

CHAPTER 7

Many-Electron Atoms



Helium, whose atoms have only closed electron shells, is inert chemically and cannot burn or explode. Because it is also less dense than air, it is used in airships.

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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.

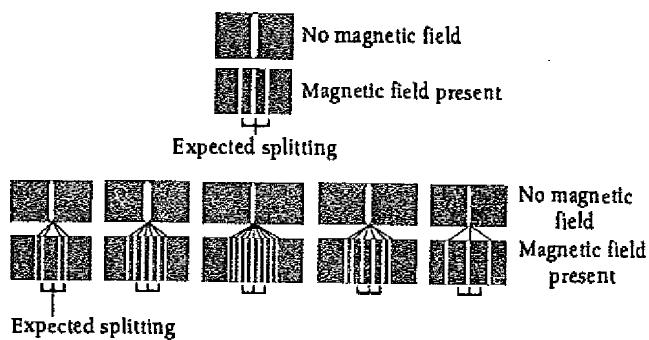


Figure 7.1 The normal and anomalous Zeeman effects in various spectral lines.

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 μ_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

$$\text{Spin angular momentum} \quad S = \sqrt{s(s+1)}\hbar = \frac{\sqrt{3}}{2}\hbar \quad (7.1)$$

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, ...	Electron energy
Orbital	l	0, 1, 2, ..., $n - 1$	Orbital angular-momentum magnitude
Magnetic	m_l	$-l, \dots, 0, \dots, +l$	Orbital angular-momentum direction
Spin magnetic	m_s	$-\frac{1}{2}, +\frac{1}{2}$	Electron spin direction

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

$$S_z = m_s \hbar = \pm \frac{1}{2} \hbar \quad (7.2)$$

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 μ_s of an electron is related to its spin angular momentum S by

Spin magnetic
moment

$$\mu_s = -\frac{e}{m} S \quad (7.3)$$

The possible components of μ_s along any axis, say the z axis, are therefore limited to

z component of
spin magnetic
moment

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

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

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.

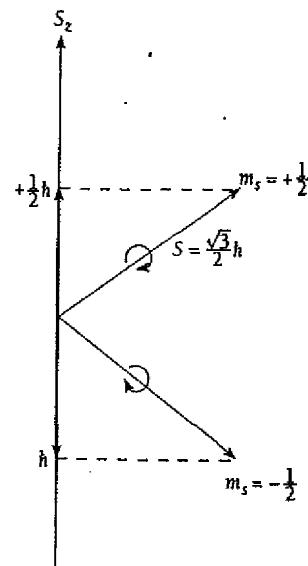


Figure 7.2 The two possible orientations of the spin angular-momentum vector are "spin up" ($m_s = +\frac{1}{2}$) and "spin down" ($m_s = -\frac{1}{2}$).

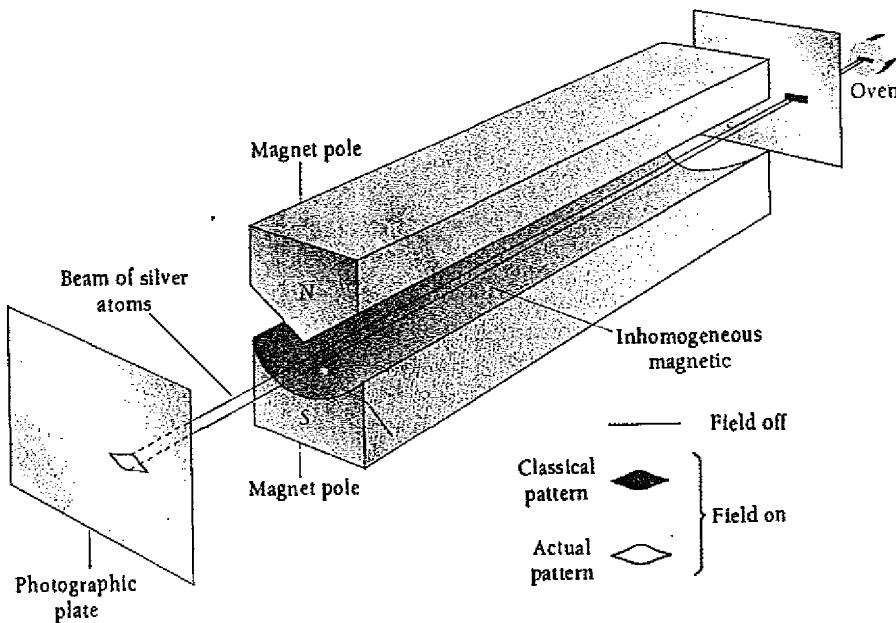


Figure 7.3 The Stern-Gerlach experiment.

The Stern-Gerlach Experiment

Space quantization was first explicitly 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 determining atomic structures, it is interesting to look into its quantum-mechanical implications.

The complete wave function $\psi(1, 2, 3, \dots, n)$ of a system of n noninteracting particles can be expressed as the product of the wave functions $\psi(1), \psi(2), \psi(3), \dots, \psi(n)$ of the individual particles. That is,

$$\psi(1, 2, 3, \dots, n) = \psi(1)\psi(2)\psi(3)\dots\psi(n) \quad (7.5)$$

Let us use Eq. (7.5) to look into the kinds of wave functions that can be used to describe a system of two identical particles.

Suppose one of the particles is in quantum state a and the other in state b . Because the particles are identical, it should make no difference in the probability density $|\psi|^2$ of the system if the particles are exchanged, with the one in state a replacing the one in state b , and vice versa. Symbolically, we require that

$$|\psi|^2(1, 2) = |\psi|^2(2, 1) \quad (7.6)$$

The wave function $\psi(2, 1)$ that represents the exchanged particles can be either

$$\text{Symmetric} \quad \psi(2, 1) = \psi(1, 2) \quad (7.7)$$

or

$$\text{Antisymmetric} \quad \psi(2, 1) = -\psi(1, 2) \quad (7.8)$$

and still fulfill Eq. (7.6). The wave function of the system is not itself a measurable quantity, and so it can be altered in sign by the exchange of the particles. Wave functions that are unaffected by an exchange of particles are said to be **symmetric**, while those that reverse sign upon such an exchange are said to be **antisymmetric**.

If particle 1 is in state a and particle 2 is in state b , the wave function of the system is, according to Eq. (7.5),

$$\psi_1 = \psi_a(1)\psi_b(2) \quad (7.9)$$

If particle 2 is in state a and particle 1 is in state b , the wave function is

$$\psi_{11} = \psi_a(2)\psi_b(1) \quad (7.10)$$

Because the two particles are indistinguishable, we have no way to know at any moment whether ψ_1 or ψ_{11} describes the system. The likelihood that ψ_1 is correct at any moment is the same as the likelihood that ψ_{11} is correct.

Equivalently, we can say that the system spends half the time in the configuration whose wave function is ψ_1 and the other half in the configuration whose wave function is ψ_{11} . Therefore a linear combination of ψ_1 and ψ_{11} is the proper description of the system. Two such combinations, symmetric and antisymmetric, are possible:

$$\text{Symmetric} \quad \psi_S = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)] \quad (7.11)$$

$$\text{Antisymmetric} \quad \psi_A = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)] \quad (7.12)$$

The factor $1/\sqrt{2}$ is needed to normalize ψ_S and ψ_A . Exchanging particles 1 and 2 leaves ψ_S unaffected, while it reverses the sign of ψ_A . Both ψ_S and ψ_A obey Eq. (7.6).

There are a number of important distinctions between the behavior of particles in systems whose wave functions are symmetric and that of particles in systems whose wave functions are antisymmetric. The most obvious is that in the symmetric case, both particles 1 and 2 can simultaneously exist in the same state, with $a = b$. In the antisymmetric case, if we set $a = b$, we find that

$$\psi_A = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_a(2) - \psi_a(2)\psi_a(1)] = 0$$

Hence the two particles *cannot* be in the same quantum state. Pauli found that no two electrons in an atom can be in the same quantum state, so we conclude that systems of electrons are described by wave functions that reverse sign upon the exchange of any pair of them.

Fermions and Bosons

The results of various experiments show that *all* particles which have odd half-integral spins ($\frac{1}{2}, \frac{3}{2}, \dots$) have wave functions that are antisymmetric to an exchange of any pair of them. Such particles, which include protons and neutrons as well as electrons, obey the exclusion principle when they are in the same system. That is, when they move in a common force field, each member of the system must be in a different quantum state. Particles of odd half-integral spin are often referred to as fermions because, as we shall learn in Chap. 9, the behavior of systems of them (such as free electrons in a metal) is governed by a statistical distribution law discovered by Fermi and Dirac.

Particles whose spins are 0 or an integer have wave functions that are symmetric to an exchange of any pair of them. These particles, which include photons, alpha particles, and helium atoms, do not obey the exclusion principle. Particles of 0 or integral spin are often referred to as bosons because the behavior of systems of them (such as photons in a cavity) is governed by a statistical distribution law discovered by Bose and Einstein.

There are other consequences of the symmetry or antisymmetry of particle wave functions besides that expressed in the exclusion principle. It is these consequences that make it useful to classify particles according to the natures of their wave functions rather than merely according to whether or not they obey the exclusion principle.

7.4 PERIODIC TABLE

Organizing the elements

In 1869 the Russian chemist Dmitri Mendeleev formulated the periodic law whose modern statement is

When the elements are listed in order of atomic number, elements with similar chemical and physical properties recur at regular intervals.

Although the modern quantum theory of the atom was many years in the future, Mendeleev was fully aware of the significance his work would turn out to have. As he



Dmitri Mendeleev (1834–1907) was born in Siberia and grew up there, going on to Moscow and later France and Germany to study chemistry. In 1866 he became professor of chemistry at the University of St. Petersburg and three years later published the first version of the periodic table. The notion of atomic number was then unknown and Mendeleev had to deviate from the strict sequence of atomic masses for some elements and leave

gaps in the table in order that the known elements (only 63 at that time) occupy places appropriate to their properties. Other chemists of the time were thinking along the same lines, but Mendeleev went further in 1871 by proposing that the gaps correspond to then-unknown elements. When his detailed predictions of the properties of these elements were fulfilled upon their discovery, Mendeleev became world famous. A further triumph for the periodic table came at the end of the nineteenth century, when the inert gases were discovered. Here were six elements of whose existence Mendeleev had been unaware, but they fit perfectly as a new group in the table. The element of atomic number 101 is called mendelevium in his honor.

remarked, "The periodic law, together with the revelations of spectrum analysis, have contributed to again revive an old but remarkably long-lived hope—that of discovering, if not by experiment, at least by mental effort, the *primary matter*."

A periodic table is an arrangement of the elements according to atomic number in a series of rows such that elements with similar properties form vertical columns. Table 7.2 is a simple form of periodic table.

Elements with similar properties form the groups shown as vertical columns in Table 7.2 (Fig. 7.4). Thus group 1 consists of hydrogen plus the alkali metals, which are all soft, have low melting points, and are very active chemically. Lithium, sodium, and potassium are examples. Hydrogen, although physically a nonmetal, behaves chemically much like an active metal. Group 7 consists of the halogens, volatile nonmetals that form diatomic molecules in the gaseous state. Like the alkali metals, the halogens are chemically active, but as oxidizing agents rather than as reducing agents. Fluorine, chlorine, bromine, and iodine are examples; fluorine is so active it can corrode platinum. Group 8 consists of the inert gases, of which helium, neon, and argon are examples. As their name suggests, they are inactive chemically: they form virtually no compounds with other elements, and their atoms do not join together into molecules.

The horizontal rows in Table 7.2 are called periods. The first three periods are broken in order to keep their members aligned with the most closely related elements of the long periods below. Most of the elements are metals (Fig. 7.5). Across each period is a more or less steady transition from an active metal through less active metals and weakly active nonmetals to highly active nonmetals and finally to an inert gas (Fig. 7.6). Within each column there are also regular changes in properties, but they are far less conspicuous than those in each period. For example, increasing atomic number in the alkali metals is accompanied by greater chemical activity, while the reverse is true in the halogens.

A series of transition elements appears in each period after the third between the group 2 and group 3 elements (Fig. 7.7). The transition elements are metals, in general hard and brittle with high melting points, that have similar chemical behavior. Fifteen of the transition elements in period 6 are virtually indistinguishable in their properties and are known as the lanthanide elements (or rare earths). Another group of closely related metals, the actinide elements, is found in period 7.

For over a century the periodic law has been indispensable to chemists because it provides a framework for organizing their knowledge of the elements. It is one of the

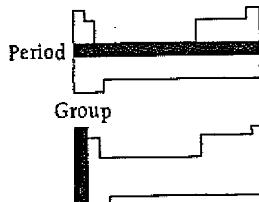


Figure 7.4 The elements in a group of the periodic table have similar properties, while those in a period have different properties.

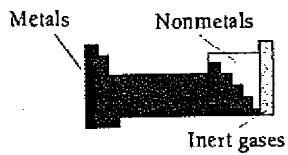


Figure 7.5 The majority of the elements are metals.

