

9

Atomic Structure

Chapter Outline

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Much of what we have learned about the hydrogen atom with its single electron can be used directly to describe such single-electron ions as He^+ and Li^{2+} , which are hydrogen-like in their electronic structure. Multielectron atoms, however, such as neutral helium and lithium, introduce extra complications that stem from the interactions among the atomic electrons. Thus, the study of the atom inevitably involves us in the complexities of systems consisting of many interacting electrons. In this chapter we will learn some of the basic principles needed to treat such systems effectively and apply these principles to describe the physics of electrons in atoms.

Being of like charge and confined to a small space, the electrons of an atom repel one another strongly through the Coulomb force. In addition, we shall discover that the atomic electrons behave like tiny bar magnets, interacting magnetically with one another as well as with any external magnetic field applied to the atom. These magnetic properties derive in part from a new concept—electron spin—which will be explored at some length in this chapter.

Another new physical idea, known as the exclusion principle, is also presented in this chapter. This principle is extremely important in understanding the properties of multielectron atoms and the periodic table. In fact, the implications of the exclusion principle are almost as far-reaching as those of the Schrödinger equation itself.

9.1 ORBITAL MAGNETISM AND THE NORMAL ZEEMAN EFFECT

An electron orbiting the nucleus of an atom should give rise to magnetic effects, much like those arising from an electric current circulating in a wire loop. In particular, the motion of charge generates a magnetic field within the atom, and the atom as a whole is subject to forces and torques when it is placed in an external magnetic field. These magnetic interactions can all be described in terms of a single property of the atom—the magnetic dipole moment.

To calculate the magnetic moment of an orbiting charge, we reason by analogy with a current-carrying loop of wire. The moment $\boldsymbol{\mu}$ of such a loop has magnitude $|\boldsymbol{\mu}| = iA$, where i is the current and A is the area bounded by the loop. The direction of this moment is perpendicular to the plane of the loop, and its sense is given by a right-hand rule, as shown in Figure 9.1a. This characterization of a current loop as a magnetic dipole implies that its magnetic behavior is similar to that of a bar magnet with its north-south axis directed along $\boldsymbol{\mu}$ (Fig. 9.1b).

For a circulating charge q , the (time-averaged) current is simply q/T , where T is the orbital period. Furthermore, A/T is just the area swept out per unit time and equals the magnitude of the angular momentum $|\mathbf{L}|$ of the orbiting charge divided by twice the particle mass m .¹ This relation is

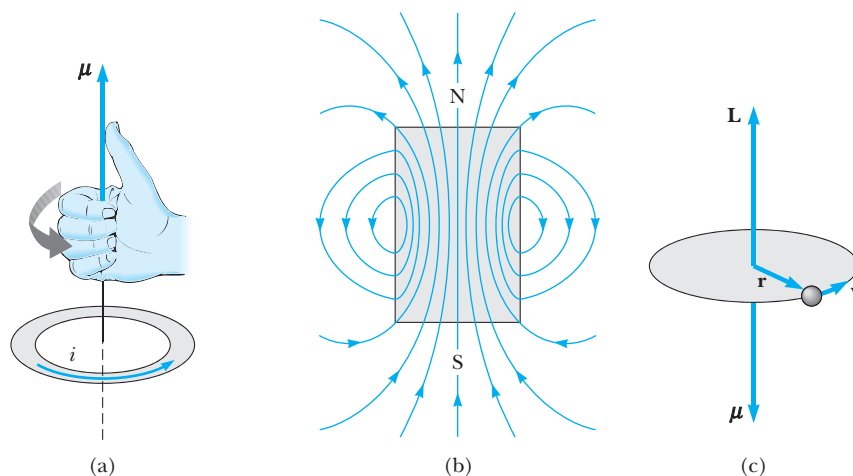


Figure 9.1 (a) The magnetic field in the space surrounding a current-carrying wire loop is that of a magnetic dipole with moment $\boldsymbol{\mu}$ perpendicular to the plane of the loop. The vector $\boldsymbol{\mu}$ points in the direction of the thumb if the fingers of the right hand are curled in the sense of the current i (right-hand rule). (b) The magnetic field in the space surrounding a bar magnet is also that of a magnetic dipole. The dipole moment vector $\boldsymbol{\mu}$ points from the south to the north pole of the magnet. (c) The magnetic moment $\boldsymbol{\mu}$ of an orbiting electron with angular momentum \mathbf{L} . Since the electron is negatively charged, $\boldsymbol{\mu}$ and \mathbf{L} point in opposite directions.

¹This is one of Kepler's laws of planetary motion, later shown by Newton to be a consequence of any central force.

easily verified for circular orbits, where $|\mathbf{L}| = mvr$, $v = 2\pi r/T$, and $A = \pi r^2$, so that

$$|\mathbf{L}| = m \left(\frac{2\pi r}{T} \right) r = 2m \left(\frac{\pi r^2}{T} \right) = 2m \left(\frac{A}{T} \right) \quad \text{or} \quad \frac{A}{T} = \frac{|\mathbf{L}|}{2m}$$

The same result holds for orbital motion of any kind (see Problem 2), so that $|\boldsymbol{\mu}| = iA$ becomes

$$\boldsymbol{\mu} = \frac{q}{2m} \mathbf{L} \quad (9.1)$$

Magnetic moment of an orbiting charge

for the magnetic moment of an orbiting charge q . Since \mathbf{L} is perpendicular to the orbital plane, so too is $\boldsymbol{\mu}$. You may verify that the sense of the vector described by Equation 9.1 is consistent with that expected from the right-hand rule. Thus, the magnetic moment vector is directed along the angular momentum vector, and its magnitude is fixed by the proportionality constant $q/2m$, called the *gyromagnetic ratio*. For electrons, $q = -e$ so the direction of $\boldsymbol{\mu}$ is opposite the direction of \mathbf{L} (Fig. 9.1c).

On the atomic scale, the elemental unit of angular momentum is \hbar . It follows that the natural unit for atomic moments is the quantity $e\hbar/2m_e$, called the **Bohr magneton** and designated by the symbol μ_B . Its value in SI units (joules/tesla) is

$$\mu_B = \frac{e\hbar}{2m_e} = 9.274 \times 10^{-24} \text{ J/T} \quad (9.2)$$

Bohr magneton

Because $\boldsymbol{\mu}$ is proportional to \mathbf{L} , the orbital magnetic moment is subject to **space quantization**, as illustrated in Figure 9.2. In particular, the z component of the orbital magnetic moment is fixed by the value of the magnetic quantum number m_ℓ as

$$\mu_z = -\frac{e}{2m_e} L_z = -\frac{e\hbar}{2m_e} m_\ell = -\mu_B m_\ell \quad (9.3)$$

Just as with angular momentum, the magnetic moment vector can be visualized as precessing about the z -axis, thereby preserving this sharp value of μ_z while depicting the remaining components μ_x and μ_y as fuzzy.

The interaction of an atom with an applied magnetic field depends on the size and orientation of the atom's magnetic moment. Suppose an external field \mathbf{B} is applied along the z -axis of an atom. According to classical electromagnetism, the atom experiences a torque

$$\boldsymbol{\tau} = \boldsymbol{\mu} \times \mathbf{B} \quad (9.4)$$

A magnetic moment precesses in a magnetic field

that tends to align its moment with the applied field. Instead of aligning itself with \mathbf{B} , however, the moment actually precesses around the field direction! This unexpected precession arises because $\boldsymbol{\mu}$ is proportional to the angular momentum \mathbf{L} . The motion is analogous to that of a spinning top precessing in the Earth's gravitational field. The gravitational torque acting to tip it over instead results in precession because of the angular

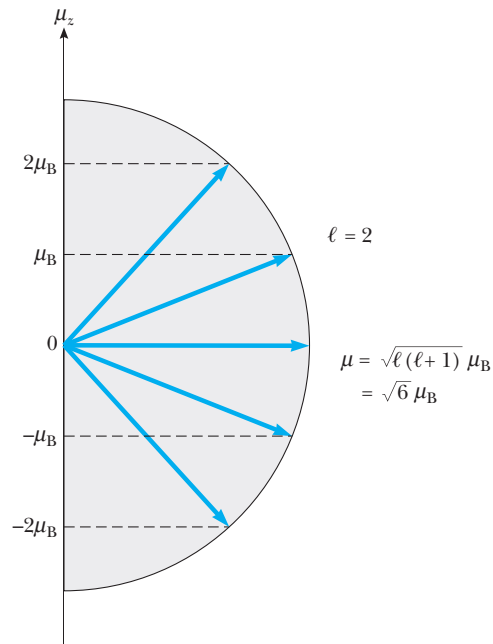


Figure 9.2 The orientations in space and z components of the orbital magnetic moment for the case $\ell = 2$. There are $2\ell + 1 = 5$ different possible orientations.

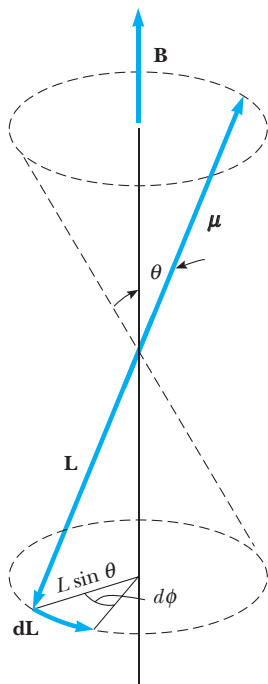


Figure 9.3 Larmor precession of the orbital moment μ in an applied magnetic field \mathbf{B} . Since μ is proportional to \mathbf{L} , the torque of the applied field causes the moment vector μ to precess around the direction of \mathbf{B} with frequency $\omega_L = eB/2m_e$.

momentum possessed by the spinning top. Returning to the atomic case, because $\boldsymbol{\tau} = d\mathbf{L}/dt$, we see from Equation 9.4 that the change in angular momentum, $d\mathbf{L}$, is always perpendicular to both \mathbf{L} and \mathbf{B} . Figure 9.3 depicts the motion (precession) that results. For atoms in a magnetic field this is known as **Larmor precession**.

From the geometry of Figure 9.3, we see that in a time dt the precession angle increases by $d\phi$, where

$$L \sin \theta \cdot d\phi = |d\mathbf{L}|$$

But Equations 9.1 and 9.4 can be combined to give

$$|d\mathbf{L}| = |\boldsymbol{\tau}| dt = \left| \frac{q}{2m_e} LB \sin \theta \right| dt$$

For electrons we take $q = -e$ and the frequency of precession, or **Larmor frequency** ω_L , becomes

$$\omega_L = \frac{d\phi}{dt} = \frac{1}{L \sin \theta} \frac{|d\mathbf{L}|}{dt} = \frac{e}{2m_e} B \tag{9.5}$$

It is useful to introduce the quantum of energy $\hbar\omega_L$ associated with the Larmor frequency ω_L . This energy is related to the work required to reorient the atomic moment against the torque of the applied field. Remembering that

the work of a torque τ to produce an angular displacement $d\theta$ is $dW = \tau d\theta$, we have from Equation 9.4

$$dW = -\mu B \sin \theta d\theta = d(\mu B \cos \theta) = d(\boldsymbol{\mu} \cdot \mathbf{B})$$

The minus sign signifies that the external torque must *oppose* that produced by the magnetic field \mathbf{B} . The work done is stored as orientational potential energy of the dipole in the field. Writing $dW = -dU$, we identify the **magnetic potential energy** U as

$$U = -\boldsymbol{\mu} \cdot \mathbf{B} \quad (9.6)$$

The energy of a magnetic moment depends on its orientation in a magnetic field

Equation 9.6 expresses the fact that the energy of a magnetic dipole in an external magnetic field \mathbf{B} depends on its orientation in this field. The magnetic energy is minimal when $\boldsymbol{\mu}$ and \mathbf{B} are aligned; therefore, this alignment is the preferred orientation. Because the possible orientations for $\boldsymbol{\mu}$ are restricted by space quantization, the magnetic energy is quantized accordingly. Taking the z -axis along \mathbf{B} , and combining Equations 9.1, 9.3, and 9.6, we find

$$U = \frac{e}{2m_e} \mathbf{L} \cdot \mathbf{B} = \frac{eB}{2m_e} L_z = \hbar \omega_L m_\ell \quad (9.7)$$

From Equation 9.7 we see that **the magnetic energy of an atomic electron depends on the magnetic quantum number m_ℓ** (so named for this dependence!) and, therefore, **is quantized**. The total energy of this electron is the sum of its magnetic energy U plus whatever energy it had in the absence of an applied field—say, E_0 . Therefore,

$$E \equiv E_0 + \hbar \omega_L m_\ell \quad (9.8)$$

For atomic hydrogen, E_0 depends only on the principal quantum number n ; in more complex atoms, the atomic energy also varies according to the subshell label ℓ , as discussed further in Section 9.5.

Unlike energies, the wavefunctions of atomic electrons are unaffected by the application of a magnetic field. This somewhat surprising result can be partly understood by recognizing that according to classical physics, the only effect of the field is to cause (Larmor) precession around the direction of \mathbf{B} . For atomic electrons, this translates into precession of \mathbf{L} about the z -axis. However, such a precession is already implicit in our semiclassical picture of electron orbits in the absence of external fields, as required by the sharpness of L_z while L_x and L_y remain fuzzy. From this viewpoint, the introduction of an applied magnetic field merely transforms this *virtual precession*² into a real one at the Larmor frequency!

²In zero magnetic field, the precession of the classical vector may be termed virtual (not real) since even though the same value may not be obtained for L_x (or L_y) in successive measurements, the average value $\langle L_x \rangle$ (or $\langle L_y \rangle$) does not change over time. With \mathbf{B} nonzero, however, it can be shown that $(d^2/dt^2) \langle L_x \rangle = -\omega_L^2 \langle L_x \rangle$ (and similarly for $\langle L_y \rangle$), indicating that $\langle L_x \rangle$ (and $\langle L_y \rangle$) oscillates at the Larmor frequency ω_L .

