

Electron Spin and the Spin–Statistics Theorem

10.1 Electron Spin

All chemists are familiar with the yellow color imparted to a flame by sodium atoms. The strongest yellow line (the D line) in the sodium spectrum is actually two closely spaced lines. The sodium D line arises from a transition from the excited configuration $1s^2 2s^2 2p^6 3p$ to the ground state. The doublet nature of this and other lines in the Na spectrum indicates a doubling of the expected number of states available to the valence electron.

To explain this *fine structure* of atomic spectra, Uhlenbeck and Goudsmit proposed in 1925 that the electron has an *intrinsic* (built-in) angular momentum in addition to the orbital angular momentum due to its motion about the nucleus. If we picture the electron as a sphere of charge spinning about one of its diameters, we can see how such an intrinsic angular momentum can arise. Hence we have the term **spin angular momentum** or, more simply, **spin**. However, electron “spin” is not a classical effect, and the picture of an electron rotating about an axis has no physical reality. The intrinsic angular momentum is real, but no easily visualizable model can properly explain its origin. We cannot hope to understand microscopic particles based on models taken from our experience in the macroscopic world. Other elementary particles besides the electron have spin angular momentum.

In 1928, Dirac developed the relativistic quantum mechanics of an electron, and in his treatment electron spin arises naturally.

In the nonrelativistic quantum mechanics to which we are confining ourselves, electron spin must be introduced as an additional hypothesis. We have learned that each physical property has its corresponding linear Hermitian operator in quantum mechanics. For such properties as orbital angular momentum, we can construct the quantum-mechanical operator from the classical expression by replacing p_x, p_y, p_z by the appropriate operators. The inherent spin angular momentum of a microscopic particle has no analog in classical mechanics, so we cannot use this method to construct operators for spin. For our purposes, we shall simply use symbols for the spin operators, without giving an explicit form for them.

Analogous to the orbital angular-momentum operators $\hat{L}^2, \hat{L}_x, \hat{L}_y, \hat{L}_z$, we have the spin angular-momentum operators $\hat{S}^2, \hat{S}_x, \hat{S}_y, \hat{S}_z$, which are postulated to be linear and Hermitian. $\hat{S}^2$ is the operator for the square of the magnitude of the total spin angular

momentum of a particle. $\hat{S}_z$ is the operator for the z component of the particle's spin angular momentum. We have

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 \quad (10.1)$$

We postulate that the spin angular-momentum operators obey the same commutation relations as the orbital angular-momentum operators. Analogous to $[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z$, $[\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x$, $[\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y$ [Eqs. (5.46) and (5.48)], we have

$$[\hat{S}_x, \hat{S}_y] = i\hbar\hat{S}_z, \quad [\hat{S}_y, \hat{S}_z] = i\hbar\hat{S}_x, \quad [\hat{S}_z, \hat{S}_x] = i\hbar\hat{S}_y \quad (10.2)$$

From (10.1) and (10.2), it follows, by the same operator algebra used to obtain (5.49) and (5.50), that

$$[\hat{S}^2, \hat{S}_x] = [\hat{S}^2, \hat{S}_y] = [\hat{S}^2, \hat{S}_z] = 0 \quad (10.3)$$

Since Eqs. (10.1) and (10.2) are of the form of Eqs. (5.107) and (5.108), it follows from the work of Section 5.4 (which depended only on the commutation relations and not on the specific forms of the operators) that the eigenvalues of $\hat{S}^2$ are [Eq. (5.142)]

$$s(s+1)\hbar^2, \quad s = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots \quad (10.4)$$

and the eigenvalues of $\hat{S}_z$ are [Eq. (5.141)]

$$m_s\hbar, \quad m_s = -s, -s+1, \dots, s-1, s \quad (10.5)$$

The quantum number s is called the **spin** of the particle. Although nothing in Section 5.4 restricts electrons to a single value for s , experiment shows that all electrons do have a single value for s , namely, $s = \frac{1}{2}$. Protons and neutrons also have $s = \frac{1}{2}$. Pions have $s = 0$. Photons have $s = 1$. However, Eq. (10.5) does not hold for photons. Photons travel at speed c in vacuum. Because of their relativistic nature, it turns out that photons can have either $m_s = +1$ or $m_s = -1$, but not $m_s = 0$ (see *Merzbacher*, Chapter 22). These two m_s values correspond to left circularly polarized and right circularly polarized light.

With $s = \frac{1}{2}$, the magnitude of the total spin angular momentum of an electron is given by the square root of (10.4) as

$$[\frac{1}{2}(\frac{3}{2})\hbar^2]^{1/2} = \frac{1}{2}\sqrt{3}\hbar \quad (10.6)$$

For $s = \frac{1}{2}$, Eq. (10.5) gives the possible eigenvalues of $\hat{S}_z$ of an electron as $+\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$. The electron spin eigenfunctions that correspond to these $\hat{S}_z$ eigenvalues are denoted by α and β :

$$\hat{S}_z\alpha = +\frac{1}{2}\hbar\alpha \quad (10.7)$$

$$\hat{S}_z\beta = -\frac{1}{2}\hbar\beta \quad (10.8)$$

Since $\hat{S}_z$ commutes with $\hat{S}^2$, we can take the eigenfunctions of $\hat{S}_z$ to be eigenfunctions of $\hat{S}^2$ also, with the eigenvalue given by (10.4) with $s = \frac{1}{2}$:

$$\hat{S}^2\alpha = \frac{3}{4}\hbar^2\alpha, \quad \hat{S}^2\beta = \frac{3}{4}\hbar^2\beta \quad (10.9)$$

$\hat{S}_z$ does not commute with $\hat{S}_x$ or $\hat{S}_y$, so α and β are not eigenfunctions of these operators. The terms *spin up* and *spin down* refer to $m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$, respectively. See [Fig. 10.1](#). We shall later show that the two possibilities for the quantum number m_s give the doubling of lines in the spectra of the alkali metals.

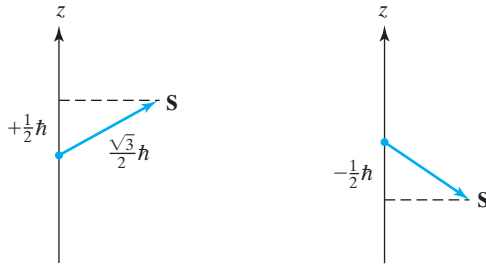


FIGURE 10.1 Possible orientations of the electron spin vector with respect to the z axis. In each case, $\mathbf{S}$ lies on the surface of a cone whose axis is the z axis.

The wave functions we have dealt with previously are functions of the spatial coordinates of the particle: $\psi = \psi(x, y, z)$. We might ask: What is the variable for the spin eigenfunctions α and β ? Sometimes one talks of a spin coordinate ω , without really specifying what this coordinate is. Most often, one takes the spin quantum number m_s as being the variable on which the spin eigenfunctions depend. This procedure is quite unusual as compared with the spatial wave functions; but because we have only two possible electronic spin eigenfunctions and eigenvalues, this is a convenient choice. We have

$$\alpha = \alpha(m_s), \quad \beta = \beta(m_s) \quad (10.10)$$

As usual, we want the eigenfunctions to be normalized. The three variables of a one-particle spatial wave function range continuously from $-\infty$ to $+\infty$, so normalization means

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

The variable m_s of the electronic spin eigenfunctions takes on only the two discrete values $+\frac{1}{2}$ and $-\frac{1}{2}$. Normalization of the one-particle spin eigenfunctions therefore means

$$\sum_{m_s=-1/2}^{1/2} |\alpha(m_s)|^2 = 1, \quad \sum_{m_s=-1/2}^{1/2} |\beta(m_s)|^2 = 1 \quad (10.11)$$

Since the eigenfunctions α and β correspond to different eigenvalues of the Hermitian operator $\hat{S}_z$, they are orthogonal:

$$\sum_{m_s=-1/2}^{1/2} \alpha^*(m_s) \beta(m_s) = 0 \quad (10.12)$$

Taking $\alpha(m_s) = \delta_{m_s, 1/2}$ and $\beta(m_s) = \delta_{m_s, -1/2}$, where δ_{jk} is the Kronecker delta function, we can satisfy (10.11) and (10.12).

When we consider the complete wave function for an electron including both space and spin variables, we shall normalize it according to

$$\sum_{m_s=-1/2}^{1/2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |\psi(x, y, z, m_s)|^2 dx dy dz = 1 \quad (10.13)$$

The notation

$$\int |\psi(x, y, z, m_s)|^2 d\tau$$

will denote summation over the spin variable and integration over the full range of the spatial variables, as in (10.13). The symbol $\int dv$ will denote integration over the full range of the system's spatial variables.

An electron is currently considered to be a pointlike elementary particle with no substructure. High-energy electron–positron collision experiments show no evidence for a nonzero electron size and put an upper limit of 3×10^{-19} m on the radius of an electron [D. Bourilkov, *Phys. Rev. D*, **62**, 076005 (2000); arxiv.org/abs/hep-ph/0002172]. Protons and neutrons are made of quarks, and so are not elementary particles. The proton rms charge radius is 0.88×10^{-15} m.

10.2 Spin and the Hydrogen Atom

The wave function specifying the state of an electron depends not only on the coordinates x , y , and z but also on the spin state of the electron. What effect does this have on the wave functions and energy levels of the hydrogen atom?

To a very good approximation, the Hamiltonian operator for a system of electrons does not involve the spin variables but is a function only of spatial coordinates and derivatives with respect to spatial coordinates. As a result, we can separate the stationary-state wave function of a single electron into a product of space and spin parts:

$$\psi(x, y, z)g(m_s)$$

where $g(m_s)$ is either one of the functions α or β , depending on whether $m_s = \frac{1}{2}$ or $-\frac{1}{2}$. [More generally, $g(m_s)$ might be a linear combination of α and β ; $g(m_s) = c_1\alpha + c_2\beta$.] Since the Hamiltonian operator has no effect on the spin function, we have

$$\hat{H}[\psi(x, y, z)g(m_s)] = g(m_s)\hat{H}\psi(x, y, z) = E[\psi(x, y, z)g(m_s)]$$

and we get the same energies as previously found without taking spin into account. The only difference spin makes is to double the possible number of states. Instead of the state $\psi(x, y, z)$, we have the two possible states $\psi(x, y, z)\alpha$ and $\psi(x, y, z)\beta$. When we take spin into account, the degeneracy of the hydrogen-atom energy levels is $2n^2$ rather than n^2 .

10.3 The Spin–Statistics Theorem

Suppose we have a system of several identical particles. In classical mechanics the identity of the particles leads to no special consequences. For example, consider identical billiard balls rolling on a billiard table. We can follow the motion of any individual ball, say by taking a motion picture of the system. We can say that ball number one is moving along a certain path, ball two is on another definite path, and so on, the paths being determined by Newton's laws of motion. Thus, although the balls are identical, we can distinguish among them by specifying the path each takes. The identity of the balls has no special effect on their motions.