Table 7.2
The Periodic Table of the Elements

Period	Group	1	2	3	4	5	6	7	8
1	H	Hydrogen 1.008							
2	3	Lithium 6.941	Boron 9.012						
3	11	Sodium 22.99	Magnesium 24.31						
4	19	K	Calcium 40.08	Scandium 44.96	Titanium 47.88	Vanadium 50.94	Cr 52.00	Mn 54.94	Fe 55.8
5	37	Rb	Strontium 87.62	Sr 85.47	Niobium 91.91	Zirconium 91.22	Tantalum 95.94	Tungsten (98)	Technetium 41
6	55	Cs	Barium 137.3	Barium 132.9	Hafnium 178.5	Tantalum 180.9	Tungsten 183.9	Rhenium 186.2	Rhenium 190.2
7	87	Fr	Ra		Dubnium (262)	Seaborgium (263)	Nielsbohrium (262)	Hessium (264)	Mt (265)
		Francium (223)	Radium 226.0						
		Alkali metals							
		Lanthanides (rare earths)							
		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd
		Lanthanum 138.9	Cerium 140.1	Praseodymium 140.9	Neodymium 144.2	Promethium (145)	Samarium 150.4	Euroium 152.0	Terbium 157.3
		Ac	Th	Pa	U	Np	Pu	Am	Dy
		Actinium (227)	Thorium 232.0	Protactinium 231.0	Uranium 238.0	Neptunium (237)	Plutonium (244)	Americum (243)	Tb
		Actinides							
		Lu	Yttrium 175.0	Terbium 173.0	Europium 169.9	Erbium 167.3	Thulium 165.9	Ytterbium 163.9	Lu
		Lutetium 175.0	Yttrium 173.0	Terbium 171.9	Europium 168.7	Thulium 167.6	Ytterbium 166.9	No	LW
		Actinium (227)	Thorium 232.0	Protactinium 231.0	Uranium 238.0	Neptunium (237)	Plutonium (244)	Americum (243)	Mendelevium (257)
		Halogens (next group)							
		He	Helium 4.003						
		Ar	Argon 39.95						
		Cl	Chlorine 35.45						
		S	Sulfur 32.07						
		P	Phosphorus 30.97						
		As	Gallium 72.59						
		Se	Germanium 74.92						
		Br	Antimony 78.95						
		Kr	Boron 79.90						
		Xe	Selenium 83.80						
		I	Iodine 126.9						
		Te	Tellurium 127.6						
		S	Polonium (209)						
		At	Lead 209.0						
		Asmiline (210)							
		Halogenes (next group)							

The number above the symbol of each element is its atomic number, and the number below its name is its average atomic mass. The elements whose atomic masses are given in parentheses do not occur in nature but have been created in nuclear reactions. The atomic mass in such a case is the mass number of the most long-lived radioisotope of the element. Elements with atomic numbers 110, 111, 112, 114, and 116 have also been created but not yet named.

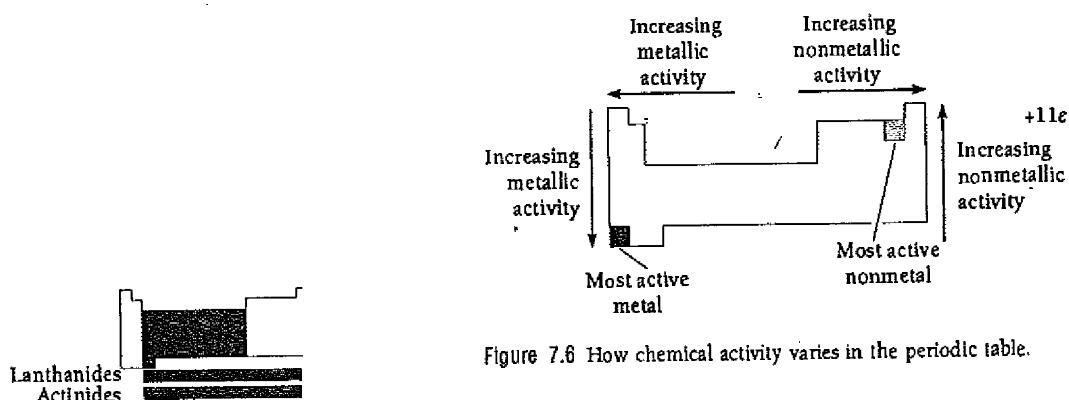


Figure 7.6 How chemical activity varies in the periodic table.

Figure 7.7 The transition elements are metals.

triumphs of the quantum theory of the atom that it enables us to account in a natural way for the periodic law without invoking any new assumptions.

7.5 ATOMIC STRUCTURES

Shells and subshells of electrons

Two basic principles determine the structures of atoms with more than one electron:

- 1 A system of particles is stable when its total energy is a minimum.
- 2 Only one electron can exist in any particular quantum state in an atom.

Before we apply these rules to actual atoms, let us examine the variation of electron energy with quantum state.

While the various electrons in a complex atom certainly interact directly with one another, much about atomic structure can be understood by simply considering each electron as though it exists in a constant mean electric field. For a given electron this effective field is approximately that of the nuclear charge Z_e decreased by the partial shielding of those other electrons that are closer to the nucleus (see Fig. 7.9 in Sec. 7.6).

Electrons that have the same principal quantum number n usually (though not always) average roughly the same distance from the nucleus. These electrons therefore interact with roughly the same electric field and have similar energies. It is conventional to speak of such electrons as occupying the same atomic shell. Shells are denoted by capital letters according to the following scheme:

$$\begin{array}{ccccccc} \text{Atomic shells} & & & n = 1 & 2 & 3 & 4 & 5 \dots \\ & & & K & L & M & N & O \dots \end{array} \quad (7.13)$$

The energy of an electron in a particular shell also depends to a certain extent on its orbital quantum number l , though not as much as on n . In a complex atom the degree to which the full nuclear charge is shielded from a given electron by intervening shells of other electrons varies with its probability-density distribution. An electron of small l is more likely to be found, near the nucleus where it is poorly shielded by the other electrons than is one of higher l (see Fig. 6.11). The result is a lower total energy (that is, higher binding energy) for the electron. The electrons in each shell

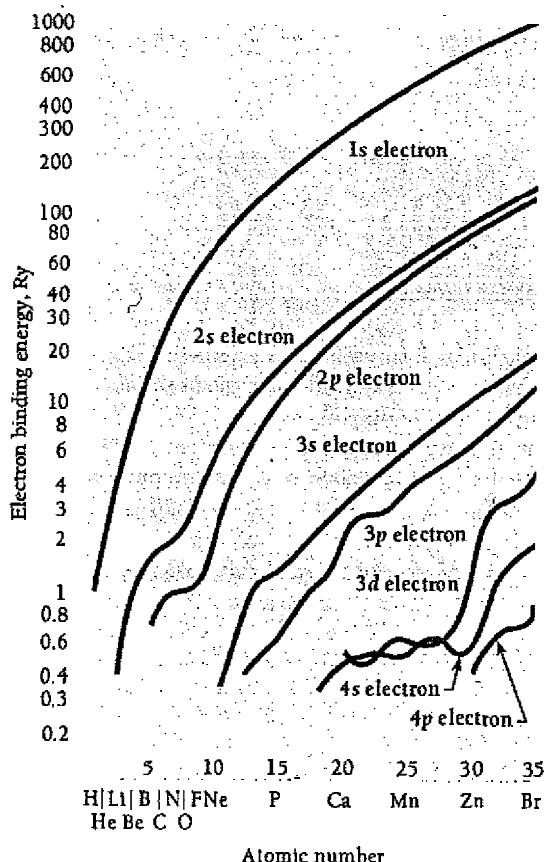


Figure 7.8 The binding energies of atomic electrons in rydbergs. (1 Ry = 13.6 eV = ground-state energy of H atom.)

accordingly increase in energy with increasing l . This effect is illustrated in Fig. 7.8, which is a plot of the binding energies of various atomic electrons as a function of atomic number for the lighter elements.

Electrons that share a certain value of l in a shell are said to occupy the same subshell. All the electrons in a subshell have almost identical energies, since the dependence of electron energy upon m_l and m_s is comparatively minor.

The occupancy of the various subshells in an atom is usually expressed with the help of the notation introduced in the previous chapter for the various quantum states of the hydrogen atom. As indicated in Table 6.2, each subshell is identified by its principal quantum number n followed by the letter corresponding to its orbital quantum number l . A superscript after the letter indicates the number of electrons in that subshell. For example, the electron configuration of sodium is written

$$1s^2 2s^2 2p^6 3s^1$$

which means that the 1s ($n = 1, l = 0$) and 2s ($n = 2, l = 0$) subshells contain two electrons each, the 2p ($n = 2, l = 1$) subshell contains six electrons, and the 3s ($n = 3, l = 0$) subshell contains one electron.

Table 7.3 Subshell Capacities in the M ($n = 3$) Shell of an Atom

	$m_l = 0$	$m_l = -1$	$m_l = +1$	$m_l = -2$	$m_l = +2$	
$l = 0:$	$\uparrow\downarrow$					$\uparrow m_s = +\frac{1}{2}$
$l = 1:$	$\uparrow\downarrow$	$\downarrow\uparrow$	$\uparrow\downarrow$	$\downarrow\uparrow$	$\uparrow\downarrow$	$\downarrow m_s = -\frac{1}{2}$
$l = 2:$	$\uparrow\downarrow$	$\downarrow\uparrow$	$\uparrow\downarrow$	$\downarrow\uparrow$	$\uparrow\downarrow$	

Shell and Subshell Capacities

The exclusion principle limits the number of electrons that can occupy a given subshell. A subshell is characterized by a certain principal quantum number n and orbital quantum number l , where l can have the values $0, 1, 2, \dots, (n - 1)$. There are $2l + 1$ different values of the magnetic quantum number m_l for any l , since $m_l = 0, \pm 1, \pm 2, \dots, \pm l$. Finally, the spin magnetic quantum number m_s has the two possible values of $+\frac{1}{2}$ and $-\frac{1}{2}$ for any m_l . The result is that each subshell can contain a maximum of $2(2l + 1)$ electrons (Table 7.3).

The maximum number of electrons a shell can hold is the sum of the electrons in its filled subshells. This number is

$$N_{\max} = \sum_{l=0}^{l=n-1} 2(2l + 1) = 2[1 + 3 + 5 + \dots + 2(n - 1) + 1] \\ = 2[1 + 3 + 5 + \dots + 2n - 1]$$

The quantity in brackets has n terms whose average value is $\frac{1}{2}[1 + (2n - 1)]$. The number of electrons in a filled shell is therefore

$$N_{\max} = (n)(2)(\frac{1}{2})[1 + (2n - 1)] = 2n^2 \quad (7.14)$$

Thus a closed K shell holds 2 electrons, a closed L shell holds 8 electrons, a closed M shell holds 18 electrons, and so on.

7.6 EXPLAINING THE PERIODIC TABLE

How an atom's electron structure determines its chemical behavior

The notion of electron shells and subshells fits perfectly into the pattern of the periodic table, which mirrors the atomic structures of the elements. Let us see how this pattern arises.

An atomic shell or subshell that contains its full quota of electrons is said to be **closed**. A closed s subshell ($l = 0$) holds two electrons, a closed p subshell ($l = 1$) six electrons, a closed d subshell ($l = 2$) ten electrons, and so on.

The total orbital and spin angular momenta of the electrons in a closed subshell are zero, and their effective charge distributions are perfectly symmetrical (see Exercise 23 of Chap. 6). The electrons in a closed shell are all very tightly bound, since the positive nuclear charge is large relative to the negative charge of the inner shielding electrons (Fig. 7.9). Because an atom with only closed shells has no dipole moment, it does not attract other electrons, and its electrons cannot be easily

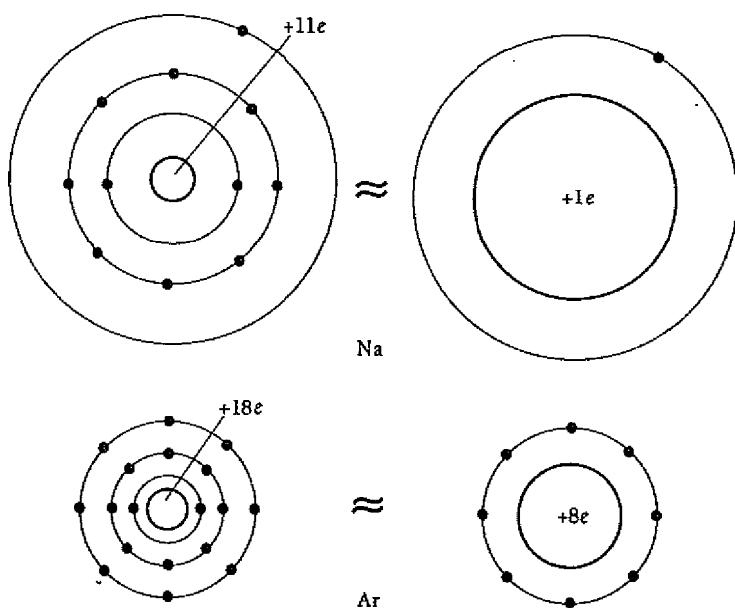


Figure 7.9 Schematic representation of electron shielding in the sodium and argon atoms. In this crude model, each outer electron in an Ar atom is acted upon by an effective nuclear charge 8 times greater than that acting upon the outer electron in a Na atom. The Ar atom is accordingly smaller in size and has a higher ionization energy. In the actual atoms, the probability-density distributions of the various electrons overlap in complex ways and thus alter the amount of shielding, but the basic effect remains the same.

detached. We expect such atoms to be passive chemically, like the inert gases—and the inert gases all turn out to have closed-shell electron configurations or their equivalents. This is evident from Table 7.4, which shows the electron configurations of the elements.

