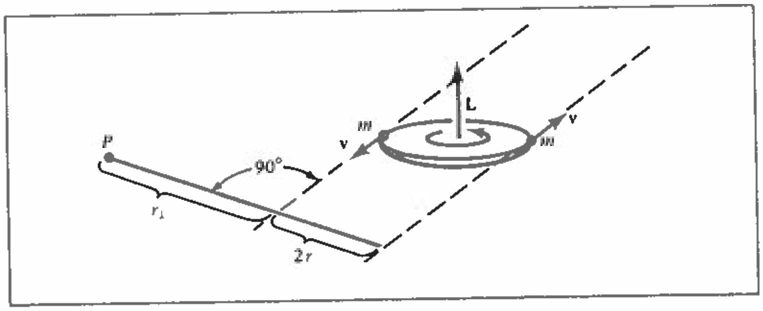

FIGURE 7-5. *The total spin angular momentum* **L**, *relative to an arbitrary point P, of two particles symmetrically located with respect to the spin axis.*

is *independent* of the location of P (independent of $r_\perp$). Since the spinning object is taken to be symmetrical about the rotation axis, we can imagine it to be composed of such pairs of particles, each contributing an angular momentum independent of the choice of axis. Thus, the object's total spin angular momentum is independent of axis. It is customary to locate the spin-angular-momentum vector along the spin axis, as shown in Figure 7-5; from the proof given above, it could be located *anywhere*. It is not hard to show that spin angular momentum is independent of the inertial frame, too. The angular momentum of a spinning symmetrical object is, then, an intrinsic property of the object; it is sometimes referred to as *intrinsic angular momentum.*

The total angular momentum of a system of objects consists of the vector sum of the orbital and spin angular momenta; when the system is isolated, its total angular momentum is constant. We shall see that such particles as electrons must be assigned intrinsic angular momenta in addition to their orbital angular momenta.

7-2 Quantization of Orbital Angular Momentum

The Bohr theory of a one-electron atom introduces the principal quantum number n, whose integral value determines the total energy of the atom according to the relation $E_n = -E_I/n^2$, where E_I is the ionization energy. The quantum number n also specifies the magnitude of the angular momentum **L**. This value comes from the electron's orbiting the nucleus in a circular path, according to $L = n\hbar$, where $\hbar$ is Planck's constant divided by 2π. It is, however, not proper from the point of view of wave mechanics to visualize the electron as moving in a well-defined path, circular or otherwise.

Although the Bohr theory agrees with wave mechanics on the quantized energy values E_n, the Bohr rule for the quantization of the magnitude of the orbital angular momentum is *not* correct. Wave mechanics does show that there is quantization of the orbital angular momentum for a one-electron atomic system, but the rules are more complicated than what the simple Bohr model provides. Because the mathematical analysis of this quantum problem is lengthy and involved, we shall state only the results here.[†]

First, one finds that the magnitude of the orbital angular momentum **L** of an atomic system is quantized; the possible values are given by

$$L = \sqrt{l(l+1)}\hbar \qquad (7\text{-}1)$$

[†] See any textbook on elementary quantum mechanics.

where l is an integer called the *orbital-angular-momentum quantum number*. Furthermore, for a given value of the principal quantum number n, the only permitted values of l are integers ranging from zero to $(n - 1)$:

$$l = 0, 1, 2, 3, \ldots, n - 1$$

Thus, for $n = 1$ (ground state), the only possible value of l is 0, and from Equation 7–1, the value of L is 0. For $n = 2$, the value of l is restricted to 0 or 1, and the corresponding values of L are 0 and $\sqrt{2}\hbar$, respectively. Generally for a given n, there are n possible values of l, and therefore n possible values of the orbital angular momentum. The integral values of the quantum number l are often represented by letter symbols (the reasons are historical), as follows:

$$\begin{aligned} l &= 0,\ 1,\ 2,\ 3,\ 4,\ 5,\ \ldots \\ \text{Symbol} &= \text{S, P, D, F, G, H, } \ldots \end{aligned}$$

Whereas in the Bohr theory, the state of an atom is specified completely by the one quantum number n (hence, the radius of the circular orbit, or the total energy), in wave mechanics the state of an atom is specified by the values of *all* the appropriate quantum numbers. To every state there corresponds a distinctive wave function ψ, differing from the others in the way in which it depends on the spatial coordinates. Those states for which, say, n is 3 and l is 0, 1, and 2 are called 3S, 3P, and 3D states, respectively. From Equation 7–1, the corresponding magnitudes of the orbital angular momentum **L** are 0, $\sqrt{2}\hbar$, $\sqrt{6}\hbar$; see Figure 7–6. Since the 3S, 3P, and 3D states have a common value of the principal quantum number, $n = 3$, then for a single electron under the influence of a Coulomb force from a nucleus assumed to be a point charge, the three states have identical energies E but different angular momenta; they also differ in the spatial dependence of the wave function. Such states, which are identical in total energy but different in some other respect, are said to be *degenerate*.

