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.

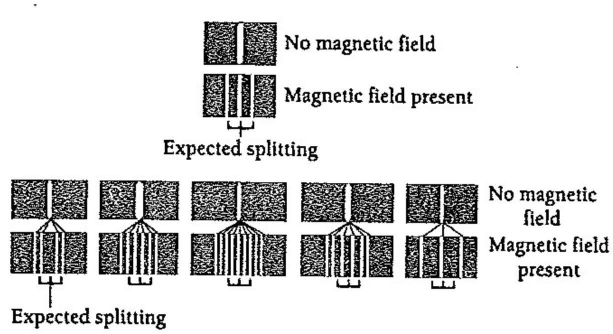

Figure 7.1 The normal and anomalous Zeeman effects in various spectral lines.

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

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

$$v = \left(\frac{5\sqrt{3}}{4}\right)\frac{\hbar}{mr} = \frac{(5\sqrt{3})(1.055 \times 10^{-34}\ \text{J}\cdot\text{s})}{(4)(9.11 \times 10^{-31}\ \text{kg})(5.00 \times 10^{-17}\ \text{m})} = 5.01 \times 10^{12}\ \text{m/s} = 1.67 \times 10^4 c$$

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

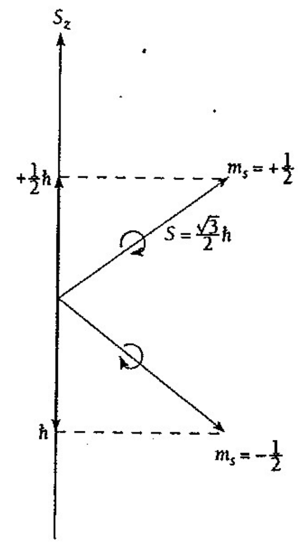

Figure 7.2 The two possible orientations of the spin angular-momentum vector are "spin up" ($m_s = +\frac{1}{2}$) and "spin down" ($m_s = -\frac{1}{2}$).

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 $\mathbf{S}$ 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.

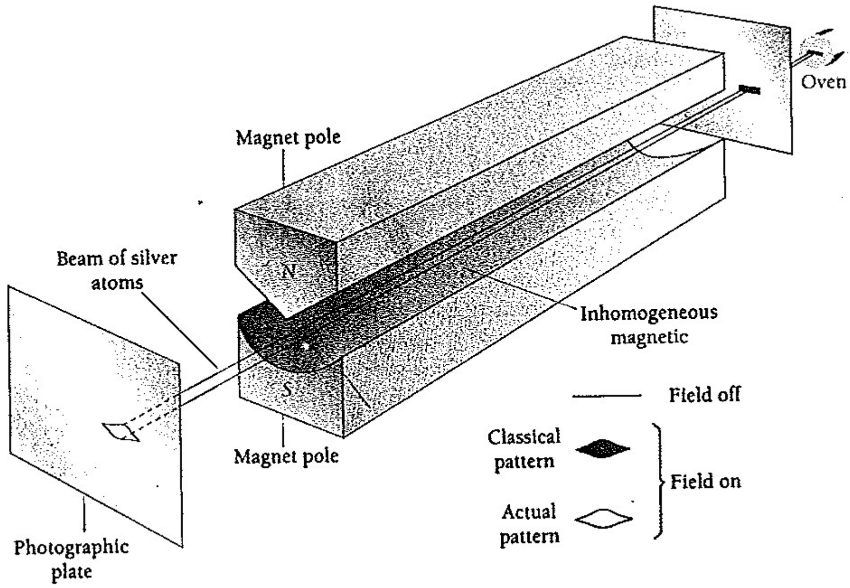

Figure 7.3 The Stern-Gerlach experiment.

The Stern-Gerlach Experiment

Space quantization was first explictly demonstrated in 1921 by Otto Stern and Walter Gerlach. They directed a beam of neutral silver atoms from an oven through a set of collimating slits into an inhomogeneous magnetic field as in Fig. 7.3. A photographic plate recorded the shape of the beam after it had passed 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 without 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.

An example is the great difference in chemical behavior shown by certain elements whose atomic structures differ by only one electron. Thus the elements that have the atomic numbers 9, 10, and 11 are respectively the chemically active halogen gas fluorine, the inert gas neon, and the alkali metal sodium. Since the electron structure of an atom controls how it interacts with other atoms, it makes no sense that the chemical properties of the elements should change so sharply with a small change in atomic number if all the electrons in an atom were in the same quantum state.

Wolfgang Pauli (1900–1958) was born in Vienna and at nineteen had prepared a detailed account of special and general relativity that impressed Einstein and remained the standard work on the subject for many years. Pauli received his doctorate from the University of Munich in 1922 and then spent short periods in Göttingen, Copenhagen, and Hamburg before becoming professor of physics at the Institute of Technology in Zurich, Switzerland, in 1928. In 1925 he proposed that four quantum numbers (what one of them governed was then unknown) are needed to characterize each atomic electron and that no two electrons in an atom have the same set of quantum numbers. This exclusion principle turned out to be the missing link in understanding the arrangement of electrons in an atom.

Late in 1925 Goudsmit and Uhlenbeck, two young Dutch physicists, showed that the electron possesses intrinsic angular momentum, so it must be thought of as spinning, and that Pauli's fourth quantum number described the direction of the spin. The American physicist Ralph Kronig had conceived of electron spin a few months earlier and had told Pauli about it. However, because Pauli had "ridiculed the idea" Kronig did not publish his work.

In 1931 Pauli resolved the problem of the apparently missing energy in the beta decay of a nucleus by proposing that a neutral, massless particle leaves the nucleus together with the electron emitted. Two years later Fermi developed the theory of beta decay with the help of this particle (today believed to have a small mass), which he called the neutrino ("small neutral one" in Italian). Pauli spent the war years in the United States, and received the Nobel Prize in 1945.

In 1925 Wolfgang Pauli discovered the fundamental principle that governs the electronic configurations of atoms having more than one electron. His **exclusion principle** states that

> No two electrons in an atom can exist in the same quantum state. Each electron must have a different set of quantum numbers n, l, m_l, m_s.

Pauli was led to the exclusion principle by a study of atomic spectra. The various states of an atom can be determined from its spectrum, and the quantum numbers of these states can be inferred. In the spectra of every element but hydrogen a number of lines are *missing* that correspond to transitions to and from states having certain combinations of quantum numbers. For instance, no transitions are observed in helium to or from the ground-state configuration in which the spins of both electrons are in the same direction. However, transitions *are* observed to and from the other ground-state configuration, in which the spins are in opposite directions.

In the absent state in helium the quantum numbers of *both* electrons would be $n = 1, l = 0, m_l = 0, m_s = \frac{1}{2}$. On the other hand, in the state known to exist one of the electrons has $m_s = \frac{1}{2}$ and the other $m_s = -\frac{1}{2}$. Pauli showed that every unobserved atomic state involves two or more electrons with identical quantum numbers, and the exclusion principle is a statement of this finding.

7.3 SYMMETRIC AND ANTISYMMETRIC WAVE FUNCTIONS

Fermions and bosons

Before we explore the role of the exclusion principle in de... it is interesting to look into its quantum-mechanical implica...