An atom of any of the alkali metals of group 1 has a single s electron in its outer shell. Such an electron is relatively far from the nucleus. It is also shielded by the inner electrons from all but an effective nuclear charge of approximately $+e$ rather than $+Ze$. Relatively little work is needed to detach an electron from such an atom, and the alkali metals accordingly form positive ions of charge $+e$ readily.

Example 7.2

The ionization energy of lithium is 5.39 eV. Use this figure to find the effective charge that acts on the outer (2s) electron of the lithium atom.

Solution

If the effective nuclear charge is Ze instead of e , Eq. (4.15) becomes

$$E_n = \frac{Z^2 E_1}{n^2}$$

Table 7.4 Electron Configurations of the Elements

	<i>K</i>	<i>L</i>		<i>M</i>			<i>N</i>				<i>O</i>				<i>P</i>			<i>Q</i>	
		1 <i>s</i>	2 <i>s</i>	2 <i>p</i>	3 <i>s</i>	3 <i>p</i>	3 <i>d</i>	4 <i>s</i>	4 <i>p</i>	4 <i>d</i>	4 <i>f</i>	5 <i>s</i>	5 <i>p</i>	5 <i>d</i>	5 <i>f</i>	6 <i>s</i>	6 <i>p</i>	6 <i>d</i>	7 <i>s</i>
1 H	1																		
2 He	2	2		Inert gas															
3 Li	2		1	1 ← Alkali metal															
4 Be	2	2																	
5 B	2	2	2	1															
6 C	2	2	2	2															
7 N	2	2	2	3															
8 O	2	2	2	4															
9 F	2	2	5	5 ← Halogen															
10 Ne	2	2	6	6 ← Inert gas															
11 Na	2	2	6	1 ← Alkali metal															
12 Mg	2	2	6	2															
13 Al	2	2	6	2	1														
14 Si	2	2	6	2	2														
15 P	2	2	6	2	3														
16 S	2	2	6	2	4														
17 Cl	2	2	6	2	5 ← Halogen														
18 Ar	2	2	6	2	6 ← Inert gas														
19 K	2	2	6	2	6							1 ← Alkali metal							
20 Ca	2	2	6	2	6							2							
21 Sc	2	2	6	2	6	1						2							
22 Ti	2	2	6	2	6	2						2							
23 V	2	2	6	2	6	3						2							
24 Cr	2	2	6	2	6	5						1							
25 Mn	2	2	6	2	6	5						2							
26 Fe	2	2	6	2	6	6						2							
27 Co	2	2	6	2	6	7						2							
28 Ni	2	2	6	2	6	8						2							
29 Cu	2	2	6	2	6	10						1							
30 Zn	2	2	6	2	6	10						2							
31 Ga	2	2	6	2	6	10						2	1						
32 Ge	2	2	6	2	6	10						2	2						
33 As	2	2	6	2	6	10						2	3						
34 Se	2	2	6	2	6	10						2	4						
35 Br	2	2	6	2	6	10						2	5 ← Halogen						
36 Kr	2	2	6	2	6	10						2	6 ← Inert gas						
37 Rb	2	2	6	2	6	10						2	6			1 ← Alkali metal			
38 Sr	2	2	6	2	6	10						2	6			2			
39 Y	2	2	6	2	6	10						2	6	1		2			
40 Zr	2	2	6	2	6	10						2	6	2		2			
41 Nb	2	2	6	2	6	10						2	6	4		1			
42 Mo	2	2	6	2	6	10						2	6	5		1			
43 Tc	2	2	6	2	6	10						2	6	5		2			
44 Ru	2	2	6	2	6	10						2	6	7		1			
45 Rh	2	2	6	2	6	10						2	6	8		1			
46 Pd	2	2	6	2	6	10						2	6	10		1			
47 Ag	2	2	6	2	6	10						2	6	10		2			
48 Cd	2	2	6	2	6	10						2	6	10		2	1		
49 In	2	2	6	2	6	10						2	6	10		2	2		
50 Sn	2	2	6	2	6	10						2	6	10		2	3		
51 Sb	2	2	6	2	6	10						2	6	10		2	4		
52 Te	2	2	6	2	6	10						2	6	10					

Table 7.4 (Cont.)

	<i>K</i>			<i>L</i>			<i>M</i>			<i>N</i>				<i>O</i>				<i>P</i>			<i>Q</i>
	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s			
53 I	2	2	6	2	6	10	2	6	10		2	5	↔ Halogen								
54 Xe	2	2	6	2	6	10	2	6	10		2	6	↔ Inert gas								
55 Cs	2	2	6	2	6	10	2	6	10		2	6									
56 Ba	2	2	6	2	6	10	2	6	10		2	6									
57 La	2	2	6	2	6	10	2	6	10	2	6	1									
58 Ce	2	2	6	2	6	10	2	6	10	2	6	2									
59 Pr	2	2	6	2	6	10	2	6	10	3	2	6									
60 Nd	2	2	6	2	6	10	2	6	10	4	2	6									
61 Pm	2	2	6	2	6	10	2	6	10	5	2	6									
62 Sm	2	2	6	2	6	10	2	6	10	6	2	6									
63 Eu	2	2	6	2	6	10	2	6	10	7	2	6									
64 Gd	2	2	6	2	6	10	2	6	10	7	2	6	1								
65 Tb	2	2	6	2	6	10	2	6	10	9	2	6									
66 Dy	2	2	6	2	6	10	2	6	10	10	2	6									
67 Ho	2	2	6	2	6	10	2	6	10	11	2	6									
68 Er	2	2	6	2	6	10	2	6	10	12	2	6									
69 Tm	2	2	6	2	6	10	2	6	10	13	2	6									
70 Yb	2	2	6	2	6	10	2	6	10	14	2	6									
71 Lu	2	2	6	2	6	10	2	6	10	14	2	6	1								
72 Hf	2	2	6	2	6	10	2	6	10	14	2	6	2								
73 Ta	2	2	6	2	6	10	2	6	10	14	2	6	3								
74 W	2	2	6	2	6	10	2	6	10	14	2	6	4								
75 Re	2	2	6	2	6	10	2	6	10	14	2	6	5								
76 Os	2	2	6	2	6	10	2	6	10	14	2	6	6								
77 Ir	2	2	6	2	6	10	2	6	10	14	2	6	7								
78 Pt	2	2	6	2	6	10	2	6	10	14	2	6	9								
79 Au	2	2	6	2	6	10	2	6	10	14	2	6	10	1							
80 Hg	2	2	6	2	6	10	2	6	10	14	2	6	10	2							
81 Tl	2	2	6	2	6	10	2	6	10	14	2	6	10	2	1						
82 Pb	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2						
83 Bi	2	2	6	2	6	10	2	6	10	14	2	6	10	2	3						
84 Po	2	2	6	2	6	10	2	6	10	14	2	6	10	2	4						
85 At	2	2	6	2	6	10	2	6	10	14	2	6	10	2	5	↔ Halogen					
86 Rn	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	↔ Inert gas					
87 Fr	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	1	↔ Alkali metal				
88 Ra	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	1	2				
89 Ac	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	2	2				
90 Th	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	2	2				
91 Pa	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	1	2				
92 U	2	2	6	2	6	10	2	6	10	14	2	6	10	3	2	6	1	2			
93 Np	2	2	6	2	6	10	2	6	10	14	2	6	10	4	2	6	1	2			
94 Pu	2	2	6	2	6	10	2	6	10	14	2	6	10	5	2	6	1	2			
95 Am	2	2	6	2	6	10	2	6	10	14	2	6	10	6	2	6	1	2			
96 Cm	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	1	2			
97 Bk	2	2	6	2	6	10	2	6	10	14	2	6	10	8	2	6	1	2			
98 Cf	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6	2	2			
99 Es	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6	2	2			
100 Fm	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6	2	2			
101 Md	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6	2	2			
102 No	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	2	2			
103 Lr	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	2	2			

Transition elements
Lanthanides
Actinides

Here $n = 2$ for the $2s$ electron, its ionization energy is $E_2 = -5.39$ eV, and $E_1 = -13.6$ eV is the ionization energy of the hydrogen atom. Hence

$$Z = n \sqrt{\frac{E_2}{E_1}} = 2 \sqrt{\frac{5.39 \text{ eV}}{13.6 \text{ eV}}} = 1.26$$

The effective charge is $1.26e$ and not e because the shielding of $2e$ of the nuclear charge of $3e$ by the two $1s$ electrons is not complete: as we can see in Fig. 6.11, the $2s$ electron has a certain probability of being found inside the $1s$ electrons.

Ionization Energy

Figure 7.10 shows how the ionization energies of the elements vary with atomic number. As we expect, the inert gases have the highest ionization energies and the alkali metals the lowest. The larger an atom, the farther the outer electron is from the nucleus and the weaker the force is that holds it to the atom. This is why the ionization energy generally decreases as we go down a group in the periodic table. The increase in ionization energy from left to right across any period is accounted for by the increase in nuclear charge while the number of inner shielding electrons stays constant. In period 2, for instance, the outer electron in a lithium atom is held by an effective charge of about $+e$, while each outer electron in beryllium, boron, carbon, and so on, is held by effective charges of about $+2e$, $+3e$, $+4e$, and so on. The ionization energy of lithium is 5.4 eV whereas that of neon, which ends the period, is 21.6 eV.

At the other extreme from alkali metal atoms, which tend to lose their outermost electrons, are halogen atoms, whose imperfectly shielded nuclear charges tend to complete their outer subshells by picking up an additional electron each. Halogen

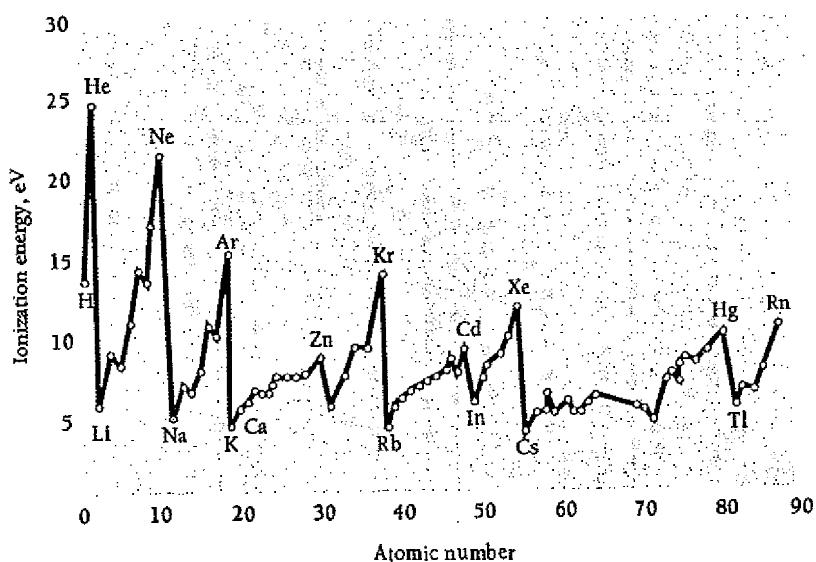


Figure 7.10 The variation of ionization energy with atomic number.

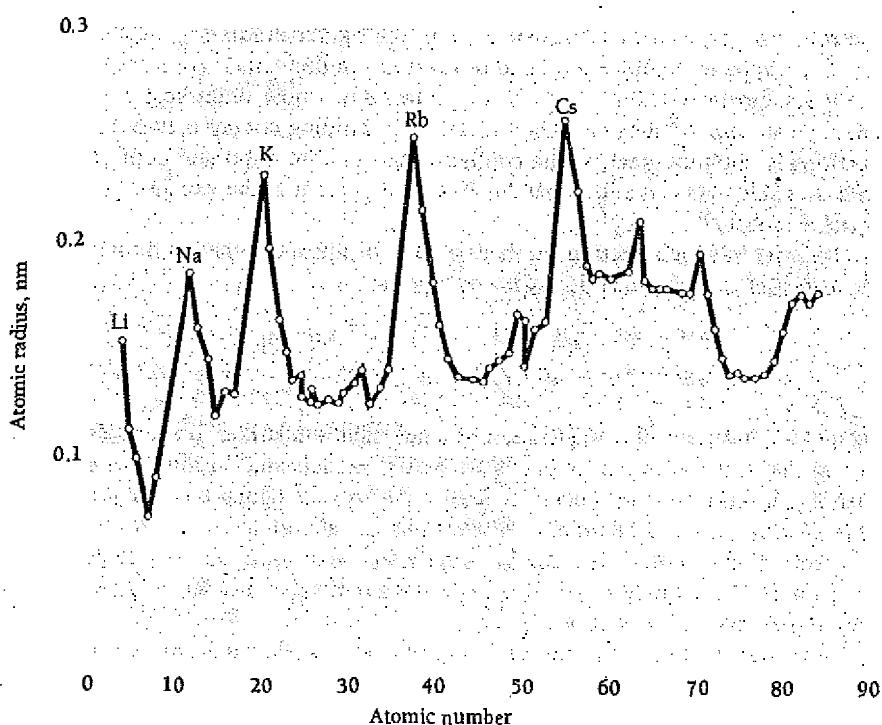


Figure 7.11 Atomic radii of the elements.

atoms accordingly form negative ions of charge $-e$ readily. Reasoning of this kind accounts for the similarities of the members of the various groups of the periodic table.