EXAMPLE 9.1 Magnetic Energy of the Electron in Hydrogen

Calculate the magnetic energy and Larmor frequency for an electron in the $n = 2$ state of hydrogen, assuming the atom is in a magnetic field of strength $B = 1.00$ T.

Solution Taking the z -axis along \mathbf{B} , we calculate the magnetic energy from Equation 9.7 as

$$U = \frac{eB}{2m_e} L_z = \frac{e\hbar}{2m_e} B m_\ell = \hbar\omega_L m_\ell$$

For a 1.00 T field, the energy quantum $\hbar\omega_L$ has the value

$$\hbar\omega_L = \frac{e\hbar}{2m_e} B = \mu_B B = (9.27 \times 10^{-24} \text{ J/T})(1.00 \text{ T})$$

$$= 9.27 \times 10^{-24} \text{ J} = 5.79 \times 10^{-5} \text{ eV}$$

With $n = 2$, ℓ can be 0 or 1, and m_ℓ is 0 (twice) and ± 1 . Thus, the magnetic energy U can be 0, $+\hbar\omega_L$, or $-\hbar\omega_L$. In such applications, the energy quantum $\hbar\omega_L$ is called the Zeeman energy. This Zeeman energy divided by \hbar is the Larmor frequency:

$$\omega_L = \frac{5.79 \times 10^{-5} \text{ eV}}{6.58 \times 10^{-16} \text{ eV}\cdot\text{s}} = 8.80 \times 10^{10} \text{ rad/s}$$

Evidence for the existence of atomic moments is the appearance of extra lines in the spectrum of an atom that is placed in a magnetic field. Consider a hydrogen atom in its first excited ($n = 2$) state. For $n = 2$, ℓ can have values 0 and 1. The magnetic field has no effect on the state for which $\ell = 0$, since then $m_\ell = 0$. For $\ell = 1$, however, m_ℓ can take values of 1, 0, and -1 , and the first excited level is split into three levels by the magnetic field (Figure 9.4).

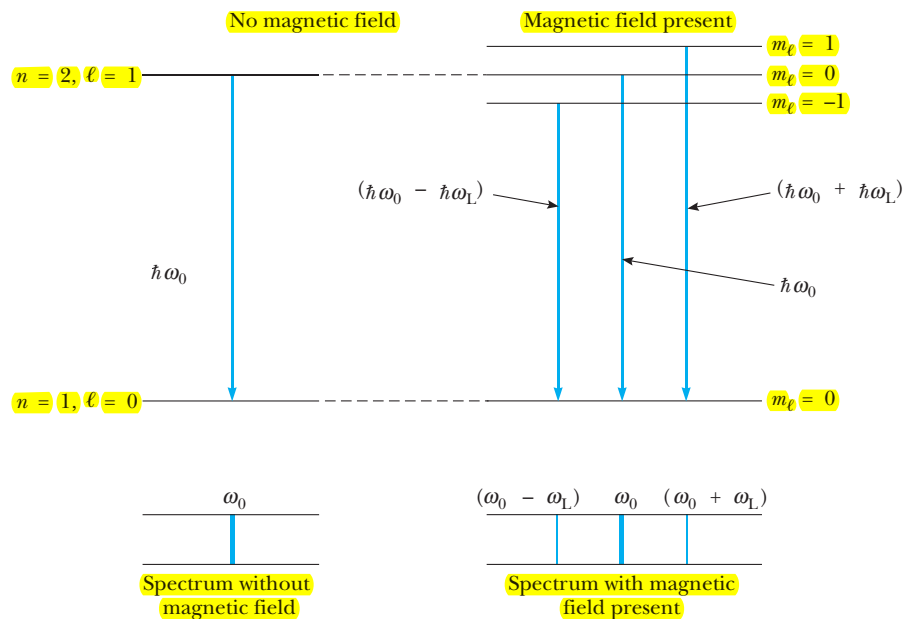


Figure 9.4 Level splittings for the ground and first excited states of a hydrogen atom immersed in a magnetic field \mathbf{B} . An electron in one of the excited states decays to the ground state with the emission of a photon, giving rise to emission lines at ω_0 , $\omega_0 + \omega_L$, and $\omega_0 - \omega_L$. This is the normal Zeeman effect. When $\mathbf{B} = 0$, only the line at ω_0 is observed.

The original (Lyman) emission line is replaced by the three lines depicted in Figure 9.4. The central line appears at the same frequency ω_0 as it would without a magnetic field. This is flanked on both sides by new lines at frequencies $\omega_0 \pm \omega_L$. Therefore, the magnetic field splits the original emission line into three lines. Because ω_L is proportional to B , the amount of splitting increases linearly with the strength of the applied field. **This effect of spectral line splitting by a magnetic field is known as the normal Zeeman effect after its discoverer, Pieter Zeeman.**

The normal Zeeman effect

Zeeman spectra of atoms excited to higher states should be more complex, because many more level splittings are involved. For electrons excited to the $n = 3$ state of hydrogen, the expected Zeeman lines and the atomic transitions that give rise to them are shown in Figure 9.5. Accompanying each hydrogen line are anywhere from two to six satellites at frequencies removed from the original by multiples of the Larmor frequency. But the observed Zeeman spectrum is not this complicated, owing to selection rules that limit the transitions

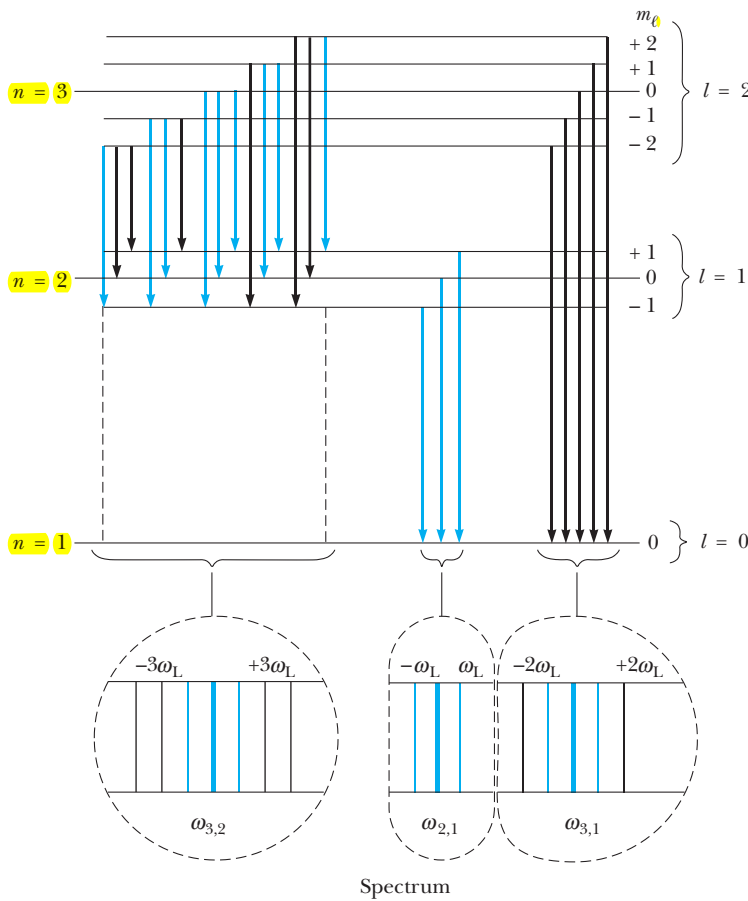


Figure 9.5 Zeeman spectral lines and the underlying atomic transitions that give rise to them for an electron excited to the $n = 3$ state of hydrogen. **Because of selection rules, only the transitions drawn in color actually occur.** Transitions from the $n = 3$, $l = 1$ orbitals (not shown) to the $n = 1$ state give rise to the colored lines in the illustration at the bottom right.

to those for which ℓ changes by 1 and m_ℓ changes by 0, +1, or -1 . The result is that satellites appear at the Larmor frequency *only* and not at multiples of this frequency. The selection rules express conservation of angular momentum for the system, taking into account the angular momentum of the emitted photon. (See Section 8.5.)

Finally, even the splitting of an emission line into a triplet of equally spaced lines as predicted here, called the normal Zeeman effect, frequently is not observed. More commonly, splittings into four, six, or even more unequally spaced lines are seen. This is the anomalous Zeeman effect, which has its roots in the existence of electron spin.

9.2 THE SPINNING ELECTRON

The anomalous Zeeman splittings are only one of several phenomena not explained by the magnetic interactions discussed thus far. Another is the observed doubling of many spectral lines referred to as fine structure. Both effects are attributed to the existence of a new magnetic moment—the spin moment—that arises from the electron spinning on its axis.

We have seen that the orbital motion of charge gives rise to magnetic effects that can be described in terms of the orbital magnetic moment $\boldsymbol{\mu}$ given by Equation 9.1. Similarly, a charged object in rotation produces magnetic effects related to the spin magnetic moment $\boldsymbol{\mu}_s$. The spin moment is found by noting that a rotating body of charge can be viewed as a collection of charge elements Δq with mass Δm all rotating in circular orbits about a fixed line, the axis of rotation (Fig. 9.6). To each of these we should apply Equation 9.1 with \mathbf{L} replaced by \mathbf{L}_i , the orbital angular momentum of the i th charge element (Fig. 9.6b). If the charge-to-mass ratio is uniform throughout the

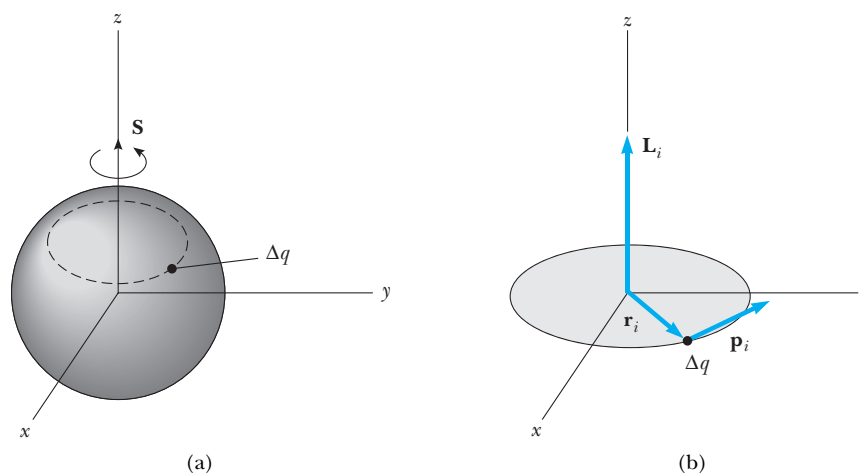


Figure 9.6 (a) A spinning charge q may be viewed as a collection of charge elements Δq orbiting a fixed line, the axis of rotation. (b) The circular path followed by one such charge element. The angular momentum of this charge element $\mathbf{L}_i = \mathbf{r}_i \times \mathbf{p}_i$ lies along the axis of rotation. The magnetic moments accompanying these orbiting charge elements are summed to give the total magnetic moment of rotation, or spin magnetic moment, of the charge q .

Otto Stern was one of the finest experimental physicists of the 20th century. Born and educated in Germany (Ph.D. in physical chemistry in 1912), he at first worked with Einstein on theoretical issues in molecular theory, in particular applying the new quantum ideas to theories of the specific heat of solids. From about 1920, Stern devoted himself to his real life's work, the development of the molecular beam method, which enabled him to investigate the properties of free or isolated atoms and culminated in a Nobel prize in 1945. In this method, a thin stream of atoms is introduced into a high-vacuum chamber where the atoms are free, and hence the properties of individual atoms may be investigated by applying external fields or by some other technique.

Stern first used this method to confirm that silver atoms obey the Maxwell speed distribution. Shortly after, in a series of elegant and difficult experiments with Walter Gerlach, Stern showed that silver atoms obey space quantization and succeeded in measuring the magnetic moment of the silver atom. In the period from 1923 to 1933, Stern directed a remarkably productive molecular beam laboratory at the University of Hamburg. With his students and coworkers he directly demonstrated the wave

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OTTO STERN

(1888–1969)

nature of helium atoms and measured the magnetic moments of many atoms. Finally, with a great deal of effort, he succeeded in measuring the very small magnetic moments of the proton and deuteron. For these last important fundamental measurements he was awarded the Nobel prize. In connection with the measurement of the proton's magnetic moment, an interesting story is told by Victor Weisskopf, which should gladden the hearts of experimentalists everywhere:

“There was a seminar held by the theoretical group in Göttingen, and Stern came down and gave a talk on

the measurements he was about to finish of the magnetic moment of the proton. He explained his apparatus, but he did not tell us the result. He took a piece of paper and went to each of us saying, ‘What is your prediction of the magnetic moment of the proton?’ Every theoretician from Max Born down to Victor Weisskopf said, ‘Well, of course, the great thing about the Dirac equation is that it predicts a magnetic moment of one Bohr magneton for a particle of spin one-half!’ Then he asked us to write down the prediction; everybody wrote ‘one magneton.’ Then, two months later, he came to give again a talk about the finished experiment, which showed that the value was 2.8 magnetons. He then projected the paper with our predictions on the screen. It was a sobering experience.”*

In protest over Nazi dismissals of some of his closest coworkers, Stern resigned his post in Hamburg and came to the Carnegie Institute of Technology in the United States in 1933. Here he worked on molecular beam research until his retirement in 1946.

