7.1 ELECTRON SPIN 電子自旋

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 精細結構 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).

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

内在自旋角动量

振幅对所有 e^- 都一样

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

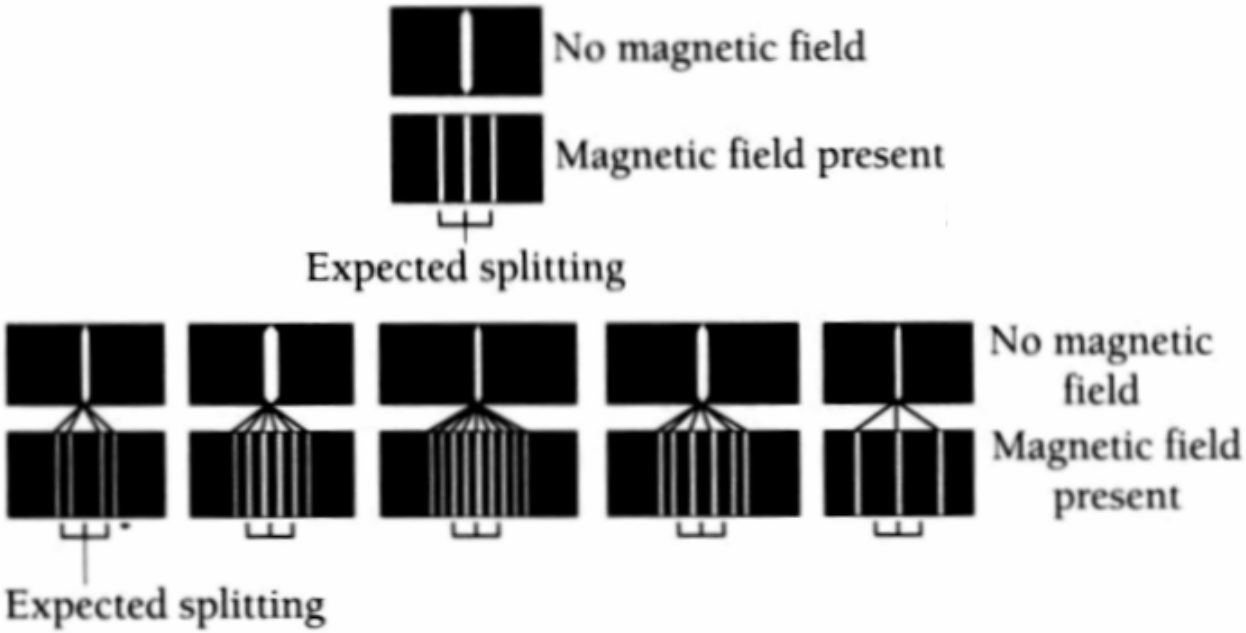


Figure 7.1 The normal and anomalous Zeeman effects in various spectral lines.

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

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

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

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

$S = \sqrt{(\frac{1}{2})(\frac{3}{2})}\,\hbar = \frac{\sqrt{3}}{2}\hbar$

Spin angular momentum 自旋角动量

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

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

Example 7.1

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

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

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

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

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 objection.

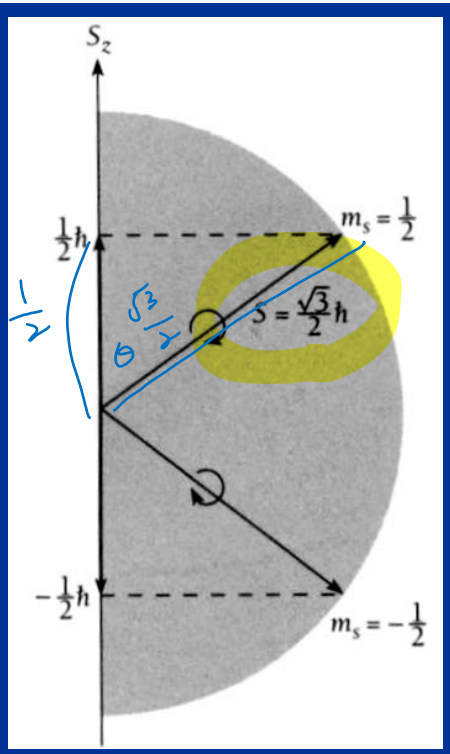
The space quantization of electron spin is described by the spin magnetic quantum number m_s. We recall that the orbital angular-momentum vector can have the $2l + 1$ orientations in a magnetic field from $+l$ to $-l$. Similarly the spin angular-momentum vector can have the $2s + 1 = 2$ orientations 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

$S = \frac{\sqrt{3}}{2}\hbar$

z component of spin angular momentum

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

$\pm\frac{1}{2}$



$\cos\theta = \sqrt{3}$ $\theta = 54.°$

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

The gyromagnetic ratio characteristic of electron spin is almost exactly twice that characteristic of electron orbital motion. Taking this ratio as equal to 2, the spin magnetic moment $\boldsymbol{\mu}_s$ of an electron is related to its spin angular momentum $\mathbf{S}$ by

Spin magnetic moment 自旋磁动量

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

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

$S_z = \pm \frac{1}{2}\hbar$

z component of spin magnetic moment

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

波耳磁子
Bohr magneton

where μ_B is the Bohr magneton.

The Stern-Gerlach Experiment

空間量子化

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.

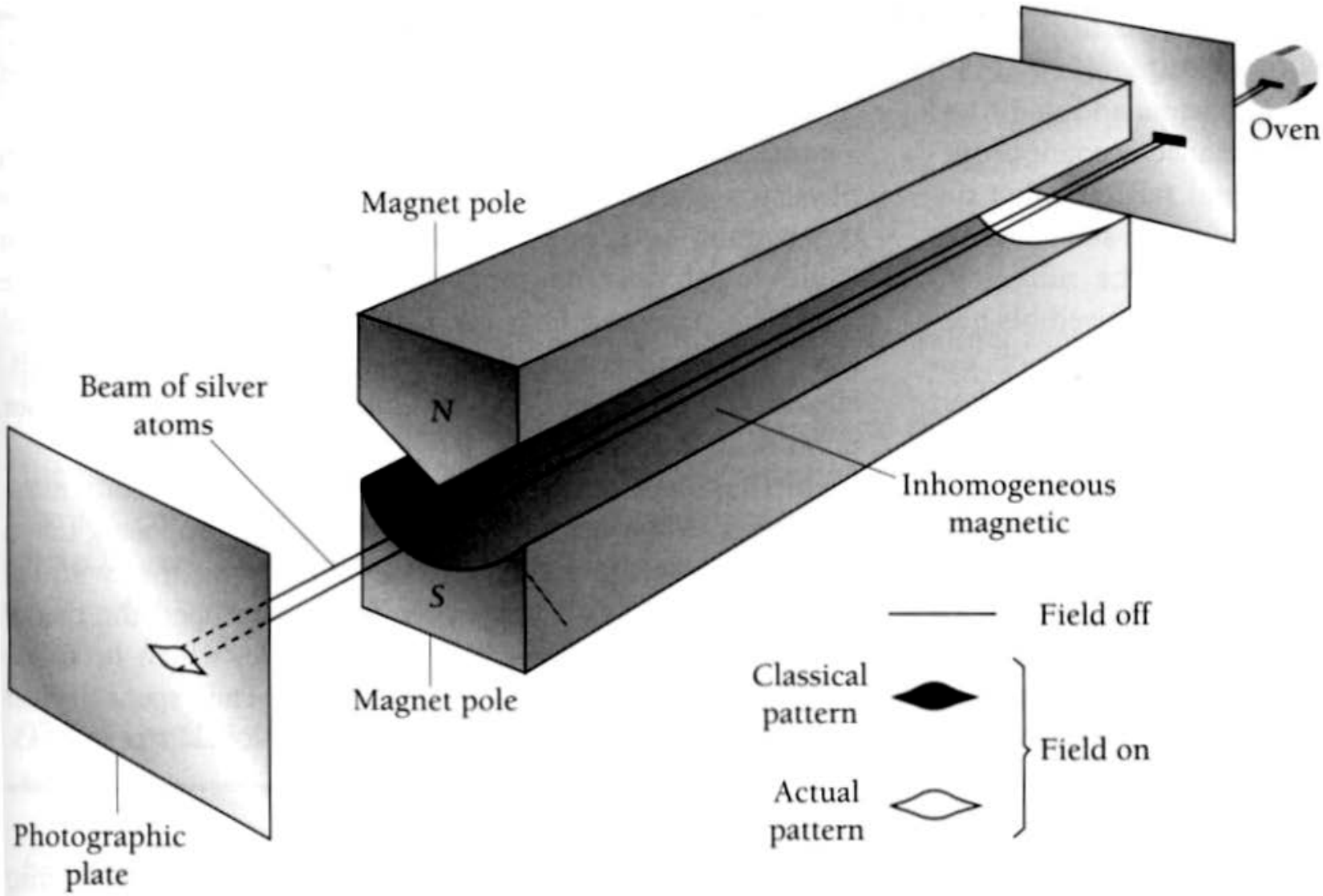


Figure 7.3 The Stern-Gerlach experiment.