Size

Although, strictly speaking, an atom of a certain kind cannot be said to have a definite size, from a practical point of view a fairly definite size can usually be attributed to it on the basis of the observed interatomic spacings in closely packed crystal lattices. Figure 7.11 shows how the resulting radii vary with atomic number. The periodicity here is as conspicuous as in the case of ionization energy and has a similar origin in the partial shielding by inner electrons of the full nuclear charge. The greater the shielding, the lower the binding energy of an outer electron and the farther it is on the average from the nucleus.

The relatively small range of atomic radii is not surprising in view of the binding-energy curves of Fig. 7.8. There we see that in contrast to the enormous increase in the binding energies of the unshielded 1s electrons with Z , the binding energies of the outermost electrons (whose probability-density distributions are what determine atomic size) vary through a narrow range. The heaviest atoms, with over 90 electrons, have radii only about 3 times that of the hydrogen atom, and even the cesium atom, the largest in size, has a radius only 4.4 times that of the hydrogen atom.

Transition Elements

The origin of the transition elements lies in the tighter binding of s electrons than d or f electrons in complex atoms, discussed in the previous section (see Fig. 7.8). The first element to exhibit this effect is potassium, whose outermost electron is in a 4s instead of a 3d substate. The difference in binding energy between 3d and 4s electrons is not very great, as the configurations of chromium and copper show. In both these elements an additional 3d electron is present at the expense of a vacancy in the 4s subshell.

The order in which electron subshells tend to be filled, together with the maximum occupancy of each subshell, is usually as follows:

$$\begin{array}{cccccccccc} 1s^2 & 2s^2 & 2p^6 & 3s^2 & 3p^6 & 4s^2 & 3d^{10} & 4p^6 & 5s^2 \\ & & & & & & & & \\ 4d^{10} & 5p^6 & 6s^2 & 4f^{14} & 5d^{10} & 6p^6 & 7s^2 & 6d^{10} & 5f^{14} \end{array}$$

Figure 7.12 illustrates this sequence. The remarkable similarities in chemical behavior among the lanthanides and actinides are easy to understand on the basis of this sequence. All the lanthanides have the same $5s^2 5p^6 6s^2$ configurations but have incomplete 4f subshells. The addition of 4f electrons has almost no effect on the chemical properties of the lanthanide elements, which are determined by the outer electrons. Similarly, all the actinides have $6s^2 6p^6 7s^2$ configurations and differ only in the numbers of their 5f and 6d electrons.

These irregularities in the binding energies of atomic electrons are also responsible for the lack of completely full outer shells in the heavier inert gases. Helium ($Z = 2$) and neon ($Z = 10$) contain closed K and L shells, respectively, but argon ($Z = 18$) has only 8 electrons in its M shell, corresponding to closed 3s and 3p subshells. The reason the 3d subshell is not filled next is that 4s electrons have higher binding energies

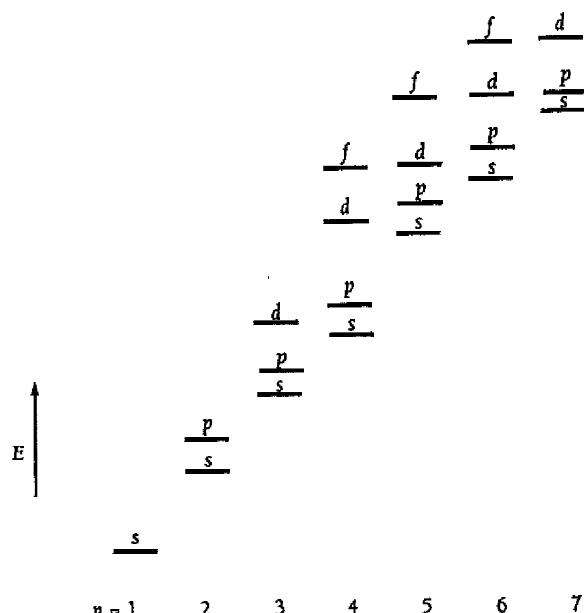


Figure 7.12 The sequence of quantum states in an atom. Not to scale.

Table 7.5 Electron Configurations of Elements from $Z = 5$ to $Z = 10$. The p electrons have parallel spins whenever possible, in accord with Hund's rule.

Element	Atomic Number	Configuration	Spins of p Electrons		
Boron	5	$1s^2 2s^2 2p^1$	↑		
Carbon	6	$1s^2 2s^2 2p^2$	↑	↑	
Nitrogen	7	$1s^2 2s^2 2p^3$	↑	↑	↑
Oxygen	8	$1s^2 2s^2 2p^4$	↑↓	↑	↑
Fluorine	9	$1s^2 2s^2 2p^5$	↑↓	↑↓	↑
Neon	10	$1s^2 2s^2 2p^6$	↑↓	↑↓	↑↓

than do $3d$ electrons. Hence the $4s$ subshell is filled first in potassium and calcium. As the $3d$ subshell is filled in successively heavier transition elements, there are still one or two outer $4s$ electrons that make possible chemical activity. Not until krypton ($Z = 36$) is another inert gas reached, and here a similarly incomplete outer shell occurs with only the $4s$ and $4p$ subshells filled. Following krypton is rubidium ($Z = 37$), which skips both the $4d$ and $4f$ subshells to have a $5s$ electron. The next inert gas is xenon ($Z = 54$), which has filled $4d$, $5s$, and $5p$ subshells, but now even the inner $4f$ subshell is empty as well as the $5d$ and $5f$ subshells. The same pattern recurs with the last inert gas, radon.

Hund's Rule

In general, the electrons in a subshell remain unpaired—that is, have parallel spins—whenever possible (Table 7.5). This principle is called *Hund's rule*. The ferromagnetism of iron, cobalt, and nickel ($Z = 26, 27, 28$) is in part a consequence of Hund's rule. The $3d$ subshells of their atoms are only partially occupied, and the electrons in these subshells do not pair off to permit their spin magnetic moments to cancel out. In iron, for instance, five of the six $3d$ electrons have parallel spins, so that each iron atom has a large resultant magnetic moment.

The origin of Hund's rule lies in the mutual repulsion of atomic electrons. Because of this repulsion, the farther apart the electrons in an atom are, the lower the energy of the atom. Electrons in the same subshell with the same spin must have different m_l values and accordingly are described by wave functions whose spatial distributions are different. Electrons with parallel spins are therefore more separated in space than they would be if they paired off. This arrangement, having less energy, is the more stable one.

7.7 SPIN-ORBIT COUPLING

Angular momenta linked magnetically

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

Spin-orbit coupling can be understood in terms of a straightforward classical model. An electron revolving about a nucleus finds itself in a magnetic field because in its own frame of reference, the nucleus is circling about it (Fig. 7.13). This magnetic field then acts upon the electron's own spin magnetic moment to produce a kind of internal Zeeman effect.

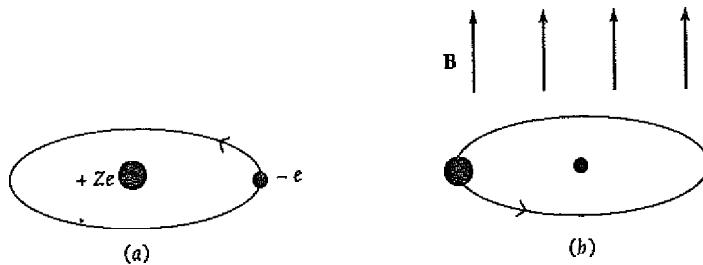


Figure 7.13 (a) An electron circles an atomic nucleus, as viewed from the frame of reference of the nucleus. (b) From the electron's frame of reference, the nucleus is circling it. The magnetic field the electron experiences as a result is directed upward from the plane of the orbit. The interaction between the electron's spin magnetic moment and this magnetic field leads to the phenomenon of spin-orbit coupling.

The potential energy U_m of a magnetic dipole of moment μ in a magnetic field B is, as we know,

$$U_m = -\mu B \cos \theta \quad (6.38)$$

where θ is the angle between μ and B . The quantity $\mu \cos \theta$ is the component of μ parallel to B . In the case of the spin magnetic moment of the electron this component is $\mu_{sz} = \pm \mu_B$. Hence

$$\mu \cos \theta = \pm \mu_B$$

and so

$$\text{Spin-orbit coupling} \quad U_m = \pm \mu_B B \quad (7.15)$$

Depending on the orientation of its spin vector S , the energy of an atomic electron will be higher or lower by $\mu_B B$ than its energy without spin-orbit coupling. The result is that every quantum state (except s states in which there is no orbital angular momentum) is split into two substates.

The assignment of $s = \frac{1}{2}$ is the only one that agrees with the observed fine-structure doubling. Because what would be single states without spin are in fact twin states, the $2s + 1$ possible orientations of the spin vector S must total 2. With $2s + 1 = 2$, the result is $s = \frac{1}{2}$.

Example 7.3

Estimate the magnetic energy U_m for an electron in the $2p$ state of a hydrogen atom using the Bohr model, whose $n = 2$ state corresponds to the $2p$ state.

Solution

A circular wire loop of radius r that carries the current I has a magnetic field at its center of magnitude

$$B = \frac{\mu_0 I}{2r}$$

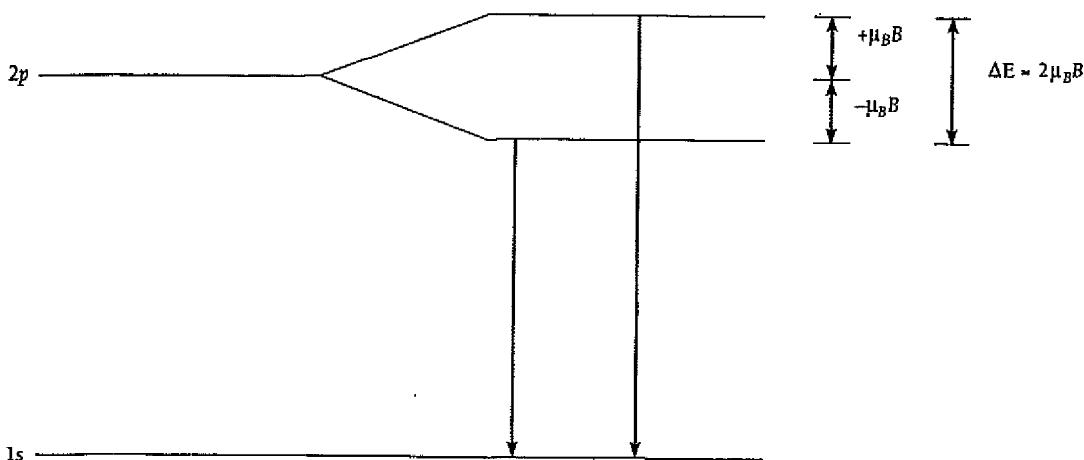


Figure 7.14 Spin-orbit coupling splits the $2p$ state in the hydrogen atom into two substates ΔE apart. The result is a doublet (two closely spaced lines) instead of a single spectral line for the $2p \rightarrow 1s$ transition.

The orbiting electron "sees" itself circled f times per second by the proton of charge $+e$ that is the nucleus, for a resulting magnetic field of

$$B = \frac{\mu_0 f e}{2r}$$

The frequency of revolution and orbital radius for $n = 2$ are, from Eqs. (4.4) and (4.14),

$$f = \frac{v}{2\pi r} = 8.4 \times 10^{14} \text{ s}^{-1}$$

$$r = n^2 a_0 = 4a_0 = 2.1 \times 10^{-10} \text{ m}$$

Hence the magnetic field experienced by the electron is

$$B = \frac{(4\pi \times 10^{-7} \text{ T} \cdot \text{m/A})(8.4 \times 10^{14} \text{ s}^{-1})(1.6 \times 10^{-19} \text{ C})}{(2)(2.1 \times 10^{-10} \text{ m})} = 0.40 \text{ T}$$

which is a fairly strong field. Since the value of the Bohr magneton is $\mu_B = e\hbar/2m = 9.27 \times 10^{-24} \text{ J/T}$, the magnetic energy of the electron is

$$U_m = \mu_B B = 3.7 \times 10^{-24} \text{ J} = 2.3 \times 10^{-5} \text{ eV}$$

The energy difference between the upper and lower substates is twice this, $4.6 \times 10^{-5} \text{ eV}$, which is not far from what is observed (Fig. 7.14).

7.8 TOTAL ANGULAR MOMENTUM

Both magnitude and direction are quantized

Each electron in an atom has a certain orbital angular momentum L and a certain spin angular momentum S , both of which contribute to the total angular momentum J of the atom. Let us first consider an atom whose total angular momentum is provided by a single electron. Atoms of the elements in group 1 of the periodic

table—hydrogen, lithium, sodium, and so on—are of this kind. They have single electrons outside closed inner shells (except for hydrogen, which has no inner electrons) and the exclusion principle ensures that the total angular momentum and magnetic moment of a closed shell are zero. Also in this category are the ions He^+ , Be^+ , Mg^+ , B^{2+} , Al^{2+} , and so on.