*From Victor F. Weisskopf, *Physics in the Twentieth Century; Selected Essays: My Life as a Physicist*, Cambridge, MA, The MIT Press, 1972.

body, then $\Delta q/\Delta m$ is the ratio of total charge q to total mass m_e and we get for the spin moment

$$\boldsymbol{\mu}_s = \frac{q}{2m_e} \sum \mathbf{L}_i = \frac{q}{2m_e} \mathbf{S} \quad (9.9)$$

A rotating charge gives rise to a spin magnetic moment

where \mathbf{S} , the *spin* angular momentum, is the total angular momentum of rotation. The spin angular momentum \mathbf{S} points along the axis of rotation according to a right-hand rule, as shown in Figure 9.6; its magnitude depends on the size and shape of the object, as well as its speed of rotation. If the charge-to-mass ratio is not uniform, the gyromagnetic ratio in Equation 9.9, $q/2m_e$, must be multiplied by a dimensionless constant, the **g factor**, whose value reflects the detailed charge-to-mass distribution within the body. Note that g factors different from unity imply a distribution of charge that is not

tightly linked to the distribution of mass, an unusual circumstance but one that cannot be excluded.³

The existence of a spin magnetic moment for the electron was first demonstrated in 1921 in a classic experiment performed by Otto Stern and Walter Gerlach. Electron spin was unknown at that time; the Stern–Gerlach experiment was originally conceived to demonstrate the space quantization associated with orbiting electrons in atoms. In their experiment, a beam of silver atoms was passed through a nonuniform magnetic field created in the gap between the pole faces of a large magnet. The beam was then detected by being deposited on a glass collector plate (Fig. 9.7). A nonuniform field exerts a force on any magnetic moment, so that each atom is deflected in the gap by an amount governed by the orientation of its moment with respect to the direction of inhomogeneity (the z -axis), as illustrated in Figure 9.7b. If the moment directions are restricted by space quantization as in Figure 9.2, so too are the deflections. Thus, the atomic beam should split into a number of discrete components, one for each distinct moment orientation present in the beam. This is contrary to the classical expectation that any moment orientation (and hence any beam deflection) is possible, and all would combine to produce a continuous fanning of the atomic beam (Fig. 9.7c).

The Stern–Gerlach experiment produced a staggering result: The silver atomic beam was clearly split—but into only *two* components, not the odd number $(2\ell + 1)$ expected from the space quantization of orbital moments! This is all the more remarkable when we realize that silver atoms in their ground state have no orbital angular momentum ($\ell = 0$), because the outermost electron in silver normally would be in an s state. The result was so surprising that the experiment was repeated in 1927 by T. E. Phipps and J. B. Taylor with a beam of hydrogen atoms replacing silver, thereby eliminating any uncertainties arising from the use of the more complex silver atoms. The results, however, were unchanged. From these experiments, we are forced to conclude that there is some contribution to the atomic magnetic moment other than the orbital motion of electrons and that this moment is subject to space quantization.

Our present understanding of the situation dates to the 1925 paper of Samuel Goudsmit and George Uhlenbeck, then graduate students at the University of Leiden. Goudsmit and Uhlenbeck believed that the unknown moment had its origin in the spinning motion of atomic electrons, with the spin angular momentum obeying the same quantization rules as orbital angular momentum. The magnetic moment seen in the Stern–Gerlach experiment is attributed to the spin of the outermost electron in silver. Because all allowed orientations of the spin moment should be represented in the atomic beam, the observed splitting presents a dramatic confirmation of space quantization as applied to electron spin, with the number of components $(2s + 1)$ indicating the value of the spin quantum number s .

The spin magnetic moment suggests that the electron can be viewed as a charge in rotation, although the classical picture of a spinning body of

³It is only fair to caution the reader at this point not to take the classical view of an electron as a tiny charged ball spinning on its axis too literally. Although such a picture is useful in first introducing and visualizing electron spin, it is not technically correct. Several shortcomings of the classical picture are discussed in detail on pp. 306 and 307.

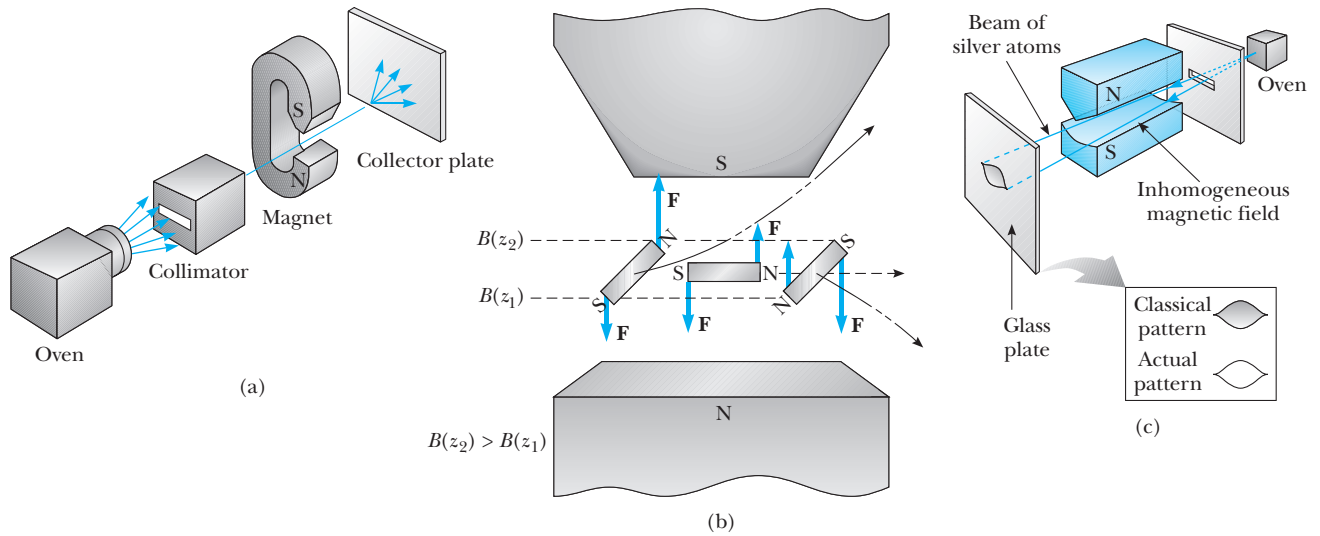


Figure 9.7 The Stern–Gerlach experiment to detect space quantization. (a) A beam of silver atoms is passed through a nonuniform magnetic field and detected on a collector plate. (b) The atoms, with their magnetic moment, are equivalent to tiny bar magnets. In a nonuniform field, each atomic magnet experiences a net force that depends on its orientation. (c) If any moment orientation were possible, a continuous fanning of the beam would be seen at the collector. For space quantization, the fanning is replaced by a set of discrete lines, one for each distinct moment orientation present in the beam.

charge must be adjusted to accommodate the wave properties of matter. The resulting semiclassical model of electron spin can be summarized as follows:

- The spin quantum number s for the electron is $\frac{1}{2}$! This value is dictated by the observation that an atomic beam passing through the Stern–Gerlach magnet is split into just two components ($= 2s + 1$). Accordingly, there are exactly two orientations possible for the spin axis, described as the “spin-up” and “spin-down” states of the electron. This is space quantization again, according to the quantization rules for angular momentum⁴ as applied to a spin of $\frac{1}{2}$:

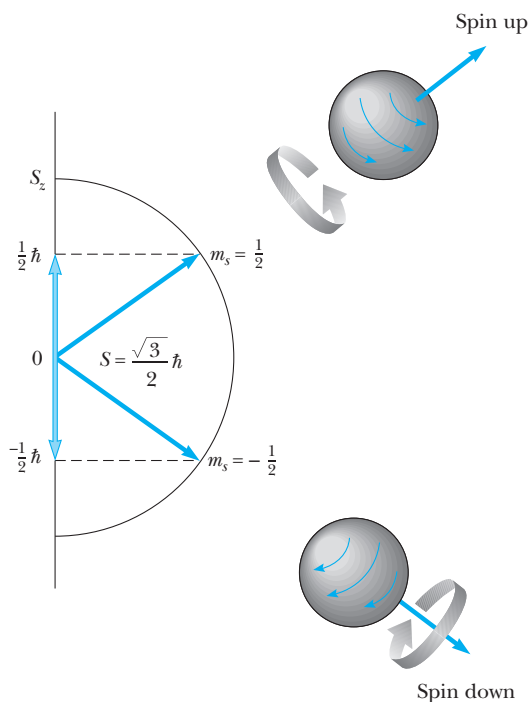
$$S_z = m_s \hbar \quad \text{where } m_s = \frac{1}{2} \text{ or } -\frac{1}{2} \quad (9.10)$$

The two values $\pm\hbar/2$ for S_z correspond to the two possible orientations for \mathbf{S} shown in Figure 9.8. The value $m_s = +\frac{1}{2}$ refers to the spin-up case, sometimes designated with an up arrow (\uparrow) or simply a plus sign (+). Likewise, $m_s = -\frac{1}{2}$ is the spin-down case, (\downarrow) or (-). The fact that s has a nonintegral value suggests that spin is not merely another manifestation of orbital motion, as the classical picture implies.

Properties of electron spin

⁴For integer angular momentum quantum numbers, the z component is quantized as $m_s = 0, \pm 1, \dots, \pm s$, which can also be written as $m_s = s, s - 1, \dots, -s$. For $s = \frac{1}{2}$, the latter implies $m_s = \frac{1}{2}$ or $-\frac{1}{2}$.

Figure 9.8 The spin angular momentum also exhibits space quantization. This figure shows the two allowed orientations of the spin vector \mathbf{S} for a spin $\frac{1}{2}$ particle, such as the electron.



- The magnitude of the spin angular momentum is

$$|\mathbf{S}| = \sqrt{s(s+1)} \hbar = \frac{\sqrt{3}}{2} \hbar \quad (9.11)$$

The spin angular momentum of an electron

and never changes! This angular momentum of rotation cannot be changed in any way, but is an intrinsic property of the electron, like its mass or charge. The notion that $|\mathbf{S}|$ is fixed contradicts classical laws, where a rotating charge would be slowed down by the application of a magnetic field owing to the Faraday emf that accompanies the changing magnetic field (the diamagnetic effect). Furthermore, if the electron were viewed as a spinning ball with angular momentum $\hbar\sqrt{3}/2$ subject to classical laws, parts of the ball near its surface would be rotating with velocities in excess of the speed of light!⁵ All of this is taken to mean that the classical picture of the electron as a charge in rotation must not be pressed too far; ultimately, the spinning electron is a quantum entity defying any simple classical description.

- The spin magnetic moment is given by Equation 9.9 with a **g factor of 2**; that is, the moment is twice as large as would be expected for a body with

⁵This follows from the extremely small size of the electron. The exact size of the electron is unknown, but an upper limit of 10^{-6} Å is deduced from experiments in which electrons are scattered from other electrons. According to some current theories, the electron may be a true point object, that is, a particle with zero size!

spin angular momentum given by Equation 9.10. The value $g = 2$ is required by the amount of beam deflection produced by the Stern–Gerlach magnet; the larger the magnetic moment, the greater will be the deflection of the atomic beam. As already mentioned, any g factor other than unity implies a nonuniform charge-to-mass ratio in the classical picture. The g factor of 2 can be realized classically but suggests a bizarre picture that cannot be taken seriously (see Problem 8). The correct g factor of 2 is predicted by the relativistic quantum theory of the electron put forth by Paul Dirac in 1929.⁶

With the recognition of electron spin we see that an additional quantum number, m_s , is needed to specify the internal, or spin, state of an electron. Therefore, the state of an electron in hydrogen must be described by the four quantum numbers n , ℓ , m_ℓ , and m_s . Furthermore, the total magnetic moment now has orbital and spin contributions:

$$\boldsymbol{\mu} = \boldsymbol{\mu}_0 + \boldsymbol{\mu}_s = \frac{-e}{2m_e} \{\mathbf{L} + g\mathbf{S}\} \quad (9.12)$$

The total magnetic moment of an electron

Because of the electron g factor, the total moment $\boldsymbol{\mu}$ is no longer in the same direction as the total (orbital plus spin) angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$. The component of the total moment $\boldsymbol{\mu}$ along \mathbf{J} is sometimes referred to as the **effective moment**. When the magnetic field \mathbf{B} applied to an atom is weak, the effective moment determines the magnetic energy of atomic electrons according to Equation 9.6. As we shall discover in Section 9.3, the number of possible orientations for \mathbf{J} (and, hence, for the effective moment) is even, leading to the even number of spectral lines seen in the anomalous Zeeman effect.

EXAMPLE 9.2 Semiclassical Model for Electron Spin

Calculate the angles between the z -axis and the spin angular momentum \mathbf{S} of the electron in the up and down spin states. How should we portray the fuzziness inherent in the x and y components of the spin angular momentum?

Solution For the electron, the magnitude of the spin angular momentum is $|\mathbf{S}| = \hbar\sqrt{3}/2$, and the z component of spin is $S_z = \pm\hbar/2$. Thus, the spin vector \mathbf{S} is inclined from the z -axis at angles given by

$$\cos \theta = \frac{S_z}{|\mathbf{S}|} = \pm \frac{1}{\sqrt{3}}$$

For the up spin state, we take the plus sign and get $\cos \theta = 0.577$, or $\theta = 54.7^\circ$. The down spin orientation is described by the minus sign and gives $\cos \theta = -0.577$, or $\theta = 125.3^\circ$. Because the axis of rotation coincides with the direction of the spin vector, these are the angles the rotation axis makes with the z -axis.

While S_z is sharp in either the up or down spin orientation, both S_x and S_y are fuzzy. This fuzziness may be depicted by allowing the spin vector to precess about the z -axis, as we did for the orbital angular momentum in Chapter 8.

⁶The g factor for the electron is not exactly 2. The best value to date is $g = 2.00232$. The discrepancy between Dirac's predicted value and the observed value is attributed to the electron interacting with the "vacuum." Such effects are the subject of quantum electrodynamics, developed by Richard Feynman in the early 1950s.

Exercise 1 The photon is a spin 1 particle, that is, $s = 1$ for the photon. Calculate the possible angles between the z -axis and the spin vector of the photon.

Answer $45^\circ, 90^\circ,$ and 135°

EXAMPLE 9.3 Zeeman Spectrum of Hydrogen Including Spin

Examine the Zeeman spectrum produced by hydrogen atoms initially in the $n = 2$ state when electron spin is taken into account, assuming the atoms to be in a magnetic field of magnitude $B = 1.00$ T.

