CHAPTER **7**

MANY-ELECTRON ATOMS

Despite the accuracy with which quantum mechanics accounts for certain of the properties of the hydrogen atom, and despite the elegance and essential simplicity of the theory, it cannot approach a complete description of this atom or of other atoms without taking into account electron spin and the exclusion principle associated with it. In this chapter we shall be introduced to the role of electron spin in atomic phenomena and to why the exclusion principle is the key to understanding the structures and spectra of atoms with more than one electron.

7.1 ELECTRON SPIN

Round and round it seems to go

Fine structure in spectral lines

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.

Anomalous Zeeman effect

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. (6.42). 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. (6.42). Several anomalous Zeeman patterns are shown in Fig. 7.1 together with the predictions of Eq. (6.42).

Electron spin

In an effort to account for both fine structure in spectral lines and the anomalous Zeeman effect, S. A. Goudsmit and G. E. Uhlenbeck proposed in 1925 that **the electron possesses an intrinsic angular momentum independent of any orbital angular momentum it might have and, associated with this angular momentum, a certain magnetic moment.**

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 $\mathbf{L}_s$. 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.

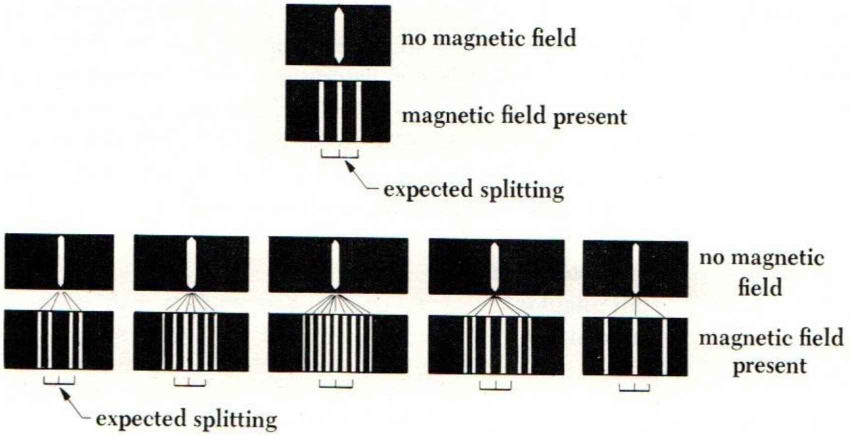


FIGURE 7.1 The normal and anomalous Zeeman effects in various spectral lines.

The electron as a spinning sphere is a model, not reality

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.

Dirac's theory of the electron

But the inapplicability of a model taken from everyday life does not invalidate the idea of electron spin. We have already been introduced to plenty of ideas in relativity and quantum physics that are consistent with 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. Instead of starting from the nonrelativistic energy equation $E = p^2/2m + V$ as Schrödinger did, Dirac used the relativistic equation $E = \sqrt{m_0^2c^4 + p^2c^2} + V$ [see Eq. (1.23)]. He found that a particle having the mass and charge of the electron *must* have the intrinsic angular momentum and magnetic moment attributed to the electron by Goudsmit and Uhlenbeck.

Spin angular momentum

The quantum number s is used to describe the spin angular momentum of the electron. The only value s can have is $s = \frac{1}{2}$; this restriction follows from Dirac's theory and, as we shall see below, may also be obtained empirically 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 the formula