In these atoms and ions, the outer electron's total angular momentum J is the vector sum of L and S :

$$\begin{array}{ll} \text{Total atomic} & J = L + S \\ \text{angular momentum} & \end{array} \quad (7.16)$$

Like all angular momenta, J is quantized in both magnitude and direction. The magnitude of J is given by

$$J = \sqrt{j(j+1)}\hbar \quad j = l+s = l \pm \frac{1}{2} \quad (7.17)$$

If $l = 0$, j has the single value $j = \frac{1}{2}$. The component J_z of J in the z direction is given by

$$J_z = m_j\hbar \quad m_j = -j, -j+1, \dots, j-1, j \quad (7.18)$$

Because of the simultaneous quantization of J , L , and S they can have only certain specific relative orientations. This is a general conclusion; in the case of a one-electron atom, there are only two relative orientations possible. One relative orientation corresponds to $j = l+s$, so that $J > L$, and the other to $j = l-s$, so that $J < L$. Figure 7.15 shows the two ways in which L and S can combine to form J when $l = 1$. Evidently the orbital and spin angular-momentum vectors can never be exactly parallel or antiparallel to each other or to the total angular-momentum vector.

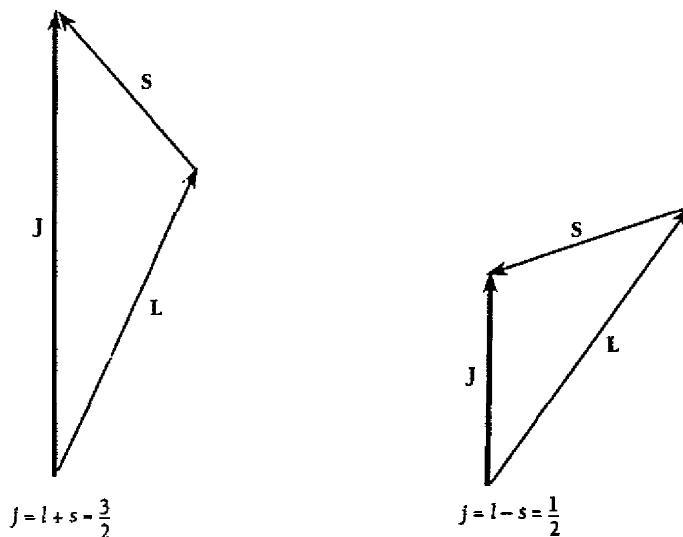


Figure 7.15 The two ways in which L and S can be added to form J when $l = 1$, $s = \frac{1}{2}$.

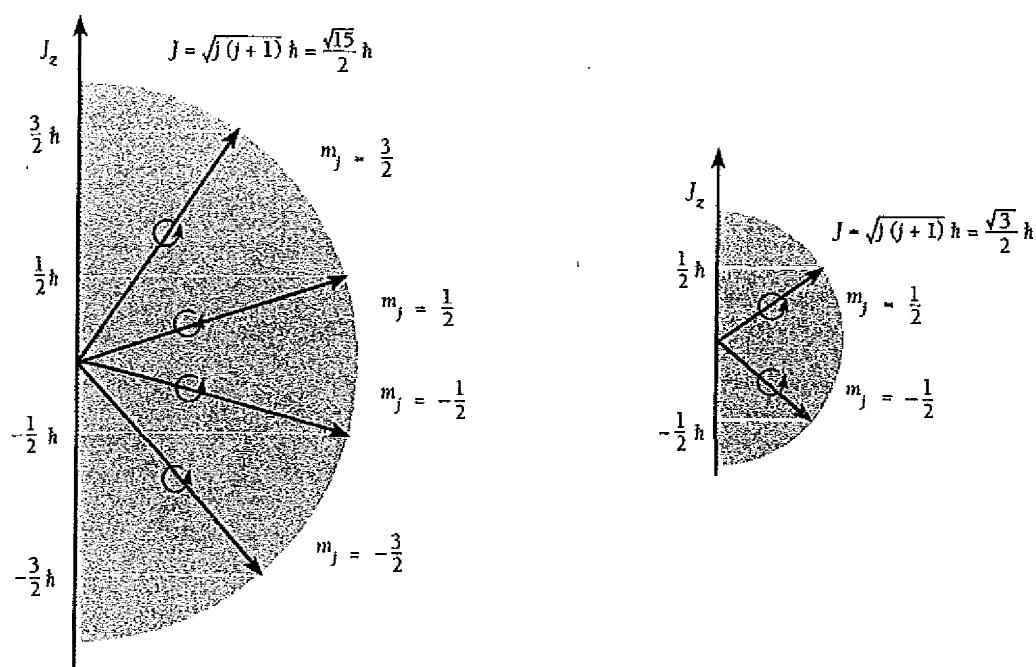


Figure 7.16 Space quantization of total angular momentum when the orbital angular momentum is $l = 1$.

Example 7.4

What are the possible orientations of \mathbf{J} for the $j = \frac{3}{2}$ and $j = \frac{1}{2}$ states that correspond to $l = 1$?

Solution

For the $j = \frac{3}{2}$ state, Eq. (7.18) gives $m_j = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$. For the $j = \frac{1}{2}$ state, $m_j = -\frac{1}{2}, \frac{1}{2}$. Figure 7.16 shows the orientations of \mathbf{J} relative to the z axis for these values of j .

The angular momenta \mathbf{L} and \mathbf{S} interact magnetically, as we saw in Sec. 7.7. If there is no external magnetic field, the total angular momentum \mathbf{J} is conserved in magnitude and direction, and the effect of the internal torques is the precession of \mathbf{L} and \mathbf{S} around the direction of their resultant \mathbf{J} (Fig. 7.17). However, if there is an external magnetic field \mathbf{B} present, then \mathbf{J} precesses about the direction of \mathbf{B} while \mathbf{L} and \mathbf{S} continue precessing about \mathbf{J} , as in Fig. 7.18. The precession of \mathbf{J} about \mathbf{B} is what gives rise to the anomalous Zeeman effect, since different orientations of \mathbf{J} involve slightly different energies in the presence of \mathbf{B} .

LS Coupling

When more than one electron contributes orbital and spin angular momenta to the total angular momentum \mathbf{J} of an atom, \mathbf{J} is still the vector sum of these individual momenta. The usual pattern for all but the heaviest atoms is that the orbital angular momenta \mathbf{L}_i of

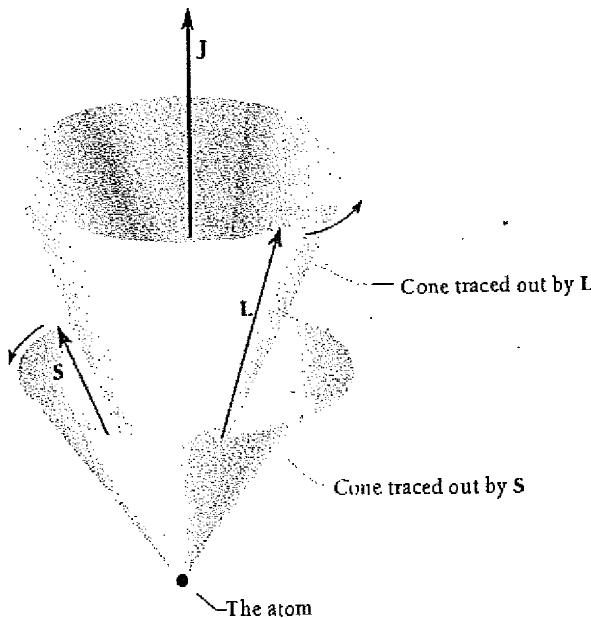


Figure 7.17 The orbital and spin angular-momentum vectors L and S precess about J .

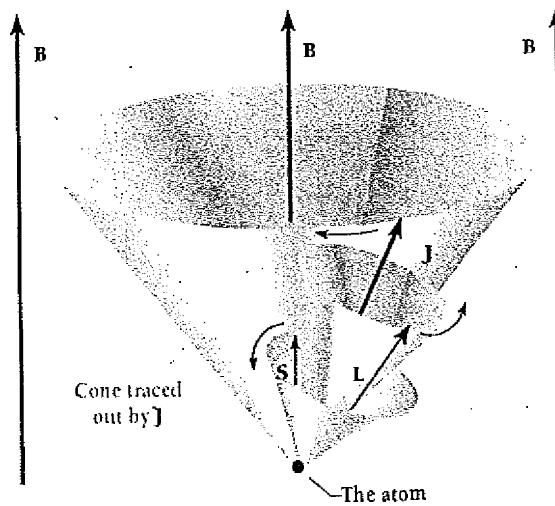


Figure 7.18 In the presence of an external magnetic field B , the total angular-momentum vector J precesses about B .

the various electrons are coupled together into a single resultant L . The spin angular momenta S_i are also coupled together into another single resultant S . The momenta L and S then interact via the spin-orbit effect to form a total angular momentum J . This scheme, called **LS coupling**, can be summarized as follows:

$$\begin{aligned} L &= \sum L_i \\ \text{LS coupling} \quad S &= \sum S_i \\ J &= L + S \end{aligned} \quad (7.19)$$

The angular momentum magnitudes L , S , J and their z components L_z , S_z , and J_z are all quantized in the usual ways, with the respective quantum numbers L , S , J , M_L , M_S , and M_J . Hence

$$\begin{aligned} L &= \sqrt{L(L+1)}\hbar \\ L_z &= M_L\hbar \\ S &= \sqrt{S(S+1)}\hbar \\ S_z &= M_S\hbar \\ J &= \sqrt{J(J+1)}\hbar \\ J_z &= M_J\hbar \end{aligned} \quad (7.20)$$

Both L and M_L are always integers or 0, while the other quantum numbers are half-integral if an odd number of electrons is involved and integral or 0 if an even number of electrons is involved. When $L > S$, J can have $2S + 1$ values; when $L < S$, J can have $2L + 1$ values.

Example 7.5

Find the possible values of the total angular-momentum quantum number J under LS coupling of two atomic electrons whose orbital quantum numbers are $l_1 = 1$ and $l_2 = 2$.

Solution

As in Fig. 7.19a, the vectors L_1 and L_2 can be combined in three ways into a single vector L that is quantized according to Eq. (7.20). These correspond to $L = 1, 2$, and 3 since all values of L are possible from $|l_1 - l_2| (= 1 \text{ here})$ to $l_1 + l_2$. The spin quantum number s is always $\frac{1}{2}$, which gives the two possibilities for $S_1 + S_2$ shown in Fig. 7.19b, corresponding to $S = 0$ and $S = 1$.

We note that if the vector sums are not 0 , L_1 and L_2 can never be exactly parallel to L , nor can S_1 and S_2 be parallel to S . Because J can have any value between $|L - S|$ and $L + S$, the five possible values here are $J = 0, 1, 2, 3$, and 4 .

Atomic nuclei also have intrinsic angular momenta and magnetic moments, and these contribute to the total atomic angular momenta and magnetic moments. Such contributions are small because nuclear magnetic moments are $\sim 10^{-3}$ the magnitude of electronic moments. They lead to the hyperfine structure of spectral lines with typical spacings between components of $\sim 10^{-3}$ nm as compared with typical fine-structure spacings a hundred times greater.

Term Symbols

In Sec. 6.5 we saw that individual orbital angular-momentum states are customarily described by a lowercase letter, with s corresponding to $l = 0$, p to $l = 1$, d to $l = 2$, and so on. A similar scheme using capital letters is used to designate the entire electronic state of an atom according to its total orbital angular-momentum quantum number L as follows:

$$\begin{array}{ccccccc} L & = & 0 & 1 & 2 & 3 & 4 & 5 & 6 \dots \\ & & S & P & D & F & G & H & I \dots \end{array}$$

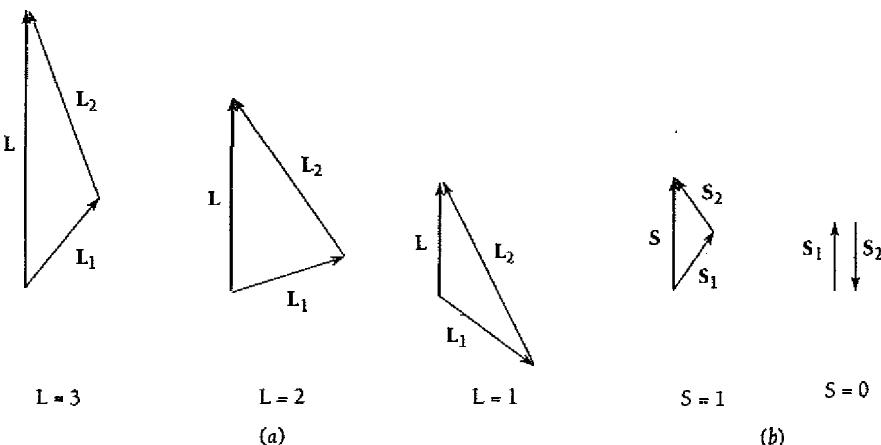


Figure 7.19 When $l_1 = 1$, $s_1 = \frac{1}{2}$, and $l_2 = 2$, $s_2 = \frac{1}{2}$, there are three ways in which L_1 and L_2 can combine to form L and two ways in which S_1 and S_2 can combine to form S .

A superscript number before the letter (2P , for instance) is used to indicate the multiplicity of the state, which is the number of different possible orientations of L and S and hence the number of different possible values of J . The multiplicity is equal to $2S + 1$ in the usual situation where $L > S$, since J ranges from $L - S$ to $L + S$. Thus when $S = 0$, the multiplicity is 1 (a singlet state) and $J = L$; when $S = \frac{1}{2}$, the multiplicity is 2 (a doublet state) and $J = L \pm \frac{1}{2}$; when $S = 1$, the multiplicity is 3 (a triplet state) and $J = L + 1, L$, or $L - 1$; and so on. (In a configuration in which $S > L$, the multiplicity is given by $2L + 1$.) The total angular-momentum quantum number J is used as a subscript after the letter, so that a $^2P_{3/2}$ state (read as "doublet P three-halves") refers to an electronic configuration in which $S = \frac{1}{2}$, $L = 1$, and $J = \frac{3}{2}$. For historical reasons, these designations are called term symbols.