Solution The electron energies now have a magnetic contribution from both the orbital and spin motions. Choosing the z -axis along the direction of \mathbf{B} , we calculate the magnetic energy from Equations 9.6 and 9.12:

$$U = -\boldsymbol{\mu} \cdot \mathbf{B} = \frac{e\hbar}{2m_e} B(L_z + gS_z) = \frac{e\hbar}{2m_e} B(m_\ell + gm_s)$$

The energy $(e\hbar/2m_e)B$ is the Zeeman energy $\mu_B B$ or $\hbar\omega_L$; its value in this example is

$$\begin{aligned} \mu_B B &= (9.27 \times 10^{-24} \text{ J/T})(1.00 \text{ T}) = 9.27 \times 10^{-24} \text{ J} \\ &= 5.79 \times 10^{-5} \text{ eV} \end{aligned}$$

For the $n = 2$ state of hydrogen, the shell energy is $E_2 = -(13.6 \text{ eV})/2^2 = -3.40 \text{ eV}$. Because m_ℓ takes the

values 0 (twice) and ± 1 , there is an orbital contribution to the magnetic energy $U_0 = m_\ell \hbar\omega_L$ that introduces new levels at $E_2 \pm \hbar\omega_L$, as discussed in Example 9.1. The presence of electron spin splits each of these into a pair of levels, the additional (spin) contribution to the energy being $U_s = (gm_s)\hbar\omega_L$ (Fig. 9.9). Because $g = 2$ and m_s is $\pm \frac{1}{2}$ for the electron, the spin energy in the field $|U_s|$ is again the Zeeman energy $\hbar\omega_L$. Therefore, an electron in this shell can have any one of the energies

$$E_2, \quad E_2 \pm \hbar\omega_L, \quad E_2 \pm 2\hbar\omega_L$$

In making a downward transition to the $n = 1$ shell with energy $E_1 = -13.6 \text{ eV}$, the final state of the electron may have energy $E_1 + \hbar\omega_L$ or $E_1 - \hbar\omega_L$, depending on the orientation of its spin in the applied field. Therefore, the energy of transition may be any one of the following possibilities:

$$\Delta E_{2,1}, \quad \Delta E_{2,1} \pm \hbar\omega_L, \quad \Delta E_{2,1} \pm 2\hbar\omega_L, \quad \Delta E_{2,1} \pm 3\hbar\omega_L$$

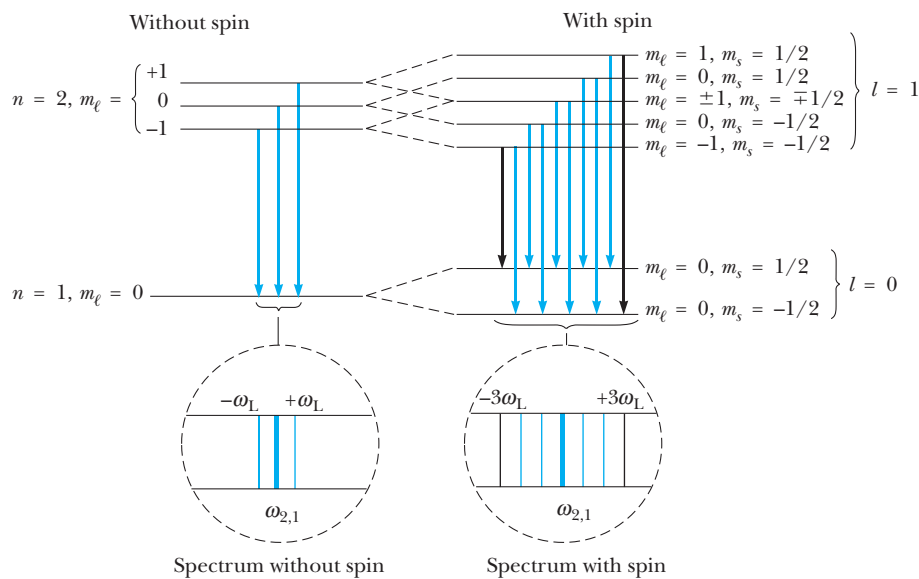


Figure 9.9 (Example 9.3) Predicted Zeeman pattern and underlying atomic transitions for an electron excited to the $n = 2$ state of hydrogen, when electron spin is taken into account. Again, selection rules prohibit all but the colored transitions. Because of the neglect of the spin-orbit interaction, the effect shown here (called the Paschen-Back effect) is observed only in very intense applied magnetic fields.

Photons emitted with these energies have frequencies

$$\omega_{2,1}, \quad \omega_{2,1} \pm \omega_L, \quad \omega_{2,1} \pm 2\omega_L, \quad \omega_{2,1} \pm 3\omega_L$$

Therefore the spectrum should consist of the original line at $\omega_{2,1}$ flanked on both sides by satellite lines separated from the original by the Larmor frequency, twice the Larmor frequency, and three times this frequency. Notice that the lines at $\omega_{2,1} \pm 2\omega_L$ and $\omega_{2,1} \pm 3\omega_L$ appear solely because of electron spin.

Again, however, the observed pattern is not the predicted one. Selection rules inhibit transitions unless $m_\ell \pm m_s$ changes by 0, +1, or -1. This has the effect of

eliminating the satellites at $\omega_{2,1} \pm 3\omega_L$. Furthermore, the spin moment and the orbital moment of the electron interact with each other, a circumstance not recognized in our calculation. Only when this spin-orbit interaction energy is small compared with the Zeeman energy, $\hbar\omega_L$, do we observe the spectral lines predicted here. This is the case for the **Paschen-Back effect**, in which the magnetic field applied to the atom is intense enough to make $\hbar\omega_L$ the dominant energy. Typically, to observe the Paschen-Back effect requires magnetic fields in excess of several tesla.

9.3 THE SPIN-ORBIT INTERACTION AND OTHER MAGNETIC EFFECTS

The existence of both spin and orbital magnetic moments for the electron inevitably leads to their mutual interaction. This so-called **spin-orbit interaction** is best understood from the vantage point of the orbiting electron, which “sees” the atomic nucleus circling it (Fig. 9.10). The apparent orbital motion of the nucleus generates a magnetic field at the electron site, and the electron spin moment acquires magnetic energy in this field according to Equation 9.6. This can be thought of as an internal Zeeman effect, with **B** arising from the orbital motion of the electron itself. The electron has a higher energy when its spin is up, or aligned with **B**, than when its spin is down, or aligned opposite to **B** (Fig. 9.10b).

The energy difference between the two spin orientations is responsible for the **fine structure doubling** of many atomic spectral lines. For example, the $2p \rightarrow 1s$ transition in hydrogen is split into two lines because the $2p$ level is actually a spin doublet with a level spacing of about 5×10^{-5} eV (Fig. 9.11), while the $1s$ level remains unsplit (there is no orbital field in a state with zero orbital angular momentum). Similarly, the spin-orbit doubling of the sodium $3p$ level gives rise to the well-known sodium D lines to be discussed in Example 9.4.

The coupling of spin and orbital moments implies that **neither orbital angular momentum nor spin angular momentum is conserved separately**. But **total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$ is conserved**, so long as no external torques are present. Consequently, quantum states exist for which $|\mathbf{J}|$ and J_z are sharp observables quantized in the manner we have come to expect for angular momentum:

$$|\mathbf{J}| = \sqrt{j(j+1)}\hbar \tag{9.13}$$

$$J_z = m_j\hbar \quad \text{with } m_j = j, j-1, \dots, -j$$

Permissible values for the total angular momentum quantum number j are

$$j = \ell \pm s, \quad \ell + s - 1, \dots, |\ell - s| \tag{9.14}$$

in terms of the orbital (ℓ) and spin (s) quantum numbers. For an atomic electron $s = \frac{1}{2}$ and $\ell = 0, 1, 2, \dots$, so $j = \frac{1}{2}$ (for $\ell = 0$) and $j = \ell \pm \frac{1}{2}$ (for $\ell > 0$).

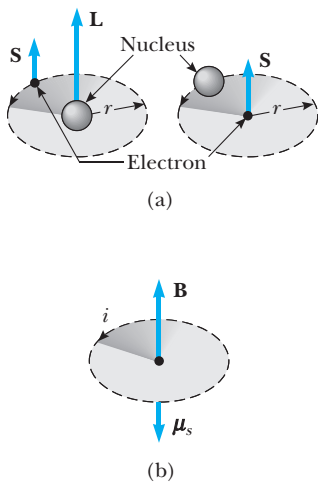


Figure 9.10 (a) *Left:* An electron with angular momentum \mathbf{L} orbiting the nucleus of an atom. In the spin-up orientation shown here, the spin angular momentum \mathbf{S} of the electron is “aligned” with \mathbf{L} . *Right:* From the viewpoint of the orbiting electron, the nucleus circulates as shown. (b) The apparently circulating nuclear charge is represented by the current i and causes a magnetic field \mathbf{B} at the site of the electron. In the presence of \mathbf{B} , the electron spin moment $\boldsymbol{\mu}_s$ acquires magnetic energy $U = -\boldsymbol{\mu}_s \cdot \mathbf{B}$. The spin moment $\boldsymbol{\mu}_s$ is opposite the spin vector \mathbf{S} for the negatively charged electron. The direction of \mathbf{B} is given by a right-hand rule: With the thumb of the right hand pointing in the direction of the current i , the fingers give the sense in which the \mathbf{B} field circulates about the orbit path. The magnetic energy is highest for the case shown, where \mathbf{S} and \mathbf{L} are “aligned.”

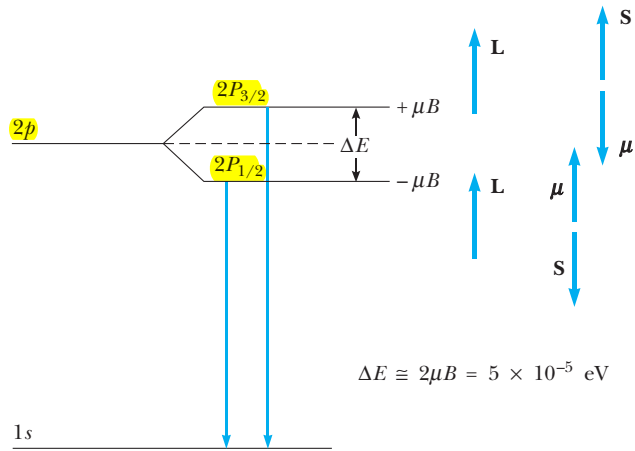


Figure 9.11 The $2p$ level of hydrogen is split by the spin-orbit effect into a doublet separated by the spin-orbit energy $\Delta E = 5 \times 10^{-5} \text{ eV}$. The higher energy state is the one for which the spin angular momentum of the electron is “aligned” with its orbital angular momentum. The $1s$ level is unaffected, since no magnetic field arises for orbital motion with zero angular momentum.

These results can be deduced from the vector addition model shown in Figure 9.12a. With $j = \frac{1}{2}$, there are only two possibilities for m_j , namely $m_j = \pm \frac{1}{2}$. For $j = \ell \pm \frac{1}{2}$, the number of possibilities $(2j + 1)$ for m_j becomes either 2ℓ or $2\ell + 2$. Notice that the number of m_j values is always *even* for a single electron, leading to an even number of orientations in the semiclassical model for \mathbf{J}

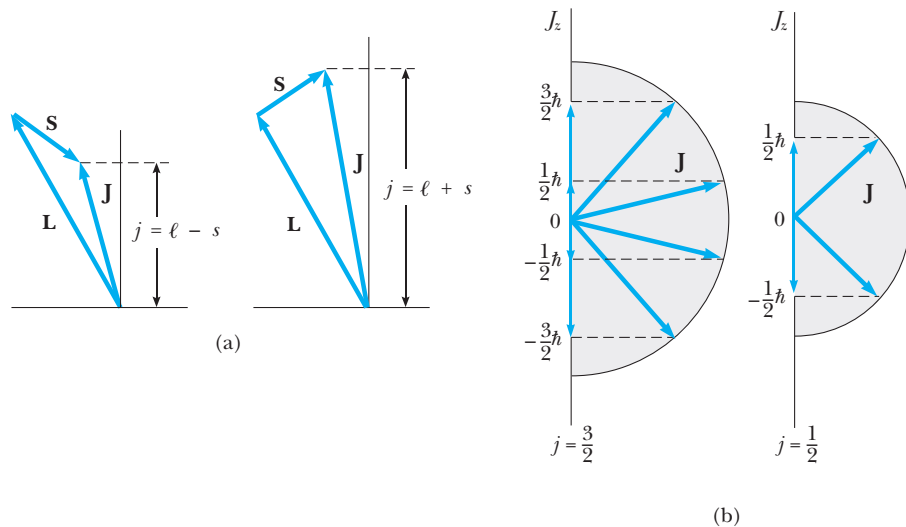


Figure 9.12 (a) A vector model for determining the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$ of a single electron. (b) The allowed orientations of the total angular momentum \mathbf{J} for the states $j = \frac{3}{2}$ and $j = \frac{1}{2}$. Notice that there are now an even number of orientations possible, not the odd number familiar from the space quantization of \mathbf{L} alone.

(Fig. 9.12b), rather than the odd number predicted for the orbital angular momentum \mathbf{L} alone.

A common spectroscopic notation is to use a subscript after a letter to designate the total angular momentum of an atomic electron, where the letter itself (now uppercase) describes its orbital angular momentum. For example, the notation $1S_{1/2}$ describes the ground state of hydrogen, where the 1 indicates $n = 1$, the S tells us that $\ell = 0$, and the subscript $\frac{1}{2}$ denotes $j = \frac{1}{2}$. Likewise, the spectroscopic notations for the $n = 2$ states of hydrogen are $2S_{1/2}$ ($\ell = 0, j = \frac{1}{2}$), $2P_{3/2}$ ($\ell = 1, j = \frac{3}{2}$), and $2P_{1/2}$ ($\ell = 1, j = \frac{1}{2}$). Again, the spin-orbit interaction splits the latter two states in energy by about 5×10^{-5} eV.

