Chapter 8

Identical Particles

Up to this point, we have dealt mainly with the motion of a single particle. Now we want to examine how to describe systems with *many particles*. We shall focus on systems of *identical* particles and examine how to construct their wave functions.

8.1 Many-Particle Systems

Most physical systems—nucleons, nuclei, atoms, molecules, solids, fluids, gases, etc.—involve many particles. They are known as *many-particle* or *many-body* systems. While atomic, nuclear, and subnuclear systems involve intermediate numbers of particles ($\sim$ 2 to 300), solids, fluids, and gases are truly many-body systems, since they involve very large numbers of particles ($\sim 10^{23}$).

8.1.1 Schrödinger Equation

How does one describe the dynamics of a system of N particles? This description can be obtained from a generalization of the dynamics of a single particle. The state of a system of N spinless particles (we ignore their spin for the moment) is described by a wave function $\Psi(\vec{r}_1, \vec{r}_2, \ldots \vec{r}_N, t)$, where $|\Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, t)|^2 d^3r_1\, d^3r_2 \cdots d^3r_N$ represents the probability at time t of finding particle 1 in the volume element d^3r_1 centered about $\vec{r}_1$, particle 2 in the volume d^3r_2 about $\vec{r}_2$, $\ldots$, and particle N in the volume d^3r_N about $\vec{r}_N$. The normalization condition of the state is given by

$$\int d^3r_1 \int d^3r_2 \cdots \int |\Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, t)|^2 d^3r_N = 1. \tag{8.1}$$

The wave function Ψ evolves in time according to the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, t) = \hat{H} \Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, t). \tag{8.2}$$

The form of $\hat{H}$ is obtained by generalizing the one-particle Hamiltonian $\vec{P}^2/(2m) + \vec{V}(\vec{r})$ to N

particles:

$$\hat{H} = \sum_{j=1}^{N} \frac{\hat{\vec{P}}_j^2}{2m_j} + \hat{V}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, t) = -\sum_{j=1}^{N} \frac{\hbar^2}{2m_j} \nabla_j^2 + \hat{V}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, t), \tag{8.3}$$

where m_j and $\hat{\vec{P}}_j$ are the mass and the momentum of the jth particle and $\hat{V}$ is the operator corresponding to the total potential energy ($\hat{V}$ accounts for all forms of interactions—internal and external—the mutual interactions between the various particles of the system and for the interactions of the particles with the outside world).

The formalism of quantum mechanics for an N-particle system can be, in principle, inferred from that of a single particle. Operators corresponding to different particles commute; for instance, the commutation relations between the position and momentum operators are

$$[\hat{X}_j,\ \hat{P}_{x_k}] = i\hbar\delta_{j,k}, \qquad [\hat{X}_j,\ \hat{X}_k] = [\hat{P}_{x_j},\ \hat{P}_{x_k}] = 0 \qquad (j, k = 1, 2, 3, \ldots, N), \tag{8.4}$$

where $\hat{X}_j$ is the x-position operator of the jth particle, and $\hat{P}_{x_k}$ the x-momentum operator of the kth particle; similar relations can be obtained for the y and z components.

Stationary states

In the case where the potential $\hat{V}$ is *time independent*, the solutions of (8.2) are given by *stationary* states

$$\Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, t) = \psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)\, e^{-iEt/\hbar}, \tag{8.5}$$

where E is the total energy of the system and ψ is the solution to the time-independent Schrödinger equation $\hat{H}\psi = E\psi$, i.e.,

$$\left[-\sum_{j=1}^{N} \frac{\hbar^2}{2m_j} \vec{\nabla}_j^2 + V(\vec{r}_1, \ldots, \vec{r}_N) \right] \psi(\vec{r}_1, \vec{r}_2,\ \ldots, \vec{r}_N) = E\ \psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N). \tag{8.6}$$

The properties of stationary states for a single particle also apply to N-particle systems. For instance, the probability density $\langle \psi \mid \psi \rangle$, the probability current density $\vec{j}$, and the expectation values of time-independent operators are conserved, since they do not depend on time:

$$\langle \Psi \mid \hat{A} \mid \Psi \rangle = \langle \psi \mid \hat{A} \mid \psi \rangle = \int d^3r_1 \int d^3r_2 \cdots \int \psi^*(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \hat{A} \psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)\, d^3r_N. \tag{8.7}$$

In particular, the energy of a stationary state is conserved.

Multielectron atoms

As an illustration, let us consider an atom with Z electrons. If $\vec{R}$ is used to represent the position of the center of mass of the nucleus, the wave function of the atom depends on $3(Z+1)$ coordinates $\psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_Z, \vec{R})$, where $\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_Z$ are the position vectors of the Z electrons. The time-independent Schrödinger equation for this atom, neglecting contributions from the spin–orbit correction, the relativistic correction, and similar terms, is given by

$$\begin{aligned} &\left[-\frac{\hbar^2}{2m_e} \sum_{i=1}^{Z} \vec{\nabla}_{r_i}^2 - \frac{\hbar^2}{2M} \vec{\nabla}_R^2 - \sum_{i=1}^{Z} \frac{Z e^2}{|\vec{r}_i - \vec{R}|} + \sum_{i>j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \right] \psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_Z, \vec{R}) \\ &\qquad = E\psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_Z, \vec{R}), \end{aligned} \tag{8.8}$$

where M is the mass of the nucleus and $-\hbar^2\vec{\nabla}_R^2/2M$ is its kinetic energy operator. The term $-\sum_{i=1}^{Z} Ze^2/|\vec{r}_i - \vec{R}|$ represents the attractive Coulomb interaction of each electron with the nucleus and $\sum_{i>j} e^2/|\vec{r}_i - \vec{r}_j|$ is the repulsive Coulomb interaction between the ith and the jth electrons; $|\vec{r}_i - \vec{r}_j|$ is the distance separating them. As these (Coulomb) interactions are independent of time, the states of atoms are stationary.

We should note that the Schrödinger equations (8.3), (8.6), and (8.8) are all many-particle differential equations. As these equations cannot be separated into one-body equations, it is difficult, if not impossible, to solve them. For the important case where the N particles of the system do not interact—this is referred to as an *independent particle system*—the Schrödinger equation can be trivially reduced to N one-particle equations (Section 8.1.3); we have seen how to solve these equations exactly (Chapters 4 and 6) and approximately (Chapters 9 and 10).

8.1.2 Interchange Symmetry

Although the exact eigenstates of the many-body Hamiltonian (8.3) are generally impossible to obtain, we can still infer some of their properties by means of symmetry schemes. Let ξ_i represent the coordinates (position $\vec{r}_i$, spin $\vec{s}_i$, and any other internal degrees of freedom such as isospin, color, flavor) of the ith particle and let $\psi(\xi_1, \xi_2, \ldots, \xi_N)$ designate the wave function of the N-particle system.

We define a *permutation operator* (also called *exchange operator*) $\hat{P}_{ij}$ as an operator that, when acting on an N-particle wave function $\psi(\xi_1, \ldots, \xi_i, \ldots, \xi_j, \ldots, \xi_N)$, interchanges the ith and the jth particles

$$\hat{P}_{ij}\psi(\xi_1, \ldots, \xi_i, \ldots, \xi_j, \ldots \xi_N) = \psi(\xi_1, \ldots, \xi_j, \ldots, \xi_i, \ldots, \xi_N); \tag{8.9}$$

i and j are arbitrary ($i,\ j = 1, 2, \cdots, N$). Since

$$\begin{aligned} \hat{P}_{ji}\psi(\xi_1, \ldots, \xi_i, \ldots, \xi_j, \ldots \xi_N) &= \psi(\xi_1, \ldots, \xi_j, \ldots, \xi_i, \ldots, \xi_N) \\ &= \hat{P}_{ij}\psi(\xi_1, \ldots, \xi_i, \ldots, \xi_j, \ldots \xi_N), \end{aligned} \tag{8.10}$$

we have $\hat{P}_{ij} = \hat{P}_{ji}$. In general, permutation operators do not commute:

$$\hat{P}_{ij}\hat{P}_{kl} \neq \hat{P}_{kl}\hat{P}_{ij} \qquad \text{or} \qquad [\hat{P}_{ij}, \hat{P}_{kl}] \neq 0 \qquad (ij \neq kl). \tag{8.11}$$

For instance, in the case of a four-particle state $\psi(\xi_1, \xi_2, \xi_3, \xi_4) = (3\xi_4/\xi_2\xi_3)e^{-i\xi_1}$, we have

$$\hat{P}_{12}\hat{P}_{14}\psi(\xi_1, \xi_2, \xi_3, \xi_4) = \hat{P}_{12}\psi(\xi_4, \xi_2, \xi_3, \xi_1) = \psi(\xi_2, \xi_4, \xi_3, \xi_1) = \frac{3\xi_1}{\xi_4\xi_3}e^{-i\xi_2}, \tag{8.12}$$

$$\hat{P}_{14}\hat{P}_{12}\psi(\xi_1, \xi_2, \xi_3, \xi_4) = \hat{P}_{14}\psi(\xi_2, \xi_1, \xi_3, \xi_4) = \psi(\xi_4, \xi_1, \xi_3, \xi_2) = \frac{3\xi_2}{\xi_1\xi_3}e^{-i\xi_4}. \tag{8.13}$$

Since two successive applications of $\hat{P}_{ij}$ leave the wave function unchanged,

$$\begin{aligned} \hat{P}_{ij}^2\psi(\xi_1, \ldots, \xi_i, \ldots, \xi_j, \ldots, \xi_N) &= \hat{P}_{ij}\psi(\xi_1, \ldots, \xi_j, \ldots, \xi_i, \ldots, \xi_N) \\ &= \psi(\xi_1, \ldots, \xi_i, \ldots, \xi_j, \ldots, \xi_N), \end{aligned} \tag{8.14}$$

we have $\hat{P}_{ij}^2 = 1$; hence $\hat{P}_{ij}$ has two eigenvalues ± 1:

$$\hat{P}_{ij}\psi(\xi_1, \ldots, \xi_i, \ldots, \xi_j, \ldots, \xi_N) = \pm\psi(\xi_1, \ldots, \xi_i, \ldots, \xi_j, \ldots \xi_N). \tag{8.15}$$

The wave functions corresponding to the eigenvalue $+1$ are *symmetric* and those corresponding to -1 are *antisymmetric* with respect to the interchange of the pair $(i,\ j)$. Denoting these functions by ψ_s and ψ_a, respectively, we have

$$\begin{aligned}\psi_s(\xi_1,\ldots,\xi_i,\ldots,\xi_j,\ldots,\xi_N) &= \psi_s(\xi_1,\ldots,\xi_j,\ldots,\xi_i,\ldots,\xi_N), &(8.16)\\ \psi_a(\xi_1,\ldots,\xi_i,\ldots,\xi_j,\ldots,\xi_N) &= -\psi_a(\xi_1,\ldots,\xi_j,\ldots,\xi_i,\ldots,\xi_N). &(8.17)\end{aligned}$$

Example 8.1

Specify the symmetry of the following functions:

(a) $\psi(x_1,x_2)=4(x_1-x_2)^2+\frac{10}{x_1^2+x_2^2}$,

(b) $\phi(x_1,x_2)=-\frac{3(x_1-x_2)}{2(x_1-x_2)^2+7}$,

(c) $\chi(x_1,x_2,x_3)=6x_1x_2x_3+\frac{x_1^2+x_2^2+x_3^2-1}{2x_1^3+2x_2^3+2x_3^3+5}$,

(d) $\Phi(x_1,x_2)=\frac{1}{x_2+3}e^{-|x_1|}$.

Solution

(a) The function $\psi(x_1,x_2)$ is symmetric, since $\psi(x_2,x_1)=\psi(x_1,x_2)$.

(b) The function $\phi(x_1,x_2)$ is antisymmetric, since $\phi(x_2,x_1)=-\phi(x_1,x_2)$, and ϕ is zero when $x_1=x_2$: $\phi(x_1,x_1)=0$.

(c) The function $\chi(x_1,x_2,x_3)$ is symmetric because

$$\begin{aligned}\chi(x_1,x_2,x_3) &= \chi(x_1,x_3,x_2)=\chi(x_2,x_1,x_3)=\chi(x_2,x_3,x_1)\\ &= \chi(x_3,x_1,x_2)=\chi(x_3,x_2,x_1). &(8.18)\end{aligned}$$

(d) The function $\Phi(x_2,x_1)$ is neither symmetric nor antisymmetric, since $\Phi(x_2,x_1)=\frac{1}{x_1+3}e^{-|x_2|}\neq\pm\Phi(x_1,x_2)$.

8.1.3 Systems of Distinguishable Noninteracting Particles

For a system of N noninteracting particles that are distinguishable—each particle has a different mass m_i and experiences a different potential $\hat{V}_i(\xi_i)$—the potential $\hat{V}$ is given by

$$\hat{V}(\xi_1,\xi_2,\ldots,\xi_N)=\sum_{i=1}^{N}\hat{V}_i(\xi_i) \tag{8.19}$$

and the Hamiltonian of this system of N independent particles by

$$\hat{H}=\sum_{i=1}^{N}\hat{H}_i=\sum_{i=1}^{N}\left[-\frac{\hbar^2}{2m_i}\nabla_i^2+\hat{V}_i(\xi_i)\right], \tag{8.20}$$

where $\hat{H}_i=-\hbar^2\nabla_i^2/2m_i+\hat{V}_i(\xi_i)$ is the Hamiltonian of the ith particle, known as the single particle Hamiltonian. The Hamiltonians of different particles commute $[\hat{H}_i,\hat{H}_j]=0$, since $[\hat{X}_i,\ \hat{X}_j]=[\hat{P}_i,\ \hat{P}_j]=0$.

The Schrödinger equation of the N-particle system

$$\hat{H}\psi_{n_1,n_2,\cdots,n_N}(\xi_1,\xi_2,\cdots,\xi_N) = E_{n_1,n_2,\cdots,n_N}\psi_{n_1,n_2,\cdots,n_N}(\xi_1,\xi_2,\cdots,\xi_N) \tag{8.21}$$

separates into N one-particle equations

$$\left[-\frac{\hbar^2}{2m_i}\nabla_i^2 + \hat{V}_i(\xi_i)\right]\psi_{n_i}(\xi_i) = \varepsilon_{n_i}\psi_{n_i}(\xi_i), \tag{8.22}$$

with

$$E_{n_1,n_2,\cdots,n_N} = \varepsilon_{n_1} + \varepsilon_{n_2} + \cdots \varepsilon_{n_N} = \sum_{i=1}^{N}\varepsilon_{n_i} \tag{8.23}$$

and

$$\psi_{n_1,n_2,\cdots,n_N}(\xi_1,\xi_2,\cdots,\xi_N) = \psi_{n_1}(\xi_1)\psi_{n_2}(\xi_2)\cdots\psi_{n_N}(\xi_N) = \prod_{i=1}^{N}\psi_{n_i}(\xi_i). \tag{8.24}$$

We see that, when the interactions are neglected, the N-particle Schrödinger equation separates into N one-particle Schrödinger equations. The solutions of these equations yield the single-particle energies ε_{n_i} and states $\psi_{n_i}(\xi_i)$; the single-particle states are also known as the *orbitals*. The total energy is the sum of the single-particle energies and the total wave function is the product of the orbitals. The number n_i designates the set of all quantum numbers of the ith particle. Obviously, each particle requires one, two, or three quantum numbers for its full description, depending on whether the particles are moving in a one-, two-, or three-dimensional space; if the spin were considered, we would need to add another quantum number. For instance, if the particles moved in a one-dimensional harmonic oscillator, n_i would designate the occupation number of the ith particle. But if the particles were the electrons of an atom, then n_i would stand for four quantum numbers: the radial, orbital, magnetic, and spin quantum numbers $N_i l_i m_{l_i} m_{s_i}$.