In quantum mechanics the uncertainty principle tells us that we cannot follow the exact path taken by a microscopic “particle.” If the microscopic particles of the system all have different masses or charges or spins, we can use one of these properties to distinguish the particles from one another. But if they are all identical, then the one way we had in classical mechanics of distinguishing them, namely by specifying their paths, is lost in quantum mechanics because of the uncertainty principle. Therefore, the wave function of a system of interacting identical particles must not distinguish among the particles. For example, in the perturbation treatment of the helium-atom excited states in Chapter 9, we saw that the function $1s(1)2s(2)$, which says that electron 1 is in the $1s$ orbital and electron 2 is in the $2s$ orbital, was not a correct zeroth-order wave function.

Rather, we had to use the functions $2^{-1/2}[1s(1)2s(2) \pm 1s(2)2s(1)]$, which do not specify which electron is in which orbital. (If the identical particles are well separated from one another so that their wave functions do not overlap, they may be regarded as distinguishable.)

We now derive the restrictions on the wave function due to the requirement of indistinguishability of identical particles in quantum mechanics. The wave function of a system of n identical microscopic particles depends on the space and spin variables of the particles. For particle 1, these variables are x_1, y_1, z_1, m_{s1} . Let q_1 stand for all four of these variables. Thus $\psi = \psi(q_1, q_2, \dots, q_n)$.

We define the **exchange** or **permutation operator** $\hat{P}_{12}$ as the operator that interchanges all the coordinates of particles 1 and 2:

$$\hat{P}_{12} f(q_1, q_2, q_3, \dots, q_n) = f(q_2, q_1, q_3, \dots, q_n) \quad (10.14)$$

For example, the effect of $\hat{P}_{12}$ on the function that has electron 1 in a $1s$ orbital with spin up and electron 2 in a $3s$ orbital with spin down is

$$\hat{P}_{12}[1s(1)\alpha(1)3s(2)\beta(2)] = 1s(2)\alpha(2)3s(1)\beta(1) \quad (10.15)$$

What are the eigenvalues of $\hat{P}_{12}$? Applying $\hat{P}_{12}$ twice has no net effect:

$$\hat{P}_{12}\hat{P}_{12}f(q_1, q_2, \dots, q_n) = \hat{P}_{12}f(q_2, q_1, \dots, q_n) = f(q_1, q_2, \dots, q_n)$$

Therefore, $\hat{P}_{12}^2 = \hat{1}$. Let w_i and c_i denote the eigenfunctions and eigenvalues of $\hat{P}_{12}$. We have $\hat{P}_{12}w_i = c_i w_i$. Application of $\hat{P}_{12}$ to this equation gives $\hat{P}_{12}^2 w_i = c_i \hat{P}_{12} w_i$. Substitution of $\hat{P}_{12}^2 = \hat{1}$ and $\hat{P}_{12} w_i = c_i w_i$ in $\hat{P}_{12}^2 w_i = c_i \hat{P}_{12} w_i$ gives $w_i = c_i^2 w_i$. Since zero is not allowed as an eigenfunction, we can divide by w_i to get $1 = c_i^2$ and $c_i = \pm 1$. The eigenvalues of $\hat{P}_{12}$ (and of any linear operator whose square is the unit operator) are $+1$ and -1 .

If w_+ is an eigenfunction of $\hat{P}_{12}$ with eigenvalue $+1$, then

$$\hat{P}_{12}w_+(q_1, q_2, \dots, q_n) = (+1)w_+(q_1, q_2, \dots, q_n)$$

$$w_+(q_2, q_1, \dots, q_n) = w_+(q_1, q_2, \dots, q_n) \quad (10.16)$$

A function such as w_+ that has the property (10.16) of being unchanged when particles 1 and 2 are interchanged is said to be **symmetric** with respect to interchange of particles 1 and 2. For eigenvalue -1 , we have

$$w_-(q_2, q_1, \dots, q_n) = -w_-(q_1, q_2, \dots, q_n) \quad (10.17)$$

The function w_- in (10.17) is **antisymmetric** with respect to interchange of particles 1 and 2, meaning that this interchange multiplies w_- by -1 . There is no necessity for an arbitrary function $f(q_1, q_2, \dots, q_n)$ to be either symmetric or antisymmetric with respect to interchange of 1 and 2.

Do not confuse the property of being symmetric or antisymmetric with respect to particle interchange with the property of being even or odd with respect to inversion in space. The function $x_1 + x_2$ is symmetric with respect to interchange of 1 and 2 and is an odd function of x_1 and x_2 . The function $x_1^2 + x_2^2$ is symmetric with respect to interchange of 1 and 2 and is an even function of x_1 and x_2 .

The operator $\hat{P}_{ik}$ is defined by

$$\hat{P}_{ik} f(q_1, \dots, q_i, \dots, q_k, \dots, q_n) = f(q_1, \dots, q_k, \dots, q_i, \dots, q_n) \quad (10.18)$$

The eigenvalues of $\hat{P}_{ik}$ are, like those of $\hat{P}_{12}$, $+1$ and -1 .

We now consider the wave function of a system of n identical microscopic particles. Since the particles are indistinguishable, the way we label them cannot affect the state of the system. Thus the two wave functions

$$\psi(q_1, \dots, q_i, \dots, q_k, \dots, q_n) \quad \text{and} \quad \psi(q_1, \dots, q_k, \dots, q_i, \dots, q_n)$$

must correspond to the same state of the system. Two wave functions that correspond to the same state can differ at most by a multiplicative constant. Hence

$$\psi(q_1, \dots, q_k, \dots, q_i, \dots, q_n) = c\psi(q_1, \dots, q_i, \dots, q_k, \dots, q_n)$$

$$\hat{P}_{ik}\psi(q_1, \dots, q_i, \dots, q_k, \dots, q_n) = c\psi(q_1, \dots, q_i, \dots, q_k, \dots, q_n)$$

The last equation states that ψ is an eigenfunction of $\hat{P}_{ik}$. But we know that the only possible eigenvalues of $\hat{P}_{ik}$ are 1 and -1 . We conclude that the wave function for a system of n identical particles must be symmetric or antisymmetric with respect to interchange of any two of the identical particles, i and k . Since the n particles are all identical, we could not have the wave function symmetric with respect to some interchanges and antisymmetric with respect to other interchanges. Thus the wave function of n identical particles must be either symmetric with respect to every possible interchange or antisymmetric with respect to every possible interchange of two particles. (The argument just given is not rigorous. The statement that the wave function of a system of identical particles must be either completely symmetric or completely antisymmetric with respect to interchange of two particles is called the *symmetrization postulate*.)

We have seen that there are two possible cases for the wave function of a system of identical particles, the symmetric and the antisymmetric cases. Experimental evidence (such as the periodic table of the elements to be discussed later) shows that for electrons only the antisymmetric case occurs. Thus we have an additional postulate of quantum mechanics, which states that *the wave function of a system of electrons must be antisymmetric with respect to interchange of any two electrons*.

In 1926, Dirac concluded (based on theoretical work and experimental data) that electrons require antisymmetric wave functions and photons require symmetric wave functions. However, Dirac and other physicists erroneously believed in 1926 that all material particles required antisymmetric wave functions. In 1930, experimental data indicated that α particles (which have $s = 0$) require symmetric wave functions; physicists eventually realized that what determines whether a system of identical particles requires symmetric or antisymmetric wave functions is the spin of the particle. Particles with half-integral spin ($s = \frac{1}{2}, \frac{3}{2}$, and so on) require antisymmetric wave functions, while particles with integral spin ($s = 0, 1$, and so on) require symmetric wave functions. In 1940, the physicist Wolfgang Pauli used relativistic quantum field theory to prove this result. Particles requiring antisymmetric wave functions, such as electrons, are called **fermions** (after E. Fermi), whereas particles requiring symmetric wave functions, such as pions, are called **bosons** (after S. N. Bose). In nonrelativistic quantum mechanics, we must postulate that *the wave function of a system of identical particles must be antisymmetric with respect to interchange of any two particles if the particles have half-integral spin and must be symmetric with respect to interchange if the particles have integral spin*. This statement is called the **spin–statistics theorem** (since the statistical mechanics of a system of bosons differs from that of a system of fermions).

Many proofs of varying validity have been offered for the spin–statistics theorem; see I. Duck and E. C. G. Sudarshan, *Pauli and the Spin-Statistics Theorem*, World

Scientific, 1997; *Am. J. Phys.*, **66**, 284 (1998); Sudurshan and Duck, *Pramana-J. Phys.*, **61**, 645 (2003) (available at www.ias.ac.in/pramana/v61/p645/fulltext.pdf). Several experiments have confirmed the validity of the spin–statistics theorem to extremely high accuracy; see G. M. Tino, *Fortschr. Phys.*, **48**, 537 (2000) (available at arxiv.org/abs/quant-ph/9907028).

The spin–statistics theorem has an important consequence for a system of identical fermions. The antisymmetry requirement means that

$$\psi(q_1, q_2, q_3, \dots, q_n) = -\psi(q_2, q_1, q_3, \dots, q_n) \quad (10.19)$$

Consider the value of ψ when electrons 1 and 2 have the same coordinates, that is, when $x_1 = x_2, y_1 = y_2, z_1 = z_2$, and $m_{s1} = m_{s2}$. Putting $q_2 = q_1$ in (10.19), we have

$$\begin{aligned} \psi(q_1, q_1, q_3, \dots, q_n) &= -\psi(q_1, q_1, q_3, \dots, q_n) \\ 2\psi &= 0 \\ \psi(q_1, q_1, q_3, \dots, q_n) &= 0 \end{aligned} \quad (10.20)$$

Thus, two electrons with the same spin have zero probability of being found at the same point in three-dimensional space. (By “the same spin,” we mean the same value of m_s .) Since ψ is a continuous function, Eq. (10.20) means that the probability of finding two electrons with the same spin close to each other in space is quite small. Thus the antisymmetry requirement forces electrons of like spin to keep apart from one another. To describe this, one often speaks of a **Pauli repulsion** between such electrons. This “repulsion” is not a real physical force, but a reflection of the fact that the electronic wave function must be antisymmetric with respect to exchange.

The requirement for symmetric or antisymmetric wave functions also applies to a system containing two or more identical composite particles. Consider, for example, an $^{16}\text{O}_2$ molecule. The ^{16}O nucleus has 8 protons and 8 neutrons. Each proton and each neutron has $s = \frac{1}{2}$ and is a fermion. Therefore, interchange of the two ^{16}O nuclei interchanges 16 fermions and must multiply the molecular wave function by $(-1)^{16} = 1$. Thus the $^{16}\text{O}_2$ molecular wave function must be symmetric with respect to interchange of the nuclear coordinates. The requirement for symmetry or antisymmetry with respect to interchange of identical nuclei affects the degeneracy of molecular wave functions and leads to the symmetry number in the rotational partition function [see *McQuarrie* (2000), pp. 104–105].

For interchange of two identical composite particles containing m identical bosons and n identical fermions, the wave function is multiplied by $(+1)^m(-1)^n = (-1)^n$.