Recall that in the classical planetary model, a bound system's total energy depends only on the magnitude of the major axis of the ellipse and not on the eccentricity of the orbits or on the orbital angular momentum.

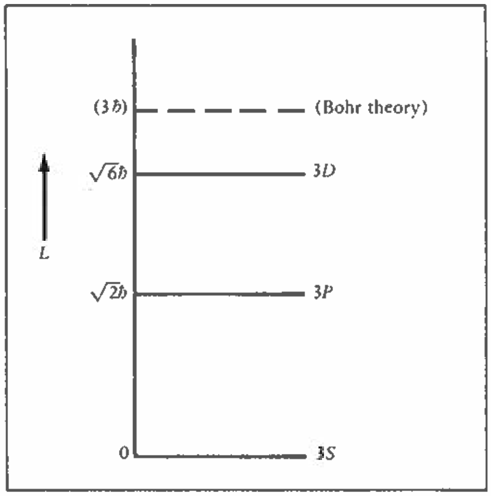

FIGURE 7–6. *Allowed values of the magnitude of the orbital angular momentum for $n = 3$.*

Quantum mechanics explains certain properties of the hydrogen atom in an accurate, straightforward, and beautiful way. However, it cannot approach a complete description of this atom or of any other without taking into account electron spin and the exclusion principle. In this chapter we will look into the role of electron spin in atomic phenomena and into why the exclusion principle is the key to understanding the structures of atoms with more than one electron.

7.1 ELECTRON SPIN

Round and round it goes forever

The theory of the atom developed in the previous chapter cannot account for a number of well-known experimental observations. One is the fact that many spectral lines actually consist of two separate lines that are very close together. An example of this **fine structure** is the first line of the Balmer series of hydrogen, which arises from transitions between the $n = 3$ and $n = 2$ levels in hydrogen atoms. Here the theoretical prediction is for a single line of wavelength 656.3 nm while in reality there are two lines 0.14 nm apart—a small effect, but a conspicuous failure for the theory.

Another failure of the simple quantum-mechanical theory of the atom occurs in the Zeeman effect, which was discussed in Sec. 6.10. There we saw that the spectral lines of an atom in a magnetic field should each be split into the three components specified by Eq. (6.43). While the normal Zeeman effect is indeed observed in the spectra of a few elements under certain circumstances, more often it is not. Four, six, or even more components may appear, and even when three components are present their spacing may not agree with Eq. (6.43). Several anomalous Zeeman patterns are shown in Fig. 7.1 together with the predictions of Eq. (6.43). (When reproached in 1923 for looking sad, the physicist Wolfgang Pauli replied, "How can one look happy when he is thinking about the anomalous Zeeman effect?")

In order to account for both fine structure in spectral lines and the anomalous Zeeman effect, two Dutch graduate students, Samuel Goudsmit and George Uhlenbeck, proposed in 1925 that

> Every electron has an intrinsic angular momentum, called spin, whose magnitude is the same for all electrons. Associated with this angular momentum is a magnetic moment.

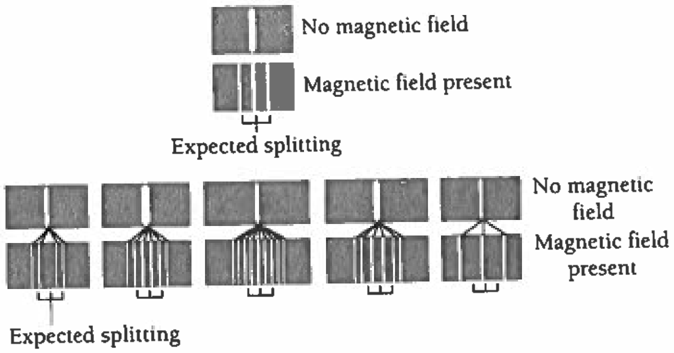

Figure 7.1 The normal and anomalous Zeeman effects in various spectral lines.

What Goudsmit and Uhlenbeck had in mind was a classical picture of an electron as a charged sphere spinning on its axis. The rotation involves angular momentum, and because the electron is negatively charged, it has a magnetic moment $\boldsymbol{\mu}_s$ opposite in direction to its angular momentum vector **S**. The notion of electron spin proved to be successful in explaining not only fine structure and the anomalous Zeeman effect but a wide variety of other atomic effects as well.