In the event that the angular momentum of the atom arises from a single outer electron, the principal quantum number n of this electron is used as a prefix. Thus the ground state of the sodium atom is described by $3^2S_{1/2}$, since its electronic configuration has an electron with $n = 3$, $l = 0$, and $s = \frac{1}{2}$ (and hence $j = \frac{1}{2}$) outside closed $n = 1$ and $n = 2$ shells. For consistency it is conventional to denote the above state by $3^2S_{1/2}$ with the superscript 2 indicating a doublet, even though there is only a single possibility for J since $L = 0$.

Example 7.6

The term symbol of the ground state of sodium is $3^2S_{1/2}$ and that of its first excited state is $3^2P_{1/2}$. List the possible quantum numbers n, l, j , and m_j of the outer electron in each case.

Solution

$$\begin{aligned} 3^2S_{1/2}: n &= 3, l = 0, j = \frac{1}{2}, m_j = \pm \frac{1}{2} \\ 3^2P_{1/2}: n &= 3, l = 1, j = \frac{1}{2}, m_j = \pm \frac{1}{2}, \pm \frac{3}{2} \\ &n = 3, l = 1, j = \frac{1}{2}, m_j = \pm \frac{1}{2} \end{aligned}$$

Example 7.7

Why is it impossible for a $2^2P_{3/2}$ state to exist?

Solution

A P state has $L = 1$ and $J = L \pm \frac{1}{2}$, so $J = \frac{5}{2}$ is impossible.

7.9 X-RAY SPECTRA

They arise from transitions to inner shells

In Chap. 2 we learned that the x-ray spectra of targets bombarded by fast electrons show narrow spikes at wavelengths characteristic of the target material. These are besides a continuous distribution of wavelengths down to a minimum wavelength inversely proportional to the electron energy (see Fig. 2.17). The continuous x-ray spectrum is the result of the inverse photoelectric effect, with electron kinetic energy being transformed into photon energy $h\nu$. The line spectrum, on the other hand, comes from electronic transitions within atoms that have been disturbed by the incident electrons.

The transitions of the outer electrons of an atom usually involve only a few electronvolts of energy, and even removing an outer electron requires at most 24.6 eV (for helium). Such transitions accordingly are associated with photons whose wavelengths lie in or near the visible part of the electromagnetic spectrum. The inner electrons of heavier elements are a quite different matter, because these electrons are not well shielded from the full nuclear charge by intervening electron shells and so are very tightly bound.

In sodium, for example, only 5.13 eV is needed to remove the outermost 3s electron, whereas the corresponding figures for the inner ones are 31 eV for each 2p electron, 63 eV for each 2s electron, and 1041 eV for each 1s electron. Transitions that involve the inner electrons in an atom are what give rise to x-ray line spectra because of the high photon energies involved.

Figure 7.20 shows the energy levels (not to scale) of a heavy atom. The energy differences between angular momentum states within a shell are minor compared with

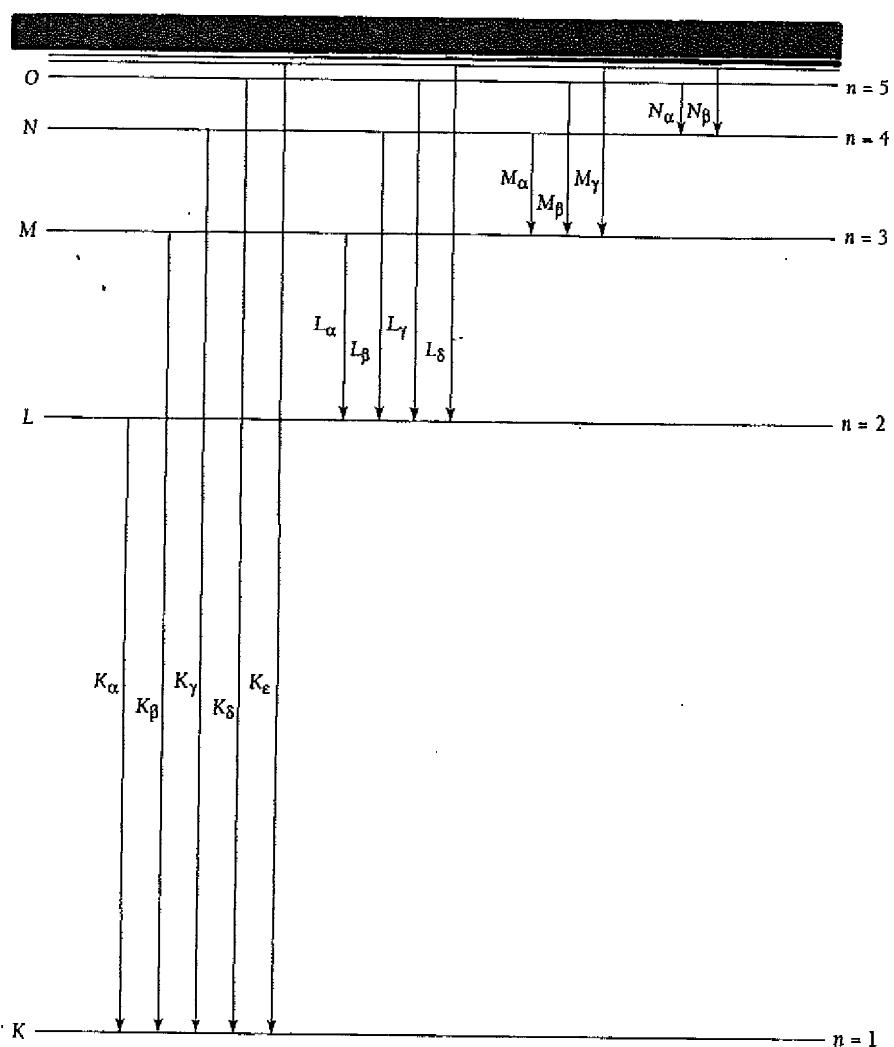


Figure 7.20 The origin of x-ray spectra.



Henry G. J. Moseley (1887–1915) was born in Weymouth, on England's south coast. He studied physics at Oxford, where his father had been professor of anatomy. After graduating in 1910, Moseley joined Rutherford at Manchester, where he began a systematic study of x-ray spectra that he later continued at Oxford. From the data he was

able to infer a relationship between the x-ray wavelengths of an element and its atomic number, a relationship that permitted him to correct ambiguities in then-current atomic number assignments and to predict the existence of several then-unknown elements. Moseley soon recognized the important link between his discovery and Bohr's atomic model. By then World War I had broken out and Moseley enlisted in the British Army. Rutherford unsuccessfully tried to have him assigned to scientific work, but in 1915 Moseley was sent to Turkey on the ill-conceived and disastrous Dardanelles campaign and was killed at the age of twenty-seven.

the energy differences between shells. Let us look at what happens when an energetic electron strikes the atom and knocks out one of the K-shell electrons. The K electron could also be raised to one of the unfilled upper states of the atom, but the difference between the energy needed to do this and that needed to remove the electron completely is insignificant, only 0.2 percent in sodium and still less in heavier atoms.

An atom with a missing K electron gives up most of its considerable excitation energy in the form of an x-ray photon when an electron from an outer shell drops into the "hole" in the K shell. As indicated in Fig. 7.20, the K series of lines in the x-ray spectrum of an element consists of wavelengths arising in transitions from the L, M, N, . . . levels to the K level. Similarly the longer-wavelength L series originates when an L electron is knocked out of the atom, the M series when an M electron is knocked out, and so on. The two spikes in the x-ray spectrum of molybdenum in Fig. 2.17 are the K_{α} and K_{β} lines of its K series.

It is easy to find an approximate relationship between the frequency of the K_{α} x-ray line of an element and its atomic number Z. A K_{α} photon is emitted when an L ($n = 2$) electron undergoes a transition to a vacant K ($n = 1$) state. The L electron experiences a nuclear charge of Ze that is reduced to an effective charge in the neighborhood of $(Z - 1)e$ by the shielding effect of the remaining K electron. Thus we can use Eqs. (4.15) and (4.16) to find the K_{α} photon frequency by letting $n_i = 2$ and $n_f = 1$, and replacing e^4 by $(Z - 1)^2e^4$. This gives

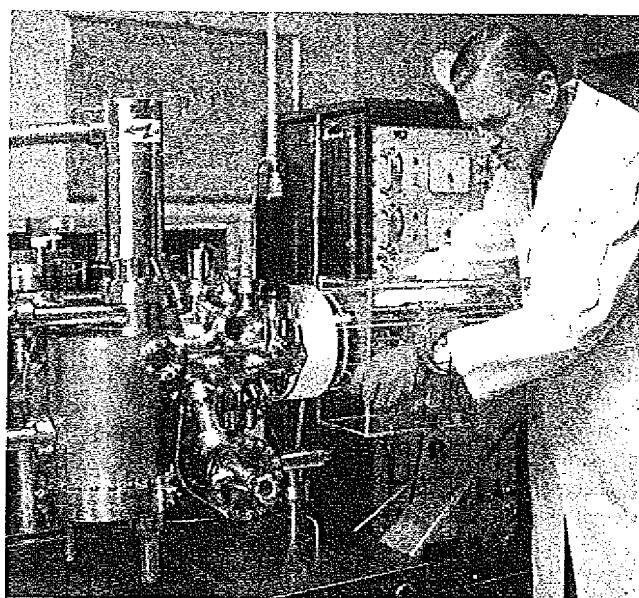
$$\nu = \frac{m(Z - 1)^2e^4}{8\epsilon_0^2h^3} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = cR(Z - 1)^2 \left(\frac{1}{1^2} - \frac{1}{2^2} \right)$$

$$K_{\alpha} \text{ x-rays} \quad \nu = \frac{3cR(Z - 1)^2}{4} \quad (7.21)$$

where $R = me^4/8\epsilon_0^2 ch^3 = 1.097 \times 10^7 \text{ m}^{-1}$ is the Rydberg constant. The energy of a K_{α} x-ray photon is given in electronvolts in terms of $(Z - 1)$ by the formula

$$E(K_{\alpha}) = (10.2 \text{ eV})(Z - 1)^2 \quad (7.22)$$

In 1913 and 1914 the young British physicist H. G. J. Moseley confirmed Eq. (7.21) by measuring the K_{α} frequencies of most of the then-known elements using the diffraction method described in Sec. 2.6. Besides supporting Bohr's newly formulated atomic model, Moseley's work provided for the first time a way to determine experimentally the atomic number Z of an element. As a result, the correct sequence of elements in the



In the operation of this x-ray spectrometer, a stream of fast electrons is directed at a sample of unknown composition. Some of the electrons knock out inner electrons in the target atoms, and when outer electrons replace them, x-ray are emitted whose wavelengths are characteristic of the elements present. The identity and relative amounts of the elements in the sample can be found in this way.

periodic table could be established. The ordering of the elements by atomic number (which is what matters) is not always the same as their ordering by atomic mass, which until then was the method used. Atomic number was originally just the number of an element in the list of atomic masses. For instance, $Z = 27$ for cobalt and $Z = 28$ for nickel, but their respective atomic masses are 58.93 and 58.71. The order dictated by atomic mass could not be understood on the basis of the chemical properties of cobalt and nickel.

In addition, Moseley found gaps in his data that corresponded to $Z = 43, 61, 72$, and 75, which suggested the existence of hitherto unknown elements that were later discovered. The first two, technetium and promethium, have no stable isotopes and were first produced in the laboratory many years later. The last two, hafnium and rhenium, were isolated in the 1920s.

Example 7.8

Which element has a K_{α} x-ray line whose wavelength is 0.180 nm?

Solution

The frequency corresponding to a wavelength of 0.180 nm = 1.80×10^{-10} m is

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{1.80 \times 10^{-10} \text{ m}} = 1.67 \times 10^{18} \text{ Hz}$$

From Eq. (7.21) we have

$$Z - 1 = \sqrt{\frac{4}{3cR}} = \sqrt{\frac{(4)(1.67 \times 10^{18} \text{ Hz})}{(3)(3.00 \times 10^8 \text{ m/s})(1.097 \times 10^7 \text{ m}^{-1})}} = 26$$

$$Z = 27$$

The element with atomic number 27 is cobalt.

Auger Effect

An atom with a missing inner electron can also lose excitation energy by the Auger effect without emitting an x-ray photon. In this effect, which was discovered by the French physicist Pierre Auger, an outer-shell electron is ejected from the atom at the same time that another outer-shell electron drops to the incomplete inner shell. Thus the ejected electron carries off the atom's excitation energy instead of a photon doing this (Fig. 7.21). In a sense the Auger effect represents an internal photoelectric effect, although the photon never actually comes into being within the atom.