Example 8.2

Find the energy levels and wave functions of a system of four distinguishable spinless particles placed in an infinite potential well of size a. Use this result to infer the energy and the wave function of the ground state and the first excited state.

Solution

Each particle moves in a potential which is defined by $\hat{V}_i(x_i) = 0$ for $0 \le x_i \le a$ and $\hat{V}_i(x_i) = \infty$ for the other values of x_i. In this case the Schrödinger equation of the four-particle system:

$$\sum_{i=1}^{4}\left[-\frac{\hbar^2}{2m_i}\frac{d^2}{dx_i^2}\right]\psi_{n_1,n_2,n_3,n_4}(x_1,x_2,x_3,x_4) = E_{n_1,n_2,n_3,n_4}\psi_{n_1,n_2,n_3,n_4}(x_1,x_2,x_3,x_4), \tag{8.25}$$

separates into four one-particle equations

$$-\frac{\hbar^2}{2m_i}\frac{d^2\psi_{n_i}(x_i)}{dx_i^2} = \varepsilon_{n_i}\psi_{n_i}(x_i), \qquad i = 1,2,3,4, \tag{8.26}$$

with

$$\varepsilon_{n_i} = \frac{\hbar^2\pi^2 n_i^2}{2m_i a^2}, \qquad \psi_{n_i}(x_i) = \sqrt{\frac{2}{a}}\sin\left(\frac{n_i\pi}{a}x_i\right). \tag{8.27}$$

The total energy and wave function are given by

$$E_{n_1,n_2,n_3,n_4} = \frac{\hbar^2\pi^2}{2a^2}\left(\frac{n_1^2}{m_1}+\frac{n_2^2}{m_2}+\frac{n_3^2}{m_3}+\frac{n_4^2}{m_4}\right), \tag{8.28}$$

$$\psi_{n_1,n_2,n_3,n_4}(x_1,x_2,x_3,x_4) = \frac{4}{a^2}\sin\left(\frac{n_1\pi}{a}x_1\right)\sin\left(\frac{n_2\pi}{a}x_2\right)\sin\left(\frac{n_3\pi}{a}x_3\right)\sin\left(\frac{n_4\pi}{a}x_4\right). \tag{8.29}$$

The ground state corresponds to the case where all four particles occupy their respective ground state orbitals, $n_1 = n_2 = n_3 = n_4 = 1$. The ground state energy and wave function are thus given by

$$E_{1,1,1,1} = \frac{\hbar^2\pi^2}{2a^2}\left(\frac{1}{m_1}+\frac{1}{m_2}+\frac{1}{m_3}+\frac{1}{m_4}\right), \tag{8.30}$$

$$\psi_{1,1,1,1}(x_1,x_2,x_3,x_4) = \frac{4}{a^2}\sin\left(\frac{\pi}{a}x_1\right)\sin\left(\frac{\pi}{a}x_2\right)\sin\left(\frac{\pi}{a}x_3\right)\sin\left(\frac{\pi}{a}x_4\right). \tag{8.31}$$

The first excited state is somewhat tricky. Since it corresponds to the next higher energy level of the system, it must correspond to the case where the particle having the largest mass occupies its first excited state while the other three particles remain in their respective ground states. For argument's sake, if the third particle were the most massive, the first excited state would correspond to the configuration $n_1 = n_2 = n_4 = 1$ and $n_3 = 2$; the energy and wave function of the first excited state would then be given by

$$E_{1,1,2,1} = \frac{\hbar^2\pi^2}{2a^2}\left(\frac{1}{m_1}+\frac{1}{m_2}+\frac{4}{m_3}+\frac{1}{m_4}\right), \tag{8.32}$$

$$\psi_{1,1,2,1}(x_1,x_2,x_3,x_4) = \frac{4}{a^2}\sin\left(\frac{\pi}{a}x_1\right)\sin\left(\frac{\pi}{a}x_2\right)\sin\left(\frac{2\pi}{a}x_3\right)\sin\left(\frac{\pi}{a}x_4\right). \tag{8.33}$$

Continuing in this way, we can obtain the entire energy spectrum of this system.

8.2 Systems of Identical Particles

8.2.1 Identical Particles in Classical and Quantum Mechanics

In classical mechanics, when a system is made of identical particles, it is possible to identify and distinguish each particle from the others. That is, although all particles have the same physical properties, we can "tag" each classical particle and follow its motion along a path. For instance, each particle can be colored differently from the rest; hence we can follow the trajectory of each particle separately at each time. *Identical classical particles, therefore, do not lose their identity; they are distinguishable.*

In quantum mechanics, however, identical particles are truly indistinguishable. The underlying basis for this is twofold. First, to describe a particle, we cannot specify more than

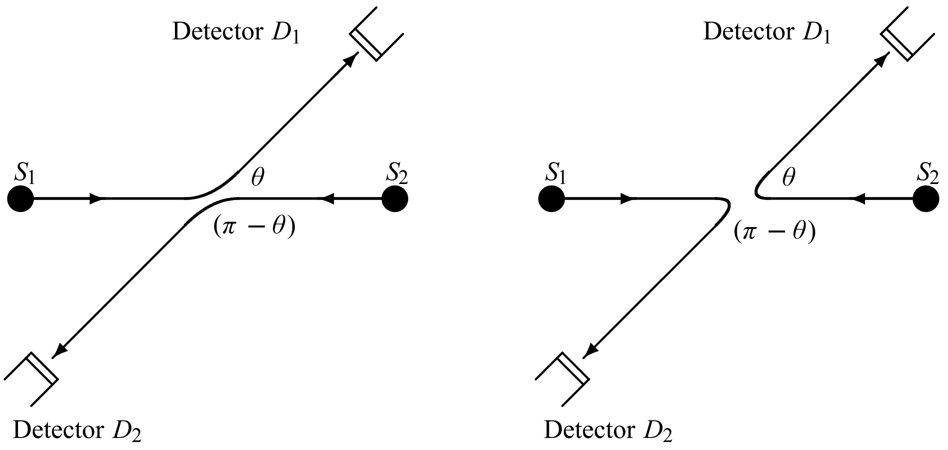

Figure 8.1 When scattering two *identical* particles in the center of mass frame, it is impossible to forcast with certitude whether the particles scatter according to the first process or to the second. For instance, we cannot tell whether the particle fired from source S_1 will make it to detector D_1 or to D_2.

a complete set of commuting observables. In particular, there exists no mechanism to tag the particles as in classical mechanics. Second, due to the uncertainty principle, the concept of the path of a particle becomes meaningless. Even if the position of a particle is exactly determined at a given time, it is not possible to specify its coordinates at the next instant. Thus, *identical particles lose their identity (individuality) in quantum mechanics*.

To illustrate this, consider an experiment in which we scatter two identical particles. As displayed in Figure 8.1, after particles 1 and 2 (fired from the sources S_1 and S_2) have scattered, it is impossible to distinguish between the first and the second outcomes. That is, we cannot determine experimentally the identity of the particles that are collected by each detector. For instance, we can in no way tell whether it is particle 1 or particle 2 that has reached detector D_1. We can only say that a particle has reached detector D_1 and another has made it to D_2, but have no information on their respective identities. There exists no experimental mechanism that allows us to follow the motion of each particle from the time it is fired out of the source till it reaches the detector. This experiment shows that *the individuality of a microscopic particle is lost the moment it is mixed with other similar particles*.

Having discussed the indistinguishability concept on a two-particle system, let us now study this concept on larger systems. For this, consider a system of N *identical* particles whose wave function is $\psi(\xi_1, \xi_2, \ldots, \xi_N)$.

The moment these N particles are mixed together, no experiment can determine which particle has the coordinates ξ_1, or which one has ξ_2, and so on. It is impossible to specify experimentally the identity of the particle which is located at ξ_1, or that located at ξ_2, and so on. The only measurements we can perform are those that specify the probability for a certain particle to be located at ξ_1, another at ξ_2, and so on, but we can never make a distinction as to which particle is which.

As a result, the probability must remain unchanged by an interchange of the particles. For instance, an interchange of particles i and j will leave the probability density unaffected:

$$\left|\psi(\xi_1, \xi_2, \ldots, \xi_i, \ldots, \xi_j, \ldots, \xi_N)\right|^2 = \left|\psi(\xi_1, \xi_2, \ldots, \xi_j, \ldots, \xi_i, \ldots, \xi_N)\right|^2; \qquad (8.34)$$

hence we have

$$\psi(\xi_1, \xi_2, \ldots, \xi_i, \ldots, \xi_j, \ldots, \xi_N) = \pm\psi(\xi_1, \xi_2, \ldots, \xi_j, \ldots, \xi_i, \ldots, \xi_N). \tag{8.35}$$

This means that the wave function of a system of N identical particles is either symmetric or antisymmetric under the interchange of a pair of particles. We will deal with the implications of this result in Section 8.2.3. We will see that the sign in (8.35) is related to the spin of the particles: the negative sign corresponds to particles with half-odd-integral spin and the positive sign corresponds to particles with integral spin; that is, the wave functions of particles with integral spins are symmetric and the wave functions of particles with half-odd-integral spins are antisymmetric. In fact, experimental observations show that, in nature, particles come in two classes:

- Particles with *integral spin*, $S_i = 0,\ 1\hbar,\ 2\hbar,\ 3\hbar, \ldots$, such as photons, pions, alpha particles. These particles are called *bosons*.
- Particles with *half-odd-integral spin*, $S_i = \hbar/2, 3\hbar/2, 5\hbar/2, 7\hbar/2, \ldots$, such as quarks, electrons, positrons, protons, neutrons. These particles are called *fermions*.

That is, particles occurring in nature are either bosons or fermions.

Before elaborating more on the properties of bosons and fermions, let us present a brief outline on the interchange (permutation) symmetry.

8.2.2 Exchange Degeneracy

How does the interchange symmetry affect operators such as the Hamiltonian? Since the Coulomb potential, which results from electron–electron and electron–nucleus interactions,

$$V(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots, \vec{r}_Z) = -\sum_{i=1}^{Z} \frac{Z\,e^2}{|\vec{r}_i - \vec{R}|} + \sum_{i>j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}, \tag{8.36}$$

is invariant under the permutation of any pair of electrons, the Hamiltonian (8.8) is also invariant under such permutations. This symmetry also applies to the orbital, spin, and angular momenta of an atom. We may thus use this symmetry to introduce another definition of the *identicalness* of particles. *The N particles of a system are said to be identical if the various observables of the system* (such as the Hamiltonian $\hat{H}$, the angular momenta, and so on) *are symmetrical when any two particles are interchanged.* If these operators were not symmetric under particle interchange, the particles would be distinguishable.

The invariance of the Hamiltonian under particle interchanges is not without physical implications: the eigenvalues of $\hat{H}$ are *degenerate*. The wave functions corresponding to all possible electron permutations have the same energy E: $\hat{H}\psi = E\psi$. This is known as the *exchange degeneracy*. For instance, the degeneracy associated with a system of two identical particles is equal to 2, since $\psi(\xi_1, \xi_2)$ and $\psi(\xi_2, \xi_1)$ correspond to the same energy E.

So the Hamiltonian of a system of N identical particles ($m_i = m$) is completely symmetric with respect to the coordinates of the particles:

$$\begin{aligned} \hat{H}(\xi_1, \ldots, \xi_i, \ldots, \xi_j, \ldots, \xi_N) &= \sum_{k=1}^{N} \frac{\vec{P}_k^2}{2m} + \hat{V}(\xi_1, \ldots, \xi_i, \ldots, \xi_j, \ldots, \xi_N) \\ &= \hat{H}(\xi_1, \ldots, \xi_j, \ldots, \xi_i, \ldots, \xi_N), \end{aligned} \tag{8.37}$$

because $\hat{V}$ is invariant under the permutation of any pair of particles $i \longleftrightarrow j$:

$$\hat{V}(\xi_1, \ldots, \xi_i, \ldots, \xi_j, \ldots, \xi_N) = \hat{V}(\xi_1, \ldots, \xi_j, \ldots, \xi_i, \ldots, \xi_N). \tag{8.38}$$

This property can also be ascertained by showing that $\hat{H}$ commutes with the particle interchange operator $\hat{P}_{ij}$. If ψ is eigenstate to $\hat{H}$ with eigenvalue E, we can write

$$\begin{aligned}\hat{H}\hat{P}_{ij}\psi(\xi_1, \ldots, \xi_i, \ldots, \xi_j, \ldots, \xi_N) &= \hat{H}\psi(\xi_1, \ldots, \xi_j, \ldots, \xi_i, \ldots, \xi_N)\\ &= E\psi(\xi_1, \ldots, \xi_j, \ldots, \xi_i, \ldots, \xi_N) = E\hat{P}_{ij}\psi(\xi_1, \ldots, \xi_i, \ldots, \xi_j, \ldots, \xi_N)\\ &= \hat{P}_{ij}E\psi(\xi_1, \ldots, \xi_i, \ldots, \xi_j, \ldots, \xi_N) = \hat{P}_{ij}\hat{H}\psi(\xi_1, \ldots, \xi_i, \ldots, \xi_j, \ldots, \xi_N)\end{aligned} \tag{8.39}$$

or

$$[\hat{H}, \hat{P}_{ij}] = 0. \tag{8.40}$$

Therefore, $\hat{P}_{ij}$ is a *constant of the motion*. That is, if we start with a wave function that is symmetric (antisymmetric), it will remain so for all subsequent times. Moreover, since $\hat{P}_{ij}$ and $\hat{H}$ commute, they possess a complete set of functions that are joint eigenstates of both. As shown in (8.15) to (8.17), these eigenstates have definite parity, either symmetric or antisymmetric.

8.2.3 Symmetrization Postulate

We have shown in (8.35) that the wave function of a system of N identical particles is either symmetric or antisymmetric under the interchange of any pair of particles:

$$\psi(\xi_1, \xi_2, \ldots, \xi_i, \ldots, \xi_j, \ldots, \xi_N) = \pm\psi(\xi_1, \xi_2, \ldots, \xi_j, \ldots, \xi_i, \ldots, \xi_N). \tag{8.41}$$

This result, which turns out to be supported by experimental evidence, is the very essence of the *symmetrization postulate* which stipulates that, in nature, the states of systems containing N identical particles are *either totally symmetric or totally antisymmetric* under the interchange of any pair of particles and that states with mixed symmetry do not exist. Besides that, this postulate states two more things:

- Particles with integral spins, or bosons, have symmetric states.
- Particles with half-odd-integral spins, or fermions, have antisymmetric states.

Fermions are said to obey *Fermi–Dirac statistics* and bosons to obey *Bose–Einstein statistics*. So the wave function of a system of identical bosons is totally symmetric and the wave function of a system of identical fermions is totally antisymmetric.

Composite particles

The foregoing discussion pertains to identical particles that are “simple” or elementary such as quarks, electrons, positrons, muons, and so on. Let us now discuss the symmetry of systems of identical *composite* “particles” where each particle is composed of two or more identical elementary particles. For instance, alpha particles, which consist of nuclei that are composed of two neutrons and two protons each, are a typical example of composite particles. A system of N hydrogen atoms can also be viewed as a system of identical composite particles where each “particle” (atom) consists of a proton and an electron. Protons, neutrons, pions, etc., are themselves composite particles, because protons and neutrons consist of three quarks and pions consist of two. *Quarks* are elementary spin $\frac{1}{2}$ particles.