To be sure, the picture of an electron as a spinning charged sphere is open to serious objections. For one thing, observations of the scattering of electrons by other electrons at high energy indicate that the electron must be less than 10^{-16} m across, and quite possibly is a point particle. In order to have the observed angular momentum associated with electron spin, so small an object would have to rotate with an equatorial velocity many times greater than the velocity of light.

But the failure of a model taken from everyday life does not invalidate the idea of electron spin. We have already found plenty of ideas in relativity and quantum physics that are mandated by experiment although at odds with classical concepts. In 1929 the fundamental nature of electron spin was confirmed by Paul Dirac's development of relativistic quantum mechanics. He found that a particle with the mass and charge of the electron *must* have the intrinsic angular momentum and magnetic moment proposed for the electron by Goudsmit and Uhlenbeck.

The quantum number s describes the spin angular momentum of the electron. The only value s can have is $s = \frac{1}{2}$, which follows both from Dirac's theory and from spectral data. The magnitude S of the angular momentum due to electron spin is given in terms of the spin quantum number s by

Spin angular momentum

$$S = \sqrt{s(s+1)}\,\hbar = \frac{\sqrt{3}}{2}\hbar \tag{7.1}$$

This is the same formula as that giving the magnitude L of the orbital angular momentum in terms of the orbital quantum number l, $L = \sqrt{l(l+1)}\,\hbar$.

Example 7.1

Find the equatorial velocity v of an electron under the assumption that it is a uniform sphere of radius $r = 5.00 \times 10^{-17}$ m that is rotating about an axis through its center.

Solution

The angular momentum of a spinning sphere is $I\omega$, where $I = \frac{2}{5}mr^2$ is its moment of inertia and $\omega = v/r$ is its angular velocity. From Eq. (7.1) the spin angular momentum of an electron is $S = (\sqrt{3}/2)\hbar$, so

$$S = \frac{\sqrt{3}}{2}\hbar = I\omega = \left(\frac{2}{5}mr^2\right)\left(\frac{v}{r}\right) = \frac{2}{5}mvr$$

$$v = \left(\frac{5\sqrt{3}}{4}\right)\frac{\hbar}{mr} = \frac{(5\sqrt{3})(1.055\times10^{-34}\ \text{J}\cdot\text{s})}{(4)(9.11\times10^{-31}\ \text{kg})(5.00\times10^{-17}\ \text{m})} = 5.01\times10^{12}\ \text{m/s} = 1.67\times10^{4}\,c$$

The equatorial velocity of an electron on the basis of this model must be over 10,000 times the velocity of light, which is impossible. No classical model of the electron can overcome this difficulty.

Table 7.1 Quantum Numbers of an Atomic Electron

Name	Symbol	Possible Values	Quantity Determined
Principal	n	$1, 2, 3, \ldots$	Electron energy
Orbital	l	$0, 1, 2, \ldots, n-1$	Orbital angular-momentum magnitude
Magnetic	m_l	$-l, \ldots, 0, \ldots, +l$	Orbital angular-momentum direction
Spin magnetic	m_s	$-\frac{1}{2}, +\frac{1}{2}$	Electron spin direction

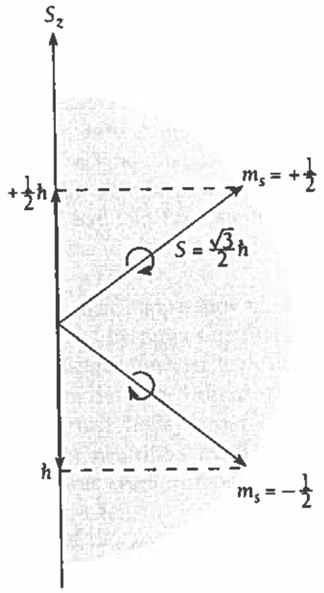

Figure 7.2 The two possible orientations of the spin angular-momentum vector are "spin up" ($m_s = +\frac{1}{2}$) and "spin down" ($m_s = -\frac{1}{2}$).

The space quantization of electron spin is described by the spin magnetic quantum number m_s. We recall that the orbital angular-momentum vector can have the $2l + 1$ orientations in a magnetic field from $+l$ to $-l$. Similarly the spin angular-momentum vector can have the $2s + 1 = 2$ orientations specified by $m_s = +\frac{1}{2}$ ("spin up") and $m_s = -\frac{1}{2}$ ("spin down"), as in Fig. 7.2. The component S_z of the spin angular momentum of an electron along a magnetic field in the z direction is determined by the spin magnetic quantum number, so that

z component of spin angular momentum

$$S_z = m_s\hbar = \pm\frac{1}{2}\hbar \tag{7.2}$$

We recall from Sec. 6.10 that gyromagnetic ratio is the ratio between magnetic moment and angular momentum. The gyromagnetic ratio for electron orbital motion is $-e/2m$. The gyromagnetic ratio characteristic of electron spin is almost exactly twice that characteristic of electron orbital motion. Taking this ratio as equal to 2, the spin magnetic moment $\boldsymbol{\mu}_s$ of an electron is related to its spin angular momentum **S** by