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.

TABLE 7.1 Quantum Numbers of an Atomic Electron

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

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7.2 EXCLUSION PRINCIPLE

不相容原理

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

原子中每一個 e^- 的量子數不同

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.

A 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.

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

每個 e^- 有不同的量子數 n, l, m_l, m_s

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 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

費米子 玻色子

Before we explore the role of the exclusion principle in determining atomic structures, it is interesting to look into its quantum-mechanical implications.

We saw in the previous chapter that the complete wave function ψ of the electron in a hydrogen atom can be expressed as the product of three separate wave functions, each describing that part of ψ which is a function of one of the three coordinates r, θ, ϕ. In an analogous way the complete wave function $\psi(1, 2, 3, \ldots, n)$ of a system of n noninteracting particles can be expressed as the product of the wave functions $\psi(1)$, $\psi(2)$, $\psi(3)$, . . . , $\psi(n)$ of the individual particles. That is,

n個不會互相作用的粒子

$$\psi(1, 2, 3, \ldots, n) = \psi(1)\,\psi(2)\,\psi(3)\ldots\psi(n) \tag{7.5}$$

Let us use this result 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

$$|\psi|^2(1, 2) = |\psi|^2(2, 1) \tag{7.6}$$

→ 分別在兩個能量態的相同粒子互換能態機率密度不變

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

開根號

Symmetric 對稱

$$\psi(2, 1) = {}^{+}\psi(1, 2) \tag{7.7}$$

or

Antisymmetric 反對稱

$$\psi(2, 1) = -\psi(1, 2) \tag{7.8}$$

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),

$$\psi_I = \psi_a(1)\psi_b(2) \tag{7.9}$$

在任意時刻
機率一樣

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

$$\psi_{II} = \psi_a(2)\psi_b(1) \tag{7.10}$$

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

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

normalize

Symmetric

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

Antisymmetric

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

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.

半整數奇數個子費米子

The results of various experiments show that *all* particles which have odd half-integral spins ($\frac{1}{2}, \frac{3}{2}, \ldots$) 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.

对称

0 or 整数

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.

轨道是波函数

填充波函数

平均位能场

概率密度

$|\psi|^2 \times P \times \int V$

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 remarked, "The periodic law, together with the relevations 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.

TABLE 7.2 The Periodic Table of the Elements

The number above the symbol of each element is its atomic mass, and the number below the symbol is its atomic number. The elements whose atomic masses are given in parentheses do not occur in nature, but have been prepared artificially in nuclear reactions. The atomic mass in such a case is the mass number of the most long-lived radioactive isotope of the element.

Group	I	II											III	IV	V	VI	VII	VIII		
Period 1	1.008 H 1																	4.00 He 2		
2	6.94 Li 3	9.01 Be 4											10.81 B 5	12.01 C 6	14.01 N 7	16.00 O 8	19.00 F 9	20.18 Ne 10		
3	22.99 Na 11	24.31 Mg 12											26.98 Al 13	28.09 Si 14	30.97 P 15	32.06 S 16	35.45 Cl 17	39.95 Ar 18		
4	39.10 K 19	40.08 Ca 20	3d 44.96 Sc 21	47.90 Ti 22	50.94 V 23	52.00 Cr 24	54.94 Mn 25	55.85 Fe 26	58.93 Co 27	58.70 Ni 28	63.55 Cu 29	65.38 Zn 30	69.72 Ga 31	72.59 Ge 32	74.92 As 33	78.96 Se 34	79.90 Br 35	83.8 Kr 36		
5	85.47 Rb 37	87.62 Sr 38	4d 88.91 Y 39	91.22 Zr 40	92.91 Nb 41	95.94 Mo 42	(97) Tc 43	101.1 Ru 44	102.9 Rh 45	106.4 Pd 46	107.9 Ag 47	112.4 Cd 48	114.8 In 49	118.7 Sn 50	121.8 Sb 51	127.6 Te 52	126.9 I 53	131.3 Xe 54		
6	132.9 Cs 55	137.3 Ba 56	4f * 57–71	5d 178.5 Hf 72	180.9 Ta 73	183.9 W 74	186.2 Re 75	190.2 Os 76	192.2 Ir 77	195.1 Pt 78	197.0 Au 79	200.6 Hg 80	204.4 Tl 81	207.2 Pb 82	209.0 Bi 83	(209) Po 84	(210) At 85	(222) Rn 86		
7	(223) Fr 87	226.0 Ra 88	5f † 89–105														*Halogens*	*Inert gases*		
	Alkali metals																			
				138.91 La 57	140.12 Ce 58	140.91 Pr 59	144.24 Nd 60	(145) Pm 61	150.4 Sm 62	152.0 Eu 63	157.3 Gd 64	158.9 Tb 65	162.5 Dy 66	164.9 Ho 67	167.3 Er 68	168.9 Tm 69	173.0 Yb 70	175.0 Lu 71		
			*Rare earths (Lanthanides)																	
			†Actinides	(227) Ac 89	232.0 Th 90	231.0 Pa 91	238.0 U 92	(237) Np 93	(244) Pu 94	(243) Am 95	(247) Cm 96	(247) Bk 97	(251) Cf 98	(254) Es 99	(257) Fm 100	(258) Md 101	(255) No 102	(260) Lr 103	(257) Rf 104	(260) Ha 105

Elements created in the laboratory

Elements with similar properties form the **groups** shown as vertical columns in Table 7.2 (Fig. 7.4). Thus group I 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 VII 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 VIII 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.

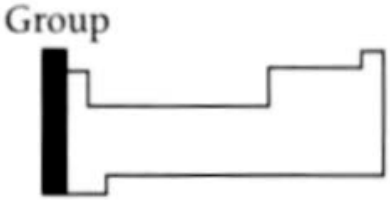

Figure 7.4 The elements in a group of the periodic table have similar properties

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.

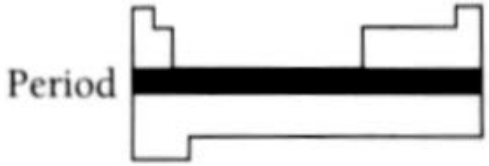

Figure 7.4 The elements in a period have different properties.

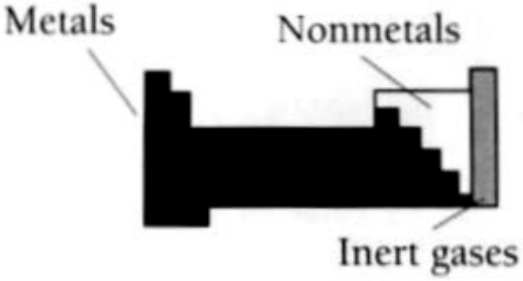

Figure 7.5 The majority of the elements are metals.