Composite particles have spin. The spin of each composite particle can be obtained by adding the spins of its constituents. If the total spin of the composite particle is half-odd-integer, this particle behaves like a fermion, and hence it obeys Fermi–Dirac statistics. If, on the other hand, its resultant spin is integer, it behaves like a boson and obeys Bose–Einstein statistics. In general, if the composite particle has an odd number of fermions; it is then a fermion, otherwise it is a boson. For instance, nucleons are fermions because they consist of three quarks; mesons are bosons because they consist of two quarks. For another illustrative example, let us consider the isotopes ^{4}He and ^{3}He of the helium atom: ^{4}He, which is called an alpha particle, is a boson for it consists of four nucleons (two protons and two neutrons), while ^{3}He is a fermion since it consists of three nucleons (one neutron and two protons). The hydrogen atom consists of two fermions (an electron and a proton), so it is a boson.

8.2.4 Constructing Symmetric and Antisymmetric Functions

Since the wave functions of systems of identical particles are either totally symmetric or totally antisymmetric, it is appropriate to study the formalism of how to construct wave functions that are totally symmetric or totally antisymmetric starting from asymmetric functions. For simplicity, consider first a system of two identical particles. Starting from any normalized asymmetric wave function $\psi(\xi_1, \xi_2)$, we can construct symmetric wave functions $\psi_s(\xi_1, \xi_2)$ as

$$\psi_s(\xi_1, \xi_2) = \frac{1}{\sqrt{2}}\Big[\, \psi(\xi_1,\ \xi_2) + \psi(\xi_2,\ \xi_1)\Big] \tag{8.42}$$

and antisymmetric wave functions $\psi_a(\xi_1, \xi_2)$ as

$$\psi_a(\xi_1,\ \xi_2) = \frac{1}{\sqrt{2}}\Big[\, \psi(\xi_1,\ \xi_2) - \psi(\xi_2,\ \xi_1)\Big], \tag{8.43}$$

where $1/\sqrt{2}$ is a normalization factor.

Similarly, for a system of three identical particles, we can construct ψ_s and ψ_a from an asymmetric function ψ as follows:

$$\begin{aligned} \psi_s(\xi_1, \xi_2, \xi_3) &= \frac{1}{\sqrt{6}}\Big[\, \psi(\xi_1, \xi_2, \xi_3) + \psi(\xi_1, \xi_3, \xi_2) + \psi(\xi_2, \xi_3, \xi_1) \\ &\qquad + \psi(\xi_2, \xi_1, \xi_3) + \psi(\xi_3, \xi_1, \xi_2) + \psi(\xi_3, \xi_2, \xi_1)\Big], \qquad (8.44) \\ \psi_a(\xi_1, \xi_2, \xi_3) &= \frac{1}{\sqrt{6}}\Big[\, \psi(\xi_1, \xi_2, \xi_3) - \psi(\xi_1, \xi_3, \xi_2) + \psi(\xi_2, \xi_3, \xi_1) \\ &\qquad - \psi(\xi_2, \xi_1, \xi_3) + \psi(\xi_3, \xi_1, \xi_2) - \psi(\xi_3, \xi_2, \xi_1)\Big]. \qquad (8.45) \end{aligned}$$

Continuing in this way, we can in principle construct symmetric and antisymmetric wave functions for any system of N identical particles.

8.2.5 Systems of Identical Noninteracting Particles

In the case of a system of N noninteracting identical particles, where all particles have equal mass $m_i = m$ and experience the same potential $\hat{V}_i(\xi_i) = \hat{V}(\xi_i)$, the Schrödinger equation of the system separates into N identical one-particle equations

$$\left[-\frac{\hbar^2}{2m}\nabla_i^2 + \hat{V}(\xi_i)\right]\psi_{n_i}(\xi_i) = \varepsilon_{n_i}\psi_{n_i}(\xi_i). \tag{8.46}$$

Whereas the energy is given, like the case of a system of N distinguishable particles, by a sum of the single-particle energies $E_{n_1,n_2,\ldots,n_N} = \sum_{i=1}^{N}\varepsilon_{n_i}$, the wave function can no longer be given by a simple product $\psi_{n_1,n_2,\ldots,n_N}(\xi_1,\xi_2,\ldots,\xi_N) = \prod_{i=1}^{N}\psi_{n_i}(\xi_i)$ for at least two reasons. First, if the wave function is given by such a product, it would imply that particle 1 is in the state ψ_{n_1}, particle 2 in the state ψ_{n_2}, ..., and particle N in the state ψ_{n_N}. This, of course, makes no sense since all we know is that one of the particles is in the state ψ_{n_1}, another in ψ_{n_2}, and so on; since the particles are identical, there is no way to tell which particle is in which state. If, however, the particles were distinguishable, then their total wave function would be given by such a product, as shown in (8.24). The second reason why the wave function of a system of identical particles cannot be given by $\prod_{i=1}^{N}\psi_{n_i}(\xi_i)$ has to do with the fact that such a product has, in general, no *definite* symmetry—a mandatory requirement for systems of N identical particles whose wave functions are either symmetric or antisymmetric. We can, however, extend the method of Section 8.2.4 to construct totally symmetric and totally antisymmetric wave functions from the single-particle states $\psi_{n_i}(\xi_i)$. For this, we are going to show how to construct symmetrized and antisymmetrized wave functions for systems of two, three, and N noninteracting identical particles.

8.2.5.1 Wave Function of Two-Particle Systems

By analogy with (8.42) and (8.43), we can construct the symmetric and antisymmetric wave functions for a system of two identical, noninteracting particles in terms of the single-particle wave functions as follows:

$$\psi_s(\xi_1,\xi_2) = \frac{1}{\sqrt{2}}\left[\psi_{n_1}(\xi_1)\psi_{n_2}(\xi_2) + \psi_{n_1}(\xi_2)\psi_{n_2}(\xi_1)\right], \tag{8.47}$$

$$\psi_a(\xi_1,\xi_2) = \frac{1}{\sqrt{2}}\left[\psi_{n_1}(\xi_1)\psi_{n_2}(\xi_2) - \psi_{n_1}(\xi_2)\psi_{n_2}(\xi_1)\right], \tag{8.48}$$

where we have supposed that $n_1 \neq n_2$. When $n_1 = n_2 = n$ the symmetric wave function is given by $\psi_s(\xi_1,\xi_2) = \psi_n(\xi_1)\psi_n(\xi_2)$ and the antisymmetric wave function is zero; we will deal later with the reason why $\psi_a(\xi_1,\xi_2) = 0$ whenever $n_1 = n_2$.

Note that we can rewrite ψ_s as

$$\boxed{\psi_s(\xi_1,\xi_2) = \frac{1}{\sqrt{2!}}\sum_P \hat{P}\psi_{n_1}(\xi_1)\psi_{n_2}(\xi_2),} \tag{8.49}$$

where $\hat{P}$ is the permutation operator and where the sum is over all possible permutations (here we have only two possible ones). Similarly, we can write ψ_a as

$$\psi_a(\xi_1,\xi_2) = \frac{1}{\sqrt{2!}}\sum_P (-1)^P \hat{P}\psi_{n_1}(\xi_1)\psi_{n_2}(\xi_2), \tag{8.50}$$

where $(-1)^P$ is equal to +1 for an even permutation (i.e., when we interchange both ξ_1 and ξ_2 and also n_1 and n_2) and equal to -1 for an odd permutation (i.e., when we permute ξ_1 and ξ_2 but not n_1, n_2, and vice versa). Note that we can rewrite ψ_a of (8.48) in the form of a determinant

$$\boxed{\psi_a(\xi_1, \xi_2) = \frac{1}{\sqrt{2!}} \begin{vmatrix} \psi_{n_1}(\xi_1) & \psi_{n_1}(\xi_2) \\ \psi_{n_2}(\xi_1) & \psi_{n_2}(\xi_2) \end{vmatrix}.} \tag{8.51}$$

8.2.5.2 Wave Function of Three-Particle Systems

For a system of three noninteracting identical particles, the symmetric wave function is given by

$$\psi_s(\xi_1, \xi_2, \xi_3) = \frac{1}{\sqrt{3!}} \sum_P \hat{P} \psi_{n_1}(\xi_1)\psi_{n_2}(\xi_2)\psi_{n_3}(\xi_3), \tag{8.52}$$

or by

$$\begin{aligned} \psi_s(\xi_1, \xi_2, \xi_3) = \frac{1}{\sqrt{3!}} \Big[& \psi_{n_1}(\xi_1)\psi_{n_2}(\xi_2)\psi_{n_3}(\xi_3) + \psi_{n_1}(\xi_1)\psi_{n_2}(\xi_3)\psi_{n_3}(\xi_2) \\ & + \psi_{n_1}(\xi_2)\psi_{n_2}(\xi_1)\psi_{n_3}(\xi_3) + \psi_{n_1}(\xi_2)\psi_{n_2}(\xi_3)\psi_{n_3}(\xi_1) \\ & + \psi_{n_1}(\xi_3)\psi_{n_2}(\xi_1)\psi_{n_3}(\xi_2) + \psi_{n_1}(\xi_3)\psi_{n_2}(\xi_2)\psi_{n_3}(\xi_1) \Big], \end{aligned} \tag{8.53}$$

and, when $n_1 \neq n_2 \neq n_3$, the antisymmetric wave function is given by

$$\psi_a(\xi_1, \xi_2, \xi_3) = \frac{1}{\sqrt{3!}} \sum_P (-1)^P \hat{P} \psi_{n_1}(\xi_1)\psi_{n_2}(\xi_2)\psi_{n_3}(\xi_3), \tag{8.54}$$

or, in the form of a determinant, by

$$\psi_a(\xi_1, \xi_2, \xi_3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_{n_1}(\xi_1) & \psi_{n_1}(\xi_2) & \psi_{n_1}(\xi_3) \\ \psi_{n_2}(\xi_1) & \psi_{n_2}(\xi_2) & \psi_{n_2}(\xi_3) \\ \psi_{n_3}(\xi_1) & \psi_{n_3}(\xi_2) & \psi_{n_3}(\xi_3) \end{vmatrix}. \tag{8.55}$$

If $n_1 = n_2 = n_3 = n$ we have $\psi_s(\xi_1, \xi_2, \xi_3) = \psi_n(\xi_1)\psi_n(\xi_2)\psi_n(\xi_3)$ and $\psi_a(\xi_1, \xi_2, \xi_3) = 0$.

8.2.5.3 Wave Function of Many-Particle Systems

We can generalize (8.52) and (8.55) and write the symmetric and antisymmetric wave functions for a system of N noninteracting identical particles as follows:

$$\psi_s(\xi_1, \xi_2, \ldots, \xi_N) = \frac{1}{\sqrt{N!}} \sum_P \hat{P} \psi_{n_1}(\xi_1)\psi_{n_2}(\xi_2)\cdots\psi_{n_N}(\xi_N), \tag{8.56}$$

$$\psi_a(\xi_1, \xi_2, \ldots, \xi_N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^P \psi_{n_1}(\xi_1)\psi_{n_2}(\xi_2)\cdots\psi_{n_N}(\xi_N), \tag{8.57}$$

or

$$\psi_a(\xi_1, \xi_2, \ldots, \xi_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{n_1}(\xi_1) & \psi_{n_1}(\xi_2) & \cdots & \psi_{n_1}(\xi_N) \\ \psi_{n_2}(\xi_1) & \psi_{n_2}(\xi_2) & \cdots & \psi_{n_2}(\xi_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_{n_N}(\xi_1) & \psi_{n_N}(\xi_2) & \cdots & \psi_{n_N}(\xi_N) \end{vmatrix}. \tag{8.58}$$

This $N \times N$ determinant, which involves one-particle states only, is known as the *Slater determinant*. An interchange of any pair of particles corresponds to an interchange of two columns of the determinant; this interchange introduces a change in the sign of the determinant. For even permutations we have $(-1)^P = 1$, and for odd permutations we have $(-1)^P = -1$.

The relations (8.56) and (8.58) are valid for the case where the numbers $n_1, n_2, \ldots, n_N$ are all different from one another. What happens if some, or all, of these numbers are equal? In the symmetric case, if $n_1 = n_2 = \ldots = n_N$ then ψ_s is given by

$$\psi_s(\xi_1, \xi_2, \ldots, \xi_N) = \prod_{i=1}^{N} \psi_n(\xi_i) = \psi_n(\xi_1)\psi_n(\xi_2)\cdots\psi_n(\xi_N). \tag{8.59}$$

When there is a multiplicity in the numbers $n_1, n_2, \ldots, n_N$ (i.e., when some of the numbers n_i occur more than once), we have to be careful and avoid double counting. For instance, if n_1 occurs N_1 times in the sequence $n_1, n_2, \ldots, n_N$, if n_2 occurs N_2 times, and so on, the symmetric wave function will be given by

$$\psi_s(\xi_1, \xi_2, \ldots, \xi_N) = \sqrt{\frac{N_1!N_2!\cdots N_N!}{N!}} \sum_P \hat{P}\psi_{n_1}(\xi_1)\psi_{n_2}(\xi_2)\cdots\psi_{n_N}(\xi_N); \tag{8.60}$$

the summation $\sum_P$ is taken only over permutations which lead to *distinct* terms and includes $N!/N_1!N_2!\cdots N_n!$ different terms. For example, in the case of a system of three independent, identical bosons where $n_1 = n_2 = n$ and $n_3 \neq n$, the multiplicity of n_1 is $N_1 = 2$; hence ψ_s is given by

$$\begin{aligned}\psi_s(\xi_1, \xi_2, \xi_3) &= \sqrt{\frac{2!}{3!}} \sum_P \hat{P}\psi_n(\xi_1)\psi_n(\xi_2)\psi_{n_3}(\xi_3) = \frac{1}{\sqrt{3}}\Big[\psi_n(\xi_1)\psi_n(\xi_2)\psi_{n_3}(\xi_3) \\ &\quad + \psi_n(\xi_1)\psi_{n_3}(\xi_2)\psi_n(\xi_3) + \psi_{n_3}(\xi_1)\psi_n(\xi_2)\psi_n(\xi_3)\Big].\end{aligned} \tag{8.61}$$

Unlike the symmetric case, the antisymmetric case is quite straightforward: if, among the numbers $n_1, n_2, \ldots, n_N$, only two are equal, the antisymmetric wave function vanishes. For instance, if $n_i = n_j$, the ith and jth rows of the determinant (8.58) will be identical; hence the determinant vanishes identically. Antisymmetric wave functions, therefore, are nonzero only for those cases where all the numbers $n_1, n_2, \ldots, n_N$ are different.

8.3 The Pauli Exclusion Principle

As mentioned above, if any two particles occupy the same single-particle state, the determinant (8.58), and hence the total wave function, will vanish since two rows of the determinant will be identical. We can thus infer that *in a system of N identical particles, no two fermions can occupy the same single-particle state at a time*; every single-particle state can be occupied by at most one fermion. This is the *Pauli exclusion principle*, which was first postulated in 1925 to explain the periodic table. It states that *no two electrons can occupy simultaneously the same (single-particle) quantum state on the same atom*; there can be only one (or at most one) electron occupying a state of quantum numbers $n_i l_i m_{l_i} m_{s_i}$: $\psi_{n_i l_i m_{l_i} m_{s_i}}(\vec{r}_i, \vec{S}_i)$. The exclusion principle plays an important role in the structure of atoms. It has a direct effect on the *spatial distribution* of fermions.