A composite particle is thus a fermion if it contains an odd number of fermions and is a boson otherwise.

When the variational principle (Section 8.1) is used to get approximate electronic wave functions of atoms and molecules, the requirement that the trial variation function be well-behaved includes the requirement that it be antisymmetric.

10.4 The Helium Atom

We now reconsider the helium atom from the standpoint of electron spin and the antisymmetry requirement. In the perturbation treatment of helium in Section 9.3, we found the zeroth-order wave function for the ground state to be $1s(1)1s(2)$. To take spin into account, we must multiply this spatial function by a spin eigenfunction. We therefore consider the possible spin eigenfunctions for two electrons. We shall use the notation $\alpha(1)\alpha(2)$ to indicate a state where electron 1 has spin up and electron 2 has spin up; $\alpha(1)$ stands for

$\alpha(m_{s1})$. Since each electron has two possible spin states, we have at first sight the four possible spin functions:

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

There is nothing wrong with the first two functions, but the third and fourth functions violate the principle of indistinguishability of identical particles. For example, the third function says that electron 1 has spin up and electron 2 has spin down, which *does* distinguish between electrons 1 and 2. More formally, if we apply $\hat{P}_{12}$ to these functions, we find that the first two functions are symmetric with respect to interchange of the two electrons, but the third and fourth functions are neither symmetric nor antisymmetric and so are unacceptable.

What now? Recall that we ran into essentially the same situation in treating the helium excited states (Section 9.7), where we started with the functions $1s(1)2s(2)$ and $2s(1)1s(2)$. We found that these two functions, which distinguish between electrons 1 and 2, are not the correct zeroth-order functions and that the correct zeroth-order functions are $2^{-1/2}[1s(1)2s(2) \pm 2s(1)1s(2)]$. This result suggests pretty strongly that instead of $\alpha(1)\beta(2)$ and $\beta(1)\alpha(2)$, we use

$$2^{-1/2}[\alpha(1)\beta(2) \pm \beta(1)\alpha(2)] \quad (10.21)$$

These functions are the normalized linear combinations of $\alpha(1)\beta(2)$ and $\beta(1)\alpha(2)$ that are eigenfunctions of $\hat{P}_{12}$, that is, are symmetric or antisymmetric. When electrons 1 and 2 are interchanged, $2^{-1/2}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$ becomes $2^{-1/2}[\alpha(2)\beta(1) + \beta(2)\alpha(1)]$, which is the same as the original function. In contrast, $2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$ becomes $2^{-1/2}[\alpha(2)\beta(1) - \beta(2)\alpha(1)]$, which is -1 times the original function. To show that the functions (10.21) are normalized, we have

$$\begin{aligned} & \sum_{m_{s1}} \sum_{m_{s2}} \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) \pm \beta(1)\alpha(2)]^* \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) \pm \beta(1)\alpha(2)] \\ &= \frac{1}{2} \sum_{m_{s1}} |\alpha(1)|^2 \sum_{m_{s2}} |\beta(2)|^2 \pm \frac{1}{2} \sum_{m_{s1}} \alpha^*(1)\beta(1) \sum_{m_{s2}} \beta^*(2)\alpha(2) \\ & \quad \pm \frac{1}{2} \sum_{m_{s1}} \beta^*(1)\alpha(1) \sum_{m_{s2}} \alpha^*(2)\beta(2) + \frac{1}{2} \sum_{m_{s1}} |\beta(1)|^2 \sum_{m_{s2}} |\alpha(2)|^2 = 1 \end{aligned}$$

where we used the orthonormality relations (10.11) and (10.12).

Therefore, the four normalized two-electron spin eigenfunctions with the correct exchange properties are

symmetric:	$\alpha(1)\alpha(2)$	(10.22)
	$\beta(1)\beta(2)$	(10.23)
	$[\alpha(1)\beta(2) + \beta(1)\alpha(2)]/\sqrt{2}$	(10.24)

antisymmetric: $[\alpha(1)\beta(2) - \beta(1)\alpha(2)]/\sqrt{2}$	(10.25)
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We now include spin in the He zeroth-order ground-state wave function. The function $1s(1)1s(2)$ is symmetric with respect to exchange. The overall electronic wave function including spin must be antisymmetric. Hence we must multiply the symmetric space function $1s(1)1s(2)$ by an antisymmetric spin function. There is only one antisymmetric two-electron spin function, so the ground-state zeroth-order wave function for the helium atom including spin is

$$\psi^{(0)} = 1s(1)1s(2) \cdot 2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad (10.26)$$

$\psi^{(0)}$ is an eigenfunction of $\hat{P}_{12}$ with eigenvalue -1 .

To a very good approximation, the Hamiltonian does not contain spin terms, so the energy is unaffected by inclusion of the spin factor in the ground-state wave function. Also, the ground state of helium is still nondegenerate when spin is considered.

To further demonstrate that the spin factor does not affect the energy, we shall assume we are doing a variational calculation for the He ground state using the trial function $\phi = f(r_1, r_2, r_{12})2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$, where f is a normalized function symmetric in the coordinates of the two electrons. The variational integral is

$$\begin{aligned} \int \phi^* \hat{H} \phi d\tau &= \sum_{m_{s1}} \sum_{m_{s2}} \iint f^*(r_1, r_2, r_{12}) \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)]^* \\ &\quad \times \hat{H} f(r_1, r_2, r_{12}) \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] dv_1 dv_2 \end{aligned}$$

Since $\hat{H}$ has no effect on the spin functions, the variational integral becomes

$$\iint f^* \hat{H} f dv_1 dv_2 \sum_{m_{s1}} \sum_{m_{s2}} \frac{1}{2} |\alpha(1)\beta(2) - \beta(1)\alpha(2)|^2$$

Since the spin function (10.25) is normalized, the variational integral reduces to $\iint f^* \hat{H} f dv_1 dv_2$, which is the expression we used before we introduced spin.

Now consider the excited states of helium. We found the lowest excited state to have the zeroth-order spatial wave function $2^{-1/2}[1s(1)2s(2) - 2s(1)1s(2)]$ [Eq. (9.103)]. Since this spatial function is antisymmetric, we must multiply it by a symmetric spin function. We can use any one of the three symmetric two-electron spin functions, so instead of the nondegenerate level previously found, we have a triply degenerate level with the three zeroth-order wave functions

$$2^{-1/2}[1s(1)2s(2) - 2s(1)1s(2)]\alpha(1)\alpha(2) \quad (10.27)$$

$$2^{-1/2}[1s(1)2s(2) - 2s(1)1s(2)]\beta(1)\beta(2) \quad (10.28)$$

$$2^{-1/2}[1s(1)2s(2) - 2s(1)1s(2)]2^{-1/2}[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \quad (10.29)$$

For the next excited state, the requirement of antisymmetry of the overall wave function leads to the zeroth-order wave function

$$2^{-1/2}[1s(1)2s(2) + 2s(1)1s(2)]2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad (10.30)$$

The same considerations apply for the $1s2p$ states.

10.5 The Pauli Exclusion Principle

So far, we have not seen any very spectacular consequences of electron spin and the antisymmetry requirement. In the hydrogen and helium atoms, the spin factors in the wave functions and the antisymmetry requirement simply affect the degeneracy of the levels but do not (except for very small effects to be considered later) affect the previously obtained energies. For lithium, the story is quite different.

Suppose we take the interelectronic repulsions in the Li atom as a perturbation on the remaining terms in the Hamiltonian. By the same steps used in the treatment of helium, the unperturbed wave functions are products of three hydrogenlike functions. For the ground state,

$$\psi^{(0)} = 1s(1)1s(2)1s(3) \quad (10.31)$$

and the zeroth-order (unperturbed) energy is [Eq. (9.48) and the paragraph after (9.50)]

$$E^{(0)} = -\left(\frac{1}{1^2} + \frac{1}{1^2} + \frac{1}{1^2}\right)\left(\frac{Z^2 e^2}{8\pi\epsilon_0 a_0}\right) = -27\left(\frac{e^2}{8\pi\epsilon_0 a_0}\right) = -27(13.606 \text{ eV}) = -367.4 \text{ eV}$$

The first-order energy correction is $E^{(1)} = \langle \psi^{(0)} | \hat{H}' | \psi^{(0)} \rangle$. The perturbation $\hat{H}'$ consists of the interelectronic repulsions, so

$$E^{(1)} = \int |1s(1)|^2 |1s(2)|^2 |1s(3)|^2 \frac{e^2}{4\pi\epsilon_0 r_{12}} dv + \int |1s(1)|^2 |1s(2)|^2 |1s(3)|^2 \frac{e^2}{4\pi\epsilon_0 r_{23}} dv \\ + \int |1s(1)|^2 |1s(2)|^2 |1s(3)|^2 \frac{e^2}{4\pi\epsilon_0 r_{13}} dv$$

The way we label the dummy integration variables in these definite integrals cannot affect their value. If we interchange the labels 1 and 3 on the variables in the second integral, it is converted to the first integral. Hence these two integrals are equal. Interchange of the labels 2 and 3 in the third integral shows it to be equal to the first integral also. Therefore

$$E^{(1)} = 3 \int \int |1s(1)|^2 |1s(2)|^2 \frac{e^2}{4\pi\epsilon_0 r_{12}} dv_1 dv_2 \int |1s(3)|^2 dv_3$$

The integral over electron 3 gives 1 (normalization). The integral over electrons 1 and 2 was evaluated in the perturbation treatment of helium, and [Eqs. (9.52) and (9.53)]

$$E^{(1)} = 3\left(\frac{5Z}{4}\right)\left(\frac{e^2}{8\pi\epsilon_0 a_0}\right) = \frac{45}{4}(13.606 \text{ eV}) = 153.1 \text{ eV}$$

$$E^{(0)} + E^{(1)} = -214.3 \text{ eV}$$

Since we can use the zeroth-order perturbation wave function as a trial variation function (recall the discussion at the beginning of Section 9.4), $E^{(0)} + E^{(1)}$ must be, according to the variation principle, equal to or greater than the true ground-state energy. The experimental value of the lithium ground-state energy is found by adding up the first, second, and third ionization energies, which gives [C. E. Moore, “Ionization Potentials and Ionization Limits,” publication NSRDS-NBS 34 of the National Bureau of Standards (1970); available at www.nist.gov/data/nsrds/NSRDS-NBS34.pdf]

$$-(5.39 + 75.64 + 122.45) \text{ eV} = -203.5 \text{ eV}$$

We thus have $E^{(0)} + E^{(1)}$ as less than the true ground-state energy, which is a violation of the variation principle. Moreover, the supposed configuration $1s^3$ for the Li ground state disagrees with the low value of the first ionization potential and with all chemical evidence. If we continued in this manner, we would have a $1s^Z$ ground-state configuration for the element of atomic number Z . We would not get the well-known periodic behavior of the elements.