Spectroscopic notation extended to include spin

EXAMPLE 9.4 The Sodium Doublet

The famed sodium doublet arises from the spin-orbit splitting of the sodium $3p$ level, and consists of the closely spaced pair of spectral lines at wavelengths of 588.995 nm and 589.592 nm. Show on an energy-level diagram the electronic transitions giving rise to these lines, labeling the participating atomic states with their proper spectroscopic designations. From the doublet spacing, determine the magnitude of the spin-orbit energy.

Solution The outer electron in sodium is the first electron to occupy the $n = 3$ shell, and it would go into the lowest-energy subshell, the $3s$ or $3S_{1/2}$ level. The next-highest levels belong to the $3p$ subshell. The $2(2\ell + 1) = 6$ states of this subshell are grouped into the $3P_{1/2}$ level with two states, and the $3P_{3/2}$ level with four states. The spin-orbit effect splits these levels by the spin-orbit energy. The outer electron, once it is excited to either of these levels by some means (such as an electric discharge in the sodium vapor lamp), returns to the $3S_{1/2}$ level with the emission of a photon. The two possible transitions $3P_{3/2} \rightarrow 3S_{1/2}$ and $3P_{1/2} \rightarrow 3S_{1/2}$ are shown in Figure 9.13. The emitted photons have nearly the same energy but differ by the small amount ΔE representing the spin-orbit splitting of the initial levels. Since $E = hc/\lambda$ for photons, ΔE is found as

$$\Delta E = \frac{hc}{\lambda_1} - \frac{hc}{\lambda_2} = \frac{hc(\lambda_2 - \lambda_1)}{\lambda_1\lambda_2}$$

For the sodium doublet, the observed wavelength difference is

$$\lambda_2 - \lambda_1 = 589.592 \text{ nm} - 588.995 \text{ nm} = 0.597 \text{ nm}$$

Using this with $hc = 1240 \text{ eV}\cdot\text{nm}$ gives

$$\Delta E = \frac{(1240 \text{ eV}\cdot\text{nm})(0.597 \text{ nm})}{(589.592 \text{ nm})(588.995 \text{ nm})} = 2.13 \times 10^{-3} \text{ eV}$$

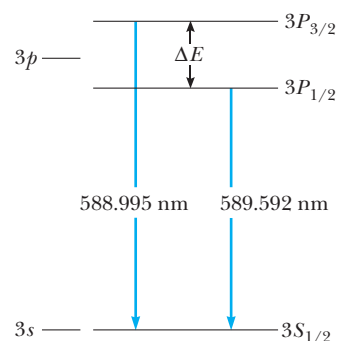


Figure 9.13 (Example 9.4). The transitions $3P_{3/2} \Rightarrow 3S_{1/2}$ and $3P_{1/2} \Rightarrow 3S_{1/2}$ that give rise to the sodium doublet. The $3p$ level of sodium is split by the spin-orbit effect, but the $3s$ level is unaffected. In the sodium vapor lamp, electrons normally in the $3s$ level are excited to the $3p$ levels by an electric discharge.

Exercise 2 Using the spin-orbit interaction energy calculated in Example 9.4, calculate the magnitude of the magnetic field at the site of the orbiting $3p$ electron in sodium.

Answer $B = 18.38 \text{ T}$, a large field by laboratory standards.

9.4 EXCHANGE SYMMETRY AND THE EXCLUSION PRINCIPLE

As mentioned earlier, the existence of spin requires that the state of an atomic electron be specified with four quantum numbers. In the absence of spin-orbit effects these could be n , ℓ , m_ℓ , and m_s ; if the spin-orbit interaction is taken into account, m_ℓ and m_s are replaced by j and m_j . In either case, four quantum numbers are required, one for each of the four degrees of freedom possessed by a single electron.

In those systems where two or more electrons are present, we might expect to describe each electronic state by giving the appropriate set of four quantum numbers. In this connection an interesting question arises, namely, “How many electrons in an atom can have the same four quantum numbers, that is, be in the same state?” This important question was answered by Wolfgang Pauli in 1925 in a powerful statement known as the exclusion principle. **The exclusion principle states that no two**

Wolfgang Pauli was an extremely talented Austrian theoretical physicist who made important contributions in many areas of modern physics.

At the age of 21, Pauli gained public recognition with a masterful review article on relativity, which is still considered to be one of the finest and most comprehensive introductions to the subject. Other major contributions were the discovery of the exclusion principle, the explanation of the connection between particle spin and statistics, theories of relativistic quantum electrodynamics, the neutrino hypothesis, and the hypothesis of nuclear spin. An article entitled “The Fundamental Principles of Quantum Mechanics,” written by Pauli in 1933 for the *Handbuch der Physik*, is widely acknowledged to be one of the best treatments of quantum physics ever written. Pauli was a forceful and colorful character, well known for his witty and often caustic remarks directed at those who presented new theories in a less than perfectly clear manner. Pauli exerted great influence on his students and colleagues by forcing them with his sharp criticism to a deeper and clearer under-

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WOLFGANG PAULI

(1900–1958)

standing. Victor Weisskopf, one of Pauli’s famous students, has aptly described him as “the conscience of theoretical physics.” Pauli’s sharp sense of humor was also nicely captured by Weisskopf in the following anecdote:

“In a few weeks, Pauli asked me to come to Zurich. I came to the big door of his office, I knocked, and no answer. I knocked again and no answer. After about five minutes he said, rather roughly, “Who is it? Come in!”

I opened the door, and here was Pauli—it was a very big office—at the other side of the room, at his desk, writing and writing. He said, “Who is this? First I must finish calculating.” Again he let me wait for about five minutes and then: “Who is that?” “I am Weisskopf.” “Uhh, Weisskopf, ja, you are my new assistant.” Then he looked at me and said, “Now, you see I wanted to take Bethe, but Bethe works now on the solid state. Solid state I don’t like, although I started it. This is why I took you.” Then I said, “What can I do for you, sir?” and he said “I shall give you right away a problem.” He gave me a problem, some calculation, and then he said, “Go and work.” So I went, and after 10 days or so, he came and said, “Well, show me what you have done.” And I showed him. He looked at it and exclaimed: “I should have taken Bethe!”*

*From Victor F. Weisskopf, *Physics in the Twentieth Century: Selected Essays: My Life as a Physicist*. Cambridge, MA, The MIT Press, 1972, p. 10.

electrons in an atom can have the same set of quantum numbers. We should point out that if this principle were not valid, every electron would occupy the $1s$ atomic state (this being the state of lowest energy), the chemical behavior of the elements would be drastically different, and nature as we know it would not exist!

The exclusion principle follows from our belief that electrons are identical particles—that it is impossible to distinguish one electron from another. This seemingly innocuous statement takes on added importance in view of the wave nature of matter, and has far-reaching consequences. To gain an appreciation for this point, let us consider a collision between two electrons, as shown in Figure 9.14. Figures 9.14a and 9.14b depict two distinct events, the scattering effect being much stronger in the latter where the electrons are turned through a larger angle. Each event, however, arises from the same initial condition and leads to the same outcome—both electrons are scattered and emerge at angles θ relative to the axis of incidence. Had we not followed their paths, we could not decide which of the two collisions actually occurred, and the separate identities of the electrons would have been lost in the process of collision.

But paths are classical concepts, blurred by the wave properties of matter according to the uncertainty principle. That is, there is an inherent fuzziness to these paths, which blends them inextricably in the collision region, where the electrons may be separated by only a few de Broglie wavelengths. The quantum viewpoint is better portrayed in Figure 9.14c, where the two distinct possibilities (from a classical standpoint) merge into a single quantum event—the scattering of two electrons through an angle θ . Note that indistinguishability plays no role in classical physics: All particles, even identical ones, are distinguishable classically through their *paths!* **With our acceptance of matter waves, we must conclude that identical particles cannot be told**

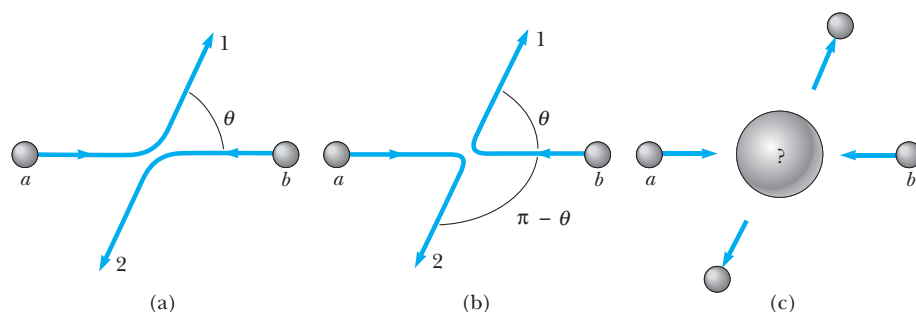


Figure 9.14 The scattering of two electrons as a result of their mutual repulsion. The events depicted in (a) and (b) produce the same outcome for identical electrons but are nonetheless distinguishable classically because the path taken by each electron is different in the two cases. In this way, the electrons retain their separate identities during collision. (c) According to quantum mechanics, the paths taken by the electrons are blurred by the wave properties of matter. In consequence, once they have interacted, the electrons cannot be told apart in any way!

Electrons are truly indistinguishable apart in any way—they are truly indistinguishable. Incorporating this remarkable fact into the quantum theory leads to the exclusion principle discovered by Pauli.

Let us see how indistinguishability affects our mathematical description of a two-electron system, say, the helium atom. Each electron has kinetic energy and the atom has electrostatic potential energy associated with the interaction of the two electrons with the doubly charged helium nucleus. These contributions are represented in Schrödinger's equation for one electron by terms

$$-\frac{\hbar^2}{2m_e} \nabla_1^2 \psi + \frac{k(2e)(-e)}{r_1} \psi$$

where ∇_1^2 is the Laplacian in this electron's coordinate, \mathbf{r}_1 . For brevity, let us write the sum of both terms simply as $h(1)\psi$, with the label 1 referring to \mathbf{r}_1 . For the second electron, we write the same expression, except that \mathbf{r}_1 must be replaced everywhere by \mathbf{r}_2 , the coordinate of the second electron. The stationary states for our two-electron system satisfy Schrödinger's time-independent equation,

$$h(1)\psi + h(2)\psi = E\psi \quad (9.15)$$

The fact that $h(1)$ and $h(2)$ are the *same* but for their arguments reflects the indistinguishability of the two electrons.

Equation 9.15 accounts for the electrons' kinetic energy and the atom's potential energy, but ignores the interaction between the two electrons. In fact, the electrons repel each other through the Coulomb force, leading to an interaction energy that must be added to the left-hand side of Equation 9.15. For simplicity, we shall ignore this interaction and treat the electrons as independent objects, each unaffected by the other's presence. In Section 9.5 we show how this *independent particle approximation* can be improved to give a better description of reality.

The two-electron wavefunction depends on the coordinates of both particles, $\psi = \psi(\mathbf{r}_1, \mathbf{r}_2)$, with $|\psi(\mathbf{r}_1, \mathbf{r}_2)|^2$ representing the probability density for finding one electron at \mathbf{r}_1 and the other at \mathbf{r}_2 . The indistinguishability of electrons requires that a formal interchange of particles produce no observable effects. In particular, all probabilities are unaffected by the interchange, so the wavefunction ψ must be one for which

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)|^2 = |\psi(\mathbf{r}_2, \mathbf{r}_1)|^2$$

We say that such a wavefunction exhibits **exchange symmetry**. The wavefunction itself may be either even or odd under particle exchange. The former is characterized by the property

Exchange symmetry for bosons

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi(\mathbf{r}_2, \mathbf{r}_1) \quad (9.16)$$

and describes a class of particles called **bosons**. Photons belong to this class, as do some more exotic particles such as pions. Electrons, as well as protons and neutrons, are examples of **fermions**, for which

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = -\psi(\mathbf{r}_2, \mathbf{r}_1) \quad (9.17)$$

**Exchange symmetry
for fermions**

Therefore, our two-electron helium wavefunction must obey Equation 9.17 to account for the indistinguishability of electrons.⁷

To recover the Pauli principle, we must examine the wavefunction more closely. For independent electrons, solutions to Equation 9.15 are easily found. Because each electron “sees” only the helium nucleus, the wavefunction in each coordinate must be an atomic function of the type discussed in Chapter 8. We denote these atomic functions by ψ_a where a is a collective label for the four quantum numbers n , ℓ , m_ℓ , and m_s (or n , ℓ , j , and m_j if spin-orbit effects are included). The products $\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)$ satisfy our equation, because

$$h(1)\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) = E_a\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)$$

$$h(2)\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) = E_b\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)$$

E_a and E_b are hydrogen-like energies for the states labeled a and b (see Eq. 8.38). Therefore,

$$[h(1) + h(2)]\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) = (E_a + E_b)\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) \quad (9.18)$$

and $E = E_a + E_b$ is the total energy of this two-electron state.

Notice that the one-electron energies are simply additive, as we might have anticipated for independent particles. Furthermore, the solution $\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)$ describes one electron occupying the atomic state labeled a and the other the state labeled b . But this product is *not* odd under particle exchange, as required for identical fermions. However, you can verify that $\psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)$ also is a solution to Equation 9.15 with energy $E = E_a + E_b$, corresponding to our two electrons having exchanged states. The antisymmetric combination of these two

$$\psi_{ab}(\mathbf{r}_1, \mathbf{r}_2) = \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) - \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1) \quad (9.19)$$

does display the correct exchange symmetry, that is,

$$\begin{aligned} \psi_{ab}(\mathbf{r}_2, \mathbf{r}_1) &= \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1) - \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) \\ &= -\psi_{ab}(\mathbf{r}_1, \mathbf{r}_2) \end{aligned}$$

Therefore, Equation 9.19 furnishes an acceptable description of the system. Notice, however, that it is now impossible to decide which electron occupies which state—as it should be for identical electrons! Finally, we see that when a and b label the same state ($a = b$), ψ_{ab} is identically zero—the theory allows no solution (description) in this case, in agreement with the familiar statement of the exclusion principle.