Boson condensation

What about bosons? Do they have any restriction like fermions? Not at all. There is no restriction on the number of bosons that can occupy a single state. Instead of the exclusion principle of fermions, bosons tend to condense all in the same state, the ground state; this is called *boson condensation*. For instance, all the particles of liquid ^{4}He (a boson system) occupy the same ground state. This phenomenon is known as *Bose–Einstein condensation*. The properties of liquid ^{3}He are, however, completely different from those of liquid ^{4}He, because ^{3}He is a fermion system.

Remark

We have seen that when the Schrödinger equation involves the spin, the wave function of a single particle is equal to the product of the spatial part and the spin part: $\Psi(\vec{r}, \vec{S}) = \psi(\vec{r})\chi(\vec{S})$. The wave function of a system of N particles, which have spins, is the product of the spatial part and the spin part:

$$\Psi(\vec{r}_1, \vec{S}_1;\ \vec{r}_2, \vec{S}_2;\ \ldots;\ \vec{r}_N, \vec{S}_N) = \psi(\vec{r}_1,\ \vec{r}_2,\ \ldots,\ \vec{r}_N)\chi(\vec{S}_1,\ \vec{S}_2,\ \ldots,\ \vec{S}_N). \tag{8.62}$$

This wave function must satisfy the appropriate symmetry requirements when the N particles are identical. In the case of a system of N identical bosons, the wave function must be symmetric; hence the spatial and spin parts must have the same parity:

$$\Psi_s(\vec{r}_1, \vec{S}_1;\ \vec{r}_2, \vec{S}_2;\ \ldots;\ \vec{r}_N, \vec{S}_N) = \left\{ \begin{array}{l} \psi_a(\vec{r}_1,\ \vec{r}_2,\ \ldots,\ \vec{r}_N)\chi_a(\vec{S}_1,\ \vec{S}_2,\ \ldots,\ \vec{S}_N), \\ \psi_s(\vec{r}_1,\ \vec{r}_2,\ \ldots,\ \vec{r}_N)\chi_s(\vec{S}_1,\ \vec{S}_2,\ \ldots,\ \vec{S}_N). \end{array} \right. \tag{8.63}$$

In the case of a system of N identical fermions, however, the space and spin parts must have different parities, leading to an overall wave function that is antisymmetric:

$$\Psi_a(\vec{r}_1, \vec{S}_1;\ \vec{r}_2, \vec{S}_2;\ \ldots;\ \vec{r}_N, \vec{S}_N) = \left\{ \begin{array}{l} \psi_a(\vec{r}_1,\ \vec{r}_2,\ \ldots,\ \vec{r}_N)\chi_s(\vec{S}_1,\ \vec{S}_2,\ \ldots,\ \vec{S}_N), \\ \psi_s(\vec{r}_1,\ \vec{r}_2,\ \ldots,\ \vec{r}_N)\chi_a(\vec{S}_1,\ \vec{S}_2,\ \ldots,\ \vec{S}_N). \end{array} \right. \tag{8.64}$$

Example 8.3 (Wave function of two identical, noninteracting particles)

Find the wave functions of two systems of identical, noninteracting particles: the first consists of two bosons and the second of two spin $\frac{1}{2}$ fermions.

Solution

For a system of two identical, noninteracting bosons, (8.47) and (8.48) yield

$$\Psi_s(\vec{r}_1, \vec{S}_1; \vec{r}_2, \vec{S}_2) = \frac{1}{\sqrt{2}} \left\{ \begin{array}{l} \left[\, \psi_{n_1}(\vec{r}_1)\psi_{n_2}(\vec{r}_2) - \psi_{n_1}(\vec{r}_2)\psi_{n_2}(\vec{r}_1)\right] \chi_a(\vec{S}_1,\ \vec{S}_2), \\ \left[\, \psi_{n_1}(\vec{r}_1)\psi_{n_2}(\vec{r}_2) + \psi_{n_1}(\vec{r}_2)\psi_{n_2}(\vec{r}_1)\right] \chi_s(\vec{S}_1,\ \vec{S}_2), \end{array} \right. \tag{8.65}$$

and for a system of two spin $\frac{1}{2}$ fermions

$$\Psi_a(\vec{r}_1, \vec{S}_1; \vec{r}_2, \vec{S}_2) = \frac{1}{\sqrt{2}} \left\{ \begin{array}{l} \left[\, \psi_{n_1}(\vec{r}_1)\psi_{n_2}(\vec{r}_2) - \psi_{n_1}(\vec{r}_2)\psi_{n_2}(\vec{r}_1)\right] \chi_s(\vec{S}_1,\ \vec{S}_2), \\ \left[\, \psi_{n_1}(\vec{r}_1)\psi_{n_2}(\vec{r}_2) + \psi_{n_1}(\vec{r}_2)\psi_{n_2}(\vec{r}_1)\right] \chi_a(\vec{S}_1,\ \vec{S}_2), \end{array} \right. \tag{8.66}$$

where, from the formalism of angular momentum addition, there are three states (a triplet) that are symmetric, $\chi_s(\vec{S}_1, \vec{S}_2)$:

$$\chi_{triplet}(\vec{S}_1, \vec{S}_2) = \begin{cases} \left|\frac{1}{2}\,\frac{1}{2}\right\rangle_1 \left|\frac{1}{2}\,\frac{1}{2}\right\rangle_2, \\ \frac{1}{\sqrt{2}}\left(\left|\frac{1}{2}\,\frac{1}{2}\right\rangle_1 \left|\frac{1}{2}\,-\frac{1}{2}\right\rangle_2 + \left|\frac{1}{2}\,-\frac{1}{2}\right\rangle_1 \left|\frac{1}{2}\,\frac{1}{2}\right\rangle_2 \right), \\ \left|\frac{1}{2}\,-\frac{1}{2}\right\rangle_1 \left|\frac{1}{2}\,-\frac{1}{2}\right\rangle_2, \end{cases} \tag{8.67}$$

and one state (a singlet) that is antisymmetric, $\chi_a(\vec{S}_1, \vec{S}_2)$:

$$\chi_{singlet}(\vec{S}_1, \vec{S}_2) = \frac{1}{\sqrt{2}}\left(\left|\frac{1}{2}\,\frac{1}{2}\right\rangle_1 \left|\frac{1}{2}\,-\frac{1}{2}\right\rangle_2 - \left|\frac{1}{2}\,-\frac{1}{2}\right\rangle_1 \left|\frac{1}{2}\,\frac{1}{2}\right\rangle_2 \right). \tag{8.68}$$

8.4 The Exclusion Principle and the Periodic Table

Explaining the periodic table is one of the most striking successes of the Schrödinger equation. When combined with the Pauli exclusion principle, the equation offers insightful information on the structure of multielectron atoms.

In Chapter 6, we saw that the state of the hydrogen's electron, which moves in the spherically symmetric Coulomb potential of the nucleus, is described by four quantum numbers n, l, m_l, and m_s: $\Psi_{nlm_lm_s}(\vec{r}) = \psi_{nlm_l}(\vec{r})\chi_{m_s}$, where $\psi_{nlm_l}(\vec{r}) = R_{nl}(r)Y_{lm_l}(\theta, \varphi)$ is the electron's wave function when the spin is ignored and $\chi_{m_s} = \left|\frac{1}{2}, \pm\frac{1}{2}\right\rangle$ is the spin's state. This representation turns out to be suitable for any atom as well.

In a multielectron atom, the average potential in which every electron moves is different from the Coulomb potential of the nucleus; yet, to a good approximation, it can be assumed to be spherically symmetric. We can therefore, as in hydrogen, characterize the electronic states by the four quantum numbers n, l, m_l, and m_s, which respectively represent the principal quantum number, the orbital quantum number, the magnetic (or azimuthal) quantum number, and the spin quantum number; m_l represents the z-component of the electron orbital angular momentum and m_s the z-component of its spin.

Atoms have a *shell structure*. Each atom has a number of major shells that are specified by the radial or principal quantum number n. Shells have subshells which are specified by the orbital quantum number l. Subshells in turn have subsubshells, called *orbitals*, specified by m_l; so *an orbital is fully specified by three quantum numbers* n, l, m_l; i.e., it is defined by $|nlm_l\rangle$. Each shell n therefore has n subshells corresponding to $l = 0, 1, 2, 3, \ldots, n-1$, and in turn each subshell has $2l+1$ orbitals (or subsubshells), since to $m_l = -l, -l+1, -l+2, \ldots, l-2, l-1, l$. As in hydrogen, individual electrons occupy single-particle states or orbitals; the states corresponding to the respective numerical values $l = 0, 1, 2, 3, 4, 5, \ldots$ are called s, p, d, f, g, h, … states. Hence for a given n an s-state has 1 orbital ($m_l = 0$), a p-state has 3 orbitals ($m_l = -1, 0, 1$), a d-state has 5 orbitals ($m_l = -2, -1, 0, 1, 2$), and so on (Chapter 6). We will label the electronic states by nl where, as before, l refers to s, p, d, f, etc.; for example $1s$ corresponds to $(n, l) = (1, 0)$, $2s$ corresponds to $(n, l) = (2, 0)$, $2p$ corresponds to $(n, l) = (2, 1)$, $3s$ corresponds to $(n, l) = (3, 0)$, and so on.

How do electrons fill the various shells and subshells in an atom? If electrons were bosons, they would all group in the ground state $|nlm_l\rangle = |100\rangle$; we wouldn't then have the rich diversity of elements that exist in nature. But since electrons are identical fermions, they are

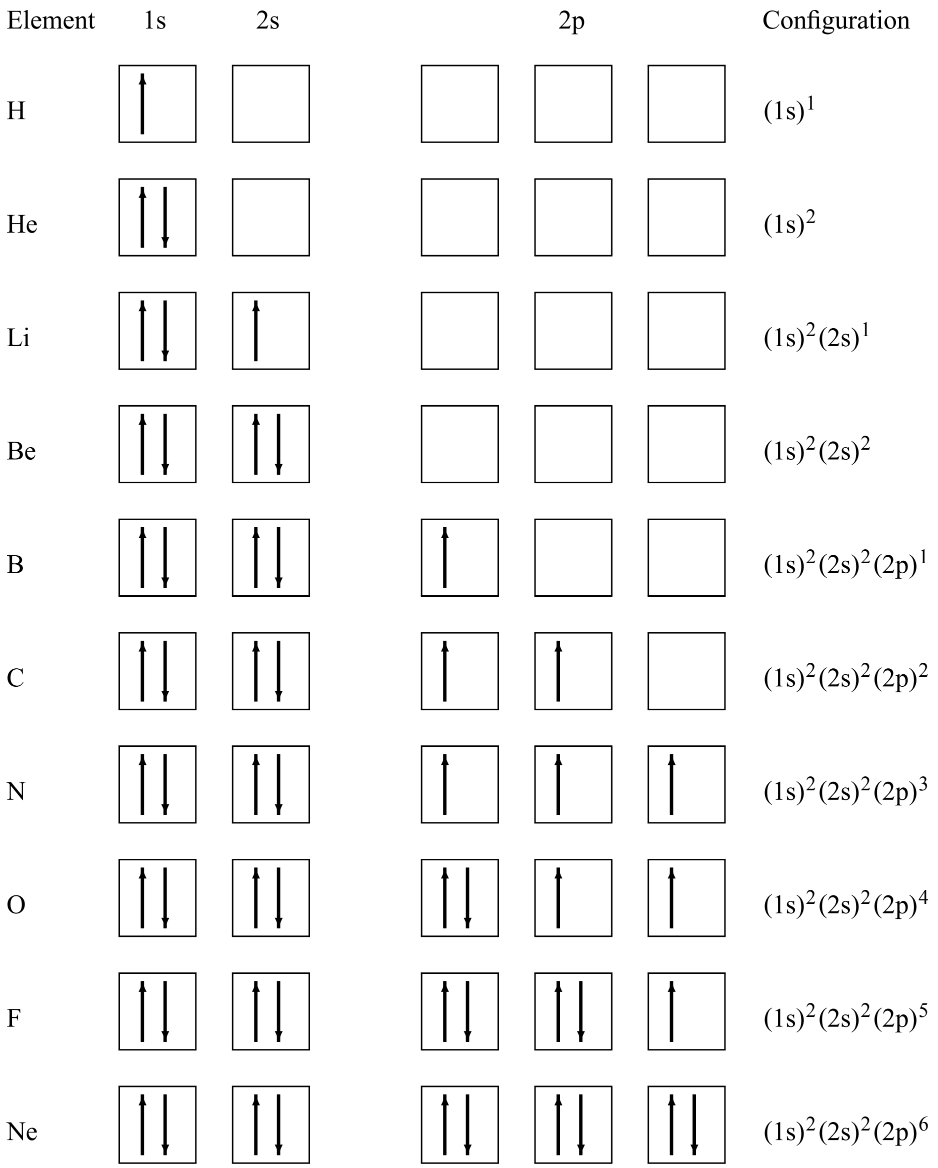

Figure 8.2 Filling orbitals according to the Pauli exclusion principle.

governed by the Pauli exclusion principle, which states that *no two electrons can occupy simultaneously the same quantum state* $|nlm_lm_s\rangle$ *on the same atom*. Hence each orbital state $|nlm_l\rangle$ can be occupied by two electrons *at most*: one having spin-up $m_s = +\frac{1}{2}$, the other spin-down $m_s = -\frac{1}{2}$. Hence, each state nl can accommodate $2(2l+1)$ electrons. So an s-state (i.e., $|n00\rangle$) can at most hold 2 electrons, a p-state (i.e., $|n1m_l\rangle$) at most 6 electrons, a d-state (i.e., $|n2m_l\rangle$) at most 10 electrons, an f-state (i.e., $|n3m_l\rangle$) at most 14 electrons, and so on (Figure 8.2).

For an atom in the ground state, the *electrons fill the orbitals in order of increasing energy*; once a subshell is filled, the next electron goes into the vacant subshell whose energy is just above the previous subshell. When all orbitals in a major electronic shell are filled up, we get a *closed shell*; the next electron goes into the next major shell, and so on. By filling the atomic orbitals one after the other in order of increasing energy, one obtains all the elements of the periodic table (Table 8.1).

Elements $1 \leq Z \leq 18$

As shown in Table 8.1, the first period (or first horizontal row) of the periodic table has two elements, hydrogen H and helium He; the second period has 8 elements, lithium Li to neon Ne; the third period also has 8 elements, sodium Na to argon Ar; and so on. The orbitals of the 18 lightest elements, $1 \leq Z \leq 18$, are filled in order of increasing energy according to the sequence: 1s, 2s, 2p, 3s, 3p. The electronic state of an atom is determined by specifying the occupied orbitals or by what is called the *electronic configuration*. For example, hydrogen has one electron, its ground state configuration is $(1s)^1$; helium He has two electrons: $(1s)^2$; lithium Li has three electrons: $(1s)^2(2s)^1$; beryllium Be has four: $(1s)^2(2s)^2$, and so on.