Of course, our error is failure to consider spin and the antisymmetry requirement. The hypothetical zeroth-order wave function $1s(1)1s(2)1s(3)$ is symmetric with respect to interchange of any two electrons. If we are to have an antisymmetric $\psi^{(0)}$, we must multiply this symmetric space function by an antisymmetric spin function. It is easy to construct completely symmetric spin functions for three electrons, such as $\alpha(1)\alpha(2)\alpha(3)$. However, it is impossible to construct a completely antisymmetric spin function for three electrons.

Let us consider how we can systematically construct an antisymmetric function for three electrons. We shall use f , g , and h to stand for three functions of electronic coordinates, without specifying whether we are considering space coordinates or spin coordinates or both. We start with the function

$$f(1)g(2)h(3) \tag{10.32}$$

which is certainly not antisymmetric. The antisymmetric function we desire must be converted into its negative by each of the permutation operators $\hat{P}_{12}$, $\hat{P}_{13}$, and $\hat{P}_{23}$. Applying each of these operators in turn to $f(1)g(2)h(3)$, we get

$$f(2)g(1)h(3), \quad f(3)g(2)h(1), \quad f(1)g(3)h(2) \quad (10.33)$$

We might try to construct the antisymmetric functions as a linear combination of the four functions (10.32) and (10.33), but this attempt would fail. Application of $\hat{P}_{12}$ to the last two functions in (10.33) gives

$$f(3)g(1)h(2) \quad \text{and} \quad f(2)g(3)h(1) \quad (10.34)$$

which are not included in (10.32) or (10.33). We must therefore include all six functions (10.32) to (10.34) in the desired antisymmetric linear combination. These six functions are the six $(3 \cdot 2 \cdot 1)$ possible permutations of the three electrons among the three functions f , g , and h . If $f(1)g(2)h(3)$ is a solution of the Schrödinger equation with eigenvalue E , then, because of the identity of the particles, each of the functions (10.32) to (10.34) is also a solution with the same eigenvalue E (exchange degeneracy), and any linear combination of these functions is an eigenfunction with eigenvalue E .

The antisymmetric linear combination will have the form

$$\begin{aligned} c_1 f(1)g(2)h(3) + c_2 f(2)g(1)h(3) + c_3 f(3)g(2)h(1) + c_4 f(1)g(3)h(2) \\ + c_5 f(3)g(1)h(2) + c_6 f(2)g(3)h(1) \end{aligned} \quad (10.35)$$

Since $f(2)g(1)h(3) = \hat{P}_{12}f(1)g(2)h(3)$, in order to have (10.35) be an eigenfunction of $\hat{P}_{12}$ with eigenvalue -1 , we must have $c_2 = -c_1$. Likewise, $f(3)g(2)h(1) = \hat{P}_{13}f(1)g(2)h(3)$ and $f(1)g(3)h(2) = \hat{P}_{23}f(1)g(2)h(3)$, so $c_3 = -c_1$ and $c_4 = -c_1$. Since $f(3)g(1)h(2) = \hat{P}_{12}\hat{P}_{13}f(1)g(2)h(3)$, we must have $c_5 = -c_3 = c_1$. Similarly, we find $c_6 = c_1$. We thus arrive at the linear combination

$$\begin{aligned} c_1 [f(1)g(2)h(3) - f(2)g(1)h(3) - f(3)g(2)h(1) - f(1)g(3)h(2) \\ + f(3)g(1)h(2) + f(2)g(3)h(1)] \end{aligned} \quad (10.36)$$

which is easily verified to be antisymmetric with respect to 1–2, 1–3, and 2–3 interchange. [Taking all signs as plus in (10.36), we would get a completely symmetric function.]

Let us assume f , g , and h to be orthonormal and choose c_1 so that (10.36) is normalized. Multiplying (10.36) by its complex conjugate, we get many terms, but because of the assumed orthogonality the integrals of all products involving two different terms of (10.36) vanish. For example,

$$\begin{aligned} \int [f(1)g(2)h(3)]^* f(2)g(1)h(3) d\tau \\ = \int f^*(1)g(1) d\tau_1 \int g^*(2)f(2) d\tau_2 \int h^*(3)h(3) d\tau_3 = 0 \cdot 0 \cdot 1 = 0 \end{aligned}$$

Integrals involving the product of a term of (10.36) with its own complex conjugate are equal to 1, because f , g , and h are normalized. Therefore,

$$\begin{aligned} 1 &= \int |(10.36)|^2 d\tau = |c_1|^2 (1 + 1 + 1 + 1 + 1 + 1) \\ c_1 &= 1/\sqrt{6} \end{aligned}$$

We could work with (10.36) as it stands, but its properties are most easily found if we recognize it as the expansion [Eq. (8.24)] of the following third-order determinant:

$$\boxed{\frac{1}{\sqrt{6}} \begin{vmatrix} f(1) & g(1) & h(1) \\ f(2) & g(2) & h(2) \\ f(3) & g(3) & h(3) \end{vmatrix}} \quad (10.37)$$

(See also Prob. 8.22.) The antisymmetry property holds for (10.37) because interchange of two electrons amounts to interchanging two rows of the determinant, which multiplies it by -1 .

We now use (10.37) to prove that it is impossible to construct an antisymmetric spin function for three electrons. The functions f , g , and h may each be either α or β . If we take $f = \alpha$, $g = \beta$, $h = \alpha$, then (10.37) becomes

$$\frac{1}{\sqrt{6}} \begin{vmatrix} \alpha(1) & \beta(1) & \alpha(1) \\ \alpha(2) & \beta(2) & \alpha(2) \\ \alpha(3) & \beta(3) & \alpha(3) \end{vmatrix} \quad (10.38)$$

Although (10.38) is antisymmetric, we must reject it because it is equal to zero. The first and third columns of the determinant are identical, so (Section 8.3) the determinant vanishes. No matter how we choose f , g , and h , at least two columns of the determinant must be equal, so we cannot construct a nonzero antisymmetric three-electron spin function.

We now use (10.37) to construct the zeroth-order ground-state wave function for lithium, including both space and spin variables. The functions f , g , and h will now involve both space and spin variables. We choose

$$f(1) = 1s(1)\alpha(1) \quad (10.39)$$

We call a function like (10.39) a **spin-orbital**. A spin-orbital is the product of a one-electron spatial orbital and a one-electron spin function.

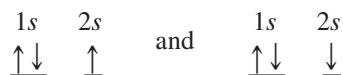
If we were to take $g(1) = 1s(1)\alpha(1)$, this would make the first and second columns of (10.37) identical, and the wave function would vanish. This is a particular case of the **Pauli exclusion principle**: No two electrons can occupy the same spin-orbital. Another way of stating this is to say that no two electrons in an atom can have the same values for all their quantum numbers. The Pauli exclusion principle is a consequence of the more general antisymmetry requirement for the wave function of a system of identical spin- $\frac{1}{2}$ particles and is less satisfying than the antisymmetry statement, since the exclusion principle is based on approximate (zeroth-order) wave functions.

We therefore take $g(1) = 1s(1)\beta(1)$, which puts two electrons with opposite spin in the $1s$ orbital. For the spin-orbital h , we cannot use either $1s(1)\alpha(1)$ or $1s(1)\beta(1)$, since these choices make the determinant vanish. We take $h(1) = 2s(1)\alpha(1)$, which gives the familiar Li ground-state configuration $1s^2 2s$ and the zeroth-order wave function

$$\psi^{(0)} = \frac{1}{\sqrt{6}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3) \end{vmatrix} \quad (10.40)$$

Note especially that (10.40) is *not* simply a product of space and spin parts (as we found for H and He), but is a linear combination of terms, each of which is a product of space and spin parts.

Since we could just as well have taken $h(1) = 2s(1)\beta(1)$, the ground state of lithium is, like hydrogen, doubly degenerate, corresponding to the two possible orientations of the spin of the $2s$ electron. We might use the orbital diagrams



to indicate this. Each spatial orbital such as $1s$ or $2p_0$ can hold two electrons of opposite spin. A spin-orbital such as $2s\alpha$ can hold one electron.

Although the $1s^2 2p$ configuration will have the same unperturbed energy $E^{(0)}$ as the $1s^2 2s$ configuration, when we take electron repulsion into account by calculating $E^{(1)}$ and

higher corrections, we find that the $1s^2 2s$ configuration lies lower for the same reason as in helium.

Consider some points about the Pauli exclusion principle, which we restate as follows: *In a system of identical fermions, no two particles can occupy the same state.* If we have a system of n interacting particles (for example, an atom), there is a single wave function (involving $4n$ variables) for the entire system. Because of the interactions between the particles, the wave function cannot be written as the product of wave functions of the individual particles. Hence, strictly speaking, we cannot talk of the states of individual particles, only the state of the whole system. If, however, the interactions between the particles are not too large, then as an initial approximation we can neglect them and write the zeroth-order wave function of the system as a product of wave functions of the individual particles. In this zeroth-order wave function, no two fermions can have the same wave function (state).

Since bosons require a wave function symmetric with respect to interchange, there is no restriction on the number of bosons in a given state.

In 1925, Einstein showed that in an ideal gas of noninteracting bosons, there is a very low temperature T_c (called the condensation temperature) above which the fraction f of bosons in the ground state is negligible but below which f becomes appreciable and goes to 1 as the absolute temperature T goes to 0. The equation for f for noninteracting bosons in a cubic box is $f = 1 - (T/T_c)^{3/2}$ for $T < T_c$ [McQuarrie (2000), Section 10-4]. The phenomenon of a significant fraction of bosons falling into the ground state is called *Bose–Einstein condensation*. Bose–Einstein condensation is important in determining the properties of superfluid liquid ^4He (whose atoms are bosons), but the interatomic interactions in the liquid make theoretical analysis difficult.

In 1995, physicists succeeded in producing Bose–Einstein condensation in a gas [Physics Today, August 1995, p. 17; C. E. Wieman, *Am. J. Phys.*, **64**, 847 (1996)]. They used a gas of ^{87}Rb atoms. An ^{87}Rb atom has 87 nucleons and 37 electrons. With an even number (124) of fermions, ^{87}Rb is a boson. With a combination of laser light, an applied inhomogeneous magnetic field, and applied radiofrequency radiation, a sample of 10^4 ^{87}Rb atoms was cooled to 10^{-7} K, thereby condensing a substantial fraction of the atoms into the ground state. The radiofrequency radiation was then used to remove most of the atoms in excited states, leaving a condensate of 2000 atoms, nearly all of which were in the ground state. Each Rb atom in this experiment was subject to a potential-energy function $V(x, y, z)$ produced by the interaction of the atom's total spin magnetic moment with the applied magnetic field (Sections 6.8 and 10.9). The inhomogeneous applied magnetic field was such that the potential energy V was that of a three-dimensional harmonic oscillator (Prob. 4.20) plus a constant. The Rb atoms in the Bose–Einstein condensate are in the ground state of this harmonic-oscillator potential.

10.6 Slater Determinants

Slater pointed out in 1929 that a determinant of the form (10.40) satisfies the antisymmetry requirement for a many-electron atom. A determinant like (10.40) is called a **Slater determinant**. All the elements in a given column of a Slater determinant involve the same spin-orbital, whereas elements in the same row all involve the same electron. (Since interchanging rows and columns does not affect the value of a determinant, we could write the Slater determinant in another, equivalent form.)