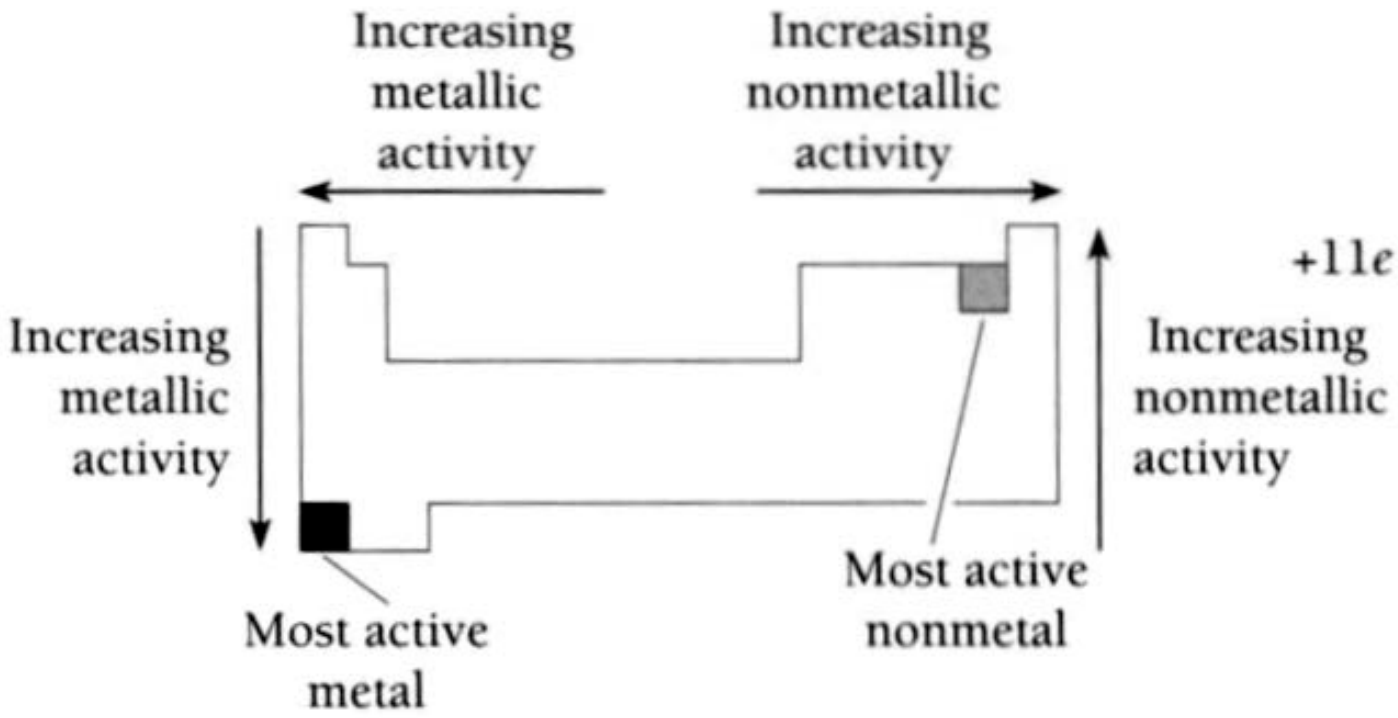

Figure 7.6 How chemical activity varies in the periodic table.

A series of **transition elements** appears in each period after the third between the group II and group III 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 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.

Figure 7.7 The transition elements are metals.

( ) → 多 e^- 的差别

↓

∵ e^- 和 e^- 間的位能

x, y, z x, y, z

7.5 ATOMIC STRUCTURES

Shells and subshells of electrons

子軌道

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. → 能量最低

2 Only one electron can exist in any particular quantum state in an atom. → 互立不相害

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

每個 e^- 視為在固定平均电場中

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 Ze decreased by the partial shielding of those other electrons that are closer to the nucleus (see Fig. 7.9).

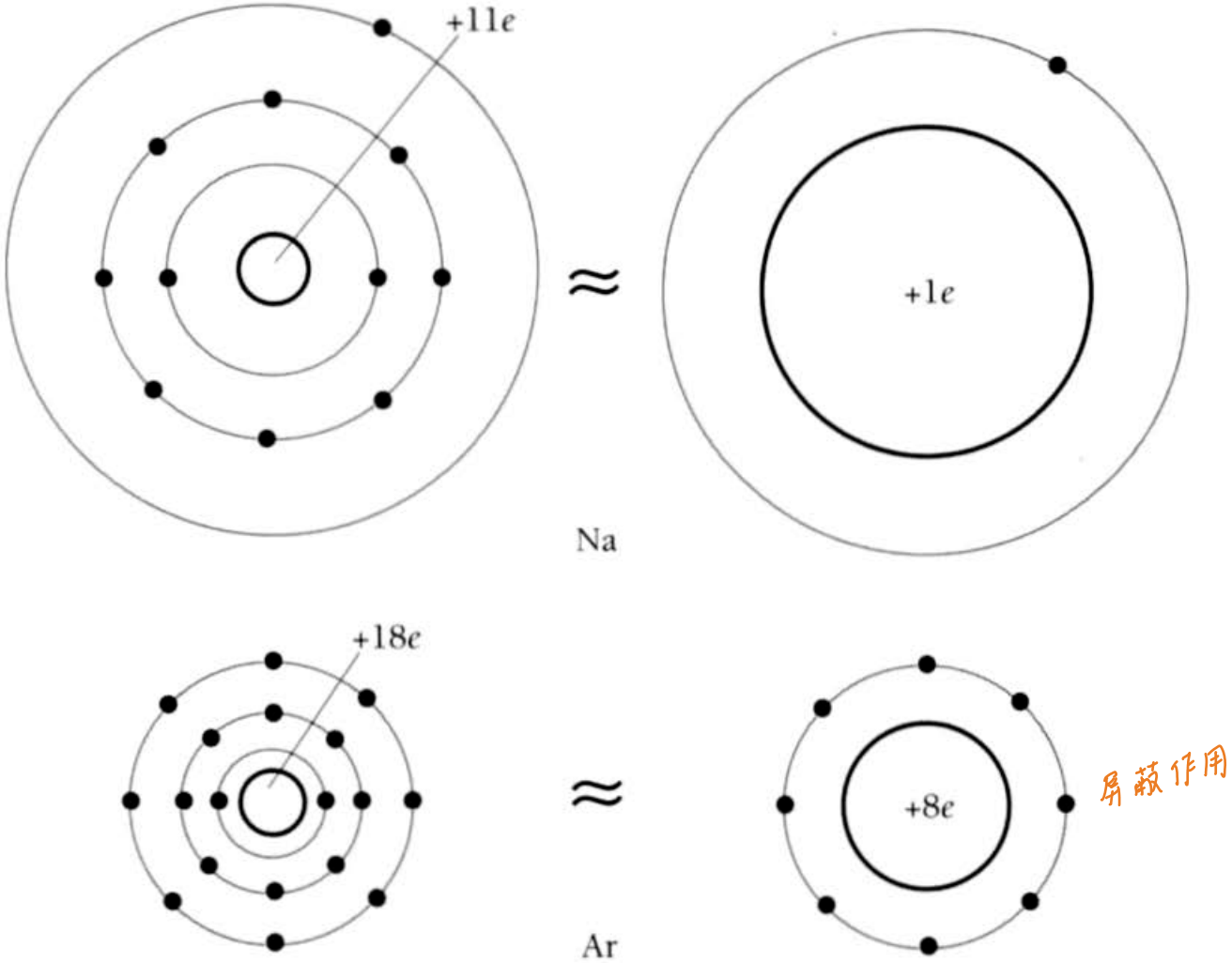

Figure 7.9 Schematic representation of electron shielding in the sodium and argon atoms. In this crude model, each outer electron in an Ar atom is acted upon by an effective nuclear charge 8 times greater than that acting upon the outer electron in a Na atom. The Ar atom is accordingly smaller in size 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.

<Back>

shell 用 n
sub shell 用 n, l

r 的方程和 l 有関 ∴ e⁻ 和 e⁻ 的作用

Self-Consistent Field Method (Hartree-Fock)
⇒ single-electron wave functions and energy levels for many-electron atoms

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:

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

Atomic shells

$$\begin{array}{cccccc} n = 1 & 2 & 3 & 4 & 5 & \ldots \\ K & L & M & N & O & \ldots \end{array} \qquad (7.13)$$

Kα

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 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.