⁷It is an experimental fact that integer spin particles are bosons, but half-integer spin particles are fermions. This connection between spin and symmetry under particle exchange can be shown to have a theoretical basis when the quantum theory is formulated so as to conform to the requirements of special relativity.

EXAMPLE 9.5 Ground State of the Helium Atom

Construct explicitly the two-electron ground-state wavefunction for the helium atom in the independent particle approximation, using the prescription of Equation 9.19. Compare the predicted energy of this state with the measured value, and account in a qualitative way for any discrepancy.

Solution In the independent-particle approximation, each helium electron “sees” only the doubly charged helium nucleus. Accordingly, the ground-state wavefunction of the helium atom is constructed from the lowest-energy hydrogen-like wavefunctions, with atomic number $Z = 2$ for helium. These are states for which $n = 1$, $\ell = 0$, and $m_\ell = 0$. Referring to Equation 8.42 of Chapter 8, we find (with $Z = 2$)

$$\psi_{100}(\mathbf{r}) = \pi^{-1/2}(2/a_0)^{3/2}e^{-2r/a_0}$$

To this orbital function we must attach a spin label (\pm) indicating the direction of electron spin. Thus, the one-electron state labels a and b in this example are given by $a = (1, 0, 0, +)$, $b = (1, 0, 0, -)$. Because there is no orbital field to interact with the electron spin, the energies of these two states are identical and are just the hydrogen-like levels of Equation 8.38 with $n = 1$ and $Z = 2$:

$$E_a = E_b = -(2^2/1^2)(13.6 \text{ eV}) = -54.4 \text{ eV}$$

The antisymmetric two-electron wavefunction for the ground state of helium is then

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{100+}(\mathbf{r}_1)\psi_{100-}(\mathbf{r}_2) - \psi_{100-}(\mathbf{r}_1)\psi_{100+}(\mathbf{r}_2)$$

Both terms have the same spatial dependence but differ as to their spin. The first term of the antisymmetric wave

describes electron 1 as having spin up and electron 2 as having spin down. These spin directions are reversed in the second term. If we introduce the notation $|+-\rangle$ to describe the two electron spins in the first term, then the second term becomes $|-+\rangle$, and the total two-electron wavefunction for the helium ground state can be written

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \pi^{-1}(2/a_0)^3 e^{-2(r_1+r_2)/a_0} \{|+-\rangle - |-+\rangle\}$$

The equal admixture of the spin states $|+-\rangle$ and $|-+\rangle$ means the spin of any one of the helium electrons is just as likely to be up as it is to be down. Notice, however, that the spin of the remaining electron is *always* opposite the first. Such spin–spin *correlations* are a direct consequence of the exclusion principle. (The valence electrons in different orbitals of many higher- Z atoms tend to align their spins. This tendency—known as **Hund’s rule**—is another example of spin–spin correlations induced by the exclusion principle.)

The total electronic energy of the helium atom in this approximation is the sum of the one-electron energies E_a and E_b :

$$E = E_a + E_b = -54.4 \text{ eV} - 54.4 \text{ eV} = -108.8 \text{ eV}$$

The magnitude of this number, 108.8 eV, represents the energy (work) required to remove both electrons from the helium atom in the independent particle model. The measured value is substantially lower, about 79.0 eV, because of the mutual repulsion of the two electrons. Specifically, it requires less energy—only about 24.6 eV—to remove the first electron from the atom, because the electron left behind *screens* the nuclear charge, making it appear less positive than a bare helium nucleus.

O P T I O N A L**9.5 ELECTRON INTERACTIONS AND SCREENING EFFECTS**

The preceding discussion of the helium atom exposes an **issue that arises whenever we treat a system with two or more electrons, namely, how to handle the effects of electron–electron repulsion.** Electrons confined to the small space of an atom are expected to exert strong repulsive electrical forces on one another. To ignore these altogether, as in the independent-particle model, is simply too crude; to include them exactly is unmanageable, since precise descriptions even for the classical motion in this case are unknown except through numerical computation. Accordingly, some workable approximation scheme is needed. A most fruitful approach to this problem begins with the notion of an effective field.

Any one atomic electron is subject to the Coulomb attraction of the nucleus as well as the Coulomb repulsion of every other electron in the atom. These influences largely cancel each other, leaving a net effective field with potential energy $U_{\text{eff}}(\mathbf{r})$.

U_{eff} may not be Coulombic—or even spherically symmetric—and may be different for each atomic electron. The success of this approach hinges on **how simply and accurately we can model the effective potential**. A few of the more obvious possibilities are outlined here.

The outermost, or valence, electrons of an atom “see” not the bare nucleus, but one shielded, or *screened*, by the intervening electrons. The attraction is more like that arising from a nucleus with an effective atomic number Z_{eff} somewhat less than the actual number Z and would be described by

$$U_{\text{eff}}(\mathbf{r}) = \frac{k(Z_{\text{eff}}e)(-e)}{r} \quad (9.20)$$

For a Z -electron atom, $Z_{\text{eff}} = Z$ would represent no screening whatever; at the opposite extreme is perfect screening by the $Z - 1$ other electrons, giving $Z_{\text{eff}} = Z - (Z - 1) = 1$. The best choice for Z_{eff} need not even be integral, and useful values may be deduced from measurements of atomic ionization potentials (see Example 9.6). Furthermore, the degree of screening depends on how much time an electron spends near the nucleus, and we should expect Z_{eff} to vary with the shell and subshell labels of the electron in question. In particular, a $4s$ electron is screened more effectively than a $3s$ electron, since its average distance from the nucleus is greater. Similarly, a $3d$ electron is better screened than a $3s$, or even a $3p$ electron (lower angular momentum implies more eccentric classical orbits, with greater penetration into the nuclear region). **The use of a Z_{eff} for valence electrons is appropriate whenever a clear distinction exists between these and inner (core) electrons of the atom, as in the alkali metals.**

EXAMPLE 9.6 Z_{eff} for the $3s$ Electron in Sodium

The outer electron of the sodium atom occupies the $3s$ atomic level. The observed value for the ionization energy of this electron is 5.14 eV . From this information, deduce a value of Z_{eff} for the $3s$ electron in sodium.

Solution Since the ionization energy, 5.14 eV , represents the amount of energy that must be expended to remove the $3s$ electron from the atom, we infer that the energy of the $3s$ electron in sodium is $E = -5.14 \text{ eV}$. This should be compared with the energy of a $3s$ electron in a hydrogen-like atom with atomic number Z_{eff} , or

$$E = -\frac{Z_{\text{eff}}^2}{3^2} (13.6 \text{ eV})$$

Equating this to -5.14 eV and solving for Z_{eff} gives

$$Z_{\text{eff}} = 3 \sqrt{\frac{5.14}{13.6}} = 1.84$$

In principle, nuclear shielding can be better described by allowing Z_{eff} to vary continuously throughout the atom in a way that mimics the tighter binding accompanying electron penetration into the core. Two functional forms commonly are used for this purpose. **For Thomas–Fermi screening we write**

$$Z_{\text{eff}}(r) = Ze^{-r/a_{\text{TF}}} \quad (9.21)$$

where a_{TF} is the Thomas–Fermi screening length. According to Equation 9.21, Z_{eff} is very nearly Z close to the nucleus ($r \approx 0$) but drops off quickly in the outer region.

The Thomas–Fermi atom

becoming essentially zero for $r \gg a_{\text{TF}}$. In this way, a_{TF} becomes an indicator of atomic size. The Thomas–Fermi model prescribes a_{TF} proportional to $Z^{-1/3}$; the weak variation with Z suggests that all atoms are essentially the same size, regardless of how many electrons they may have. Because the Thomas–Fermi potential is not Coulombic, the one-electron energies that result from the use of Equation 9.21 vary within a given shell; that is, they depend on the principal (n) and orbital (ℓ) quantum numbers. The study of these energies and their associated wavefunctions requires numerical methods, or further approximation. The Thomas–Fermi approximation improves with larger values of Z and so is especially well suited to describe the outer electronic structure of the heavier elements.

In another approach, called the quantum-defect method, nuclear shielding is described by

$$Z_{\text{eff}}(r) = 1 + \frac{b}{r} \quad (9.22)$$

where b is again a kind of screening length. This form is appropriate to the alkali metals, where a lone outer electron is responsible for the chemical properties of the atom. From Equation 9.22, this electron “sees” $Z_{\text{eff}} \approx 1$ for $r \gg b$ and larger values in the core. The special virtue of Equation 9.22 is that it leads to one-electron energies and wavefunctions that can be found without further approximation. In particular, the energy levels that follow from Equation 9.22 can be shown to be

$$E_n = \frac{ke^2}{2a_0} (n - D(\ell))^{-2} \quad (9.23)$$

where $D(\ell)$ is termed the **quantum defect**, since it measures the departure from the simple hydrogen-atom level structure. As the notation suggests, the quantum defect for an s electron differs from that for a p or d electron, but all s electrons have the same quantum defect, regardless of their shell label. Table 9.1 lists some quantum defects deduced experimentally for the sodium atom. Taking $b = 0$ in Equation 9.22 causes all quantum defects to vanish, returning us to the hydrogen-like level structure discussed in Chapter 8.

The use of a simple Z_{eff} , or the more complicated forms of the Thomas–Fermi or quantum-defect method, still results in a U_{eff} with spherical symmetry; that is, the electrons move in a central field. The **Hartree theory** discards even this feature in order to achieve more accurate results. According to Hartree, the electron “cloud” in the atom should be treated as a classical body of charge distributed with some volume charge density $\rho(\mathbf{r})$. The potential energy of any one atomic electron is then

$$U_{\text{eff}}(\mathbf{r}) = \frac{kZe^2}{r} - \int ke \left(\frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right) dV' \quad (9.24)$$

The first term is the attractive energy of the nucleus, and the second term is the repulsive energy of all other atomic electrons. This U_{eff} gives rise to a one-electron Schrödinger equation for the energies E_i and wavefunctions ψ_i of this, say the i th, atomic electron.

Table 9.1 Some Quantum Defects for the Sodium Atom

Subshell	s	p	d	f
$D(\ell)$	1.35	0.86	0.01	~ 0

Quantum defects

But the Hartree theory is *self-consistent*. That is, the charge density $\rho(\mathbf{r})$ due to the other atomic electrons is itself calculated from the electron wavefunctions as

$$\rho(\mathbf{r}) = -e \sum |\psi_j(\mathbf{r})|^2 \quad (9.25)$$

The sum in Equation 9.25 includes all occupied electron states ψ_j except the i th state. In this way the mathematical problem posed by U_{eff} is turned back on itself: We must solve not one Schrödinger equation, but N of them in a single stroke, one for each of the N electrons in the atom! This is accomplished using numerical methods in an iterative solution scheme. An educated guess is made initially for each of the N ground-state electron waves. Starting with this guess, the ρ and U_{eff} for every electron can be computed and all N Schrödinger equations solved. The resulting wavefunctions are compared with the initial guesses; if discrepancies appear, the calculation is repeated with the new set of electron wavefunctions replacing the old ones. After several such iterations, agreement is attained between the starting and calculated wavefunctions. The resulting N electron wavefunctions are said to be fully self-consistent. Implementation of the Hartree method is laborious and demands considerable skill, but the results for atomic electrons are among the best available. Indeed, the Hartree and closely related **Hartree-Fock** methods are the ones frequently used today when accurate atomic energy levels and wavefunctions are required.

Hartree's self-consistent fields

9.6 THE PERIODIC TABLE

In principle, it is possible to predict the properties of all the elements by applying the procedures of wave mechanics to each one. Because of the large number of interactions possible in multielectron atoms, however, approximations must be used for all atoms except hydrogen. Nevertheless, the electronic structure of even the most complex atoms can be viewed as a succession of filled levels increasing in energy, with the outermost electrons primarily responsible for the chemical properties of the element.

In the central field approximation, the atomic levels can be labeled by the quantum numbers n and ℓ . From the exclusion principle, the maximum number of electrons in one such subshell level is $2(2\ell + 1)$. The energy of an electron in this level depends primarily on the quantum number n , and to a lesser extent on ℓ . The levels can be grouped according to the value of n (the shell label), and all those within a group have energies that increase with increasing ℓ . The order of filling the subshell levels with electrons is as follows: Once a subshell is filled, the next electron goes into the vacant level that is lowest in energy. This **minimum energy principle** can be understood by noting that if the electron were to occupy a higher level, it would spontaneously decay to a lower one with the emission of energy.

The chemical properties of atoms are determined predominantly by the least tightly bound, or **valence, electrons**, which are in the subshell of highest energy. The most important factors are the occupancy of this subshell and the energy separation between this and the next-higher (empty) subshell. For example, an atom tends to be chemically inert if its highest subshell is full and there is an appreciable energy gap to the next-higher subshell, since then electrons are not readily shared with other atoms to

form a molecule. The quasi-periodic recurrence of similar highest-shell structures as Z increases is responsible for the periodic system of the chemical elements.

The specification of n and ℓ for each atomic electron is called the **electron configuration** of that atom. We are now in a position to describe the electron configuration of any atom in its ground state:

Hydrogen has only one electron, which, in its ground-state, is described by the quantum numbers $n = 1$, $\ell = 0$. Hence, its electron configuration is designated as $1s^1$.

Helium, with its two electrons, has a ground-state electron configuration of $1s^2$. That is, both electrons are in the same (lowest-energy) $1s$ subshell. Since two is the maximum occupancy for an s subshell, the subshell (and in this case also the shell) is said to be *closed*, and helium is inert.

Lithium has three electrons. Two of these are assigned to the $1s$ subshell, and the third must be assigned to the $2s$ subshell, because this subshell has slightly lower energy than the $2p$ subshell. Hence, the electron configuration of lithium is $1s^2 2s^1$.