Consider how the zeroth-order helium wave functions that we found previously can be written as Slater determinants. For the ground-state configuration $1s^2$, we have the spin-orbitals $1s\alpha$ and $1s\beta$, giving the Slater determinant

$$\frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) \end{vmatrix} = 1s(1)1s(2) \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad (10.41)$$

which agrees with (10.26). For the states corresponding to the excited configuration $1s2s$, we have the possible spin-orbitals $1s\alpha$, $1s\beta$, $2s\alpha$, $2s\beta$, which give the four Slater determinants

$$D_1 = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 2s(2)\alpha(2) \end{vmatrix} \quad D_2 = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\beta(1) \\ 1s(2)\alpha(2) & 2s(2)\beta(2) \end{vmatrix}$$

$$D_3 = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\beta(2) & 2s(2)\alpha(2) \end{vmatrix} \quad D_4 = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\beta(1) & 2s(1)\beta(1) \\ 1s(2)\beta(2) & 2s(2)\beta(2) \end{vmatrix}$$

Comparison with (10.27) to (10.30) shows that the $1s2s$ zeroth-order wave functions are related to these four Slater determinants as follows:

$$2^{-1/2}[1s(1)2s(2) - 2s(1)1s(2)]\alpha(1)\alpha(2) = D_1 \quad (10.42)$$

$$2^{-1/2}[1s(1)2s(2) - 2s(1)1s(2)]\beta(1)\beta(2) = D_4 \quad (10.43)$$

$$2^{-1/2}[1s(1)2s(2) - 2s(1)1s(2)]2^{-1/2}[\alpha(1)\beta(2) + \beta(1)\alpha(2)] = 2^{-1/2}(D_2 + D_3) \quad (10.44)$$

$$2^{-1/2}[1s(1)2s(2) + 2s(1)1s(2)]2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] = 2^{-1/2}(D_2 - D_3) \quad (10.45)$$

(To get a zeroth-order function that is an eigenfunction of the spin and orbital angular-momentum operators, we sometimes have to take a linear combination of the Slater determinants of a configuration; see Chapter 11.)

Next, consider some notations used for Slater determinants. Instead of writing α and β for spin functions, one often puts a bar over the spatial function to indicate the spin function β , and a spatial function without a bar implies the spin factor α . With this notation, (10.40) is written as

$$\psi^{(0)} = \frac{1}{\sqrt{6}} \begin{vmatrix} 1s(1) & \overline{1s}(1) & 2s(1) \\ 1s(2) & \overline{1s}(2) & 2s(2) \\ 1s(3) & \overline{1s}(3) & 2s(3) \end{vmatrix} \quad (10.46)$$

Given the spin-orbitals occupied by the electrons, we can readily construct the Slater determinant. Therefore, a shorthand notation for Slater determinants that simply specifies the spin-orbitals is often used. In this notation, (10.46) is written as

$$\psi^{(0)} = |1s\overline{1s}2s| \quad (10.47)$$

where the vertical lines indicate formation of the determinant and multiplication by $1/\sqrt{6}$.

We showed that the factor $1/\sqrt{6}$ normalizes a third-order Slater determinant constructed of orthonormal functions. The expansion of an n th-order determinant has $n!$ terms (Prob. 8.20). For an n th-order Slater determinant of orthonormal spin-orbitals, the same reasoning used in the third-order case shows that the normalization constant is $1/\sqrt{n!}$. We always include a factor $1/\sqrt{n!}$ in defining a Slater determinant of order n .

10.7 Perturbation Treatment of the Lithium Ground State

Let us carry out a perturbation treatment of the ground state of the lithium atom. Defining e' as $e' \equiv e/4\pi\epsilon_0$, we take

$$\hat{H}^0 = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{\hbar^2}{2m_e}\nabla_3^2 - \frac{Ze'^2}{r_1} - \frac{Ze'^2}{r_2} - \frac{Ze'^2}{r_3}, \quad \hat{H}' = \frac{e'^2}{r_{12}} + \frac{e'^2}{r_{23}} + \frac{e'^2}{r_{13}}$$

We found in Section 10.5 that to satisfy the antisymmetry requirement, the ground-state configuration must be $1s^2 2s$. The correct zeroth-order wave function is (10.40):

$$\begin{aligned} \psi^{(0)} = 6^{-1/2} [& 1s(1)1s(2)2s(3)\alpha(1)\beta(2)\alpha(3) - 1s(1)2s(2)1s(3)\alpha(1)\alpha(2)\beta(3) \\ & - 1s(1)1s(2)2s(3)\beta(1)\alpha(2)\alpha(3) + 1s(1)2s(2)1s(3)\beta(1)\alpha(2)\alpha(3) \\ & + 2s(1)1s(2)1s(3)\alpha(1)\alpha(2)\beta(3) - 2s(1)1s(2)1s(3)\alpha(1)\beta(2)\alpha(3)] \end{aligned} \quad (10.48)$$

What is $E^{(0)}$? Each term in $\psi^{(0)}$ contains the product of two $1s$ hydrogenlike functions and one $2s$ hydrogenlike function, multiplied by a spin factor. $\hat{H}^0$ is the sum of three hydrogenlike Hamiltonians, one for each electron, and does not involve spin. Thus $\psi^{(0)}$ is a linear combination of terms, each of which is an eigenfunction of $\hat{H}^0$ with eigenvalue $E_{1s}^{(0)} + E_{1s}^{(0)} + E_{2s}^{(0)}$, where these are hydrogenlike energies. Hence $\psi^{(0)}$ is an eigenfunction of $\hat{H}^0$ with eigenvalue $E_{1s}^{(0)} + E_{1s}^{(0)} + E_{2s}^{(0)}$. Therefore [Eq. (6.94)],

$$E^{(0)} = -\left(\frac{1}{1^2} + \frac{1}{1^2} + \frac{1}{2^2}\right)\left(\frac{Z^2 e'^2}{2a_0}\right) = -\frac{81}{4}(13.606 \text{ eV}) = -275.5 \text{ eV} \quad (10.49)$$

The evaluation of $E^{(1)} = \langle \psi^{(0)} | \hat{H}' | \psi^{(0)} \rangle$ is outlined in Prob. 10.15. One finds

$$\begin{aligned} E^{(1)} = 2 \iint 1s^2(1)2s^2(2) \frac{e'^2}{r_{12}} dv_1 dv_2 + \iint 1s^2(1)1s^2(2) \frac{e'^2}{r_{12}} dv_1 dv_2 \\ - \iint 1s(1)2s(2)1s(2)2s(1) \frac{e'^2}{r_{12}} dv_1 dv_2 \end{aligned} \quad (10.50)$$

These integrals are Coulomb and exchange integrals:

$$E^{(1)} = 2J_{1s2s} + J_{1s1s} - K_{1s2s} \quad (10.51)$$

We have [Eqs. (9.52), (9.53), and (9.111)]

$$\begin{aligned} J_{1s1s} = \frac{5}{8} \frac{Ze'^2}{a_0}, \quad J_{1s2s} = \frac{17}{81} \frac{Ze'^2}{a_0}, \quad K_{1s2s} = \frac{16}{729} \frac{Ze'^2}{a_0} \\ E^{(1)} = \frac{5965}{972} \left(\frac{e'^2}{2a_0}\right) = 83.5 \text{ eV} \end{aligned}$$

The energy through first order is -192.0 eV , as compared with the true ground-state energy of lithium, -203.5 eV . To improve on this result, we could calculate higher-order wave-function and energy corrections. This will mix into the wave function contributions from Slater determinants involving configurations besides $1s^2 2s$ (configuration interaction).

10.8 Variation Treatments of the Lithium Ground State

The zeroth-order perturbation wave function (10.40) uses the full nuclear charge ($Z = 3$) for both the $1s$ and $2s$ orbitals of lithium. We expect that the $2s$ electron, which is partially shielded from the nucleus by the two $1s$ electrons, will see an effective nuclear charge that is much less than 3. Even the $1s$ electrons partially shield each other (recall the treatment of the helium ground state). This reasoning suggests the introduction of two variational parameters b_1 and b_2 into (10.40).

Instead of using the $Z = 3$ $1s$ function in Table 6.2, we take

$$f \equiv \frac{1}{\pi^{1/2}} \left(\frac{b_1}{a_0}\right)^{3/2} e^{-b_1 r/a_0} \quad (10.52)$$

where b_1 is a variational parameter representing an effective nuclear charge for the $1s$ electrons. Instead of the $Z = 3$ $2s$ function in Table 6.2, we use

$$g = \frac{1}{4(2\pi)^{1/2}} \left(\frac{b_2}{a_0} \right)^{3/2} \left(2 - \frac{b_2 r}{a_0} \right) e^{-b_2 r/2a_0} \quad (10.53)$$

Our trial variation function is then

$$\phi = \frac{1}{\sqrt{6}} \begin{vmatrix} f(1)\alpha(1) & f(1)\beta(1) & g(1)\alpha(1) \\ f(2)\alpha(2) & f(2)\beta(2) & g(2)\alpha(2) \\ f(3)\alpha(3) & f(3)\beta(3) & g(3)\alpha(3) \end{vmatrix} \quad (10.54)$$

The use of different charges b_1 and b_2 for the $1s$ and $2s$ orbitals destroys their orthogonality, so (10.54) is not normalized. The best values of the variational parameters are found by setting $\partial W/\partial b_1 = 0$ and $\partial W/\partial b_2 = 0$, where the variational integral W is given by the left side of Eq. (8.9). The results are [E. B. Wilson, Jr., *J. Chem. Phys.*, **1**, 210 (1933)] $b_1 = 2.686$, $b_2 = 1.776$, and $W = -201.2$ eV. W is much closer to the true value -203.5 eV than the result -192.0 eV found in the last section. The value of b_2 shows substantial, but not complete, screening of the $2s$ electron by the $1s$ electrons.

We might try other forms for the orbitals besides (10.52) and (10.53) to improve the trial function. However, no matter what orbital functions we try, if we restrict ourselves to a trial function of the form of (10.54), we can never reach the true ground-state energy. To do this, we can introduce r_{12} , r_{23} , and r_{13} into the trial function or use a linear combination of several Slater determinants corresponding to various configurations (configuration interaction).