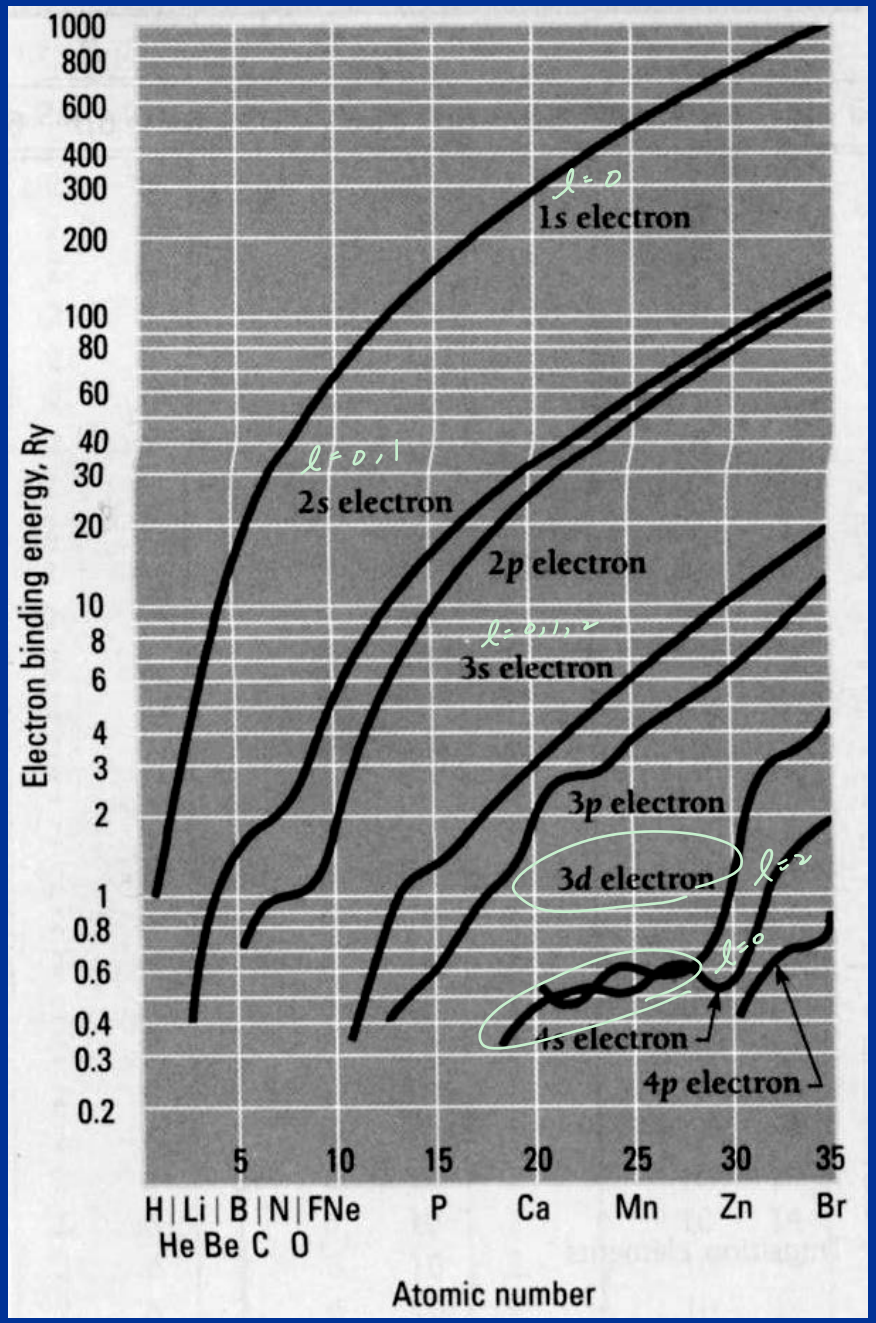

Figure 7.8 The binding energies of atomic electrons in rydbergs. (1 Ry = 13.6 eV = ground-state energy of H atom.)

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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

$$1s^2 \overset{n=2}{2s^2} 2p^6 3s^1$$

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.

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, . . . , $(n - 1)$. There are $2l + 1$ different values of the magnetic quantum number m_l for any l, since $m_l = 0, \pm 1, \pm 2, \ldots, \pm l$. 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).

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

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

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

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

$$= 2[1 + 3 + 5 + \ldots + 2n - 1]$$

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

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

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.

2e⁻

6e⁻

10e⁻

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

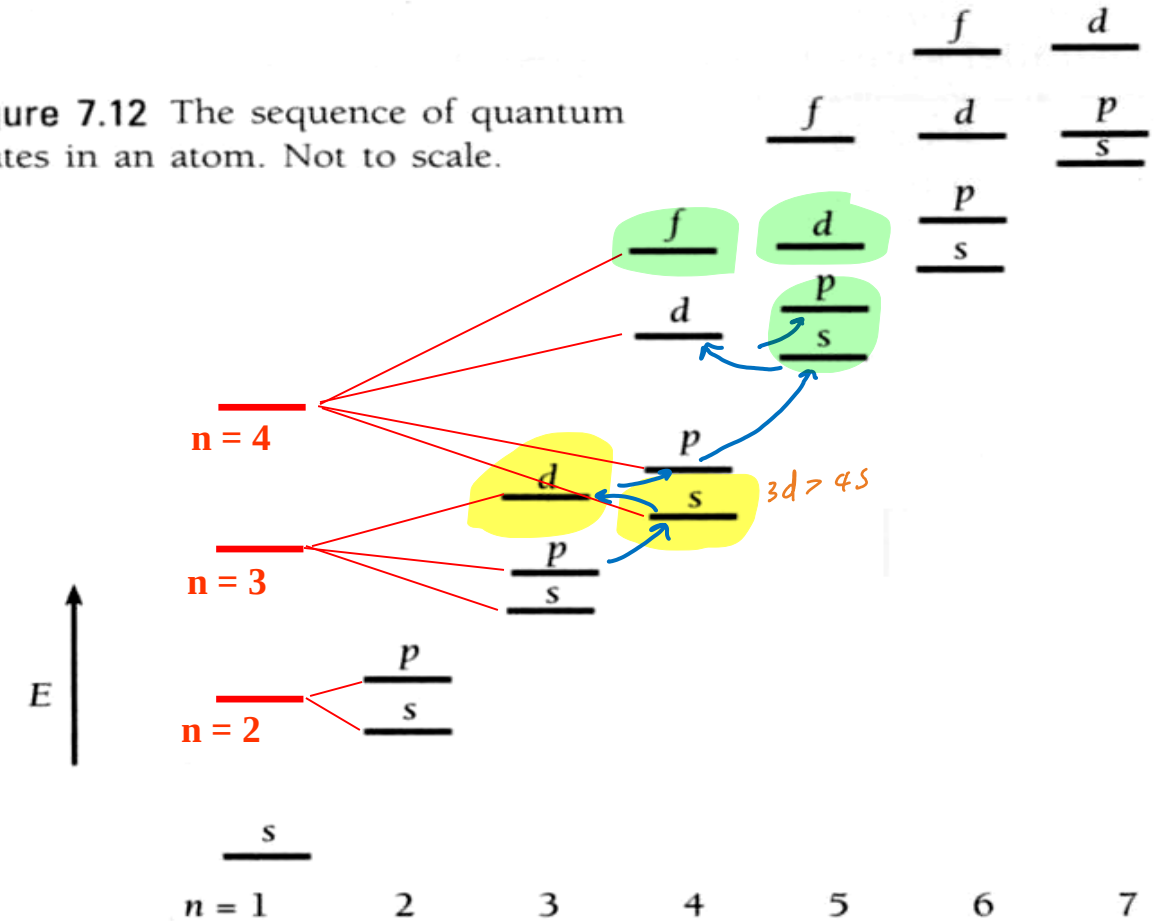

Figure 7.12 illustrates this sequence. The remarkable similarities in chemical behavior among the lanthanides and actinides are easy to understand on the basis of this sequence. All the lanthanides have the same $5s^2 5p^6 6s^2$ configurations but have incomplete $4f$ subshells. The addition of $4f$ 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.

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

$$1s^2 \quad 2s^2 \quad 2p^6 \quad 3s^2 \quad 3p^6 \quad 4s^2 \quad 3d^{10} \quad 4p^6 \quad 5s^2$$
$$4d^{10} \quad 5p^6 \quad 6s^2 \quad 4f^{14} \quad 5d^{10} \quad 6p^6 \quad 7s^2 \quad 6d^{10} \quad 5f^{14}$$

s	p	d	f
1	3	5	7
2	6	10	14

TABLE 7.4 Electron Configurations of the Elements

	K	L		M			N				O				P			Q
	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
1 H	1																	
2 He	2 ← Inert gas																	
3 Li	2	1 ← Alkali metal																
4 Be	2	2																
5 B	2	2	1															
6 C	2	2	2															
7 N	2	2	3															
8 O	2	2	4															
9 F	2	2	5 ← Halogen															
10 Ne	2	2	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											

Transition elements

填滿殼層 → closed shell
↓
不易反應

沒有真正 closed
p之前有 closed

開始填 d 軌道 → $10e^-$
↓
3d

4

9

<back>

TABLE 7.4 Electron Configurations of the Elements

	K	L		M			N				O				P			Q
	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
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									
47 Ag	2	2	6	2	6	10	2	6	10		1							
48 Cd	2	2	6	2	6	10	2	6	10		2							
49 In	2	2	6	2	6	10	2	6	10		2	1						
50 Sn	2	2	6	2	6	10	2	6	10		2	2						
51 Sb	2	2	6	2	6	10	2	6	10		2	3						
52 Te	2	2	6	2	6	10	2	6	10		2	4						

Transition elements

4d的

4f的先填5s、5p

只涂到p軌道

paramagnetic → 过渡光譜稀土元素都相似

	K	L		M			N				O				P		
	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d
53 I	2	2	6	2	6	10	2	6	10		2	5					
54 Xe	2	2	6	2	6	10	2	6	10		2	6					
55 Cs	2	2	6	2	6	10	2	6	10		2	6			1		
56 Ba	2	2	6	2	6	10	2	6	10		2	6			2		
57 La	2	2	6	2	6	10	2	6	10		2	6	1		2		
58 Ce	2	2	6	2	6	10	2	6	10	2	2	6			2		
59 Pr	2	2	6	2	6	10	2	6	10	3	2	6			2		
60 Nd	2	2	6	2	6	10	2	6	10	4	2	6			2		
61 Pm	2	2	6	2	6	10	2	6	10	5	2	6			2		
62 Sm	2	2	6	2	6	10	2	6	10	6	2	6			2		
63 Eu	2	2	6	2	6	10	2	6	10	7	2	6			2		
64 Gd	2	2	6	2	6	10	2	6	10	7	2	6	1		2		
65 Tb	2	2	6	2	6	10	2	6	10	9	2	6			2		
66 Dy	2	2	6	2	6	10	2	6	10	10	2	6			2		
67 Ho	2	2	6	2	6	10	2	6	10	11	2	6			2		
68 Er	2	2	6	2	6	10	2	6	10	12	2	6			2		
69 Tm	2	2	6	2	6	10	2	6	10	13	2	6			2		
70 Yb	2	2	6	2	6	10	2	6	10	14	2	6			2		
71 Lu	2	2	6	2	6	10	2	6	10	14	2	6	1		2		
72 Hf	2	2	6	2	6	10	2	6	10	14	2	6	2		2		
73 Ta	2	2	6	2	6	10	2	6	10	14	2	6	3		2		
74 W	2	2	6	2	6	10	2	6	10	14	2	6	4		2		
75 Re	2	2	6	2	6	10	2	6	10	14	2	6	5		2		
76 Os	2	2	6	2	6	10	2	6	10	14	2	6	6		2		
77 Ir	2	2	6	2	6	10	2	6	10	14	2	6	7		2		
78 Pt	2	2	6	2	6	10	2	6	10	14	2	6	9		1		
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		