The Auger process is competitive with x-ray emission in most atoms, but the resulting electrons are usually absorbed in the target material while the x-rays emerge to be detected. Those Auger electrons that do emerge come either from atoms on the surface of the material or just below the surface. Because the energy levels of an atom are affected by its participation in a chemical bond, the energies of Auger electrons provide insight into the chemical environment of the atoms involved. Auger spectroscopy has turned out to be a valuable method for studying the properties of surfaces, information especially needed by manufacturers of semiconductor devices that consist of thin layers of different materials deposited on one another.

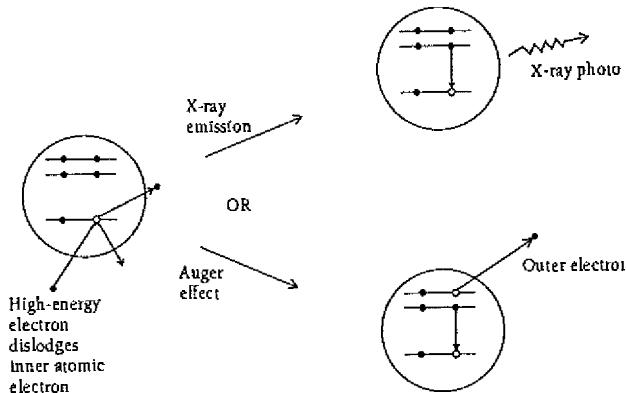


Figure 7.21 When an electron from an outer shell of an atom with a missing inner electron drops to fill the vacant state, the excitation energy can be carried off by an x-ray photon or by another outer electron. The latter process is called the Auger effect.

Appendix to Chapter 7

Atomic Spectra

We are now in a position to understand the chief features of the spectra of the various elements. Before we examine some representative examples, it should be mentioned that further complications exist which have not been considered here, for instance those that originate in relativistic effects and in the coupling between electrons and vacuum fluctuations in the electromagnetic field (see Sec. 6.9). These additional factors split certain energy states into closely spaced substates and therefore represent other sources of fine structure in spectral lines.

Hydrogen

Figure 7.22 shows the various states of the hydrogen atom classified by their total quantum number n and orbital angular-momentum quantum number l . The selection rule

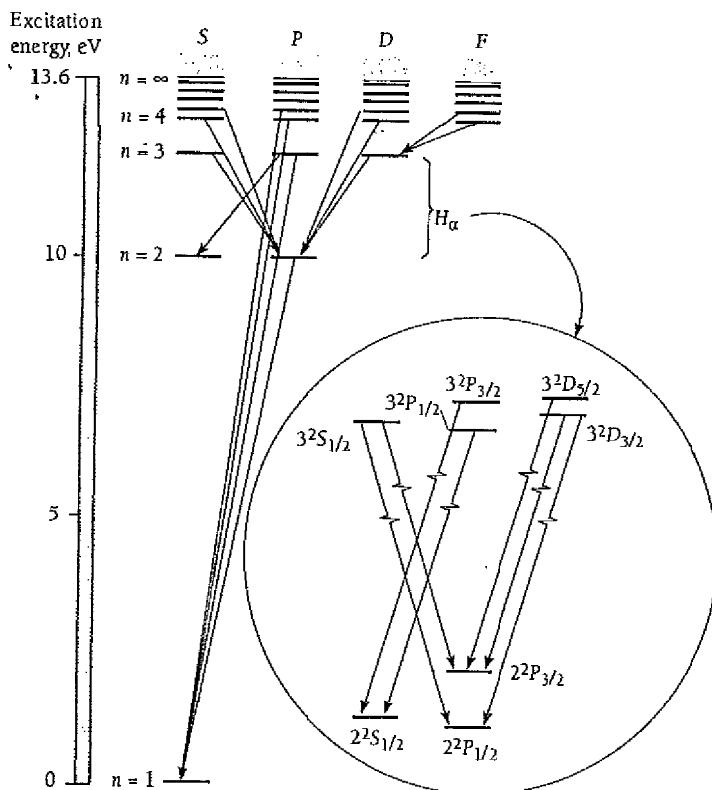


Figure 7.22 Energy-level diagram for hydrogen showing the origins of some of the more prominent spectral lines. The detailed structures of the $n = 2$ and $n = 3$ levels and the transitions that lead to the various components of the H_α line are pictured in the inset.

for allowed transitions here is

Selection rule

$$\Delta l = \pm 1$$

which is illustrated by the transitions shown. The principal quantum number n can change by any amount.

To indicate some of the detail that is omitted in a simple diagram of this kind, the detailed structures of the $n = 2$ and $n = 3$ levels are pictured. Not only are all substates of the same n and different j separated in energy, but the same is true of states of the same n and j but with different l . The latter effect is most marked for states of small n and l , and was first established in 1947 in the "Lamb shift" of the $2^2S_{1/2}$ state relative to the $2^2P_{1/2}$ state. The various separations conspire to split the H_α spectral line ($n = 3 \rightarrow n = 2$) into seven closely spaced components.

Sodium

The sodium atom has a single $3s$ electron outside closed inner shells, and so if we assume that the 10 electrons in its inner core completely shield $+10e$ of nuclear charge (which is not quite true), the outer electron is acted upon by an effective nuclear charge of $+e$ just as in the hydrogen atom. Hence we expect, as a first approximation, that the energy levels of sodium will be the same as those of hydrogen except that the lowest one will correspond to $n = 3$ instead of $n = 1$ because of the exclusion principle. Figure 7.23 is the energy-level diagram for sodium. By comparison with the hydrogen levels also shown, there is indeed agreement for the states of highest l , that is, for the states of highest angular momentum.

To understand the reason for the discrepancies at lower values of l , we need only refer to Fig. 6.11 to see how the probability for finding the electron in a hydrogen atom varies with distance from the nucleus. The smaller the value of l for a given n , the closer the electron gets to the nucleus on occasion. Although the sodium wave functions are not identical with those of hydrogen, their general behavior is similar. Accordingly we expect the outer electron in a sodium atom to penetrate the core of inner electrons most often when it is in an s state, less often when it is in a p state, still less often when it is in a d state, and so on. The less shielded an outer electron is from the full nuclear charge, the greater the average force acting on it, and the smaller (that is, the more negative) its total energy. For this reason the states of small l in sodium are displaced downward from their equivalents in hydrogen, as in Fig. 7.23, and there are pronounced differences in energy between states of the same n but different l .

Helium

A single electron is responsible for the energy levels of both hydrogen and sodium. However, there are two $1s$ electrons in the ground state of helium, and coupling affects the properties and behavior of the helium atom. These are the selection rules for allowed transitions under LS coupling:

$$\Delta L = 0, \pm 1$$

LS selection rules

$$\Delta J = 0, \pm 1$$

$$\Delta S = 0$$

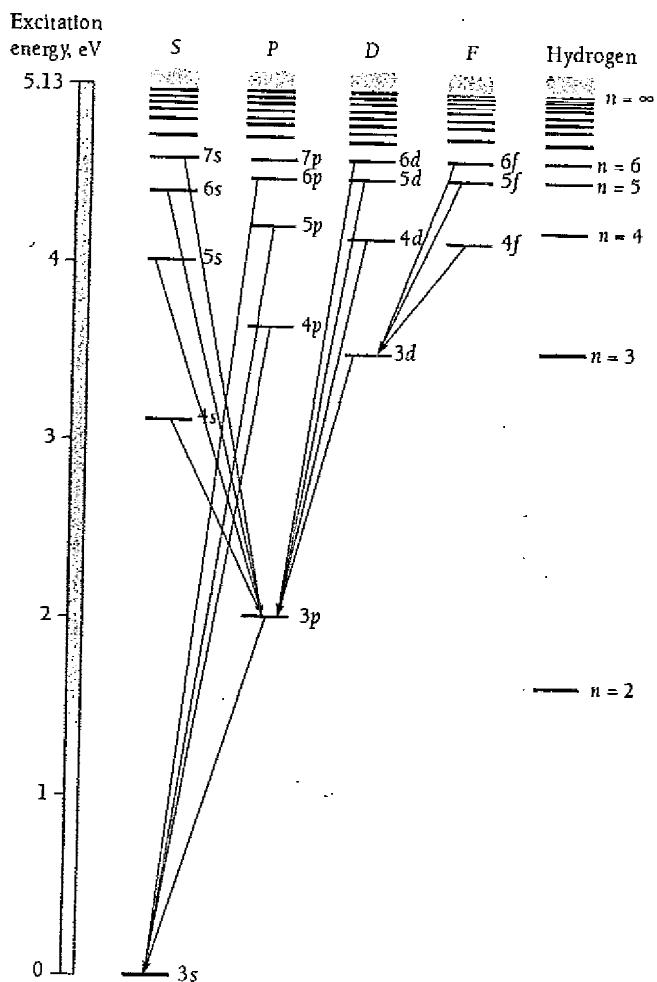


Figure 7.23 Energy-level diagram for sodium. The energy levels of hydrogen are included for comparison.

When only a single electron is involved, $\Delta L = 0$ is prohibited and $\Delta L = \Delta l = \pm 1$ is the only possibility. Furthermore, J must change when the initial state has $J = 0$, so that $J = 0 \rightarrow J = 0$ is prohibited.

The helium energy-level diagram is shown in Fig. 7.24. The various levels represent configurations in which one electron is in its ground state and the other is in an excited state. Because the angular momenta of the two electrons are coupled, the levels are characteristic of the entire atom. Three differences between this diagram and the corresponding ones for hydrogen and sodium are conspicuous:

1. There is a division into singlet and triplet states. These are, respectively, states in which the spins of the two electrons are antiparallel (to give $S = 0$) and parallel (to give $S = 1$). Because of the selection rule $\Delta S = 0$, no allowed transitions can occur between singlet states and triplet states, and the helium spectrum arises from transitions in one set or the other.

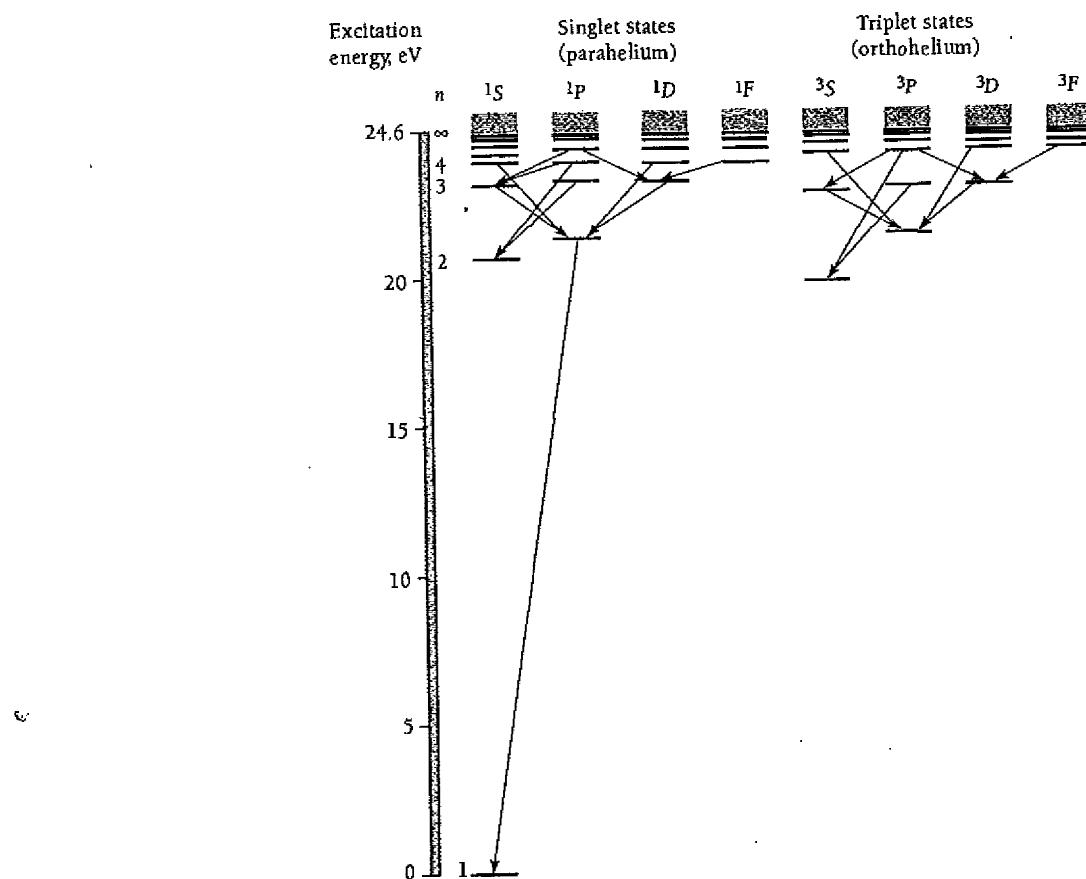


Figure 7.24 Energy-level diagram for helium showing the division into singlet (parahelium) and triplet (orthohelium) states. There is no 1^3S state because the exclusion principle prohibits two electrons with parallel spins in the same state.

Helium atoms in singlet states (antiparallel spins) constitute **parahelium** and those in triplet states (parallel spins) constitute **orthohelium**. An orthohelium atom can lose excitation energy in a collision and become one of parahelium, while a parahelium atom can gain excitation energy in a collision and become one of orthohelium. Ordinary liquid or gaseous helium is therefore a mixture of both. The lowest triplet states are metastable because, in the absence of collisions, an atom in one of them can retain its excitation energy for a relatively long time (a second or more) before radiating.