Now let us see how to determine the total angular momentum of an atom. For this, we need to calculate the total orbital angular momentum $\vec{L} = \sum_{i=1}^{Z} \vec{l}_i$, the total spin $\vec{S} = \sum_{i=1}^{Z} \vec{s}_i$, and then obtain total angular momentum by coupling $\vec{L}$ and $\vec{S}$, i.e., $\vec{J} = \vec{L} + \vec{S}$, where $\vec{l}_i$ and $\vec{s}_i$ are the orbital and spin angular momenta of individual electrons. As will be seen in Chapter 9, when the spin–orbit coupling is considered, the degeneracy of the atom's energy levels is partially lifted, introducing a splitting of the levels. The four numbers L, S, J, and M are good quantum numbers, where $|L - S| \leq J \leq L + S$ and $-J \leq M \leq J$. So there are $2S + 1$ values of J when $L \geq S$ and $2L + 1$ values when $L < S$. Since the energy depends on J, the levels corresponding to an L and S split into a $(2J + 1)$-multiplet. The issue now is to determine which one of these states has the lowest energy. Before studying this issue, let us introduce the spectroscopic notation according to which the state of an atom is labeled by

$$^{2S+1}L_J, \tag{8.69}$$

where, as before, the numbers $L = 0, 1, 2, 3, \ldots$ are designated by S, P, D, F, . . ., respectively (we should mention here that the capital letters S, P, D, F, . . . refer to the total orbital angular momentum of an atom, while the small letters s, p, d, f, . . . refer to individual electrons; that is, s, p, d, f, . . . describe the angular momentum states of individual electrons). For example, since the total angular momentum of a beryllium atom is $J = 0$, because $L = 0$ (all electrons are in s-states, $l_i = 0$) and $S = 0$ (both electrons in the $(1s)^2$ state are paired and so are the two electrons in the $(2s)^2$ state), the ground state of beryllium can be written as $^1S_0$. This applies actually to all other closed shell atoms such as helium He, neon Ne, argon Ar, and so on; their ground states are all specified by $^1S_0$ (Table 8.1).

Let us now consider boron B: the closed shells 1s and 2s have $L = S = J = 0$. Thus the angular momentum of boron is determined by the 1p electron which has $S = 1/2$ and $L = 1$. A coupling of $S = 1/2$ and $L = 1$ yields $J = 1/2$ or $3/2$, leading therefore to two possible

Table 8.1 Ground state electron configurations, spectroscopic description, and ionization energies for the first four rows of the periodic table. The brackets designate closed-shell elements.

Shell	Z	Element	Ground state configuration	Spectroscopic description	Ionization energy (eV)
1	1	H	$(1s)^1$	$^2S_{1/2}$	13.60
	2	He	$(1s)^2$	$^1S_0$	24.58
2	3	Li	$[\mathrm{He}](2s)^1 = (1s)^2(2s)^1$	$^2S_{1/2}$	5.39
	4	Be	$[\mathrm{He}](2s)^2$	$^1S_0$	9.32
	5	B	$[\mathrm{He}](2s)^2(2p)^1$	$^2P_{1/2}$	8.30
	6	C	$[\mathrm{He}](2s)^2(2p)^2$	$^3P_0$	11.26
	7	N	$[\mathrm{He}](2s)^2(2p)^3$	$^4S_{3/2}$	14.55
	8	O	$[\mathrm{He}](2s)^2(2p)^4$	$^3P_2$	13.61
	9	F	$[\mathrm{He}](2s)^2(2p)^5$	$^2P_{3/2}$	17.42
	10	Ne	$[\mathrm{He}](2s)^2(2p)^6$	$^1S_0$	21.56
3	11	Na	$[\mathrm{Ne}](3s)^1$	$^2S_{1/2}$	5.14
	12	Mg	$[\mathrm{Ne}](3s)^2$	$^1S_0$	7.64
	13	Al	$[\mathrm{Ne}](3s)^2(3p)^1$	$^2P_{1/2}$	5.94
	14	Si	$[\mathrm{Ne}](3s)^2(3p)^2$	$^3P_0$	8.15
	15	P	$[\mathrm{Ne}](3s)^2(3p)^3$	$^4S_{3/2}$	10.48
	16	S	$[\mathrm{Ne}](3s)^2(3p)^4$	$^3P_2$	10.36
	17	Cl	$[\mathrm{Ne}](3s)^2(3p)^5$	$^2P_{3/2}$	13.01
	18	Ar	$[\mathrm{Ne}](3s)^2(3p)^6$	$^1S_0$	15.76
4	19	K	$[\mathrm{Ar}](4s)^1$	$^2S_{1/2}$	4.34
	20	Ca	$[\mathrm{Ar}](4s)^2$	$^1S_0$	6.11
	21	Sc	$[\mathrm{Ar}](3d)^1(4s)^2$	$^2D_{3/2}$	6.54
	22	Ti	$[\mathrm{Ar}](3d)^2(4s)^2$	$^3F_2$	6.83
	23	V	$[\mathrm{Ar}](3d)^3(4s)^2$	$^4F_{3/2}$	6.74
	24	Cr	$[\mathrm{Ar}](3d)^4(4s)^2$	$^7S_3$	6.76
	25	Mn	$[\mathrm{Ar}](3d)^5(4s)^2$	$^6S_{3/2}$	7.43
	26	Fe	$[\mathrm{Ar}](3d)^6(4s)^2$	$^5D_4$	7.87
	27	Co	$[\mathrm{Ar}](3d)^7(4s)^2$	$^4F_{9/2}$	7.86
	28	Ni	$[\mathrm{Ar}](3d)^8(4s)^2$	$^3F_4$	7.63
	29	Cu	$[\mathrm{Ar}](3d)^{10}(4s)^1$	$^2S_{1/2}$	7.72
	30	Zn	$[\mathrm{Ar}](3d)^{10}(4s)^2$	$^1S_0$	9.39
	31	Ga	$[\mathrm{Ar}](3d)^{10}(4s)^2(4p)^1$	$^2P_{1/2}$	6.00
	32	Ge	$[\mathrm{Ar}](3d)^{10}(4s)^2(4p)^2$	$^3P_0$	7.88
	33	As	$[\mathrm{Ar}](3d)^{10}(4s)^2(4p)^3$	$^4S_{3/2}$	9.81
	34	Se	$[\mathrm{Ar}](3d)^{10}(4s)^2(4p)^4$	$^3P_2$	9.75
	35	Br	$[\mathrm{Ar}](3d)^{10}(4s)^2(4p)^5$	$^2P_{3/2}$	11.84
	36	Kr	$[\mathrm{Ar}](3d)^{10}(4s)^2(4p)^6$	$^1S_0$	9.81

states:

$$^2\mathrm{P}_{1/2} \qquad \text{or} \qquad ^2\mathrm{P}_{3/2}. \tag{8.70}$$

Which one has a lower energy? Before answering this question, let us consider another example, the carbon atom.

The ground state configuration of the carbon atom, as given by $(1\mathrm{s})^2(2\mathrm{s})^2(2\mathrm{p})^2$, implies that its total angular momentum is determined by the two 2p electrons. The coupling of the two spins $s = 1/2$, as shown in equations (7.174) to (7.177), yields two values for their total spin $S = 0$ or $S = 1$; and, as shown in Problem 7.3, page 436, a coupling of two individual orbital angular momenta $l = 1$ yields three values for the total angular momenta $L = 0$, 1, or 2. But the exclusion principle dictates that the total wave function has to be antisymmetric, i.e., the spin and orbital parts of the wave function must have opposite symmetries. Since the singlet spin state $S = 0$ is antisymmetric, the spin triplet $S = 1$ is symmetric, the orbital triplet $L = 1$ is antisymmetric, the orbital quintuplet $L = 2$ is symmetric, and the orbital singlet $L = 0$ is symmetric, the following states are antisymmetric:

$$^1\mathrm{S}_0, \qquad ^3\mathrm{P}_0, \qquad ^3\mathrm{P}_1, \qquad ^3\mathrm{P}_2, \qquad \text{or} \qquad ^1\mathrm{D}_2; \tag{8.71}$$

hence any one of these states can be the ground state of carbon. Again, which one of them has the lowest energy?

To answer this question and the question pertaining to (8.70), we may invoke *Hund's rules*: (a) the lowest energy level corresponds to the state with the largest spin S (i.e., the maximum number of electrons have unpaired spins); (b) among the states with a given value of S, the lowest energy level corresponds to the state with the largest value of L; (c) for a subshell that is less than half full the lowest energy state corresponds to $J = |L - S|$, and for a subshell that is more than half full the lowest energy state corresponds to $J = L + S$.

Hund's third rule answers the question pertaining to (8.70): since the 2p shell of boron is less than half full, the value of J corresponding to the lowest energy is given by $J = |L - S| = 1 - 1/2 = 1/2$; hence $^2\mathrm{P}_{1/2}$ is the lower energy state.

To find which one of the states (8.71) has the lowest energy, Hund's first rule dictates that $S = 1$. Since the triplet $S = 1$ is symmetric, we need an antisymmetric spatial wave function; this is given by the spatial triplet $L = 1$. We are thus left with three possible choices: $J = 0$, 1, or 2. Hund's third rule precludes the values $J = 1$ and 2. Since the 2p shell of carbon is less than half full, the value of J corresponding to the lowest energy is given by $J = |L - S| = 1 - 1 = 0$; hence $^3\mathrm{P}_0$ is the lower energy state (Table 8.1). That is, the two electrons are in different spatial states or different orbitals (Figure 8.2). Actually, we could have guessed this result: since the Coulomb repulsion between the two electrons when they are paired together is much larger than when they are unpaired, the lower energy configuration corresponds to the case where the electrons are in different spatial states. The ground state configurations of the remaining elements, oxygen to argon, can be inferred in a similar way (Table 8.1).

Elements $Z \geq 18$

When the 3p shell is filled, one would expect to place the next electron in a 3d shell. But this doesn't take place due to the occurrence of an interesting effect: the 4s states have lower energy than the 3d states. Why? In a hydrogen atom the states 3s, 3p, and 3d have the same energy ($E_3^{(0)} = -\mathcal{R}/3^2 = -1.51\,\mathrm{eV}$, since $\mathcal{R} = 13.6\,\mathrm{eV}$). But in multielectron atoms, these states have different energy values. As l increases, the effective repulsive potential $\hbar^2 l(l+1)/2mr^2$ causes the d-state electrons to be thrown outward and the s-state electrons to remain closer to the nucleus. Being closer to the nucleus, the s-state electrons therefore feel the full attraction of the nucleus, whereas the d-state electrons experience a much weaker attraction. This is known as the *screening effect*, because the inner electrons, i.e., the s-state electrons, screen the nucleus; hence the outward electrons (the d-state electrons) do not experience the full attraction of the nucleus, but instead feel a weak effective potential. As a result, the energy of the 3d-state is larger than that of the 4s-state. The screening effect also causes the energy of the 5s-state to have a lower energy than the 4d-state, and so on. So for a given n, the energies E_{nl} increase as l increases; in fact, neglecting the spin–orbit interaction and considering relativistic corrections we will show in Chapter 9 (9.90) that the ground state energy depends on the principal and orbital quantum numbers n and l as $E_{nl}^{(0)} = Z^2 E_n^{(0)}\{1 + \alpha^2 Z^2[2/(2l+1) - 3/4n]/n\}$, where $\alpha = 1/137$ is the fine structure constant and $E_n^{(0)} = -\mathcal{R}/n^2 = -13.6\,\text{eV}/n^2$.

In conclusion, the periodic table can be obtained by filling the orbitals in order of increasing energy E_{nl} as follows (Table 8.1):

$$\begin{aligned}&1s^2,\ 2s^2,\ 2p^6,\ 3s^2,\ 3p^6,\ 4s^2,\ 3d^{10},\ 4p^6,\ 5s^2,\ 4d^{10},\ 5p^6,\ 6s^2,\ 4f^{14},\\ &5d^{10},\ 6p^6, 7s^2,\ 5f^{14},\ 6d^{10},\ 7p^6,\ldots.\end{aligned} \tag{8.72}$$

Remarks

The chemical properties of an element is mostly determined by the outermost shell. Hence elements with similar electron configurations for the outside shell have similar chemical properties. This is the idea behind the structure of the periodic table: it is arranged in a way that all elements in a column have similar chemical properties. For example, the elements in the last column, helium, neon, argon, krypton, and so on, have the outer p-shell completely filled (except for helium whose outside shell is 1s). These atoms, which are formed when a shell or a subshell is filled, are very stable, interact very weakly with one another, and do not combine with other elements to form molecules or new compounds; that is, they are chemically inert. They are very reluctant to give up or to accept an electron. Due to these properties, they are called *noble gases*. They have a very low boiling point (around −200 °C). Note that each row of the periodic table corresponds to filling out a shell or subshell of the atom, up to the next noble gas. Also, there is a significant energy gap before the next level is encountered after each of these elements. As shown in Table 8.1, a large energy is required to ionize these elements; for instance, 24.58 eV is needed to ionize a helium atom.

Atoms consisting of a closed shell (or a noble gas configuration) plus an s-electron (or a valence electron), such as Li, Na, K, and so on, have the lowest binding energy; these elements are known as the alkali metals. In elements consisting of an alkali configuration plus an electron, the second s-electron is more bound than the valence electron of the alkali atom because of the higher nuclear charge. As the p-shell is gradually filled (beyond the noble gas configuration), the binding energy increases initially (as in boron, carbon, and nitrogen) till the fourth electron, then it begins to drop (Table 8.1). This is due to the fact that when the p-shell is less than half full all spins are parallel; hence all three spatial wave functions are antisymmetric. With the fourth electron (as in oxygen), two spins will be antiparallel or paired; hence the spatial wave function is not totally antisymmetric, causing a drop in the energy. Note that elements with one electron more than or one electron less than noble gas configurations are the most active chemically, because they tend to easily give up or easily accept one electron.

Example 8.4

(a) Specify the total angular momenta corresponding to ^{4}G, ^{3}H, and ^{1}D.

(b) Find the spectroscopic notation for the ground state configurations of aluminum Al ($Z = 13$) and scandium Sc ($Z = 21$).

Solution

(a) For the term ^{4}G the orbital angular momentum is $L = 4$ and the spin is $S = 3/2$, since $2S + 1 = 4$. The values of the total angular momentum corresponding to the coupling of $L = 4$ and $S = 3/2$ are given by $|4 - 3/2| \leq J \leq 4 + 3/2$. Hence we have $J = 5/2, 7/2, 9/2, 11/2$.

Similarly, for ^{3}H we have $S = 1$ and $L = 5$. Therefore, we have $|5 - 1| \leq J \leq 5 + 1$, or $J = 4, 5, 6$.

For ^{1}D we have $S = 0$ and $L = 2$. Therefore, we have $|2 - 0| \leq J \leq 2 + 0$, or $J = 2$.

(b) The ground state configuration of Al is [Ne]$(3s)^2(3p)^1$. The total angular momentum of this element is determined by the 3p electron, because $S = 0$ and $L = 0$ for both [Ne] and $(3s)^2$. Since the 3p electron has $S = 1/2$ and $L = 1$, the total angular momentum is given by $|1 - 1/2| \leq J \leq 1 + 1/2$. Hence we have $J = 1/2, 3/2$. Which of the values $J = 1/2$ and $J = 3/2$ has a lower energy? According to Hund's third rule, since the 3p shell is less than half full, the state $J = |L - S| = 1/2$ has the lower energy. Hence the ground state configuration of Al corresponds to $^2\mathrm{P}_{1/2}$ (Table 8.1), where we have used the spectroscopic notation $^{2S+1}L_J$.