Spin angular momentum

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

which is the same formula as that giving the magnitude L of the orbital angular momentum in terms of the orbital quantum number l:

$$L = \sqrt{l(l+1)}\hbar$$

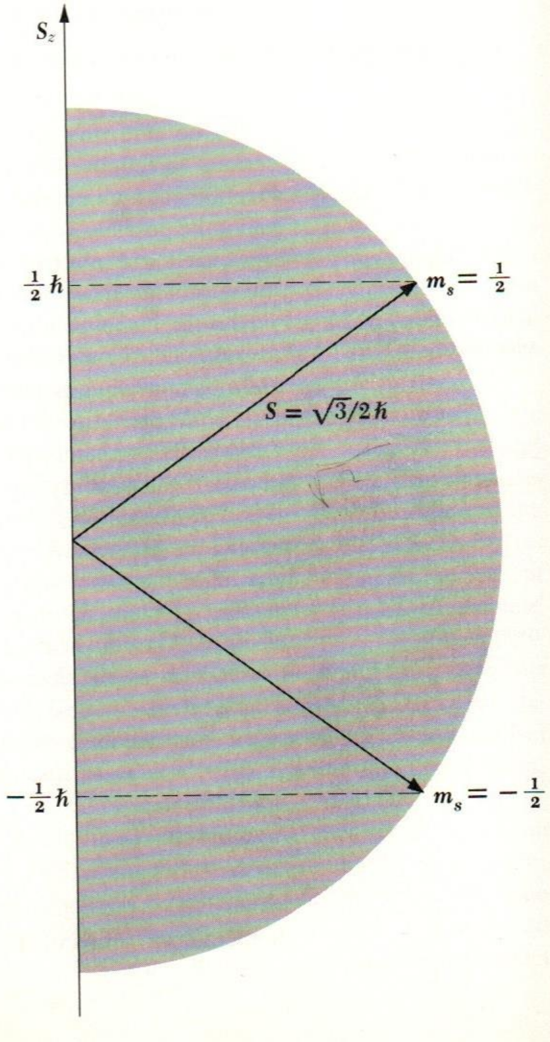
"Spin up" and "spin down" are the only possibilities

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

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

FIGURE 7.2 The two possible orientations of the spin angular-momentum vector.



Magnetic moment of the electron

The gyromagnetic ratio characteristic of electron spin is almost exactly twice that characteristic of electron orbital motion. Thus, 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

$$\boldsymbol{\mu}_s = \overset{2}{-}\frac{e}{2(m\;2)}\mathbf{S} \qquad (7.3)$$

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

z component of spin magnetic moment

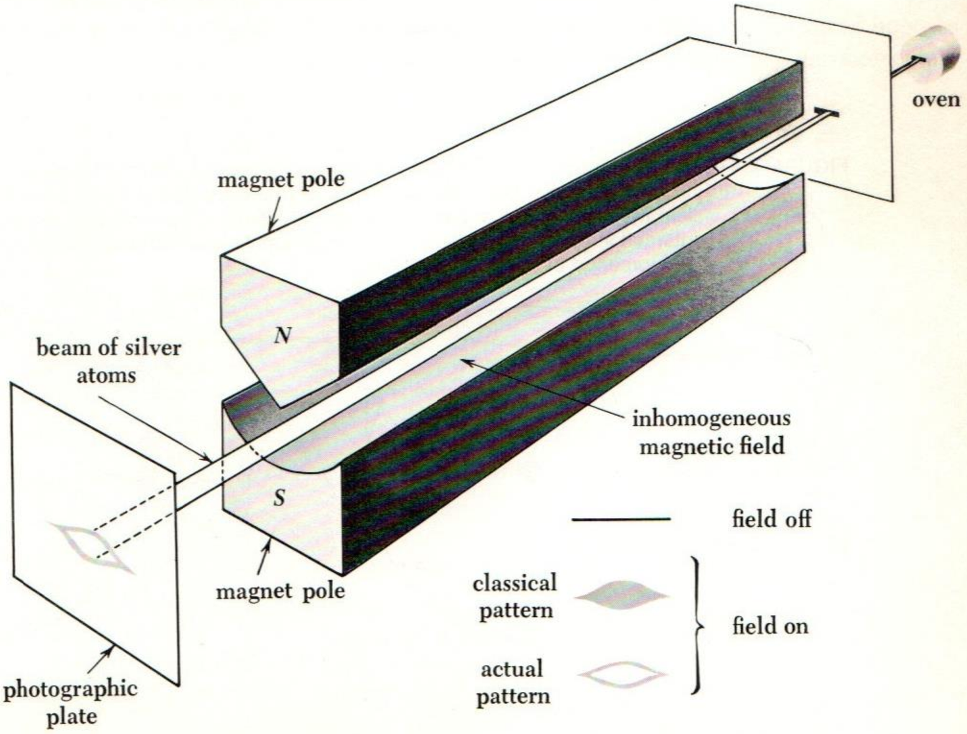
$$\mu_{sz} = \pm\frac{e\hbar}{2m} \qquad (7.4)$$