← Halogen

← Inert gas

← Alkali metal

鑭系 $5f^1$ ~ $5f^{14}$

La

$4f^1$ ~ $4f^{14}$

稀土 very similar

Lanthanides

Transition elements

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
88 Ra	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		2	metal
89 Ac	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	1	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	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	Actinides
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	
99 Es	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6		2	
100 Fm	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6		2	
101 Md	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6		2	
102 No	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6		2	
103 Lr	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	1	2	

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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 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 I 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.

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 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.

Example 7.2

外層游離能

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

Solution

$$E_n = -\frac{me^4}{32\pi\epsilon_0^2\hbar^2}\left(\frac{1}{n^2}\right) = \frac{E_1}{n^2}$$

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

$$U = \frac{(Ze^2)^2}{4\pi\epsilon_0 r} = \frac{Z^2e^4}{4\pi\epsilon_0 r}$$

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

Here $n = 2$ for the 2*s* 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

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

沒有100%的屏蔽

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

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.

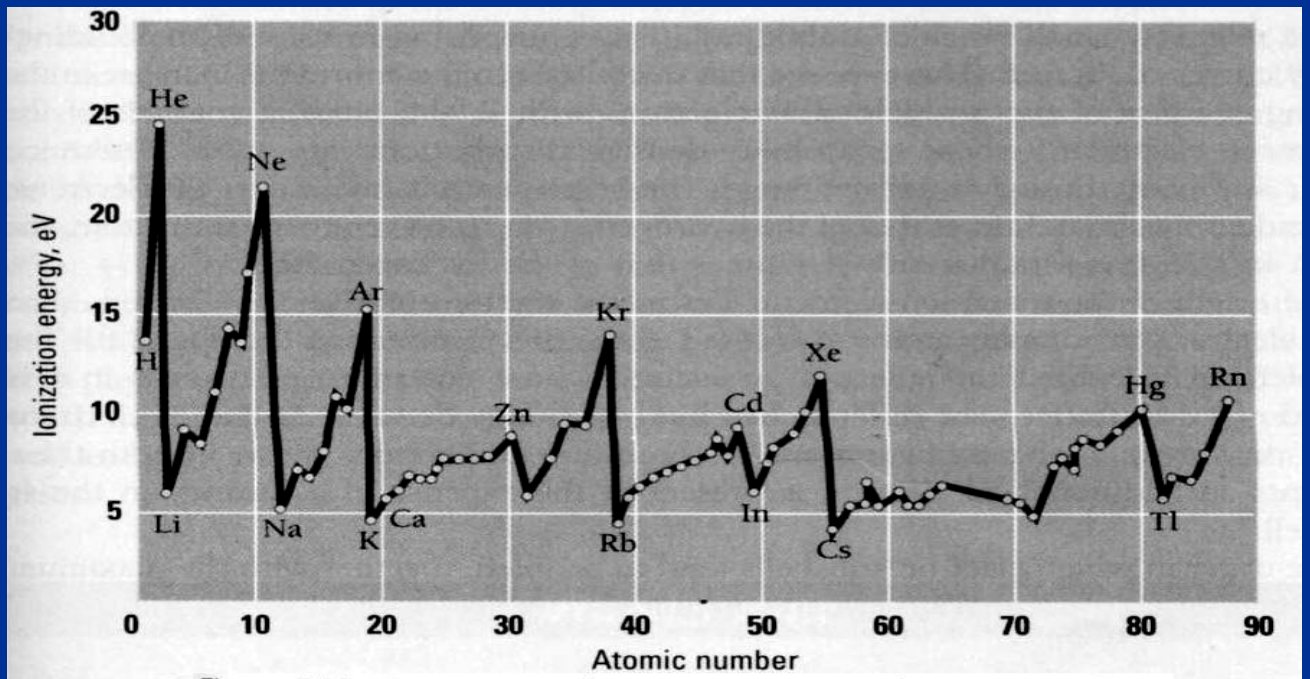
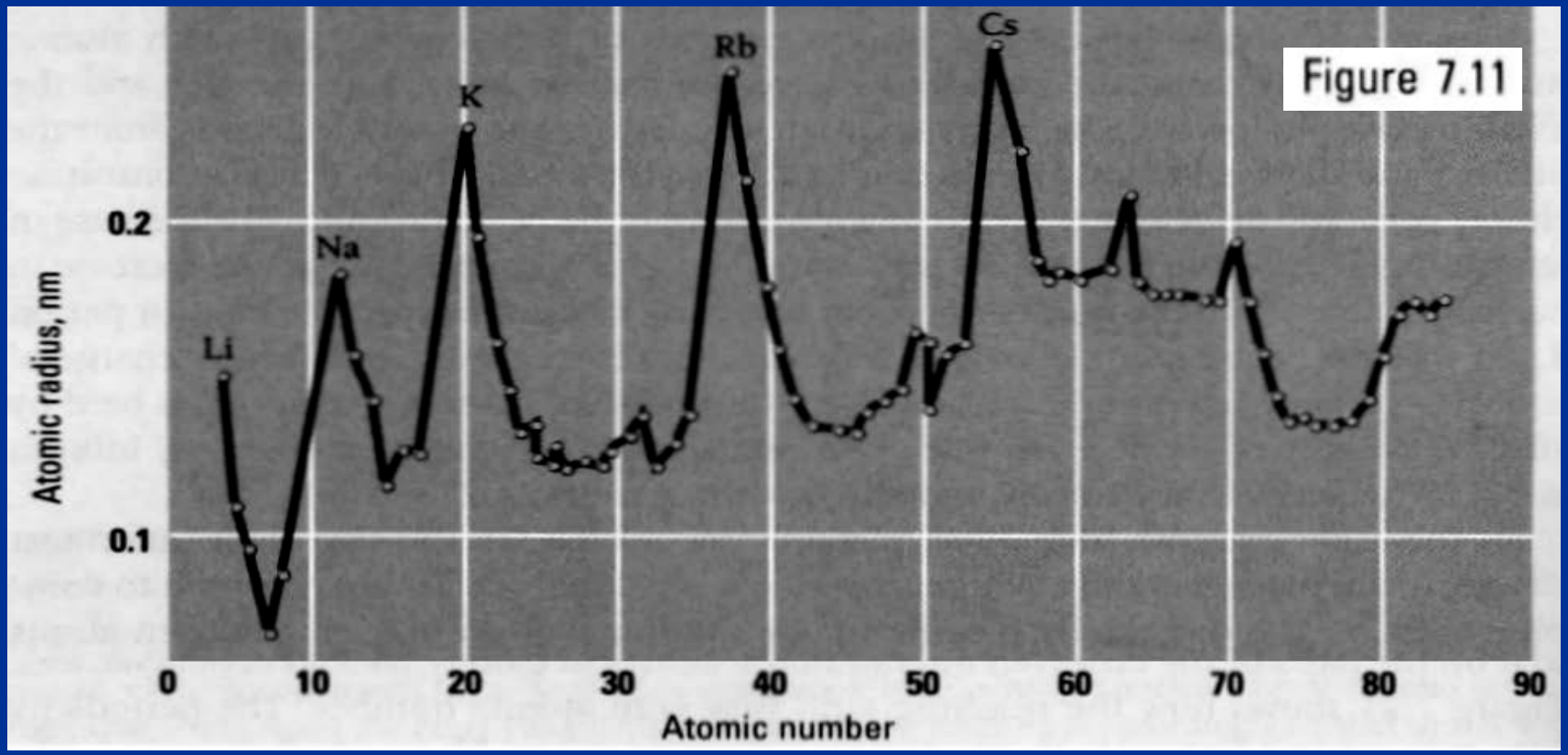


Figure 7.10 The variation of ionization energy with atomic number.

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 1*s* 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.