Since the ground state configuration of Sc is [Ar]$(4s)^2(3d)^1$, the angular momentum is given by that of the 3d electron. Since $S = 1/2$ and $L = 2$, and since the 3d shell is less than half full, Hund's third rule dictates that the total angular momentum is given by $J = |L - S| = |2 - 1/2| = 3/2$. Hence we have $^2\mathrm{D}_{3/2}$.

8.5 Solved Problems

Problem 8.1

Consider a system of three noninteracting particles that are confined to move in a one-dimensional infinite potential well of length a: $V(x) = 0$ for $0 < x < a$ and $V(x) = \infty$ for other values of x. Determine the energy and wave function of the ground state and the first and second excited states when the three particles are (a) spinless and distinguishable with $m_1 < m_2 < m_3$; (b) identical bosons; (c) identical spin $\frac{1}{2}$ particles; and (d) distinguishable spin $\frac{1}{2}$ particles.

Solution

(a) As shown in Example 8.2 on page 459, the total energy and wave function are given by

$$E_{n_1,n_2,n_3} = \frac{\hbar^2\pi^2}{2a^2}\left(\frac{n_1^2}{m_1} + \frac{n_2^2}{m_2} + \frac{n_3^2}{m_3}\right), \tag{8.73}$$

$$\psi_{n_1,n_2,n_3}(x_1, x_2, x_3) = \sqrt{\frac{8}{a^3}} \sin\left(\frac{n_1\pi}{a}x_1\right) \sin\left(\frac{n_2\pi}{a}x_2\right) \sin\left(\frac{n_3\pi}{a}x_3\right). \tag{8.74}$$

The ground state of the system corresponds to the case where all three particles occupy their respective ground state orbitals, $n_1 = n_2 = n_3 = 1$; hence

$$E^{(0)} = E_{1,1,1} = \frac{\hbar^2\pi^2}{2a^2}\left(\frac{1}{m_1} + \frac{1}{m_2} + \frac{1}{m_3}\right), \tag{8.75}$$

$$\psi^{(0)}(x_1, x_2, x_3) = \psi_{1,1,1}(x_1, x_2, x_3) = \sqrt{\frac{8}{a^3}} \sin\left(\frac{\pi}{a}x_1\right) \sin\left(\frac{\pi}{a}x_2\right) \sin\left(\frac{\pi}{a}x_3\right). \tag{8.76}$$

Since particle 3 has the highest mass, the first excited state corresponds to the case where particle 3 is in $n_3 = 2$, while particles 1 and 2 remain in $n_1 = n_2 = 1$:

$$E^{(1)} = E_{1,1,2} = \frac{\hbar^2\pi^2}{2a^2}\left(\frac{1}{m_1} + \frac{1}{m_2} + \frac{4}{m_3}\right), \tag{8.77}$$

$$\psi^{(1)}(x_1, x_2, x_3) = \psi_{1,1,2}(x_1, x_2, x_3) = \sqrt{\frac{8}{a^3}} \sin\left(\frac{\pi}{a}x_1\right) \sin\left(\frac{\pi}{a}x_2\right) \sin\left(\frac{2\pi}{a}x_3\right). \tag{8.78}$$

Similarly, the second excited state corresponds to the case where particles 2 and 3 are in $n_2 = n_3 = 2$, while particle 1 remains in $n_1 = 1$:

$$E^{(2)} = E_{1,2,2} = \frac{\hbar^2\pi^2}{2a^2}\left(\frac{1}{m_1} + \frac{4}{m_2} + \frac{4}{m_3}\right), \tag{8.79}$$

$$\psi^{(2)}(x_1, x_2, x_3) = \psi_{1,2,2}(x_1, x_2, x_3) = \sqrt{\frac{8}{a^3}} \sin\left(\frac{\pi}{a}x_1\right) \sin\left(\frac{2\pi}{a}x_2\right) \sin\left(\frac{2\pi}{a}x_3\right). \tag{8.80}$$

(b) If all three particles were identical bosons, the ground state will correspond to all particles in the lowest state $n_1 = n_2 = n_3 = 1$ (Figure 8.3):

$$E^{(0)} = E_{1,1,1} = 3\varepsilon_1 = \frac{3\hbar^2\pi^2}{2ma^2}, \tag{8.81}$$

$$\psi^{(0)} = \psi_1(x_1)\psi_1(x_2)\psi_1(x_3) = \sqrt{\frac{8}{a^3}} \sin\left(\frac{\pi}{a}x_1\right) \sin\left(\frac{\pi}{a}x_2\right) \sin\left(\frac{\pi}{a}x_3\right), \tag{8.82}$$

since $\psi_n(x_i) = \sqrt{2/a}\sin(n\pi x_i/a)$.

In the first excited state we have two particles in ψ_1 (each with energy $\varepsilon_1 = \hbar^2\pi^2/(2ma^2)$) and one in ψ_2 (with energy $\varepsilon_2 = 4\hbar^2\pi^2/(2ma^2) = 4\varepsilon_1$):

$$E^{(1)} = 2\varepsilon_1 + \varepsilon_2 = 2\varepsilon_1 + 4\varepsilon_1 = 6\varepsilon_1 = \frac{3\pi^2\hbar^2}{ma^2}. \tag{8.83}$$

The wave function is somewhat tricky again. Since the particles are identical, we can no longer say which particle is in which state; all we can say is that two particles are in ψ_1 and one in ψ_2. Since the value $n = 1$ occurs twice (two particles are in ψ_1), we infer from (8.60) and (8.61) that

$$\begin{aligned}\psi^{(1)}(x_1, x_2, x_3) \;=\; \sqrt{\frac{2!}{3!}}\Big[\, &\psi_1(x_1)\psi_1(x_2)\psi_2(x_3) + \psi_1(x_1)\psi_2(x_2)\psi_1(x_3) \\ &+ \psi_2(x_1)\psi_1(x_2)\psi_1(x_3)\Big].\end{aligned} \tag{8.84}$$

In the second excited state we have one particle in ψ_1 and two in ψ_2:

$$E^{(2)} = \varepsilon_1 + 2\varepsilon_2 = \varepsilon_1 + 8\varepsilon_2 = 9\varepsilon_1 = \frac{9\pi^2\hbar^2}{2ma^2}. \tag{8.85}$$

Now, since the value $n = 2$ occurs twice (two particles are in ψ_2) and $n = 1$ only once, (8.60) and (8.61) yield

$$\begin{aligned}\psi^{(2)}(x_1, x_2, x_3) \;=\; \sqrt{\frac{2!}{3!}}\Big[\, &\psi_1(x_1)\psi_2(x_2)\psi_2(x_3) + \psi_2(x_1)\psi_1(x_2)\psi_2(x_3) \\ &+ \psi_2(x_1)\psi_2(x_2)\psi_1(x_3)\Big].\end{aligned} \tag{8.86}$$

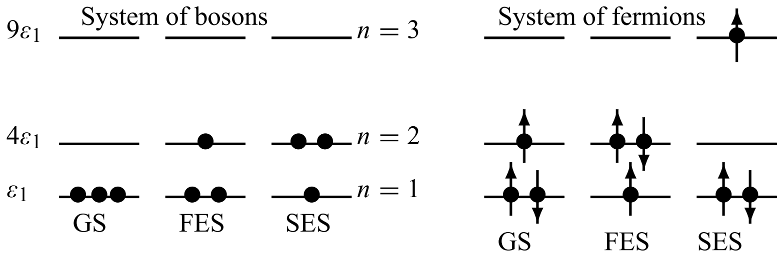

Figure 8.3 Particle distribution among the levels of the ground state (GS) and the first (FES) and second excited states (SES) for a system of three noninteracting identical bosons (left) and fermions (right) moving in an infinite well, with $\varepsilon_1 = \hbar^2\pi^2/(2ma^2)$. Each state of the fermion system is fourfold degenerate due to the various possible orientations of the spins.

(c) If the three particles were identical spin $\frac{1}{2}$ fermions, the ground state corresponds to the case where two particles are in the lowest state ψ_1 (one having a spin-up $| +\rangle = \left|\frac{1}{2}, \frac{1}{2}\right\rangle$, the other with a spin-down $| -\rangle = \left|\frac{1}{2}, -\frac{1}{2}\right\rangle$), while the third particle is in the next state ψ_2 (its spin can be either up or down, $| \pm\rangle = \left|\frac{1}{2}, \pm\frac{1}{2}\right\rangle$); see Figure 8.3. The ground state energy is

$$E^{(0)} = 2\varepsilon_1 + \varepsilon_2 = 2\varepsilon_1 + 4\varepsilon_1 = 6\varepsilon_1 = \frac{3\hbar^2\pi^2}{ma^2}. \tag{8.87}$$

The ground state wave function is antisymmetric and, in accordance with (8.55), it is given by

$$\psi^{(0)}(x_1, x_2, x_3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_1(x_1)\chi(S_1) & \psi_1(x_2)\chi(S_2) & \psi_1(x_3)\chi(S_3) \\ \psi_1(x_1)\chi(S_1) & \psi_1(x_2)\chi(S_2) & \psi_1(x_3)\chi(S_3) \\ \psi_2(x_1)\chi(S_1) & \psi_2(x_2)\chi(S_2) & \psi_2(x_3)\chi(S_3) \end{vmatrix}. \tag{8.88}$$

This state is fourfold degenerate, since there are four different ways of configuring the spins of the three fermions (the ground state (GS) shown in Figure 8.3 is just one of the four configurations). **Remark:** one should be careful not to erroneously conclude that, since the first and second rows of the determinant in (8.88) are "identical", the determinant is zero. We should keep in mind that the spin states are given by $\chi(S_1) =| \pm\rangle$, $\chi(S_2) =| \pm\rangle$, and $\chi(S_3) =| \pm\rangle$; hence, we need to select these spin states in such a way that no two rows (nor two columns) of the determinant are identical. For instance, one of the possible configurations of the ground state wave function is given by

$$\psi^{(0)}(x_1, x_2, x_3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_1(x_1) \,| +\rangle & \psi_1(x_2) \,| -\rangle & \psi_1(x_3) \,| +\rangle \\ \psi_1(x_1) \,| -\rangle & \psi_1(x_2) \,| +\rangle & \psi_1(x_3) \,| +\rangle \\ \psi_2(x_1) \,| +\rangle & \psi_2(x_2) \,| +\rangle & \psi_2(x_3) \,| -\rangle \end{vmatrix}. \tag{8.89}$$

This remark applies also to the first and second excited state wave functions (8.90) and (8.92); it also applies to the wave function (8.109).

The first excited state corresponds to one particle in the lowest state ψ_1 (its spin can be either up or down) and the other two particles in the state ψ_2 (the spin of one is up, the other is down). As in the ground state, there are also four different ways of configuring the spins of the three fermions in the first excited state (FES); the FES shown in Figure 8.3 is just one of the four configurations:

$$\psi^{(1)}(x_1, x_2, x_3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_1(x_1)\chi(S_1) & \psi_1(x_2)\chi(S_2) & \psi_1(x_3)\chi(S_3) \\ \psi_2(x_1)\chi(S_1) & \psi_2(x_2)\chi(S_2) & \psi_2(x_3)\chi(S_3) \\ \psi_2(x_1)\chi(S_1) & \psi_2(x_2)\chi(S_2) & \psi_2(x_3)\chi(S_3) \end{vmatrix}. \tag{8.90}$$

These four different states correspond to the same energy

$$E^{(1)} = \varepsilon_1 + 2\varepsilon_2 = \varepsilon_1 + 8\varepsilon_1 = 9\varepsilon_1 = \frac{9\hbar^2\pi^2}{2ma^2}. \tag{8.91}$$

The excitation energy of the first excited state is $E^{(1)} - E^{(0)} = 9\varepsilon_1 - 6\varepsilon_1 = 3\hbar^2\pi^2/(2ma^2)$.

The second excited state corresponds to two particles in the lowest state ψ_1 (one with spin-up, the other with spin-down) and the third particle in the third state ψ_3 (its spin can be either up or down). This state also has four different spin configurations; hence it is fourfold degenerate:

$$\psi^{(2)}(x_1, x_2, x_3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_1(x_1)\chi(S_1) & \psi_1(x_2)\chi(S_2) & \psi_1(x_3)\chi(S_3) \\ \psi_1(x_1)\chi(S_1) & \psi_1(x_2)\chi(S_2) & \psi_1(x_3)\chi(S_3) \\ \psi_3(x_1)\chi(S_1) & \psi_3(x_2)\chi(S_2) & \psi_3(x_3)\chi(S_3) \end{vmatrix}. \tag{8.92}$$

The energy of the second excited state is

$$E^{(2)} = 2\varepsilon_1 + \varepsilon_3 = 2\varepsilon_1 + 9\varepsilon_1 = 11\varepsilon_1 = \frac{11\hbar^2\pi^2}{2ma^2}. \tag{8.93}$$

The excitation energy of this state is $E^{(2)} - E^{(0)} = 11\varepsilon_1 - 6\varepsilon_1 = 5\varepsilon_1 = 5\hbar^2\pi^2/(2ma^2)$.

(d) If the particles were distinguishable fermions, there will be no restrictions on the symmetry of the wave function, neither on the space part nor on the spin part. The values of the energy of the ground state, the first excited state, and the second excited state will be similar to those calculated in part (a). However, the wave functions of these states are somewhat different from those found in part (a); while the states derived in (a) are nondegenerate, every state of the current system is eightfold degenerate, since the coupling of three $\frac{1}{2}$ spins yield eight different spin states (Chapter 7). So the wave functions of the system are obtained by multiplying each of the space wave functions $\psi^{(0)}(x_1, x_2, x_3)$, $\psi^{(1)}(x_1, x_2, x_3)$, and $\psi^{(2)}(x_1, x_2, x_3)$, derived in (a), by any of the eight spin states calculated in Chapter 7:

$$\left|1, \frac{3}{2}, \pm\frac{3}{2}\right\rangle = \left|\frac{1}{2}, \frac{1}{2}, \frac{1}{2}; \pm\frac{1}{2}, \pm\frac{1}{2}, \pm\frac{1}{2}\right\rangle, \tag{8.94}$$

$$\left|1, \frac{3}{2}, \pm\frac{1}{2}\right\rangle = \frac{1}{\sqrt{3}}\Big(\mid j_1, j_2, j_3; \mp, \pm, \pm\rangle + \mid j_1, j_2, j_3; \pm, \mp, \pm\rangle + \mid j_1, j_2, j_3; \pm, \pm, \mp\rangle \Big), \tag{8.95}$$

$$\left|0, \frac{1}{2}, \pm\frac{1}{2}\right\rangle = \frac{1}{\sqrt{2}}\Big(\mid j_1, j_2, j_3; \pm, \pm, \mp\rangle - \mid j_1, j_2, j_3; \mp, \pm, \pm > \Big), \tag{8.96}$$

$$\left|1, \frac{1}{2}, \pm\frac{1}{2}\right\rangle = \frac{\mp 1}{\sqrt{6}}\Big(\mid j_1, j_2, j_3;\ \pm, \pm, \mp\rangle - 2 \mid j_1, j_2, j_3;\ \pm, \mp, \pm\rangle + \mid j_1, j_2, j_3; \mp, \pm, \pm\rangle \Big). \tag{8.97}$$

Problem 8.2
Consider a system of three noninteracting identical spin $\frac{1}{2}$ particles that are in the same spin state $\left|\frac{1}{2}, \frac{1}{2}\right\rangle$ and confined to move in a one-dimensional infinite potential well of length a: $V(x) = 0$ for $0 < x < a$ and $V(x) = \infty$ for other values of x. Determine the energy and wave function of the ground state, the first excited state, and the second excited state.