10.9 Spin Magnetic Moment

Recall that the orbital angular momentum $\mathbf{L}$ of an electron has a magnetic moment $-(e/2m_e)\mathbf{L}$ associated with it [Eq. (6.128)], where $-e$ is the electron charge. It is natural to suppose that there is also a magnetic moment $\mathbf{m}_S$ associated with the electronic spin angular momentum $\mathbf{S}$. We might guess that $\mathbf{m}_S$ would be $-(e/2m_e)$ times $\mathbf{S}$. Spin is a relativistic phenomenon, however, and we cannot expect $\mathbf{m}_S$ to be related to $\mathbf{S}$ in exactly the same way that $\mathbf{m}_L$ is related to $\mathbf{L}$. In fact, Dirac's relativistic treatment of the electron gave the result that (in SI units)

$$\mathbf{m}_S = -g_e \frac{e}{2m_e} \mathbf{S} \quad (10.55)$$

where Dirac's treatment gave $g_e = 2$ for the *electron g factor* g_e . Theoretical and experimental work subsequent to Dirac's treatment has shown that g_e is slightly greater than 2; $g_e = 2(1 + \alpha/2\pi + \dots) = 2.0023$, where the dots indicate terms involving higher powers of α and where the *fine-structure constant* α is

$$\alpha \equiv \frac{e^2}{4\pi\epsilon_0\hbar c} = 0.00729735257 \quad (10.56)$$

g_e has been measured with extraordinary accuracy [D. Hanneke et al., *Phys. Rev. A*, **83**, 052122 (2011); available at arxiv.org/abs/1009.4831]: $g_e = 2.002319304361$. [Some workers prefer to omit the minus sign in (10.55) and use the convention that g_e is negative; see www.stanford.edu/group/Zarelab/publiclinks/zarepub642.pdf.]

The magnitude of the spin magnetic moment of an electron is (in SI units)

$$|\mathbf{m}_S| = g_e \frac{e}{2m_e} |\mathbf{S}| = g_e \sqrt{\frac{3}{4}} \frac{e\hbar}{2m_e} \quad (10.57)$$

The ferromagnetism of iron is due to the electron's magnetic moment.

The two possible orientations of an electron's spin and its associated spin magnetic moment with respect to an axis produce two energy levels in an externally applied magnetic field. In electron-spin-resonance (ESR) spectroscopy, one observes transitions between these two levels. ESR spectroscopy is applicable to species such as free radicals and transition-metal ions that have one or more unpaired electron spins and hence have a nonzero total electron spin and spin magnetic moment.

NMR Spectroscopy

Many atomic nuclei have a nonzero spin angular momentum $\mathbf{I}$. Similar to (10.4) and (10.5), the magnitude of $\mathbf{I}$ is $[I(I + 1)]^{1/2}\hbar$, where the nuclear-spin quantum number I can be 0, $\frac{1}{2}$, 1, and so on, and the z component of $\mathbf{I}$ has the possible values $M_I\hbar$, where $M_I = -I, -I + 1, \dots, I$. Some I values are: 0 for every nucleus with an even number of protons and an even number of neutrons (for example, $^{16}_8\text{O}$ and $^{12}_6\text{C}$); $\frac{1}{2}$ for ^1_1H , $^{13}_6\text{C}$, $^{19}_9\text{F}$, and $^{31}_{15}\text{P}$; 1 for ^2_1H and $^{14}_7\text{N}$; $\frac{3}{2}$ for $^{11}_5\text{B}$, $^{23}_{11}\text{Na}$ and $^{35}_{17}\text{Cl}$. If $I \neq 0$, the nucleus has a spin magnetic moment $\mathbf{m}_I$ given by an equation similar to (10.55):

$$\mathbf{m}_I = g_N(e/2m_p)\mathbf{I} \equiv \gamma\mathbf{I} \quad (10.58)$$

where m_p is the proton mass and the *nuclear g factor* g_N has a value characteristic of the nucleus. The quantity γ , called the **magnetogyric ratio** of the nucleus, is defined by $\gamma \equiv \mathbf{m}_I/\mathbf{I} = g_N e/2m_p$. Values of I , g_N , and γ for some nuclei are

nucleus	^1H	^{12}C	^{13}C	^{15}N	^{19}F	^{31}P
I	1/2	0	1/2	1/2	1/2	1/2
g_N	5.58569		1.40482	-0.56638	5.25773	2.2632
$\gamma/(\text{MHz/T})$	267.522		67.283	-27.126	251.815	108.39

In nuclear-magnetic-resonance (NMR) spectroscopy, one observes transitions between nuclear-spin energy levels in an applied magnetic field. The sample (most commonly a dilute solution of the compound being studied) is placed between the poles of a strong magnet. The energy of interaction between an isolated nuclear-spin magnetic moment $\mathbf{m}_I$ in an external magnetic field $\mathbf{B}$ is given by Eq. (6.131) as $E = -\mathbf{m}_I \cdot \mathbf{B}$. Using (10.58) for $\mathbf{m}_I$ and taking the z axis as coinciding with the direction of $\mathbf{B}$, we have

$$E = -\mathbf{m}_I \cdot \mathbf{B} = -\gamma(I_x\hat{\mathbf{i}} + I_y\hat{\mathbf{j}} + I_z\hat{\mathbf{k}}) \cdot (B\hat{\mathbf{k}}) = -\gamma B I_z$$

We convert this classical expression for the energy into a Hamiltonian operator by replacing the classical quantity I_z by the operator $\hat{I}_z$. Thus, $\hat{H} = -\gamma B \hat{I}_z$. Let $|M_I\rangle$ denote the function that is simultaneously an eigenfunction of the operators $\hat{I}^2$ (for the square of the magnitude of the nuclear-spin angular momentum) and $\hat{I}_z$. We have

$$\hat{H}|M_I\rangle = -\gamma B \hat{I}_z|M_I\rangle = -\gamma B M_I \hbar |M_I\rangle \quad (10.59)$$

Therefore, (10.59) gives the energy levels of the isolated nuclear spin in the applied magnetic field as

$$E = -\gamma \hbar B M_I, \quad M_I = -I, -I + 1, \dots, I$$

In NMR spectroscopy, the sample is exposed to electromagnetic radiation that induces transitions between nuclear-spin energy levels. The selection rule turns out to be $\Delta M_I = \pm 1$. The NMR transition frequency ν is found as follows:

$$\begin{aligned} h\nu &= |\Delta E| = |\gamma| \hbar B |\Delta M_I| = |\gamma| \hbar B \\ \nu &= (|\gamma|/2\pi)B = |g_N| (e/4\pi m_p)B \end{aligned} \quad (10.60)$$

The value of γ differs greatly for different nuclei, and in any one experiment, one studies the NMR spectrum of one kind of nucleus. The most commonly studied nucleus is ^1H , the proton. The second most studied nucleus is ^{13}C . The ^{13}C isotope occurs in 1% abundance in carbon.

Equation (10.60) is for a nucleus isolated except for the presence of the external magnetic field $\mathbf{B}$. For a nucleus present in a molecule, we also have to consider the contribution of the molecular electrons to the magnetic field felt by each nucleus. In most ground-state molecules, the electron spins are all paired and there is no electronic orbital angular momentum. With no electronic spin or orbital angular momentum, the electrons do not contribute to the magnetic field experienced by each nucleus. However, the application of the external applied field $\mathbf{B}$ perturbs the molecular electronic wave function, thereby producing an electronic contribution to the magnetic field at each nucleus. This electronic contribution is proportional to the magnitude of the external field B and is usually in the opposite direction to B . Therefore, the magnetic field experienced by nucleus i in a molecule is $B - \sigma_i B = (1 - \sigma_i)B$, where the proportionality constant σ_i is called the **screening constant** or **shielding constant** for nucleus i and is much less than 1. Equation (10.60) becomes for a nucleus in a molecule

$$\nu_i = (|\gamma|/2\pi)(1 - \sigma_i)B \quad (10.61)$$

The value of σ_i is the same for nuclei that are in the same electronic environment in the molecule. For example, in $\text{CH}_3\text{CH}_2\text{OH}$, the three CH_3 protons have the same σ_i , and the two CH_2 protons have the same σ_i . (A Newman projection of ethanol, which has a staggered conformation, shows that two of the three CH_3 hydrogens are closer to the OH group than is the third CH_3 hydrogen, but the low barrier to internal rotation in ethanol allows the three methyl hydrogens to be rapidly interchanged at room temperature, thereby making the electronic environment the same for these three hydrogens.)

We might thus expect the ^1H NMR spectrum of ethanol to show three peaks—one for the CH_3 protons, one for the CH_2 protons, and one for the OH proton, with the relative intensities of these peaks being 3:2:1. However, there is an additional effect, called *spin–spin coupling*, in which the nuclear spins of the protons on one carbon affect the magnetic field experienced by the protons on an adjacent carbon. Different possible orientations of the proton spins on one carbon produce different magnetic fields at the protons of the adjacent carbon, thereby splitting the NMR transition of the protons at the adjacent carbon. For example, the two CH_2 proton nuclei have the following four possible nuclear-spin orientations:

$$\uparrow\uparrow \quad \uparrow\downarrow \quad \downarrow\uparrow \quad \downarrow\downarrow \quad (10.62)$$

where the up and down arrows represent $M_I = \frac{1}{2}$ and $M_I = -\frac{1}{2}$, respectively. [Actually, because of the indistinguishability of identical particles, the middle two spin states in (10.62) must be replaced by linear combinations of these two states, to give nuclear-spin states that are analogous to the electron spin functions (10.22) to (10.25).] The middle two spin states in (10.62) have the same effect on the magnetic field felt by the CH_3 protons, so the four spin states in (10.62) produce three different magnetic fields at the CH_3 protons, thereby splitting the CH_3 proton NMR absorption line into three closely spaced lines of relative intensities 1:2:1, corresponding to the number of CH_2 proton spin states that produce each magnetic field. One might expect the CH_2 protons to also split the OH proton NMR line. However, even a trace of water present in the ethanol will catalyze a rapid exchange of the OH proton between different ethanol molecules, thereby eliminating the splitting of the OH line.

A similar analysis of the possible CH_3 proton orientations (Prob. 10.22) shows that the CH_3 protons split the ethanol CH_2 proton NMR line into four lines of relative intensities 1:3:3:1. *The general rule is that a group of n equivalent protons on an atom splits the NMR line of protons on an adjacent atom into $n + 1$ lines.* The spin–spin splitting (which is transmitted through the chemical bonds) is too weak to affect the NMR lines of protons separated by more than three bonds from the protons doing the splitting. In the proton NMR spectrum of $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{H}$, the CH_3 protons split the CH_2 proton line into 4 lines, and each of these is split into two lines by the $\text{C}(\text{O})\text{H}$ proton, so the CH_2 NMR line is split into 8 lines. (The intermolecular proton exchange in ethanol prevents the OH proton from splitting the CH_2 proton NMR absorption.)

Nuclei with $I = 0$ (for example, ^{12}C , ^{16}O) don't split proton NMR peaks. It turns out that nuclei with $I > \frac{1}{2}$ (for example, ^{35}Cl , ^{37}Cl , ^{14}N) generally don't split proton NMR peaks. The ^{19}F nucleus has $I = \frac{1}{2}$ and does split proton NMR peaks. Also, a quantum-mechanical analysis shows that the spin–spin interactions between equivalent protons don't affect the NMR spectrum.