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 4*s* instead of a 3*d* substate. The difference in binding energy between 3*d* and 4*s* electrons is not very great, as the configurations of chromium and copper show. In both these elements an additional 3*d* electron is present at the expense of a vacancy in the 4*s* subshell.

<Table 7.4>

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 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 remainder of the inert gases.

<Table 7.4>

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.

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	$1s^2 2s^2 2p^6$	↑↓	↑↓	↑↓

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 $\boldsymbol{\mu}$ in a magnetic field $\mathbf{B}$ is, as we know,

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

where θ is the angle between $\boldsymbol{\mu}$ and $\mathbf{B}$. The quantity $\mu \cos\theta$ is the component of $\boldsymbol{\mu}$ parallel to $\mathbf{B}$. 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

Spin-orbit coupling

$$U_m = \pm\mu_B B \qquad (7.15)$$

Depending on the orientation of its spin vector $\mathbf{S}$, 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 $\mathbf{S}$ 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

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

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

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

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

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

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

Hence the magnetic field experienced by the electron is

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

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

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

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

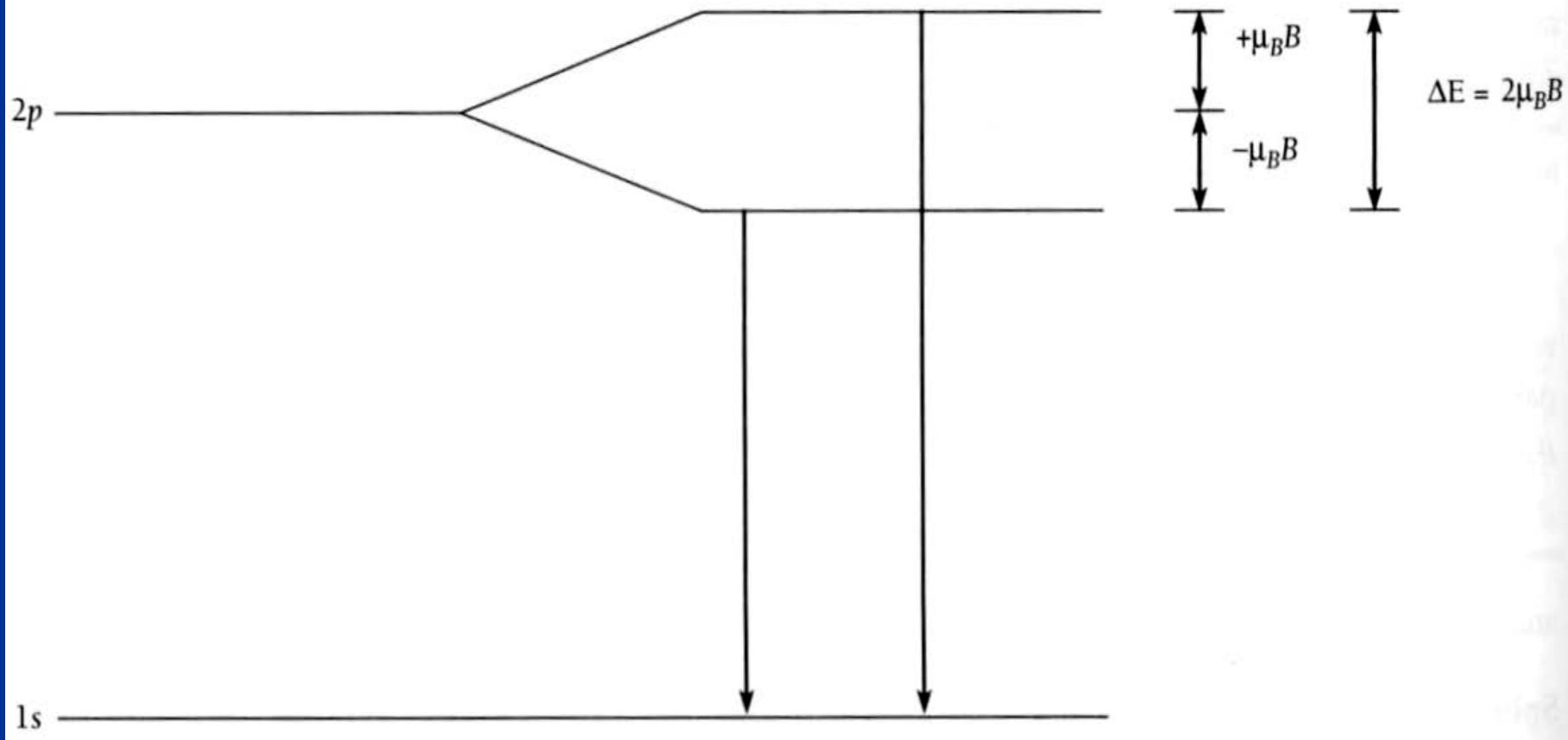


Figure 7.14 Spin-orbit coupling splits the $2p$ state in the hydrogen atom into two substates ΔE apart. The result is a doublet (two closely spaced lines) instead of a single spectral line for the $2p \rightarrow 1s$ transition.

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 I 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**:

Total atomic angular momentum

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \tag{7.16}$$

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

$$J = \sqrt{j(j+1)}\,\hbar \qquad j = l + s = l \pm \tfrac{1}{2} \tag{7.17}$$

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

$$J_z = m_j\hbar \qquad m_j = -j, -j+1, \ldots, j-1, j \tag{7.18}$$

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.

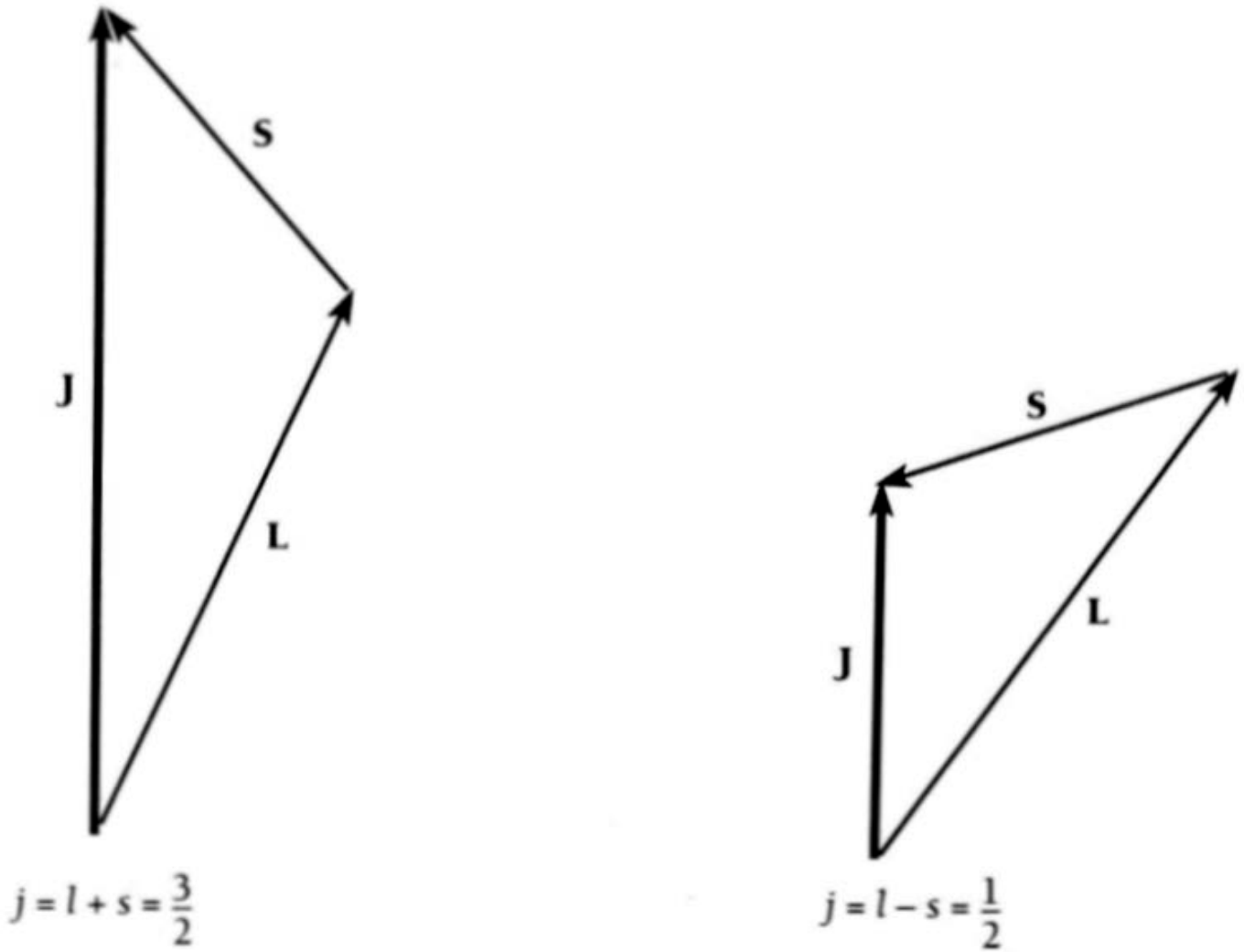


Figure 7.15 The two ways in which **L** and **S** can be added to form **J** when $l = 1$, $s = \frac{1}{2}$.