Spin magnetic moment

$$\boldsymbol{\mu}_s = -\frac{e}{m}\mathbf{S} \tag{7.3}$$

The possible components of $\boldsymbol{\mu}_s$ along any axis, say the z axis, are therefore limited to

z component of spin magnetic moment

$$\mu_{sz} = \pm\frac{e\hbar}{2m} = \pm\mu_B \tag{7.4}$$

where μ_B is the Bohr magneton ($= 9.274 \times 10^{-24}$ J/T $= 5.788 \times 10^{-5}$ eV/T).

The introduction of electron spin into the theory of the atom means that a total of four quantum numbers, n, l, m_l, and m_s, is needed to describe each possible state of an atomic electron. These are listed in Table 7.1.

7.2 EXCLUSION PRINCIPLE

A different set of quantum numbers for each electron in an atom

In a normal hydrogen atom, the electron is in its quantum state of lowest energy. What about more complex atoms? Are all 92 electrons of a uranium atom in the same quantum state, jammed into a single probability cloud? Many lines of evidence make this idea unlikely.

to whether they are singlets or triplets, that is, whether the two electron spins are antialigned or aligned, respectively. Note that the 1^3S state does *not* exist. When the atom is in an excited state, one of the electrons may remain a 1s electron in the K shell and the second electron occupy any of the higher excited levels. For example, the electron configuration of the first excited state in helium is $1s^12s^1$. Typically, transitions occur only between singlet states or only between triplet states.

The element with the next lowest atomic number, $Z = 3$, is lithium, $_3$Li. Of the three electrons in this atom, the first two occupy the two available $n = 1$ states. Therefore, as the exclusion principle requires, when lithium is in its ground state, the third electron goes to the lowest of the remaining available levels. The next-lowest available level after the K shell is $n = 2$ and $l = 0$. Then the ground-state configuration of the electrons in lithium is $1s^22s^1$, indicating two electrons in the closed K shell and one electron in the incomplete $l = 0$ subshell of the L shell; see Figure 7–28.

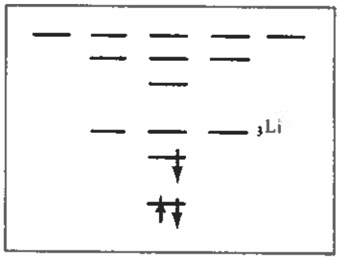

FIGURE 7–28. *Electron configuration of lithium in the ground state.*

Proceeding in this fashion—adding one electron as the nuclear charge or atomic number is increased by one unit, but always with the restriction that no *two* electrons within the atom can have the same set of quantum numbers—we can find the ground-state electron configurations of other atoms. We see from Figure 7–25 that two electrons can be accommodated in the *s* subshell of the L shell and six electrons in the p subshell, after which the L shell is completely occupied, holding its full quota of eight electrons. Table 7–4 gives the electron configurations of the elements from beryllium to sodium.

TABLE 7–4

ELEMENT	ELECTRON CONFIGURATION FOR THE GROUND STATE			
$_4$Be	$1s^2$	$2s^2$		
$_5$B	$1s^2$	$2s^2$	$2p^1$	
$_6$C	$1s^2$	$2s^2$	$2p^2$	
$_7$N	$1s^2$	$2s^2$	$2p^3$	
$_8$O	$1s^2$	$2s^2$	$2p^4$	
$_9$F	$1s^2$	$2s^2$	$2p^5$	
$_{10}$Ne	$1s^2$	$2s^2$	$2p^6$	
$_{11}$Na	$1s^2$	$2s^2$	$2p^6$	$3s^1$

We shall shortly note the chemical properties of several elements listed in Table 7–4 relative to their electron configurations and the occurrence of closed shells and subshells. First we note some of the properties of sodium that are directly related to its electron configuration, $1s^22s^22p^63s^1$. A single valence electron is outside the closed L shell, and the lowest state available to this valence electron is the 3s state. In the inner, closed subshells, the electrons' total angular momentum and magnetic moment is zero, since both their orbital angular momenta and spin angular momenta are paired off. These closed shells, $1s^2$, $2s^2$, and $2p^6$, are chemically inert and correspond to the electron configuration of the inert gas neon. The reason that sodium behaves approximately like a hydrogen atom is clear; a single valence electron moves about inner, inert, closed electron shells. The optical spectrum of sodium originates from the change in the state of the valence electron, while the ten electrons in the inner closed shells remain in their same states.