With the addition of another electron to make **beryllium**, the $2s$ subshell is closed. The electron configuration of beryllium, with four electrons altogether, is $1s^2 2s^2$. (Beryllium is not inert, however, because the energy gap separating the $2s$ level from the next available level—the $2p$ —is not very large.)

Boron has a configuration of $1s^2 2s^2 2p^1$. (With spin-orbit doubling, the $2p$ electron in boron actually occupies the $2P_{1/2}$ sublevel, corresponding to $n = 2$, $\ell = 1$, and $j = \frac{1}{2}$.)

Carbon has six electrons, and a question arises of how to assign the two $2p$ electrons. Do they go into the same orbital with paired spins ($\uparrow\downarrow$), or do they occupy different orbitals with unpaired spins ($\uparrow\uparrow$)? Experiments show that the energetically preferred configuration is the latter, in which the spins are aligned. This is one illustration of **Hund's rule**, which states that electrons usually fill different orbitals with unpaired spins, rather than the same orbital with paired spins. Hund's rule can be partly understood by noting that electrons in the same orbital tend to be closer together, where their mutual repulsion contributes to a higher energy than if they were separated in different orbitals. Some exceptions to this rule do occur in those elements with subshells that are nearly filled or half-filled. The progressive filling of the $2p$ subshell illustrating Hund's rule is shown schematically in Figure 9.15. With **neon**, the $2p$ subshell is also closed. The neon atom has ten electrons in the configuration $1s^2 2s^2 2p^6$. Because the energy gap separating the $2p$ level from the next available level—the $3s$ —is quite large, the neon configuration is exceptionally stable and the atom is chemically inert.

A complete list of electron configurations for all the known elements is given in Table 9.2. Note that beginning with **potassium** ($Z = 19$), the $4s$ subshell starts to fill while the $3d$ level remains empty. Only after the $4s$ subshell is closed to form **calcium** does the $3d$ subshell begin to fill. We infer that the $3d$ level has a higher energy than the $4s$ level, even though it belongs to a lower-indexed shell. This should come as no surprise, because the energy

Atom	1s	2s	2p			Electron configuration
Li						$1s^2 2s^1$
Be						$1s^2 2s^2$
B						$1s^2 2s^2 2p^1$
C						$1s^2 2s^2 2p^2$
N						$1s^2 2s^2 2p^3$
O						$1s^2 2s^2 2p^4$
F						$1s^2 2s^2 2p^5$
Ne						$1s^2 2s^2 2p^6$

Figure 9.15 Electronic configurations of successive elements from lithium to neon. The filling of electronic states must obey the Pauli exclusion principle and Hund's rule.

separating consecutive shells becomes smaller with increasing n (see the hydrogen-like spectrum), but the energy separating subshells is more nearly constant because of the screening discussed in Section 9.5. (In fact, the energy separating the $3d$ and $4s$ levels is very small, as evidenced by the electron configuration of *chromium*, in which the $3d$ subshell temporarily regains an electron from the $4s$.) The same phenomenon occurs again with *rubidium* ($Z = 37$), in which the $5s$ subshell begins to fill at the expense of the $4d$ and $4f$ subshells. Energetically, the electron configurations shown in the table imply the following ordering of subshells with respect to energy:

$$1s < 2s < 2p < 3s < 3p < 4s \sim 3d < 4p < 5s < 4d < 5p < 6s < 4f \sim 5d \\ < 6p < 7s < 6d \sim 5f, \dots$$

Ordering of subshells by energy

The elements from *scandium* ($Z = 21$) to *zinc* ($Z = 30$) form the first **transition series**. These transition elements are characterized by progres-

Table 9.2 Electronic Configurations of the Elements

Z	Symbol	Ground Configuration	Ionization Energy (eV)	Z	Symbol	Ground Configuration	Ionization Energy (eV)
1	H	$1s^1$	13.595	27	Co	$3d^74s^2$	7.86
2	He	$1s^2$	24.581	28	Ni	$3d^84s^2$	7.633
3	Li	$[\text{He}] 2s^1$	5.390	29	Cu	$3d^{10}4s^1$	7.724
4	Be	$2s^2$	9.320	30	Zn	$3d^{10}4s^2$	9.391
5	B	$2s^22p^1$	8.296	31	Ga	$3d^{10}4s^24p^1$	6.00
6	C	$2s^22p^2$	11.256	32	Ge	$3d^{10}4s^24p^2$	7.88
7	N	$2s^22p^3$	14.545	33	As	$3d^{10}4s^24p^3$	9.81
8	O	$2s^22p^4$	13.614	34	Se	$3d^{10}4s^24p^4$	9.75
9	F	$2s^22p^5$	17.418	35	Br	$3d^{10}4s^24p^5$	11.84
10	Ne	$2s^22p^6$	21.559	36	Kr	$3d^{10}4s^24p^6$	13.996
11	Na	$[\text{Ne}] 3s^1$	5.138	37	Rb	$[\text{Kr}] 5s^1$	4.176
12	Mg	$3s^2$	7.644	38	Sr	$5s^2$	5.692
13	Al	$3s^23p^1$	5.984	39	Y	$4d5s^2$	6.377
14	Si	$3s^23p^2$	8.149	40	Zr	$4d^25s^2$	6.835
15	P	$3s^23p^3$	10.484	41	Nb	$4d^45s^1$	6.881
16	S	$3s^23p^4$	10.357	42	Mo	$4d^55s^1$	7.10
17	Cl	$3s^23p^5$	13.01	43	Tc	$4d^55s^2$	7.228
18	Ar	$3s^23p^6$	15.755	44	Ru	$4d^75s^1$	7.365
19	K	$[\text{Ar}] 4s^1$	4.339	45	Rh	$4d^85s^1$	7.461
20	Ca	$4s^2$	6.111	46	Pd	$4d^{10}$	8.33
21	Sc	$3d4s^2$	6.54	47	Ag	$4d^{10}5s^1$	7.574
22	Ti	$3d^24s^2$	6.83	48	Cd	$4d^{10}5s^2$	8.991
23	V	$3d^34s^2$	6.74	49	In	$4d^{10}5s^25p^1$	5.785
24	Cr	$3d^54s$	6.76	50	Sn	$4d^{10}5s^25p^2$	7.342
25	Mn	$3d^54s^2$	7.432	51	Sb	$4d^{10}5s^25p^3$	8.639
26	Fe	$3d^64s^2$	7.87	52	Te	$4d^{10}5s^25p^4$	9.01

sive filling of the $3d$ subshell while the outer electron configuration is unchanged at $4s^2$ (except in the case of copper). Consequently, all the transition elements exhibit similar chemical properties. This belated occupancy of inner d subshells is encountered again in the second and third transition series, marked by the progressive filling of the $4d$ and $5d$ subshells, respectively. The second transition series includes the elements *yttrium* ($Z = 39$) to *cadmium* ($Z = 48$); the third contains the elements *lutetium* ($Z = 71$) to *mercury* ($Z = 80$).

Related behavior is also seen as the $4f$ and $5f$ subshells are filled. The **lanthanide series**, stretching from *lanthanum* ($Z = 57$) to *ytterbium* ($Z = 70$), is marked by a common $6s^2$ valence configuration, with the added electrons completing the $4f$ subshell (the nearby $5d$ levels also are occupied in some instances). The lanthanide elements, or lanthanides, also are known as the **rare earths** because of their low natural abundance. *Cerium* ($Z = 58$), which forms 0.00031% by weight of the Earth's crust, is the most abundant of the lanthanides.

Table 9.2 Electronic Configurations of the Elements

Z	Symbol	Ground Configuration	Ionization Energy (eV)	Z	Symbol	Ground Configuration	Ionization Energy (eV)
53	I	$4d^{10}5s^25p^5$	10.454	79	Au	$[\text{Xe}, 4f^{14}5d^{10}] 6s^1$	9.22
54	Xe	$4d^{10}5s^25p^6$	12.127	80	Hg	$6s^2$	10.434
55	Cs	$[\text{Xe}] 6s^1$	3.893	81	Tl	$6s^26p^1$	6.106
56	Ba	$6s^2$	5.210	82	Pb	$6s^26p^2$	7.415
57	La	$5d6s^2$	5.61	83	Bi	$6s^26p^3$	7.287
58	Ce	$4f^5d6s^2$	6.54	84	Po	$6s^26p^4$	8.43
59	Pr	$4f^36s^2$	5.48	85	At	$6s^26p^5$	9.54
60	Nd	$4f^46s^2$	5.51	86	Rn	$6s^26p^6$	10.745
61	Pm	$4f^56s^2$	5.60	87	Fr	$[\text{Rn}] 7s^1$	3.94
62	Fm	$4f^66s^2$	5.644	88	Ra	$7s^2$	5.277
63	Eu	$4f^76s^2$	5.67	89	Ac	$6d7s^2$	5.17
64	Gd	$4f^75d6s^2$	6.16	90	Th	$6d^27s^2$	6.08
65	Tb	$4f^96s^2$	6.74	91	Pa	$5f^26d7s^2$	5.89
66	Dy	$4f^{10}6s^2$	6.82	92	U	$5f^36d7s^2$	6.194
67	Ho	$4f^{11}6s^2$	6.022	93	Np	$5f^46d7s^2$	6.266
68	Er	$4f^{12}6s^2$	6.108	94	Pu	$5f^67s^2$	6.061
69	Tm	$4f^{13}6s^2$	6.185	95	Am	$5f^77s^2$	5.99
70	Yb	$4f^{14}6s^2$	6.22	96	Cm	$5f^76d7s^2$	6.02
71	Lu	$4f^{14}5d6s^2$	6.15	97	Bk	$5f^86d7s^2$	6.23
72	Hf	$4f^{14}5d^26s^2$	6.83	98	Cf	$5f^{10}7s^2$	6.30
73	Ta	$4f^{14}5d^36s^2$	7.88	99	Es	$5f^{11}7s^2$	6.42
74	W	$4f^{14}5d^46s^2$	7.98	100	Fm	$5f^{12}7s^1$	6.50
75	Re	$4f^{14}5d^56s^2$	7.87	101	Mv	$5f^{13}7s^2$	6.58
76	Os	$4f^{14}5d^66s^2$	8.71	102	No	$5f^{14}7s^2$	6.65
77	Ir	$4f^{14}5d^76s^2$	9.12	103	Lw	$5f^{14}6d7s^2$	
78	Pt	$4f^{14}5d^86s^2$	8.88	104	Ku	$5f^{14}6d^27s^2$	

Note: The bracket notation is used as a shorthand method to avoid repetition in indicating inner-shell electrons. Thus, [He] represents $1s^2$, [Ne] represents $1s^22s^22p^6$, [Ar] represents $1s^22s^22p^63s^23p^6$, and so on.

In the **actinide series** from *actinium* ($Z = 89$) to *nobelium* ($Z = 102$), the valence configuration remains $7s^2$, as the $5f$ subshell progressively fills (along with occasional occupancy of the nearby $6d$ level).

Table 9.2 also lists the ionization energies of the elements. The ionization energy for each element is plotted against its atomic number Z in Figure 9.16a. This plot shows that the ionization energy tends to increase within a shell, then drops dramatically as the filling of a new shell begins. The behavior repeats, and it is from this recurring pattern that the periodic table gets its name. A similar repetitive pattern is observed in a plot of the atomic volume per atom versus atomic number (see Fig. 9.16b).

The primary features of these plots can be understood from simple arguments. First, the larger nuclear charge that accompanies higher values of Z tends to pull the electrons closer to the nucleus and binds them more tightly. Were this the only effect, the ionization energy would increase and the atomic volume would decrease steadily with increasing Z . But the innermost, or core, electrons screen the nuclear charge, making it less effective in binding the outer electrons. The screening effect varies in a

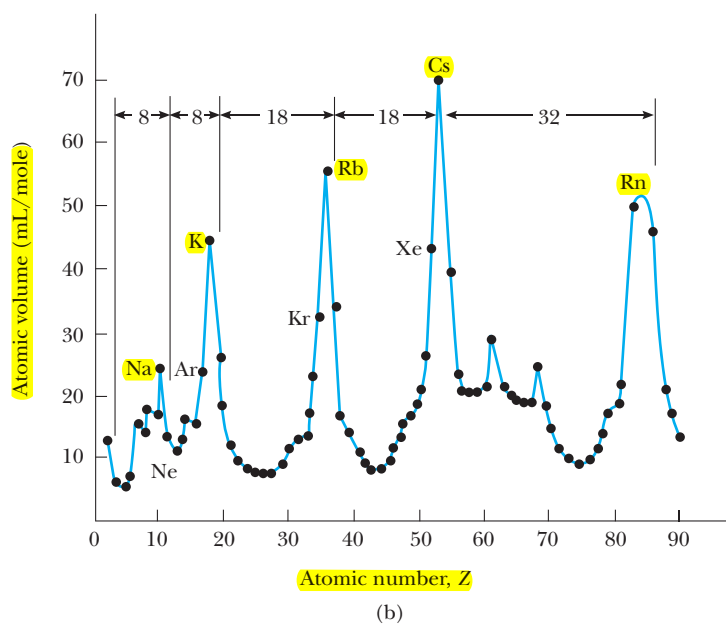
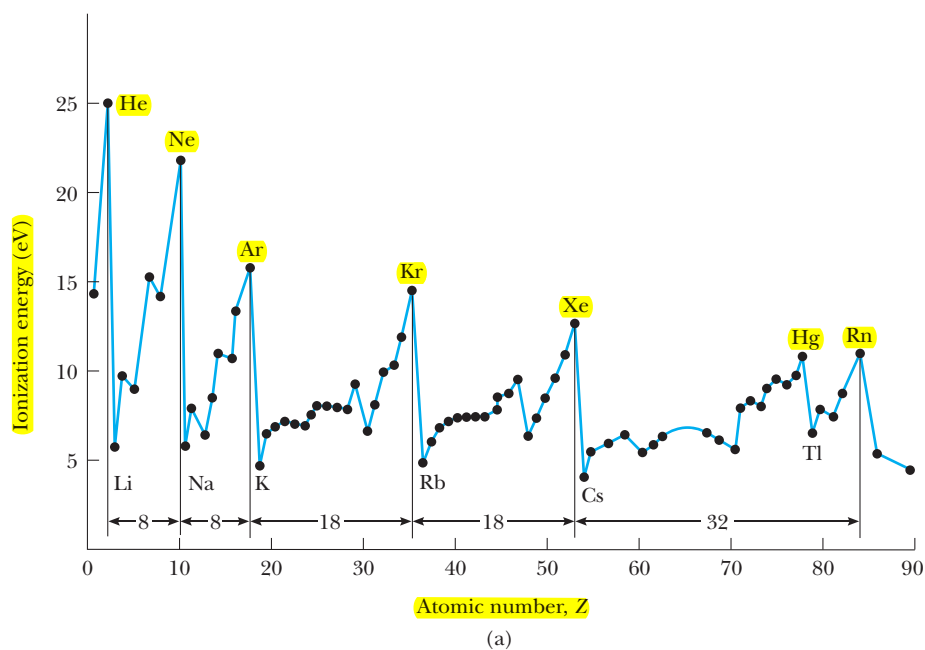


Figure 9.16 (a) Ionization energy of the elements versus atomic number Z . (b) Atomic volume of the elements versus atomic number Z . The recurring pattern with increasing atomic number exemplifies the behavior from which the periodic table gets its name.

complicated way from one element to the next, but it is most pronounced for a lone electron outside a closed shell, as in the alkali metals (Li, Na, K, Rb, Cs, and Fr). For these configurations the ionization energy drops sharply, only to rise again as the nuclear charge intensifies at higher Z . The variation in ionization energy is mirrored by the behavior of atomic volume,

which peaks at the alkali configurations and becomes smaller as the screening effect subsides.