Solution
We may mention first that the single-particle energy and wave function of a particle moving in an infinite well are given by $\varepsilon_n = n^2\hbar^2\pi^2/(2ma^2)$ and $\psi_n(x_i) = \sqrt{2/a}\sin(n\pi x_i/2)$.

The wave function of this system is antisymmetric, since it consists of identical fermions. Moreover, since all the three particles are in the same spin state, no two particles can be in the same state; every energy level is occupied by at most one particle. For instance, the ground state corresponds to the case where the three lowest levels $n = 1, 2, 3$ are occupied by one particle each. The ground state energy and wave function are thus given by

$$E^{(0)} = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 = \varepsilon_1 + 4\varepsilon_1 + 9\varepsilon_3 = 14\varepsilon_1 = \frac{7\hbar^2\pi^2}{ma^2}, \tag{8.98}$$

$$\psi^{(0)}(x_1, x_2, x_3) = \frac{1}{\sqrt{3!}}\begin{vmatrix} \psi_1(x_1) & \psi_1(x_2) & \psi_1(x_3) \\ \psi_2(x_1) & \psi_2(x_2) & \psi_2(x_3) \\ \psi_3(x_1) & \psi_3(x_2) & \psi_3(x_3) \end{vmatrix}\left|\frac{1}{2}, \frac{1}{2}\right\rangle. \tag{8.99}$$

The first excited state is obtained (from the ground state) by raising the third particle to the fourth level: the levels $n = 1$, 2, and 4 are occupied by one particle each and the third level is empty:

$$E^{(1)} = \varepsilon_1 + \varepsilon_2 + \varepsilon_4 = \varepsilon_1 + 4\varepsilon_1 + 16\varepsilon_3 = 21\varepsilon_1 = \frac{21\hbar^2\pi^2}{2ma^2}, \tag{8.100}$$

$$\psi^{(1)}(x_1, x_2, x_3) = \frac{1}{\sqrt{3!}}\begin{vmatrix} \psi_1(x_1) & \psi_1(x_2) & \psi_1(x_3) \\ \psi_2(x_1) & \psi_2(x_2) & \psi_2(x_3) \\ \psi_4(x_1) & \psi_4(x_2) & \psi_4(x_3) \end{vmatrix}\left|\frac{1}{2}, \frac{1}{2}\right\rangle. \tag{8.101}$$

In the second excited state, the levels $n = 1, 3, 4$ are occupied by one particle each; the second level is empty:

$$E^{(2)} = \varepsilon_1 + \varepsilon_3 + \varepsilon_4 = \varepsilon_1 + 9\varepsilon_1 + 16\varepsilon_3 = 26\varepsilon_1 = \frac{13\hbar^2\pi^2}{ma^2}, \tag{8.102}$$

$$\psi^{(2)}(x_1, x_2, x_3) = \frac{1}{\sqrt{3!}}\begin{vmatrix} \psi_1(x_1) & \psi_1(x_2) & \psi_1(x_3) \\ \psi_3(x_1) & \psi_3(x_2) & \psi_3(x_3) \\ \psi_4(x_1) & \psi_4(x_2) & \psi_4(x_3) \end{vmatrix}\left|\frac{1}{2}, \frac{1}{2}\right\rangle. \tag{8.103}$$

Problem 8.3
Find the ground state energy and wave function of a system of N noninteracting identical particles that are confined to a one-dimensional, infinite well when the particles are (a) bosons and (b) spin $\frac{1}{2}$ fermions.

Solution

In the case of a particle moving in an infinite well, its energy and wave function are $\varepsilon_n = n^2\hbar^2\pi^2/(2ma^2)$ and $\psi_n(x_i) = \sqrt{2/a}\sin(n\pi x_i/2)$.

(a) In the case where the N particles are bosons, the ground state is obtained by putting all the particles in the state $n = 1$; the energy and wave function are then given by

$$E^{(0)} = \varepsilon_1 + \varepsilon_1 + \varepsilon_1 + \cdots + \varepsilon_1 = N\varepsilon_1 = \frac{N\hbar^2\pi^2}{2ma^2}, \tag{8.104}$$

$$\psi^{(0)}(x_1, x_2, \ldots, x_N) = \prod_{i=1}^{N}\sqrt{\frac{2}{a}}\sin\left(\frac{\pi}{2}x_i\right) = \sqrt{\frac{2^N}{a^N}}\sin\left(\frac{\pi}{2}x_1\right)\sin\left(\frac{\pi}{2}x_2\right)\cdots\sin\left(\frac{\pi}{2}x_N\right). \tag{8.105}$$

(b) In the case where the N particles are spin $\frac{1}{2}$ fermions, each level can be occupied by at most two particles having different spin states $\left|\frac{1}{2}, \pm\frac{1}{2}\right\rangle$. The ground state is thus obtained by distributing the N particles among the $N/2$ lowest levels at a rate of two particles per level:

$$E^{(0)} = 2\varepsilon_1 + 2\varepsilon_2 + 2\varepsilon_3 + \cdots + 2\varepsilon_{N/2} = 2\sum_{n=1}^{N/2}\frac{n^2\hbar^2\pi^2}{2ma^2} = \frac{\hbar^2\pi^2}{ma^2}\sum_{n=1}^{N/2}n^2. \tag{8.106}$$

If N is large we may calculate $\sum_{n=1}^{N/2} n^2$ by using the approximation

$$\sum_{n=1}^{N/2}n^2 \simeq \int_1^{N/2} n^2 dn \simeq \frac{1}{3}\left(\frac{N}{2}\right)^3; \tag{8.107}$$

hence the ground state energy will be given by

$$E^{(0)} \simeq N^3\frac{\hbar^2\pi^2}{24ma^2}. \tag{8.108}$$

The average energy per particle is $E^{(0)}/N \simeq N^2\hbar^2\pi^2/(24ma^2)$. In the case where N is even, a possible configuration of the ground state wave function $\psi^{(0)}(x_1, x_2, \ldots, x_N)$ is given as follows:

$$\frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_1(x_1)\chi(S_1) & \psi_1(x_2)\chi(S_2) & \cdots & \psi_1(x_N)\chi(S_N) \\ \psi_1(x_1)\chi(S_1) & \psi_1(x_2)\chi(S_2) & \cdots & \psi_1(x_N)\chi(S_N) \\ \psi_2(x_1)\chi(S_1) & \psi_2(x_2)\chi(S_2) & \cdots & \psi_2(x_N)\chi(S_N) \\ \psi_2(x_1)\chi(S_1) & \psi_2(x_2)\chi(S_2) & \cdots & \psi_2(x_N)\chi(S_N) \\ \psi_3(x_1)\chi(S_1) & \psi_3(x_2)\chi(S_2) & \cdots & \psi_3(x_N)\chi(S_N) \\ \psi_3(x_1)\chi(S_1) & \psi_3(x_2)\chi(S_2) & \cdots & \psi_3(x_N)\chi(S_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_{N/2}(x_1)\chi(S_1) & \psi_{N/2}(x_2)\chi(S_2) & \cdots & \psi_{N/2}(x_N)\chi(S_N) \\ \psi_{N/2}(x_1)\chi(S_1) & \psi_{N/2}(x_2)\chi(S_2) & \cdots & \psi_{N/2}(x_N)\chi(S_N) \end{vmatrix}, \tag{8.109}$$

where $\chi(S_i) = \left|\frac{1}{2}, \pm\frac{1}{2}\right\rangle$ is the spin state of the ith particle, with $i = 1, 2, 3, \ldots, N$. If N is odd then we need to remove the last row of the determinant.

Problem 8.4

Neglecting the spin–orbit interaction and the interaction between the electrons, find the energy levels and the wave functions of the three lowest states for a two-electron atom.

Solution

Examples of such a system are the helium atom ($Z = 2$), the singly ionized Li^+ ion ($Z = 3$), the doubly ionized Be^{2+} ion ($Z = 4$), and so on. Neglecting the spin–orbit interaction and the interaction between the electrons, $V_{12} = e^2/r_{12} = e^2/|\vec{r}_1 - \vec{r}_2|$, we can view each electron as moving in the Coulomb field of the Ze nucleus. The Hamiltonian of this system is therefore equal to the sum of the Hamiltonians of the two electrons:

$$\hat{H} = H_0^{(1)} + H_0^{(2)} = \left(-\frac{\hbar^2}{2\mu}\nabla_1^2 - \frac{Ze^2}{r_1}\right) + \left(-\frac{\hbar^2}{2\mu}\nabla_2^2 - \frac{Ze^2}{r_2}\right), \tag{8.110}$$

where $\mu = Mm_e/(M + m_e)$, M is the mass of the nucleus, and m_e is the mass of the electron. We have considered here that the nucleus is placed at the origin and that the electrons are located at $\vec{r}_1$ and $\vec{r}_2$. The Schrödinger equation of the system is given by

$$\left[\hat{H}_0^{(1)} + \hat{H}_0^{(2)}\right]\Psi(\vec{r}_1,\ \vec{S}_1;\ \vec{r}_2,\ \vec{S}_2) = E_{n_1 n_2}\Psi(\vec{r}_1,\ \vec{S}_1;\ \vec{r}_2,\ \vec{S}_2), \tag{8.111}$$

where the energy $E_{n_1 n_2}$ is equal to the sum of the energies of the electrons:

$$E_{n_1 n_2} = E_{n_1}^{(0)} + E_{n_2}^{(0)} = -\frac{Z^2 e^2}{2a_0}\frac{1}{n_1^2} - \frac{Z^2 e^2}{2a_0}\frac{1}{n_2^2}, \tag{8.112}$$

where $a_0 = \hbar^2/(me^2)$ is the Bohr radius. The wave function is equal to the product of the spatial and spin parts:

$$\Psi(\vec{r}_1,\ \vec{S}_1;\ \vec{r}_2,\ \vec{S}_2) = \psi(\vec{r}_1,\ \vec{r}_2)\chi(\vec{S}_1,\ \vec{S}_2); \tag{8.113}$$

$\vec{S}_1$ and $\vec{S}_2$ are the spin vectors of the electrons.

Since this system consists of two identical fermions (electrons), its wave function has to be antisymmetric. So either the spatial part is antisymmetric and the spin part is symmetric,

$$\Psi(\vec{r}_1, \vec{S}_1; \vec{r}_2, \vec{S}_2) = \frac{1}{\sqrt{2}}\left[\phi_{n_1 l_1 m_1}(\vec{r}_1)\phi_{n_2 l_2 m_2}(\vec{r}_2) - \phi_{n_2 l_2 m_2}(\vec{r}_1)\phi_{n_1 l_1 m_1}(\vec{r}_2)\right]\chi_{triplet}(\vec{S}_1, \vec{S}_2), \tag{8.114}$$

or the spatial part is symmetric and the spin part is antisymmetric,

$$\Psi(\vec{r}_1,\ \vec{S}_1;\ \vec{r}_2,\ \vec{S}_2) = \phi_{n_1 l_1 m_1}(\vec{r}_1)\phi_{n_2 l_2 m_2}(\vec{r}_2)\chi_{singlet}(\vec{S}_1,\ \vec{S}_2), \tag{8.115}$$

where $\chi_{triplet}$ and $\chi_{singlet}$, which result from the coupling of two spins $\frac{1}{2}$, are given by (8.67) and (8.68).

Let us now specify the energy levels and wave functions of the three lowest states. The ground state corresponds to both electrons occupying the lowest state $|nlm>=|100>$ (i.e., $n_1 = n_2 = 1$); its energy and wave function can be inferred from (8.112) and (8.115):

$$E^{(0)} = E_{11} = 2E_1^{(0)} = -2\frac{Z^2 e^2}{2a_0} = -27.2Z^2\,\text{eV}, \tag{8.116}$$

$$\Psi_0(\vec{r}_1,\ \vec{S}_1;\ \vec{r}_2,\ \vec{S}_2) = \phi_{100}(\vec{r}_1)\phi_{100}(\vec{r}_2)\chi_{singlet}(\vec{S}_1,\ \vec{S}_2), \tag{8.117}$$

where $\phi_{100}(\vec{r}) = R_{10}(r)Y_{00}(\Omega) = (1/\sqrt{\pi})(Z/a_0)^{3/2}e^{-Zr/a_0}$.

In the first excited state, one electron occupies the lowest level $|nlm\rangle = |100\rangle$ and the other electron occupies the level $|nlm\rangle = |200\rangle$; this corresponds either to $n_1 = 1,\ n_2 = 2$ or to $n_1 = 2,\ n_2 = 1$. The energy and the wave function can thus be inferred from (8.112) and (8.114):

$$E^{(1)} = E_{12} = E_1^{(0)} + E_2^{(0)} = -\frac{Z^2e^2}{2a_0} - \frac{1}{4}\frac{Z^2e^2}{2a_0} = -\frac{5}{4} \times 13.6Z^2\,\text{eV} = -17.0Z^2\,\text{eV}, \tag{8.118}$$

$$\Psi_1(\vec{r}_1,\ \vec{S}_1;\ \vec{r}_2,\ \vec{S}_2) = \frac{1}{\sqrt{2}}\Big[\phi_{100}(\vec{r}_1)\phi_{200}(\vec{r}_2) - \phi_{200}(\vec{r}_1)\phi_{100}(\vec{r}_2)\Big]\chi_{triplet}(\vec{S}_1,\ \vec{S}_2), \tag{8.119}$$

where $\phi_{200}(\vec{r}) = R_{20}(r)Y_{00}(\Omega) = (1/\sqrt{8\pi})(Z/a_0)^{3/2}(1 - Zr/2a_0)e^{-Zr/2a_0}$.

Finally, the energy and wave function of the second excited state, which correspond to both electrons occupying the second level $|nlm\rangle = |200\rangle$ (i.e., $n_1 = n_2 = 2$), can be inferred from (8.112) and (8.115):

$$E^{(2)} = E_{22} = E_2^{(0)} + E_2^{(0)} = 2E_2^{(0)} = -\frac{1}{2}\frac{Z^2e^2}{2a_0} = -\frac{1}{2} \times 13.6Z^2\,\text{eV} = -6.8Z^2\,\text{eV}, \tag{8.120}$$

$$\Psi_2(\vec{r}_1,\ \vec{S}_1;\ \vec{r}_2,\ \vec{S}_2) = \phi_{200}(\vec{r}_1)\phi_{200}(\vec{r}_2)\chi_{singlet}(\vec{S}_1,\ \vec{S}_2). \tag{8.121}$$

These results are obviously not expected to be accurate because, by neglecting the Coulomb interaction between the electrons, we have made a grossly inaccurate approximation. For instance, the numerical value for the ground state energy obtained from (8.112) for the helium atom is $E_{theory}^{(0)} = -108.8\,\text{eV}$ whereas the experimental value is $E_{exp}^{(0)} = -78.975\,\text{eV}$; that is, the theoretical value is 37.8% lower than the experimental value.

In Chapter 9 we will show how to use perturbation theory and the variational method to obtain very accurate theoretical values for the energy levels of two-electron atoms.

Problem 8.5

Find the energy levels and the wave functions of the ground state and the first excited state for a system of two noninteracting identical particles moving in a common external harmonic oscillator potential for (a) two spin 1 particles with no orbital angular momentum and (b) two spin $\frac{1}{2}$ particles.