LS Coupling

When more than one electron contributes orbital and spin angular momenta to the total angular momentum **J** of an atom, **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 the various electrons are coupled together into a single resultant **L**. The spin angular momenta $\mathbf{S}_i$ 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:

***LS* coupling**

$$\begin{aligned} \mathbf{L} &= \Sigma\, \mathbf{L}_i \\ \mathbf{S} &= \Sigma\, \mathbf{S}_i \\ \mathbf{J} &= \mathbf{L} + \mathbf{S} \end{aligned} \tag{7.19}$$

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, $\mathsf{M_L}$, $\mathsf{M_S}$, and $\mathsf{M_J}$. Hence

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

Both L and $\mathsf{M_L}$ 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 $\mathsf{L} > \mathsf{S}$, J can have $2\mathsf{S} + 1$ values; when $\mathsf{L} < \mathsf{S}$, J can have $2\mathsf{L} + 1$ values.

Example 7.4

What are the possible orientations of **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 **J** relative to the z axis for these values of j.

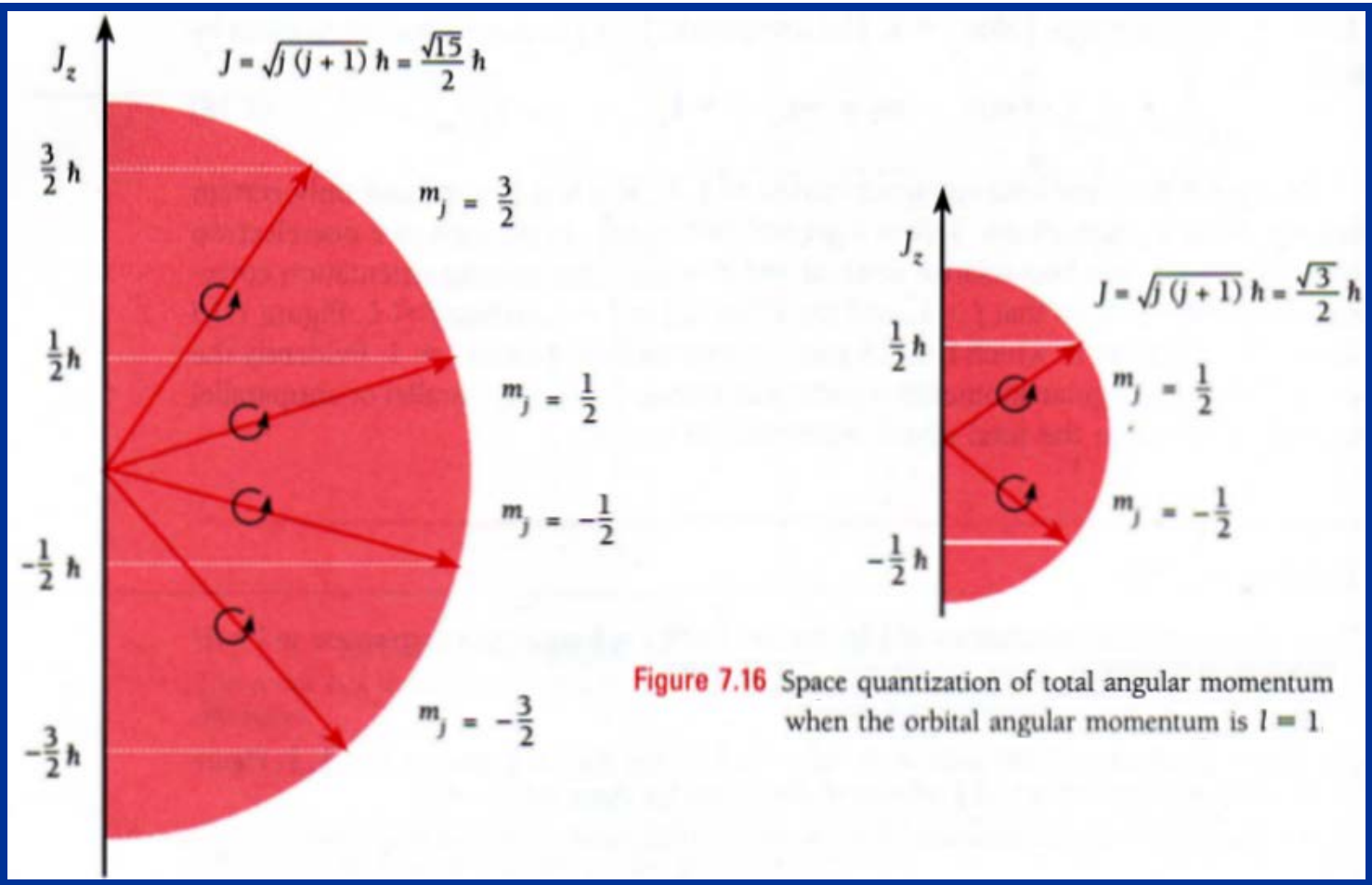


Figure 7.16 Space quantization of total angular momentum when the orbital angular momentum is $l = 1$.

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

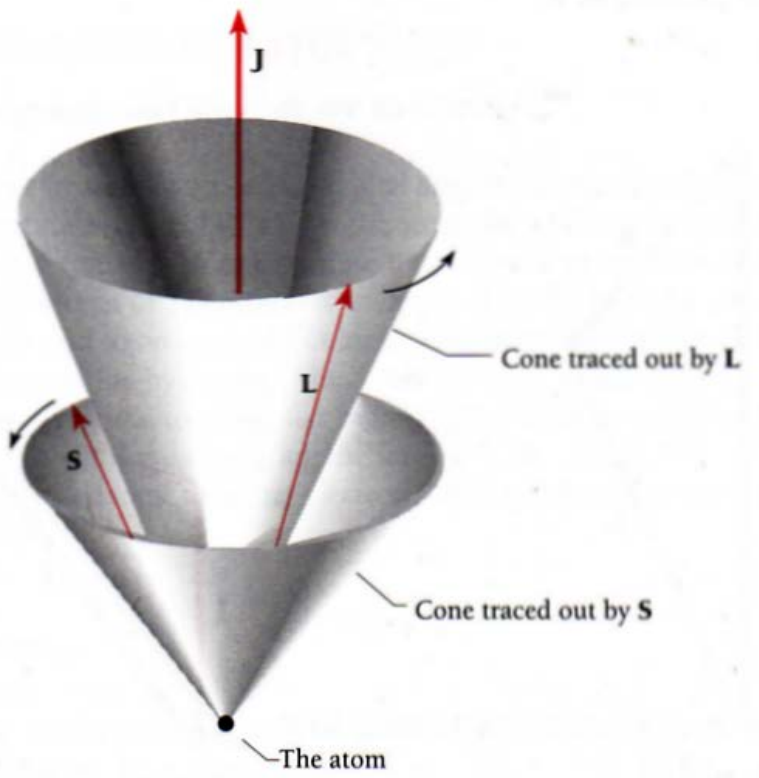


Figure 7.17 The orbital and spin angular-momentum vectors **L** and **S** precess about **J**.