9.7 X-RAY SPECTRA AND MOSELEY'S LAW

Electronic transitions within the inner shells of heavier atoms are accompanied by large energy transfers. If the excess energy is carried off by a photon, x rays are emitted at specific wavelengths peculiar to the emitting atom. This explains why discrete x-ray lines are produced when energetic electrons bombard a metal target, as discussed earlier in Section 3.5.

The inner electrons of high Z elements are bound tightly to the atom, because they see a nuclear charge essentially unscreened by the remaining electrons. Consider the case of molybdenum (Mo), with atomic number $Z = 42$ (see Table 9.2). The innermost, or K shell, electrons have $n = 1$ and energy (from Equation 8.38)

$$E_1 = -\frac{ke^2}{2a_0} \left\{ \frac{Z^2}{1^2} \right\} = -(13.6 \text{ eV})(42)^2 = -23990.4 \text{ eV}$$

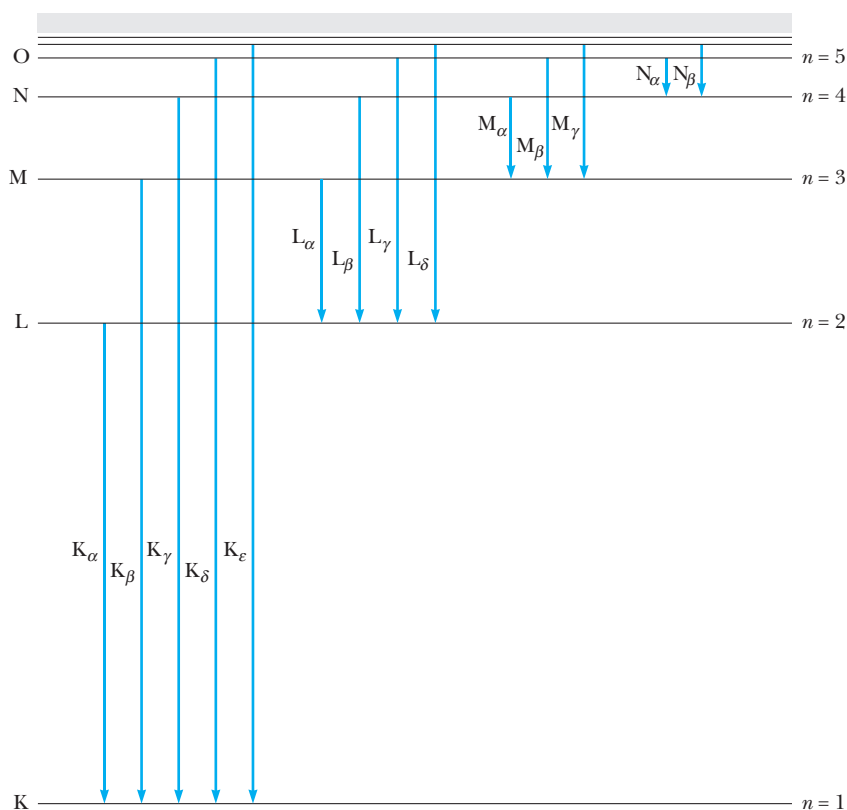


Figure 9.17 Origin of x-ray spectra. The K series ($K_\alpha, K_\beta, K_\gamma, \dots$) originates with electrons in higher-lying shells making a downward transition to fill a vacancy in the K shell. In the same way, the filling of vacancies created in higher shells produces the L series, the M series, and so on.

Thus, approximately 24 keV must be supplied to dislodge a K shell electron from the Mo atom.⁸ Energies of this magnitude are routinely delivered via electron impact: electrons accelerated to kilovolt energies collide with atoms of a molybdenum target, giving up most or all of their energy to one atom in a single collision. If large enough, the collision energy may excite one of the K shell electrons to a higher vacant level or free it from the atom altogether. (Recall there are two electrons in a filled K shell.) In either case, a vacancy, or *hole*, is left behind. This hole is quickly filled by another, higher-lying atomic electron, with the energy of transition released in the form of a photon. The exact energy (and wavelength) of the escaping photon depends on the energy of the electron filling the vacancy, giving rise to an entire K series of emission lines denoted in order of increasing energy (decreasing wavelength) by K_{α} , K_{β} , K_{γ} , In the same way, the filling of vacancies left in higher shells produces the L series, the M series, and so on, as illustrated in Figure 9.17.



Henry G. J. Moseley (1887–1915) discovered a direct way to measure Z , the atomic number, from the characteristic x-ray wavelength emitted by an element. Moseley's work not only established the correct sequence of elements in the periodic table but also provided another confirmation of the Bohr model of the atom, in this case at x-ray energies. One wonders what other major discoveries Moseley would have made if he had not been killed in action at the age of 27 in Turkey in the first world war. (*University of Oxford, Museum of the History of Science/Courtesy AIP Niels Bohr Library*)

⁸In contrast, only 7.10 eV (the ionization energy from Table 9.2) is required to free the outermost, or 5s, electron.

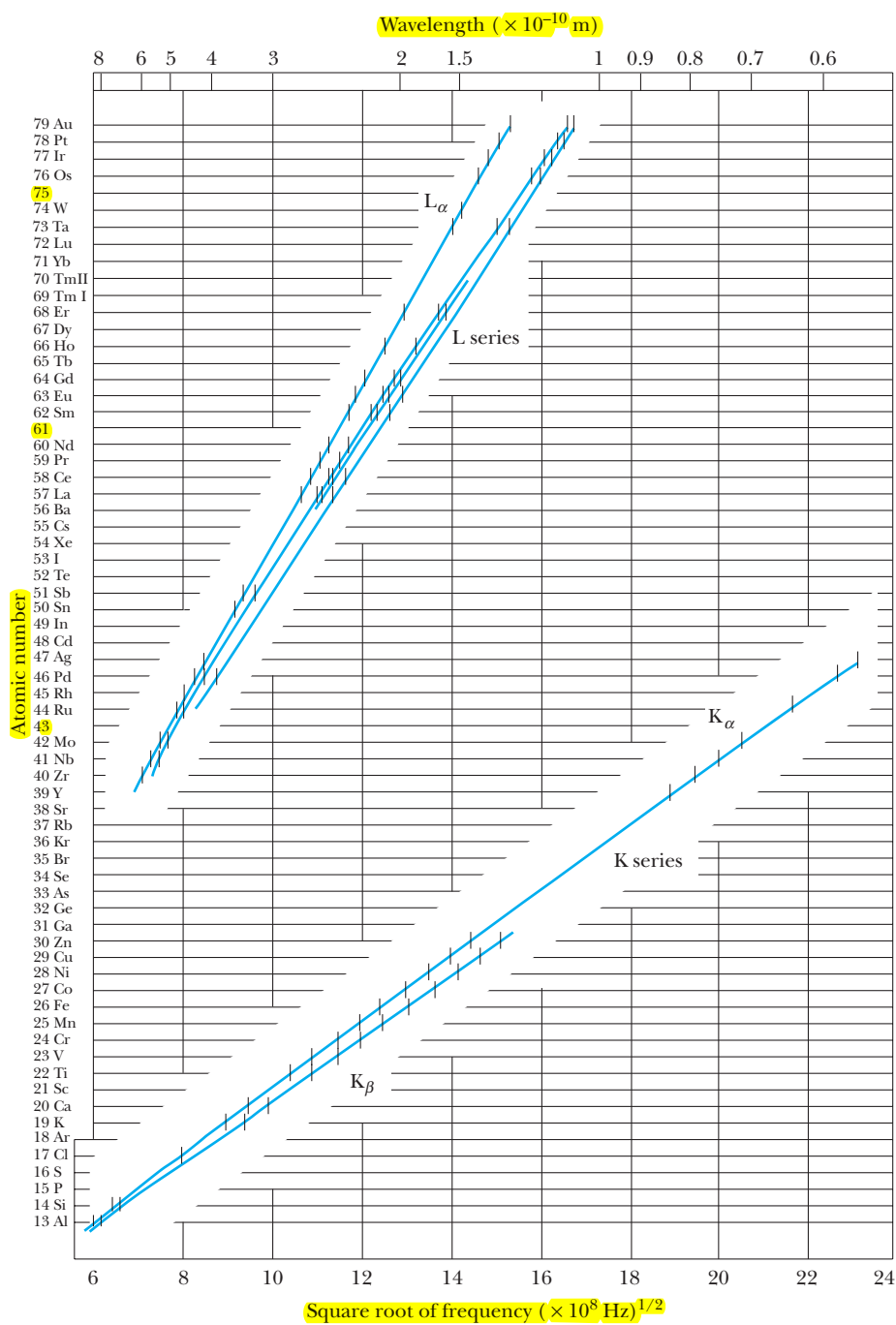


Figure 9.18 The original data of Moseley showing the relationship between atomic number Z and the characteristic x-ray frequencies. The gaps at $Z = 43, 61,$ and 75 represent elements unknown at the time of Moseley's work. (There are also several errors in the atomic number designations for the elements.) (© From *H. G. J. Moseley*, *Philos. Mag.* (6), 27:703, 1914)

The energy of the longest-wavelength photons in a series can be estimated from simple screening arguments. For the K_α line, the K shell vacancy is filled by an electron from the L shell ($n = 2$). But an electron in the L shell is partially screened from the nucleus by the one remaining K shell electron and so sees a nuclear charge of only $Z - 1$. Thus, the energy of the K_α photon can be approximated as an $n = 2$ to $n = 1$ transition in a one-electron atom with an effective nuclear charge of $Z - 1$:

$$E[K_\alpha] = -\frac{ke^2}{2a_0} \frac{(Z-1)^2}{2^2} + \frac{ke^2}{2a_0} \frac{(Z-1)^2}{1^2} = \frac{ke^2}{2a_0} \frac{3(Z-1)^2}{4} \quad (9.26)$$

For molybdenum ($Z = 42$), this is $E[K_\alpha] = 17.146$ keV, corresponding to a wavelength

$$\lambda[K_\alpha] = \frac{hc}{E[K_\alpha]} = \frac{12.4 \text{ keV} \cdot \text{\AA}}{17.146 \text{ keV}} = 0.723 \text{ \AA}$$

For comparison, the observed K_α line of molybdenum has wavelength 0.7095 \AA , in reasonable agreement with our calculation.

In a series of careful experiments conducted from 1913 to 1914, the British physicist H. G. J. Moseley measured the wavelength of K_α lines for numerous elements and confirmed the validity of Equation 9.26, known as **Moseley's law**. According to Moseley's law, a plot of the square root of photon frequency $(E/h)^{1/2}$ versus atomic number Z should yield a straight line. Such a **Moseley plot**, as it is called, is reproduced here as Figure 9.18. Before Moseley's work, atomic numbers were mere placeholders for the elements appearing in the periodic table, the elements being ordered according to their mass. By measuring their K_α lines, Moseley was able to establish the correct sequence of elements in the periodic table, a sequence properly based on atomic number rather than atomic mass. The gaps in Moseley's data at $Z = 43$, 61 , and 75 represent elements unknown at the time of his work.

SUMMARY

The magnetic behavior of atoms is characterized by their **magnetic moment**. The orbital moment of an atomic electron is proportional to its orbital angular momentum:

$$\boldsymbol{\mu} = \frac{-e}{2m_e} \mathbf{L} \quad (9.1)$$

The constant of proportionality, $-e/2m_e$, is called the **gyromagnetic ratio**. Since \mathbf{L} is subject to space quantization, so too is the atomic moment $\boldsymbol{\mu}$. Atomic moments are measured in **Bohr magnetons**, $\mu_B = e\hbar/2m_e$; the SI value of μ_B is $9.27 \times 10^{-24} \text{ J/T}$.

An atom subjected to an external magnetic field \mathbf{B} experiences a magnetic torque, which results in precession of the moment vector $\boldsymbol{\mu}$ about the field vector \mathbf{B} . The frequency of precession is the **Larmor frequency** ω_L given by

$$\omega_L = \frac{eB}{2m_e} \quad (9.5)$$