Solution

Since the particles are noninteracting and identical, their Hamiltonian is $\hat{H} = \hat{H}_1 + \hat{H}_2$, where $\hat{H}_1$ and $\hat{H}_2$ are the Hamiltonians of particles 1 and 2: $\hat{H}_j = -(\hbar^2/2m)d^2/dx_j^2 + m\omega x_j^2/2$ with $j = 1, 2$. The total energy of the system is $E_{n_1n_2} = \varepsilon_{n_1} + \varepsilon_{n_2}$, where $\varepsilon_{n_j} = \left(n_j + \frac{1}{2}\right)\hbar\omega$.

(a) When the system consists of two identical spin 1 particles, the total wave function of this system must be symmetric. Thus, the space and spin parts must be both symmetric or both antisymmetric:

$$\Psi(x_1, S_1; x_2, S_2) = \frac{1}{\sqrt{2}}\Big[\psi_s(x_1, x_2)\chi_s(S_1, S_2) + \psi_a(x_1, x_2)\chi_a(S_1, S_2)\Big], \tag{8.122}$$

where

$$\psi_s(x_1, x_2) \;=\; \frac{1}{\sqrt{2}}\Big[\, \psi_{n_1}(x_1)\psi_{n_2}(x_2) + \psi_{n_1}(x_2)\psi_{n_2}(x_1)\Big], \tag{8.123}$$

$$\psi_a(x_1, x_2) \;=\; \frac{1}{\sqrt{2}}\left[\psi_{n_1}(x_1)\psi_{n_2}(x_2) - \psi_{n_1}(x_2)\psi_{n_2}(x_1)\right], \tag{8.124}$$

where $\psi_n(x)$ is a harmonic oscillator wave function for the state n; for instance, the ground state and first excited state are

$$\psi_0(x) = \frac{1}{\sqrt{\sqrt{\pi}x_0}}\exp\left(-\frac{x^2}{2x_0^2}\right), \qquad \psi_1(x) = \sqrt{\frac{2}{\sqrt{\pi}x_0^3}}\,x\exp\left(-\frac{x^2}{2x_0^2}\right), \tag{8.125}$$

with $x_0 = \sqrt{\hbar/(m\omega)}$.

The spin states $\chi(S_1, S_2)$ can be obtained by coupling the spins of the two particles, $S_1 = 1$ and $S_2 = 1$: $\vec{S} = \vec{S}_1 + \vec{S}_2$. As shown in Chapter 7, the spin states corresponding to $S = 2$ are given by

$$|2,\ \pm 2\rangle = |11;\ \pm 1, \pm 1\rangle, \qquad |2,\ \pm 1\rangle = \frac{1}{\sqrt{2}}\Big(\,|1, 1;\ \pm 1, 0\rangle + |1, 1;\ 0, \pm 1, \rangle\Big), \tag{8.126}$$

$$|2,\ 0\rangle = \frac{1}{\sqrt{6}}\Big(\,|1, 1;\ 1,\ -1\rangle + 2|1, 1;\ 0, 0\rangle + |1, 1;\ -1, 1\rangle\Big), \tag{8.127}$$

those corresponding to $S = 1$ by

$$|1,\ \pm 1\rangle \;=\; \frac{1}{\sqrt{2}}\Big(\,\pm|1, 1;\ \pm 1, 0\rangle \mp |1, 1;\ 0, \pm 1\rangle\Big), \tag{8.128}$$

$$|1,\ 0\rangle \;=\; \frac{1}{\sqrt{2}}\Big(\,|1, 1;\ 1, -1\rangle - |1, 1;\ -1, 1\rangle\Big), \tag{8.129}$$

and the one corresponding to $S = 0$ by

$$|0,\ 0\rangle = \frac{1}{\sqrt{3}}\Big(\,|1, 1;\ 1, -1\rangle - |1, 1;\ 0, 0\rangle + |1, 1;\ -1, 1\rangle\Big). \tag{8.130}$$

Obviously, the five states $|2,\ m_s\rangle$, corresponding to $S = 2$ and $|00\rangle$, are symmetric, whereas the three states $|1,\ m_s\rangle$ are antisymmetric. Thus, $\chi_s(S_1, S_2)$ is given by any one of the six states $|2,\ \pm 2\rangle$, $|2,\ \pm 1\rangle$, $|2,\ 0\rangle$, and $|0,\ 0\rangle$; as for $\chi_a(S_1, S_2)$, it is given by any one of the three states $|2,\ \pm 1\rangle$, and $|1,\ 0\rangle$.

The ground state corresponds to the case where both particles are in their respective ground states $n_1 = n_2 = 0$. The energy is then given by $E^{(0)} = \varepsilon_0 + \varepsilon_0 = \frac{1}{2}\hbar\omega + \frac{1}{2}\hbar\omega = \hbar\omega$. Since $\psi_a(x_1, x_2)$, as given by (8.124), vanishes for $n_1 = n_2 = 0$, the ground state wave function (8.122) reduces to

$$\Psi_0(x_1, S_1; x_2, S_2) = \psi_0(x_1)\psi_0(x_2)\chi_s(S_1, S_2) = \frac{1}{\sqrt{\pi}x_0}\exp\left(-\frac{x_1^2 + x_2^2}{2x_0^2}\right)\chi_s(S_1, S_2), \tag{8.131}$$

where $\psi_0(x)$ is given by (8.125). The ground state is thus sixfold degenerate, since there are six spin states $\chi_s(S_1, S_2)$ that are symmetric.

In the first excited state, one particle occupies the ground state level $n = 0$ and the other in the first excited state $n = 1$; this corresponds to two possible configurations: either $n_1 = 0$ and $n_2 = 1$ or $n_1 = 1$ and $n_2 = 0$. The energy is then given by $E^{(1)} = \varepsilon_0 + \varepsilon_1 = \frac{1}{2}\hbar\omega + \frac{3}{2}\hbar\omega = 2\hbar\omega$. The first excited state can be inferred from (8.122) to (8.124):

$$\begin{aligned}\Psi_1(x_1, S_1; x_2, S_2) &= \frac{1}{2}\Big[\psi_0(x_1)\psi_1(x_2) + \psi_0(x_2)\psi_1(x_1)\Big]\chi_s(S_1, S_2) \\ &\quad + \frac{1}{2}\Big[\psi_0(x_1)\psi_1(x_2) - \psi_0(x_2)\psi_1(x_1)\Big]\chi_a(S_1, S_2), \qquad (8.132)\end{aligned}$$

where $\psi_0(x)$ and $\psi_1(x)$ are listed in (8.125). The first excited state is ninefold degenerate since there are six spin states, $\chi_s(S_1, S_2)$, that are symmetric and three, $\chi_a(S_1, S_2)$, that are antisymmetric.

(b) For a system of two identical fermions, the wave function must be antisymmetric and the space and spin parts must have opposite symmetries:

$$\Psi(x_1, S_1; x_2, S_2) = \frac{1}{2}\Big[\psi_s(x_1, x_2)\chi_{singlet}(S_1, S_2) + \psi_a(x_1, x_2)\chi_{triplet}(S_1, S_2)\Big], \qquad (8.133)$$

where the symmetric spin state, $\chi_{triplet}(S_1, S_2)$, is given by the triplet states listed in (8.67); the antisymmetric spin state, $\chi_{singlet}(S_1, S_2)$, is given by the (singlet) state (8.68).

The ground state for the two spin $\frac{1}{2}$ particles corresponds to the case where both particles occupy the lowest level, $n_1 = n_2 = 0$, and have different spin states. The energy is then given by $E^{(0)} = \varepsilon_0 + \varepsilon_0 = \hbar\omega$ and the wave function by

$$\begin{aligned}\Psi_0(x_1, S_1; x_2, S_2) &= \psi_0(x_1)\psi_0(x_2)\chi_{singlet}(S_1, S_2) \\ &= \frac{1}{\sqrt{\pi}x_0}\exp\left(-\frac{x_1^2 + x_2^2}{2x_0^2}\right)\chi_{singlet}(S_1, S_2), \qquad (8.134)\end{aligned}$$

since $\psi_a(x_1, x_2)$ vanishes for $n_1 = n_2 = 0$. The ground state is not degenerate, since there is only one spin state which is antisymmetric, $\chi_{singlet}(S_1, S_2)$.

The first excited state corresponds also to $n_1 = 0$ and $n_2 = 1$ or $n_1 = 1$ and $n_2 = 0$. The energy is then given by $E^{(1)} = \varepsilon_0 + \varepsilon_1 = 2\hbar\omega$ and the wave function by

$$\begin{aligned}\Psi_1(x_1, S_1; x_2, S_2) &= \frac{1}{2}\Big[\psi_0(x_1)\psi_1(x_2) + \psi_0(x_2)\psi_1(x_1)\Big]\chi_{singlet}(S_1, S_2) \\ &\quad + \frac{1}{2}\Big[\psi_0(x_1)\psi_1(x_2) - \psi_0(x_2)\psi_1(x_1)\Big]\chi_{triplet}(S_1, S_2). \qquad (8.135)\end{aligned}$$

This state is fourfold degenerate since there are three spin states, $\chi_{triplet}(S_1, S_2)$, that are symmetric and one, $\chi_{singlet}(S_1, S_2)$, that is antisymmetric.

8.6 Exercises

Exercise 8.1

Consider a system of three noninteracting identical bosons that move in a common external one-dimensional harmonic oscillator potential. Find the energy levels and wave functions of the ground state, the first excited state, and the second excited state of the system.

Exercise 8.2

Consider two identical particles of spin $\frac{1}{2}$ that are confined in a cubical box of side L. Find the energy and the wave function of this system in the case of no interaction between the particles.

Exercise 8.3

(a) Consider a system of two nonidentical particles, each of spin 1 and having no orbital angular momentum (i.e., both particles are in s states). Write down all possible states for this system.

(b) What restrictions do we get if the two particles are identical? Write down all possible states for this system of two spin 1 identical particles.

Exercise 8.4

Two identical particles of spin $\frac{1}{2}$ are enclosed in a one-dimensional box potential of length L with rigid walls at $x = 0$ and $x = L$. Assuming that the two-particle system is in a *triplet spin state*, find the energy levels, the wave functions, and the degeneracies corresponding to the three lowest states.

Exercise 8.5

Two identical particles of spin $\frac{1}{2}$ are enclosed in a one-dimensional box potential of length L with rigid walls at $x = 0$ and $x = L$. Assuming that the two-particle system is in a *singlet spin state*, find the energy levels, the wave functions, and the degeneracies corresponding to the three lowest states.

Exercise 8.6

Two identical particles of spin $\frac{1}{2}$ are moving under the influence of a one-dimensional harmonic oscillator potential. Assuming that the two-particle system is in a *triplet spin state*, find the energy levels, the wave functions, and the degeneracies corresponding to the three lowest states.

Exercise 8.7

Find the ground state energy, the average ground state energy per particle, and the ground state wave function of a system of N noninteracting, identical bosons moving under the influence of a one-dimensional harmonic oscillator potential.

Exercise 8.8

Find the ground state energy, the average ground state energy per particle, and the ground state wave function of a system of N noninteracting identical spin $\frac{1}{2}$ particles moving under the influence of a one-dimensional harmonic oscillator potential for the following two cases:

(a) when N is even and

(b) when N is odd.

Exercise 8.9

Consider a system of four noninteracting particles that are confined to move in a one-dimensional infinite potential well of length a: $V(x) = 0$ for $0 < x < a$ and $V(x) = \infty$ for other values of x. Determine the energies and wave functions of the ground state, the first excited state, and the second excited state when the four particles are

(a) distinguishable bosons such that their respective masses satisfy this relation: $m_1 < m_2 < m_3 < m_4$, and

(b) identical bosons (each of mass m).

Exercise 8.10

Consider a system of four noninteracting identical spin 1/2 particles (each of mass m) that are confined to move in a one-dimensional infinite potential well of length a: $V(x) = 0$ for $0 < x < a$ and $V(x) = \infty$ for other values of x. Determine the energies and wave functions of the ground state and the first three excited states. Draw a figure showing how the particles are distributed among the levels.

Exercise 8.11

Consider a system of four noninteracting identical spin $\frac{1}{2}$ particles that are in the same spin state $\left|\frac{1}{2}, \frac{1}{2}\right\rangle$ and confined to move in a one-dimensional infinite potential well of length a: $V(x) = 0$ for $0 < x < a$ and $V(x) = \infty$ for other values of x. Determine the energies and wave functions of the ground state, the first excited state, and the second excited state.

Exercise 8.12

Assuming the electrons in the helium atom to be spinless bosons and neglecting the interactions between them, find the energy and the wave function of the ground state and the first excited state of this (hypothetical) system.

Exercise 8.13

Assuming the electrons in the lithium atom to be spinless bosons and neglecting the interactions between them, find the energy and the wave function of the ground state and the first excited state of this (hypothetical) system.

Exercise 8.14

Consider a system of two noninteracting identical spin 1/2 particles (with mass m) that are confined to move in a one-dimensional infinite potential well of length L: $V(x) = 0$ for $0 < x < L$ and $V(x) = \infty$ for other values of x. Assume that the particles are in a state with the wave function

$$\Psi(x_1, x_2) = \frac{\sqrt{2}}{L}\left[\sin\left(\frac{2\pi x_1}{L}\right)\sin\left(\frac{5\pi x_2}{L}\right) + \sin\left(\frac{5\pi x_1}{L}\right)\sin\left(2\frac{\pi x_2}{L}\right)\right]\chi(s_1, s_2),$$

where x_1 and x_2 are the positions of particles 1 and 2, respectively, and $\chi(s_1, s_2)$ is the spin state of the two particles.

(a) Is $\chi(s_1, s_2)$ going to be a singlet or triplet state?

(b) Find the energy of this system.

Exercise 8.15

Consider a system of two noninteracting identical spin 1/2 particles (with mass m) that are confined to move in a common one-dimensional harmonic oscillator potential. Assume that the particles are in a state with the wave function

$$\Psi(x_1, x_2) = \frac{\sqrt{2}}{\sqrt{\pi}x_0^2}(x_2 - x_1)\exp\left(-\frac{x_1^2 + x_2^2}{2x_0^2}\right)\chi(s_1, s_2),$$

where x_1 and x_2 are the positions of particles 1 and 2, respectively, and $\chi(s_1, s_2)$ is the spin state of the two particles.

(a) Is $\chi(s_1, s_2)$ going to be a singlet or triplet state?

(b) Find the energy of this system.

Exercise 8.16

Consider a system of five noninteracting electrons (in the approximation where the Coulomb interaction between the electrons is neglected) that are confined to move in a common one-dimensional infinite potential well of length $L = 0.5$ nm: $V(x) = 0$ for $0 < x < L$ and $V(x) = \infty$ for other values of x.

(a) Find the ground state energy of the system.
(b) Find the energy of the first state of the system.
(c) Find the excitation energy of the first excited state.

Exercise 8.17

Determine the ground state electron configurations for the atoms having $Z = 40$, 53, 70, and 82 electrons.

Exercise 8.18

Specify the possible J values (i.e., total angular momenta) associated with each of the following states: ${}^1P$, ${}^4F$, ${}^2G$, and ${}^1H$.

Exercise 8.19

Find the spectroscopic notation ${}^{2S+1}L_J$ (i.e., find the L, S, and J) for the ground state configurations of

(a) Sc ($Z = 21$) and
(b) Cu ($Z = 29$).