The treatment just given (called a *first-order* analysis) is actually an approximation that is valid provided that the spin–spin splittings are much smaller than all the NMR frequency differences between chemically nonequivalent nuclei. In very large molecules, there will likely be chemically nonequivalent nuclei that are in only slightly different electronic environments, so the NMR frequency differences between them will be quite small and the first-order analysis will not hold. By increasing the strength of the applied magnetic field, one increases the NMR frequency differences between chemically nonequivalent nuclei, thereby tending to make the spectrum first-order, which is easier to analyze. Also, the signal strength is increased as the field is increased. Therefore, people try and use as high a field as is feasible. Current NMR research spectrometers have fields that correspond to proton NMR frequencies in the range 300 to 1000 MHz.

NMR spectroscopy is the premier structural research tool in organic chemistry, and special NMR techniques allow the structures of small proteins to be determined with the aid of NMR.

10.10 Ladder Operators for Electron Spin

The spin angular-momentum operators obey the general angular-momentum commutation relations of Section 5.4, and it is often helpful to use spin-angular-momentum ladder operators.

From (5.110) and (5.111), the raising and lowering operators for spin angular momentum are

$$\hat{S}_+ = \hat{S}_x + i\hat{S}_y \quad \text{and} \quad \hat{S}_- = \hat{S}_x - i\hat{S}_y \quad (10.63)$$

Equations (5.112) and (5.113) give

$$\hat{S}_+\hat{S}_- = \hat{S}^2 - \hat{S}_z^2 + \hbar\hat{S}_z \quad (10.64)$$

$$\hat{S}_-\hat{S}_+ = \hat{S}^2 - \hat{S}_z^2 - \hbar\hat{S}_z \quad (10.65)$$

The spin functions α and β are eigenfunctions of $\hat{S}_z$ with eigenvalues $+\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$, respectively. Since $\hat{S}_+$ is the raising operator, the function $\hat{S}_+\beta$ is an eigenfunction of $\hat{S}_z$ with eigenvalue $+\frac{1}{2}\hbar$. The most general eigenfunction of $\hat{S}_z$ with this eigenvalue is an arbitrary constant times α . Hence

$$\hat{S}_+\beta = c\alpha \quad (10.66)$$

where c is some constant. To find c , we use normalization [Eq. (10.11)]:

$$\begin{aligned}
 1 &= \sum_{m_s} [\alpha(m_s)]^* \alpha(m_s) = \sum (\hat{S}_+ \beta / c)^* (\hat{S}_+ \beta / c) \\
 |c|^2 &= \sum (\hat{S}_+ \beta)^* \hat{S}_+ \beta = \sum (\hat{S}_+ \beta)^* (\hat{S}_x + i\hat{S}_y) \beta \\
 |c|^2 &= \sum (\hat{S}_+ \beta)^* \hat{S}_x \beta + i \sum (\hat{S}_+ \beta)^* \hat{S}_y \beta
 \end{aligned} \tag{10.67}$$

We now use the Hermitian property of $\hat{S}_x$ and $\hat{S}_y$. For an operator $\hat{A}$ that acts on functions of the continuous variable x , the Hermitian property is

$$\int_{-\infty}^{\infty} f^*(x) \hat{A} g(x) dx = \int_{-\infty}^{\infty} g(x) [\hat{A} f(x)]^* dx$$

For an operator such as $\hat{S}_x$ that acts on functions of the variable m_s , which takes on discrete values, the Hermitian property is

$$\sum_{m_s} f^*(m_s) \hat{S}_x g(m_s) = \sum_{m_s} g(m_s) [\hat{S}_x f(m_s)]^* \tag{10.68}$$

Taking $f = \hat{S}_+ \beta$ and $g = \beta$, we can write (10.67) as

$$c^* c = \sum \beta (\hat{S}_x \hat{S}_+ \beta)^* + i \sum \beta (\hat{S}_y \hat{S}_+ \beta)^*$$

Taking the complex conjugate of this equation and using (10.63) and (10.65), we have

$$\begin{aligned}
 cc^* &= \sum \beta^* \hat{S}_x \hat{S}_+ \beta - i \sum \beta^* \hat{S}_y \hat{S}_+ \beta \\
 |c|^2 &= \sum \beta^* (\hat{S}_x - i\hat{S}_y) \hat{S}_+ \beta = \sum \beta^* \hat{S}_- \hat{S}_+ \beta \\
 |c|^2 &= \sum \beta^* (\hat{S}^2 - \hat{S}_z^2 - \hbar \hat{S}_z) \beta \\
 |c|^2 &= \sum \beta^* (\frac{3}{4}\hbar^2 - \frac{1}{4}\hbar^2 + \frac{1}{2}\hbar^2) \beta = \hbar^2 \sum \beta^* \beta = \hbar^2 \\
 |c| &= \hbar
 \end{aligned}$$

Choosing the phase of c as zero, we have $c = \hbar$, and (10.66) reads

$$\hat{S}_+ \beta = \hbar \alpha \tag{10.69}$$

A similar calculation gives

$$\hat{S}_- \alpha = \hbar \beta \tag{10.70}$$

Since α is the eigenfunction with the highest possible value of m_s , the operator $\hat{S}_+$ acting on α must annihilate it [Eq. (5.135)]:

$$\hat{S}_+ \alpha = 0$$

Likewise,

$$\hat{S}_- \beta = 0$$

From these last four equations, we get

$$(\hat{S}_+ + \hat{S}_-) \beta = \hbar \alpha, \quad (\hat{S}_+ - \hat{S}_-) \beta = \hbar \alpha \tag{10.71}$$

Use of (10.63) in (10.71) gives

$$\hat{S}_x \beta = \frac{1}{2} \hbar \alpha, \quad \hat{S}_y \beta = -\frac{1}{2} i \hbar \alpha \tag{10.72}$$

Similarly, we find

$$\hat{S}_x \alpha = \frac{1}{2} \hbar \beta, \quad \hat{S}_y \alpha = \frac{1}{2} i \hbar \beta \tag{10.73}$$

Matrix representatives of the spin operators are considered in Prob. 10.28.

Summary

An elementary particle possesses a spin angular momentum of magnitude $[s(s+1)\hbar^2]^{1/2}$ and z component $m_s\hbar$, where $m_s = -s, -s+1, \dots, s-1, s$. For an electron, $s = \frac{1}{2}$. The spin angular-momentum operators $\hat{S}_x$, $\hat{S}_y$, $\hat{S}_z$, and $\hat{S}^2$ obey relations analogous to those obeyed by the orbital angular-momentum operators. The electron spin eigenfunctions corresponding to the states $m_s = \frac{1}{2}$ and $m_s = -\frac{1}{2}$ are denoted by α and β . We have $\hat{S}_z\alpha = \frac{1}{2}\hbar\alpha$, $\hat{S}_z\beta = -\frac{1}{2}\hbar\beta$, $\hat{S}^2\alpha = \frac{1}{2}(\frac{3}{2})\hbar^2\alpha$, and $\hat{S}^2\beta = \frac{1}{2}(\frac{3}{2})\hbar^2\beta$. The spin functions α and β are orthonormal [Eqs. (10.11) and (10.12)]. For a one-electron system, the complete stationary-state wave function is the product of a spatial function $\psi(x, y, z)$ and a spin function (α or β or a linear combination of α and β).

According to the spin-statistics theorem, the complete wave function (including both space and spin coordinates) of a system of identical particles with half-integral spin must be antisymmetric with respect to interchange of any two such particles. The complete wave function of a system of identical particles with integral spin must be symmetric with respect to interchange of any two particles. Particles requiring antisymmetric wave functions are called fermions, and particles requiring symmetric wave functions are called bosons.

The two-electron spin eigenfunctions consist of the three symmetric functions $\alpha(1)\alpha(2)$, $\beta(1)\beta(2)$, and $[\alpha(1)\beta(2) + \beta(1)\alpha(2)]/\sqrt{2}$ and the antisymmetric function $[\alpha(1)\beta(2) - \beta(1)\alpha(2)]/\sqrt{2}$. For the helium atom, each stationary-state wave function is the product of a symmetric spatial function and an antisymmetric spin function or an antisymmetric spatial function and a symmetric spin function. Some approximate helium-atom wave functions are Eqs. (10.26) to (10.30).

A spin-orbital is the product of a one-electron spatial wave function and a one-electron spin function. An approximate wave function for a system of electrons can be written as a Slater determinant of spin-orbitals. Interchange of two electrons interchanges two rows in the Slater determinant, which multiplies the wave function by -1 , ensuring antisymmetry. In such an approximate wave function, no two electrons can be assigned to the same spin-orbital. This is the Pauli exclusion principle and is a consequence of the antisymmetry requirement.

An electron has a spin magnetic moment $\mathbf{m}_s$ that is proportional to its spin angular momentum $\mathbf{S}$. Transitions between different nuclear-spin energy levels in an applied magnetic field give rise to the NMR spectrum of a molecule.

By using ladder operators, we found the effects of $\hat{S}_x$ and $\hat{S}_y$ on α and β .

Problems

Sec.	10.1	10.3	10.4	10.6	10.7
Probs.	10.1–10.4	10.5–10.7	10.8–10.10	10.11–10.14	10.15–10.16

Sec.	10.9	10.10	general
Probs.	10.17–10.23	10.24–10.26	10.27–10.29

- 10.1** Calculate the magnitude of the spin angular momentum of a proton. Give a numerical answer.
- 10.2** Calculate the angle that the spin vector $\mathbf{S}$ makes with the z axis for an electron with spin function α .
- 10.3** The most general spin function for an electron is $c_1\alpha + c_2\beta$, where c_1 and c_2 are constants. (a) Complete these equations: $\hat{S}^2(c_1\alpha + c_2\beta) = ?$, $\hat{S}_z(c_1\alpha + c_2\beta) = ?$, and $\hat{S}_x^2(c_1\alpha + c_2\beta) = ?$. (b) The requirement that $c_1\alpha + c_2\beta$ be normalized leads to what relation between c_1 and c_2 ?
- 10.4** (a) If S_z of a particle with spin quantum number s is measured, what are the possible outcomes? (b) If S_x of a particle with spin quantum number s is measured, what are the possible outcomes? (c) In the statistical-ensemble interpretation of quantum mechanics (Section 7.9), all properties

of a particle have precise values at all times. Consider the relation $S^2 = S_x^2 + S_y^2 + S_z^2$ between a particle's spin magnitude and its spin components. For each of the spin quantum number values $s = \frac{1}{2}$, $s = 1$, and $s = \frac{3}{2}$, examine whether $S^2 = S_x^2 + S_y^2 + S_z^2$ can be obeyed with all of the four quantities S^2 , S_x , S_y , and S_z simultaneously having experimentally observable values.

10.5 State whether each of the following is a boson or a fermion: (a) an electron; (b) a proton; (c) a neutron; (d) a photon; (e) a ^{12}C nucleus; (f) a ^{13}C nucleus; (g) a ^{12}C atom; (h) a ^{13}C atom; (i) an ^{14}N atom; (j) an ^{15}N atom.