We recognize the quantity $e\hbar/2m$ as the Bohr magneton μ_b.

Stern-Gerlach experiment

Space quantization was first explicitly demonstrated by O. Stern and W. Gerlach in 1921. They directed a beam of neutral silver atoms from an oven through a set of collimating slits into an inhomogeneous magnetic field, as shown in Fig. 7.3. A

FIGURE 7.3 The Stern-Gerlach experiment.



photographic plate recorded the configuration of the beam after its passage through the field.

In its normal state, the entire magnetic moment of a silver atom is due to the spin of only one of its electrons. In a uniform magnetic field, such a dipole would merely experience a torque tending to align it with the field. In an inhomogeneous field, however, each "pole" of the dipole is subject to a force of different magnitude, and therefore there is a resultant force on the dipole that varies with its orientation relative to the field.

Classically, all orientations should be present in a beam of atoms. The result would merely be a broad trace on the photographic plate instead of the thin line formed in the absence of any magnetic field. Stern and Gerlach found, however, that the initial beam split into two distinct parts that correspond to the two opposite spin orientations in the magnetic field permitted by space quantization.

7.2 SPIN-ORBIT COUPLING

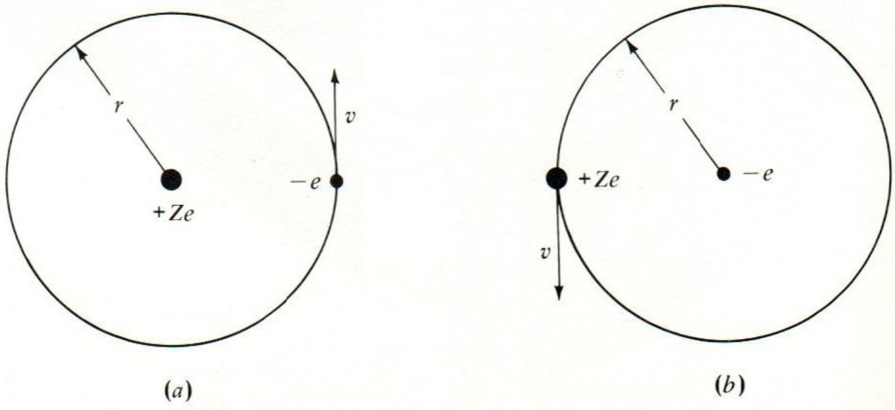
Angular momenta linked magnetically

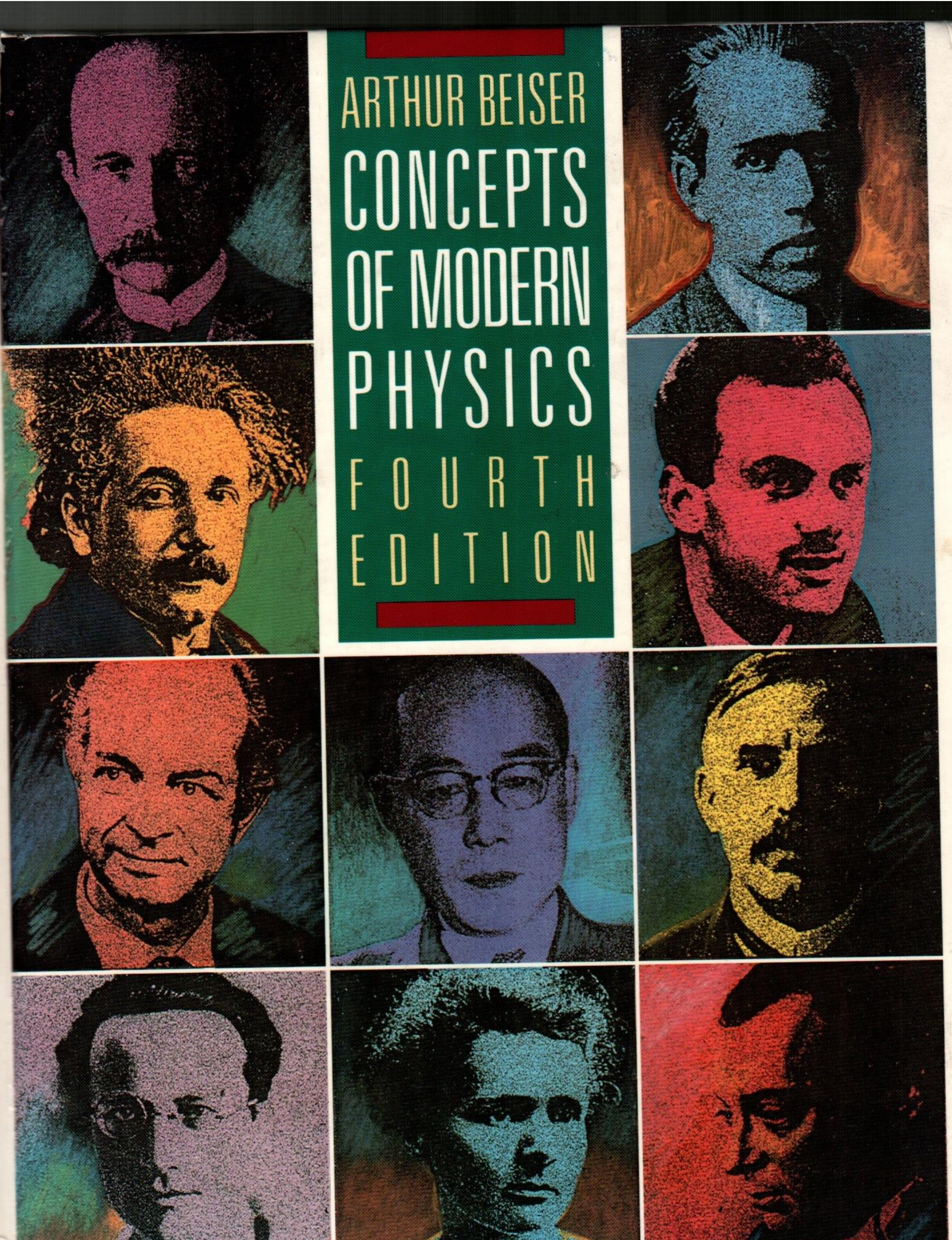
The fine-structure doubling of spectral lines arises from a magnetic interaction between the spin and orbital angular momenta of an atomic electron called *spin-orbit coupling*.

How spin and orbital angular momenta are coupled together

Spin-orbit coupling can be understood in terms of a straightforward classical model. An electron revolving about a nucleus finds itself in a magnetic field because in its own frame of reference, the nucleus is circling about *it* (Fig. 7.4). This magnetic field then acts upon the electron's own spin magnetic moment to produce a kind of internal Zeeman effect.

FIGURE 7.4 (*a*) An electron circles an atomic nucleus, as viewed from the frame of reference of the nucleus. (*b*) From the electron's frame of reference, the nucleus is circling it. The magnetic field the electron experiences as a result is directed upward from the plane of the paper. The interaction between the electron's spin magnetic moment and this magnetic field leads to the phenomenon of spin-orbit coupling.





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