2 Another obvious peculiarity in Fig. 7.24 is the absence of the 1^3S state in helium. The lowest triplet state is 2^3S , although the lowest singlet state is 1^1S . The 1^3S state is missing because of the exclusion principle, since in this state the two electrons would have parallel spins and therefore identical sets of quantum numbers.

3 The energy difference between the ground state and the lowest excited state in helium is relatively large. This reflects the tight binding of closed-shell electrons discussed earlier in this chapter. The ionization energy of helium—the work that must be done to remove an electron from a helium atom—is 24.6 eV, the highest of any element.

Mercury

The last energy-level diagram we consider is that of mercury, which has two electrons outside an inner core of 78 electrons in closed shells or subshells (Table 7.4). We expect a division into singlet and triplet states as in helium. Because the atom is so heavy we might also expect signs of a breakdown in the LS coupling of angular momenta.

As Fig. 7.25 reveals, both of these expectations are realized, and several prominent lines in the mercury spectrum arise from transitions that violate the $\Delta S = 0$ selection rule. The transition $^3P_1 \rightarrow ^1S_0$ is an example, and is responsible for the strong 253.7-nm line in the ultraviolet. To be sure, this does not mean that the transition probability is necessarily very high, since the three 3P_1 states tend to be highly populated in excited mercury vapor. The $^3P_0 \rightarrow ^1S_0$ and $^3P_2 \rightarrow ^1S_0$ transitions, respectively, violate the rules that forbid transitions from $J = 0$ to $J = 0$ and that limit ΔJ to 0 or ± 1 , as well as violating $\Delta S = 0$, and hence are considerably less likely to occur than the $^3P_1 \rightarrow ^1S_0$ transition. The 3P_0 and 3P_2 states are therefore metastable, and in the absence of collisions, an atom can persist in either of them for a relatively long time. The strong spin-orbit interaction in mercury that leads to the partial failure of LS coupling is also responsible for the wide spacing of the elements of the 3P triplet.

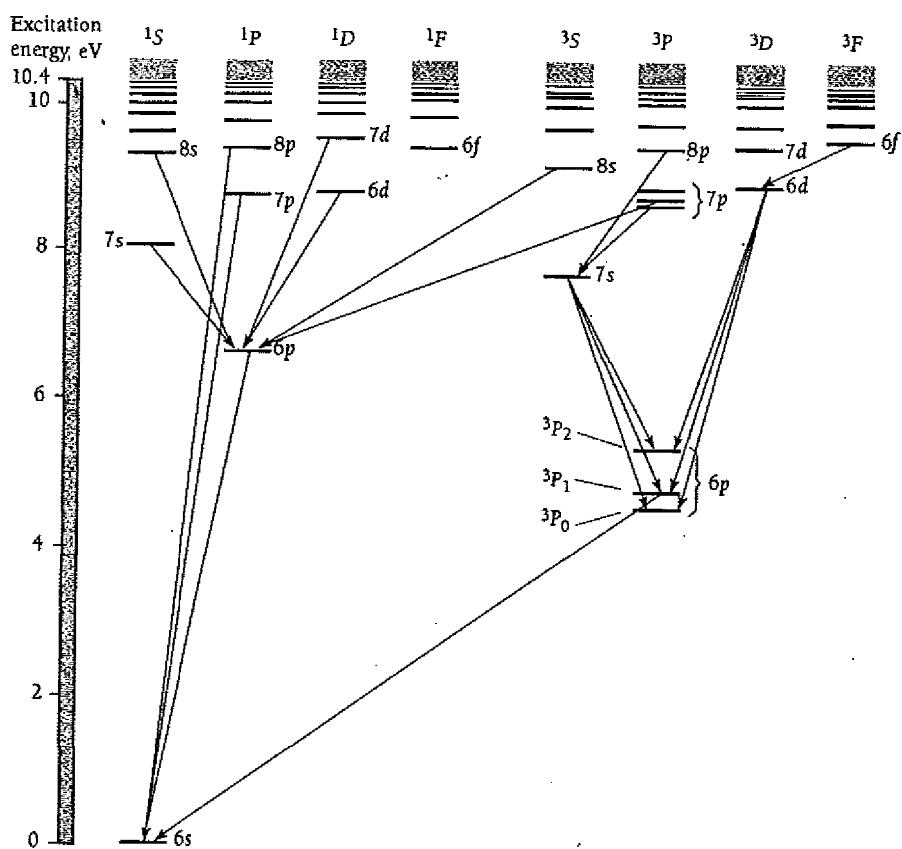


Figure 7.25 Energy-level diagram for mercury. In each excited level one outer electron is in the ground state, and the designation of the levels in the diagram corresponds to the state of the other electron.

EXERCISES

No plan survives contact with the enemy. —Field Marshal von Moltke

7.1 Electron Spin

1. A beam of electrons enters a uniform 1.20-T magnetic field.
(a) Find the energy difference between electrons whose spins are parallel and antiparallel to the field. (b) Find the wavelength of the radiation that can cause the electrons whose spins are parallel to the field to flip so that their spins are antiparallel.
2. Radio astronomers can detect clouds of hydrogen in our galaxy too cool to radiate in the optical part of the spectrum by means of the 21-cm spectral line that corresponds to the flipping of the electron in a hydrogen atom from having its spin parallel to the spin of the proton to having it antiparallel. Find the magnetic field experienced by the electron in a hydrogen atom.
3. Find the possible angles between the z axis and the direction of the spin angular-momentum vector S .

7.2 Exclusion Principle

7.3 Symmetric and Antisymmetric Wave Functions

4. In superconductivity, which occurs in certain materials at very low temperatures, electrons are linked together in "Cooper pairs" by their interaction with the crystal lattices of the materials. Cooper pairs do not obey the exclusion principle. What aspect of these pairs do you think permits this?
5. Protons and neutrons, like electrons, are spin- $\frac{1}{2}$ particles. The nuclei of ordinary helium atoms, ${}_4^{\text{He}}$, contain two protons and two neutrons each; the nuclei of another type of helium atom, ${}_3^{\text{He}}$, contain two protons and one neutron each. The properties of liquid ${}_3^{\text{He}}$ and liquid ${}_4^{\text{He}}$ are different because one type of helium atom obeys the exclusion principle but the other does not. Which is which, and why?
6. A one-dimensional potential well like those of Secs. 3.6 and 5.8 has a width of 1.00 nm and contains 10 electrons. The system of electrons has the minimum total energy possible. What is the least energy, in eV, a photon must have in order to excite a ground-state ($n = 1$) electron in this system to the lowest higher state it can occupy?

7.4 Periodic Table

7.5 Atomic Structures

7.6 Explaining the Periodic Table

7. In what way does the electron structure of an alkali metal atom differ from that of a halogen atom? From that of an inert gas atom?
8. What is true in general of the properties of elements in the same period of the periodic table? Of elements in the same group?
9. How many electrons can occupy an f subshell?

10. (a) How would the periodic table be modified if the electron had a spin of 1, so it could have spin states of $-1, 0$, and $+1$? Assume (wrongly) that such electrons are fermions and so obey the exclusion principle. Which elements would then be inert gases? (b) Such electrons would in fact be bosons. Which elements in this case would be inert gases?
11. If atoms could contain electrons with principal quantum numbers up to and including $n = 6$, how many elements would there be?
12. Verify that atomic subshells are filled in order of increasing $n + 1$, and within a group of given $n + 1$ in order of increasing n .
13. The ionization energies of Li, Na, K, Rb, and Cs are, respectively, 5.4, 5.1, 4.3, 4.2, and 3.9 eV. All are in group 1 of the periodic table. Account for the decrease in ionization energy with increasing atomic number.
14. The ionization energies of the elements of atomic numbers 20 through 29 are very nearly equal. Why should this be so when considerable variations exist in the ionization energies of other consecutive sequences of elements?
15. (a) Make a rough estimate of the effective nuclear charge that acts on each electron in the outer shell of the calcium ($Z = 20$) atom. Would you think that such an electron is relatively easy or relatively hard to detach from the atom? (b) Do the same for the sulfur ($Z = 16$) atom.
16. The effective nuclear charge that acts on the outer electron in the sodium atom is $1.84e$. Use this figure to calculate the ionization energy of sodium.
17. Why are Cl atoms more chemically active than Cl^- ions? Why are Na atoms more chemically active than Na^+ ions?
18. Account for the general trends of the variation of atomic radius with atomic number shown in Fig. 7.11.
19. In each of the following pairs of atoms, which would you expect to be larger in size? Why? Li and F; Li and Na; F and Cl; Na and Si.
20. The nucleus of a helium atom consists of two protons and two neutrons. The Bohr model of this atom has two electrons in the same orbit around the nucleus. Estimate the average separation of the electrons in a helium atom in the following way.
(1) Assume that each electron moves independently of the other in a ground-state Bohr orbit and calculate its ionization energy on this basis. (2) Use the difference between the calculated ionization energy and the measured one of 24.6 eV to find the interaction energy between the two electrons. (3) On the assumption that the interaction energy results from the repulsion between the electrons, find their separation. How does this compare with the radius of the orbit?
21. Why is the normal Zeeman effect observed only in atoms with an even number of electrons?

7.7 Spin-Orbit Coupling

22. Why is the ground state of the hydrogen atom not split into two sublevels by spin-orbit coupling?
23. The spin-orbit effect splits the $3P \rightarrow 3S$ transition in sodium (which gives rise to the yellow light of sodium-vapor highway lamps) into two lines, 589.0 nm corresponding to $3P_{3/2} \rightarrow 3S_{1/2}$ and 589.6 nm corresponding to $3P_{1/2} \rightarrow 3S_{1/2}$. Use these wavelengths to calculate the effective magnetic field experienced by the outer electron in the sodium atom as a result of its orbital motion.

7.8 Total Angular Momentum

24. An atom has a single electron outside closed inner shells. What total angular momentum J can the atom have if it is in a P state? In a D state?
25. If $j = \frac{1}{2}$, what values of l are possible?
26. (a) What are the possible values of L for a system of two electrons whose orbital quantum numbers are $l_1 = 1$ and $l_2 = 3$? (b) What are the possible values of S ? (c) What are the possible values of J ?
27. What must be true of the subshells of an atom which has a 1S_0 ground state?
28. Find the S , L , and J values that correspond to each of the following states: 1S_0 , 3P_2 , $^2D_{3/2}$, 5F_5 , $^6H_{5/2}$.
29. The lithium atom has one $2s$ electron outside a filled inner shell. Its ground state is $^2S_{1/2}$. (a) What are the term symbols of the other allowed states, if any? (b) Why would you think the $^2S_{1/2}$ state is the ground state?
30. The magnesium atom has two $3s$ electrons outside filled inner shells. Find the term symbol of its ground state.
31. The aluminum atom has two $3s$ electrons and one $3p$ electron outside filled inner shells. Find the term symbol of its ground state.
32. In a carbon atom, only the two $2p$ electrons contribute to its angular momentum. The ground state of this atom is 3P_0 , and the first four excited states, in order of increasing energy, are 3P_1 , 3P_2 , 1D_2 , and 1S_0 . (a) Give the L , S , and J values for each of these five states. (b) Why do you think the 3P_0 state is the ground state?
33. Why is it impossible for a $^2D_{3/2}$ state to exist?
34. (a) What values can the quantum number j have for a d electron in an atom whose total angular momentum is provided by this electron? (b) What are the magnitudes of the corresponding angular momenta of the electron? (c) what are the angles between the directions of L and S in each case? (d) What are the term symbols for this atom?

35. Answer the questions of Exercise 34 for an f electron in an atom whose total angular momentum is provided by this electron.

36. Show that if the angle between the directions of L and S in Fig. 7.15 is θ ,

$$\cos \theta = \frac{j(j+1) - l(l+1) - s(s+1)}{2\sqrt{l(l+1)s(s+1)}}$$

37. The magnetic moment μ_J of an atom in which LS coupling holds has the magnitude

$$\mu_J = \sqrt{J(J+1)}g_J\mu_B$$

where $\mu_B = e\hbar/2m$ is the Bohr magneton and

$$g_J = 1 + \frac{J(J+1) - L(L+1) - S(S+1)}{2J(J+1)}$$

is the Landé g factor. (a) Derive this result with the help of the law of cosines starting from the fact that averaged over time, only the components of μ_L and μ_S parallel to J contribute to μ_J . (b) Consider an atom that obeys LS coupling that is in a weak magnetic field B in which the coupling is preserved. How many substates are there for a given value of J ? What is the energy difference between different substates?

38. The ground state of chlorine is $^2P_{3/2}$. Find its magnetic moment (see previous exercise). Into how many substates will the ground state split in a weak magnetic field?

7.9 X-Ray Spectra

39. Explain why the x-ray spectra of elements of nearby atomic numbers are qualitatively very similar, although the optical spectra of these elements may differ considerably.
40. What element has a K_α x-ray line of wavelength 0.144 nm?
41. Find the energy and the wavelength of the K_α x-rays of aluminum.
42. The effective charge experienced by an M ($n = 3$) electron in an atom of atomic number Z is about $(Z - 7.4)e$. Show that the frequency of the L_α x-rays of such an element is given by $5cR(Z - 7.4)^2/36$.

Appendix: Atomic Spectra

43. Distinguish between singlet and triplet states in atoms with two outer electrons.
44. Which of the following elements would you expect to have energy levels divided into singlet and triplet states: Ne, Mg, Cl, Ca, Cu, Ag, Ba?