10.6 (a) Show that $\hat{P}_{12}$ commutes with the Hamiltonian for the lithium atom. (b) Show that $\hat{P}_{12}$ and $\hat{P}_{23}$ do not commute with each other. (c) Show that $\hat{P}_{12}$ and $\hat{P}_{23}$ commute when they are applied to antisymmetric functions.

10.7 Show that $\hat{P}_{12}$ is Hermitian.

10.8 Classify each of these functions as symmetric, antisymmetric, or neither symmetric nor antisymmetric. (a) $f(1)g(2)\alpha(1)\alpha(2)$; (b) $f(1)f(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$; (c) $f(1)f(2)f(3)\beta(1)\beta(2)\beta(3)$; (d) $e^{-a(r_1-r_2)}$; (e) $[f(1)g(2) - g(1)f(2)][\alpha(1)\beta(2) - \alpha(2)\beta(1)]$; (f) $r_{12}^2 e^{-a(r_1+r_2)}$.

10.9 If electrons had a spin of zero, what would be the zeroth-order (interelectronic repulsions neglected) wave functions for the ground state and first excited state of lithium?

10.10 Explain why the function $Ne^{-cr_1}e^{-cr_2}(r_1 - r_2)$ should not be used as a trial variation function for the helium-atom ground state.

10.11 The antisymmetrization operator $\hat{A}$ is defined as the operator that antisymmetrizes a product of n one-electron functions and multiplies it by $(n!)^{-1/2}$. For $n = 2$,

$$\hat{A}f(1)g(2) = \frac{1}{\sqrt{2}} \begin{vmatrix} f(1) & g(1) \\ f(2) & g(2) \end{vmatrix}$$

(a) For $n = 2$, express $\hat{A}$ in terms of $\hat{P}_{12}$. (b) For $n = 3$, express $\hat{A}$ in terms of $\hat{P}_{12}$, $\hat{P}_{13}$, and $\hat{P}_{23}$.

10.12 Use theorems about determinants to show that taking the lithium spin-orbitals in a Slater determinant as $1s\alpha$, $1s\beta$, and $1s(c_1\alpha + c_2\beta)$, where c_1 and c_2 are constants, gives a wave function that equals zero.

10.13 A permanent is defined by the same expansion as a determinant except that all terms are given a plus sign. Thus the second-order permanent is

$$\begin{vmatrix} + & + \\ a & b \\ c & d \end{vmatrix} = ad + bc$$

Can you think of a use for permanents in quantum mechanics?

10.14 A muon has the same charge and spin as an electron, but a heavier mass. What would be the ground-state configuration of a lithium atom with two electrons and one muon?

10.15 Derive Eq. (10.50) for $E^{(1)}$ of lithium as follows. (a) Group together terms in $\psi^{(0)}$ that have the same spin factor, to get

$$\psi^{(0)} = a\beta(1)\alpha(2)\alpha(3) + b\alpha(1)\beta(2)\alpha(3) + c\alpha(1)\alpha(2)\beta(3) = A + B + C$$

where a , b , and c are certain spatial functions and $A \equiv a\beta(1)\alpha(2)\alpha(3)$, with similar definitions for B and C . Then verify that $E^{(1)} = \int |A|^2 H' d\tau + \int |B|^2 H' d\tau + \int |C|^2 H' d\tau + \dots$, where the dots stand for six integrals that each contain two of the functions A , B , and C . Use orthogonality of spin functions [Eq. (10.12)] to show that each of the six integrals represented by dots is zero. (b) Use the normalization of spin functions to show that

$$E^{(1)} = \iiint a^2 H' dv_1 dv_2 dv_3 + \iiint b^2 H' dv_1 dv_2 dv_3 + \iiint c^2 H' dv_1 dv_2 dv_3$$

where spin is no longer involved. (c) Use relabeling of dummy integration variables to show that the three integrals in (b) are equal to one another. (d) Use orthonormality of the $1s$ and $2s$ orbitals and relabeling of integration variables to prove (10.50).

10.16 If we had incorrectly used as the zeroth-order Li ground-state wave function the nonantisymmetric function $1s(1)1s(2)2s(3)$, what would $E^{(1)}$ be calculated to be?

- 10.17** Calculate the magnitude of the spin magnetic moment of an electron.
- 10.18** (a) Use Eq. (6.131) to find the expression for the energy levels of the electron spin magnetic moment $\mathbf{m}_s$ in an applied magnetic field $\mathbf{B}$. (b) Calculate the ESR absorption frequency of an electron in a magnetic field of 1.00 T.
- 10.19** A ^{35}Cl nucleus has $I = 3/2$. (a) Find the magnitude of the spin angular momentum of a ^{35}Cl nucleus. (b) Find the possible values that can result if the z component of the spin angular momentum of a ^{35}Cl nucleus is measured. (c) The same as (b) for measurement of the y component.
- 10.20** (a) Verify the value of γ for ^1H given in the table after (10.58). (b) Calculate the NMR absorption frequency of a proton (^1H nucleus) in a magnetic field of 1.00 T.
- 10.21** (a) For a nucleus with $I = \frac{1}{2}$ and $g_N > 0$, sketch a graph of the nuclear-spin energy levels versus the applied field $\mathbf{B}$. (b) Repeat (a) for a nucleus with $I = 1$ and $g_N > 0$.
- 10.22** For the three CH_3 protons in ethanol, draw diagrams similar to (10.62) showing the possible nuclear-spin orientations. Deduce the number of lines into which the adjacent CH_2 proton NMR transition is split, and give the relative intensities of these lines.
- 10.23** The proton NMR spectrum of ethanol contains a triplet peak with relative intensities 1:2:1 for the CH_3 protons, a quartet with relative intensities 1:3:3:1 for the CH_2 protons, and a singlet peak for the OH proton. These peaks have total relative intensity ratios of 3:2:1. For each of the following molecules give a similar description of the proton NMR spectrum: (a) $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{H}$; (b) $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$; (c) benzene; (d) 1,4-dichlorobenzene; (e) 1,3-dichlorobenzene.
- 10.24** Verify the spin-operator equations (10.70) and (10.73).
- 10.25** Show that α and β are each eigenfunctions of $\hat{S}_x^2$ (but not of $\hat{S}_x$). Give a physical explanation of why these results make sense (see Prob. 10.26a).
- 10.26** (a) If the spin component S_x of an electron is measured, what possible values can result? (b) The functions α and β form a complete set, so any one-electron spin function can be written as a linear combination of them. Use Eqs. (10.72) and (10.73) to construct the two normalized eigenfunctions of $\hat{S}_x$ with eigenvalues $+\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$. (c) Suppose a measurement of S_z for an electron gives the value $+\frac{1}{2}\hbar$. If a measurement of S_x is then carried out, give the probabilities for each possible outcome. (d) Do the same as in (b) for $\hat{S}_y$ instead of $\hat{S}_x$. In the Stern–Gerlach experiment, a beam of particles is sent through an inhomogeneous magnetic field, which splits the beam into several beams each having particles with a different component of magnetic dipole moment in the field direction. For example, a beam of ground-state sodium atoms is split into two beams, corresponding to the two possible orientations of the valence electron's spin. (This neglects the effect of the nuclear spin; for a complete discussion, see H. Kopfermann, *Nuclear Moments*, Academic Press, 1958, pp. 42–51.) Problem 10.26c corresponds to setting up a Stern–Gerlach apparatus with the field in the z direction and then allowing the $+\frac{1}{2}\hbar$ beam from this apparatus to enter a Stern–Gerlach apparatus that has the field in the x direction.
- 10.27** (a) Let Y_{jm} be the *normalized* eigenfunction of the generalized angular-momentum operators (Section 5.4) $\hat{M}^2$ and $\hat{M}_z$:

$$\hat{M}^2 Y_{jm} = j(j+1)\hbar^2 Y_{jm}, \quad \hat{M}_z Y_{jm} = m\hbar Y_{jm}$$

From Section 5.4, the effect of $\hat{M}_+$ on Y_{jm} is to increase the $\hat{M}_z$ eigenvalue by $\hbar$:

$$\hat{M}_+ Y_{jm} = A Y_{j,m+1}$$

where A is a constant. Use the procedure that led to (10.69) and (10.70) to show that

$$\hat{M}_+ Y_{jm} = [j(j+1) - m(m+1)]^{1/2} \hbar Y_{j,m+1} \quad (10.74)$$

$$\hat{M}_- Y_{jm} = [j(j+1) - m(m-1)]^{1/2} \hbar Y_{j,m-1} \quad (10.75)$$

(b) Show that (10.74) and (10.75) are consistent with (10.69) and (10.70). (c) With $\mathbf{M} = \mathbf{L}$, the function Y_{jm} is the spherical harmonic $Y_l^m(\theta, \phi)$. Verify (10.74) directly for $l = 2, m = -1$.

[Actually, for consistency with the phase choice of Eqs. (10.74) and (10.75), we must add the factor $(-i)^{m+|m|}$ to the definition (5.147) of the spherical harmonics; this introduces a minus sign for odd positive values of m .]

- 10.28** The eigenfunctions α and β of the Hermitian operator $\hat{S}_z$ form a complete, orthonormal set, and any one-electron spin function can be written as $c_1\alpha + c_2\beta$. We saw in Section 7.10 that functions can be represented by column vectors and operators by square matrices. For the representation that uses α and β as the basis functions, (a) write down the column vectors that correspond to the functions α , β , and $c_1\alpha + c_2\beta$; (b) use the results of Section 10.10 to show that the matrices that correspond to $\hat{S}_x$, $\hat{S}_y$, $\hat{S}_z$, and $\hat{S}^2$ are

$$\mathbf{S}_x = \frac{1}{2}\hbar \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \mathbf{S}_y = \frac{1}{2}\hbar \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \mathbf{S}_z = \frac{1}{2}\hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \mathbf{S}^2 = \frac{1}{4}\hbar^2 \begin{pmatrix} 3 & 0 \\ 0 & 3 \end{pmatrix}$$

(c) Verify that the matrices in (b) obey $\mathbf{S}_x\mathbf{S}_y - \mathbf{S}_y\mathbf{S}_x = i\hbar\mathbf{S}_z$ [Eq. (10.2)]. (d) Find the eigenvalues and eigenvectors of the $\mathbf{S}_x$ matrix. Compare the results with those of Prob. 10.26.

- 10.29** True or false? (a) The allowed values of the quantum number s of an electron are $-\frac{1}{2}$ and $\frac{1}{2}$. (b) The magnitude of the z component S_z of the spin angular momentum of a particle with nonzero spin must always be less than the magnitude $|\mathbf{S}|$ of the spin angular momentum. (c) For every two-electron system, the spin factor in the wave function must be antisymmetric. (d) For every system of several fermions, interchange of the labels of two fermions in the wave function must multiply the wave function by -1 . (e) An atom of ^{79}Br is a boson. (f) An atom of ^3He is a fermion. (g) The magnetic moment of a nucleus is much less than the magnetic moment of an electron. (h) For a proton in an external magnetic field that points in the positive z direction, the $M_I = -\frac{1}{2}$ state is higher in energy than the $M_I = \frac{1}{2}$ state.