Link

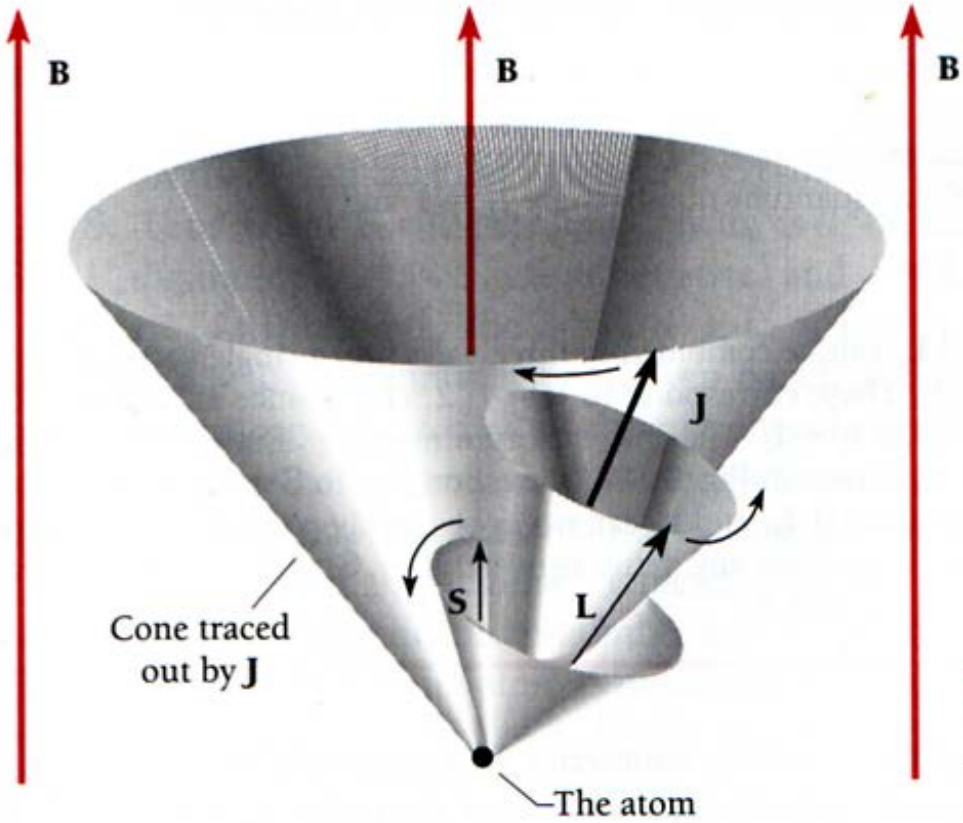


Figure 7.18 In the presence of an external magnetic field **B**, the total angular-momentum vector **J** precesses about **B**.

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. 7.19*a*, the vectors $\mathbf{L}_1$ and $\mathbf{L}_2$ can be combined in three ways into a single vector **L** that is quantized according to Eq. (7.20). These correspond to $\mathbf{L} = 1$, 2, and 3 since all values of **L** are possible from $|l_1 - l_2|$ (= 1 here) to $l_1 + l_2$. The spin quantum number s is always $\frac{1}{2}$, which gives the two possibilities for $\mathbf{S}_1 + \mathbf{S}_2$ shown in Fig. 7.19*b*, corresponding to $\mathbf{S} = 0$ and $\mathbf{S} = 1$.

We note that if the vector sums are not 0, $\mathbf{L}_1$ and $\mathbf{L}_2$ can never be exactly parallel to **L**, nor can $\mathbf{S}_1$ and $\mathbf{S}_2$ be parallel to **S**. Because J can have any value between $|\mathbf{L} - \mathbf{S}|$ and $\mathbf{L} + \mathbf{S}$, the five possible values here are $\mathbf{J} = 0$, 1, 2, 3, and 4.

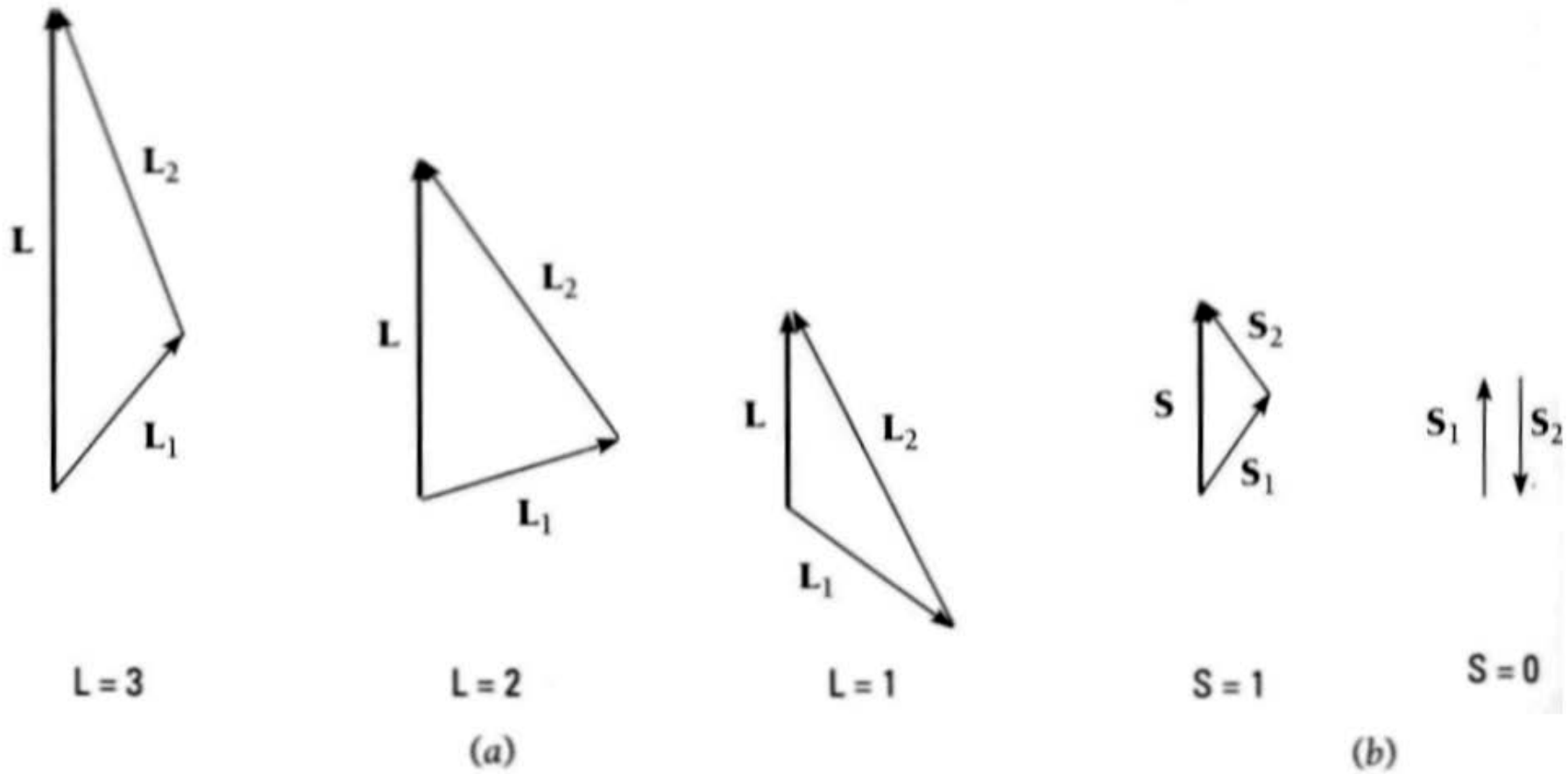


Figure 7.19 When $l_1 = 1$, $s_1 = \frac{1}{2}$, and $l_2 = 2$, $s_2 = \frac{1}{2}$, there are three ways in which $\mathbf{L}_1$ and $\mathbf{L}_2$ can combine to form $\mathbf{L}$ and two ways in which $\mathbf{S}_1$ and $\mathbf{S}_2$ can combine to form $\mathbf{S}$.

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:

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

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 $2\mathbf{S} + 1$ in the usual situation where $\mathbf{L} > \mathbf{S}$, since **J** ranges from $\mathbf{L} + \mathbf{S}$ through 0 to $\mathbf{L} - \mathbf{S}$. Thus when $\mathbf{S} = 0$, the multiplicity is 1 (a **singlet** state) and $\mathbf{J} = \mathbf{L}$; when $\mathbf{S} = \frac{1}{2}$, the multiplicity is 2 (a **doublet** state) and $\mathbf{J} = \mathbf{L} \pm \frac{1}{2}$; when $\mathbf{S} = 1$, the multiplicity is 3 (a **triplet** state) and $\mathbf{J} = \mathbf{L} + 1$, **L**, or $\mathbf{L} - 1$; and so on. (In a configuration in which $\mathbf{S} > \mathbf{L}$, the multiplicity is given by $2\mathbf{L} + 1$.) 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 $\mathbf{S} = \frac{1}{2}$, $\mathbf{L} = 1$, and $\mathbf{J} = \frac{3}{2}$. 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 $\mathbf{L} = 0$.

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

$$3^2S_{1/2}\colon\ n = 3,\ l = 0,\ j = \tfrac{1}{2},\ m_j = \pm\tfrac{1}{2}$$

$$3^2P_{1/2}\colon\ n = 3,\ l = 1,\ j = \tfrac{3}{2},\ m_j = \pm\tfrac{1}{2},\ \pm\tfrac{3}{2}$$

$$n = 3,\ l = 1,\ j = \tfrac{1}{2},\ m_j = \pm\tfrac{1}{2}$$

Example 7.7

Why is it impossible for a $2^2P_{5/2}$ state to exist?

Solution

A P state has $\mathbf{L} = 1$ and $\mathbf{J} = \mathbf{L} \pm \frac{1}{2}$, so $\mathbf{J} = \frac{5}{2}$ 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 electron-volts 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 3*s* electron, whereas the corresponding figures for the inner ones are 31 eV for each 2*p* electron, 63 eV for each 2*s* electron, and 1041 eV for each 1*s* 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 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.

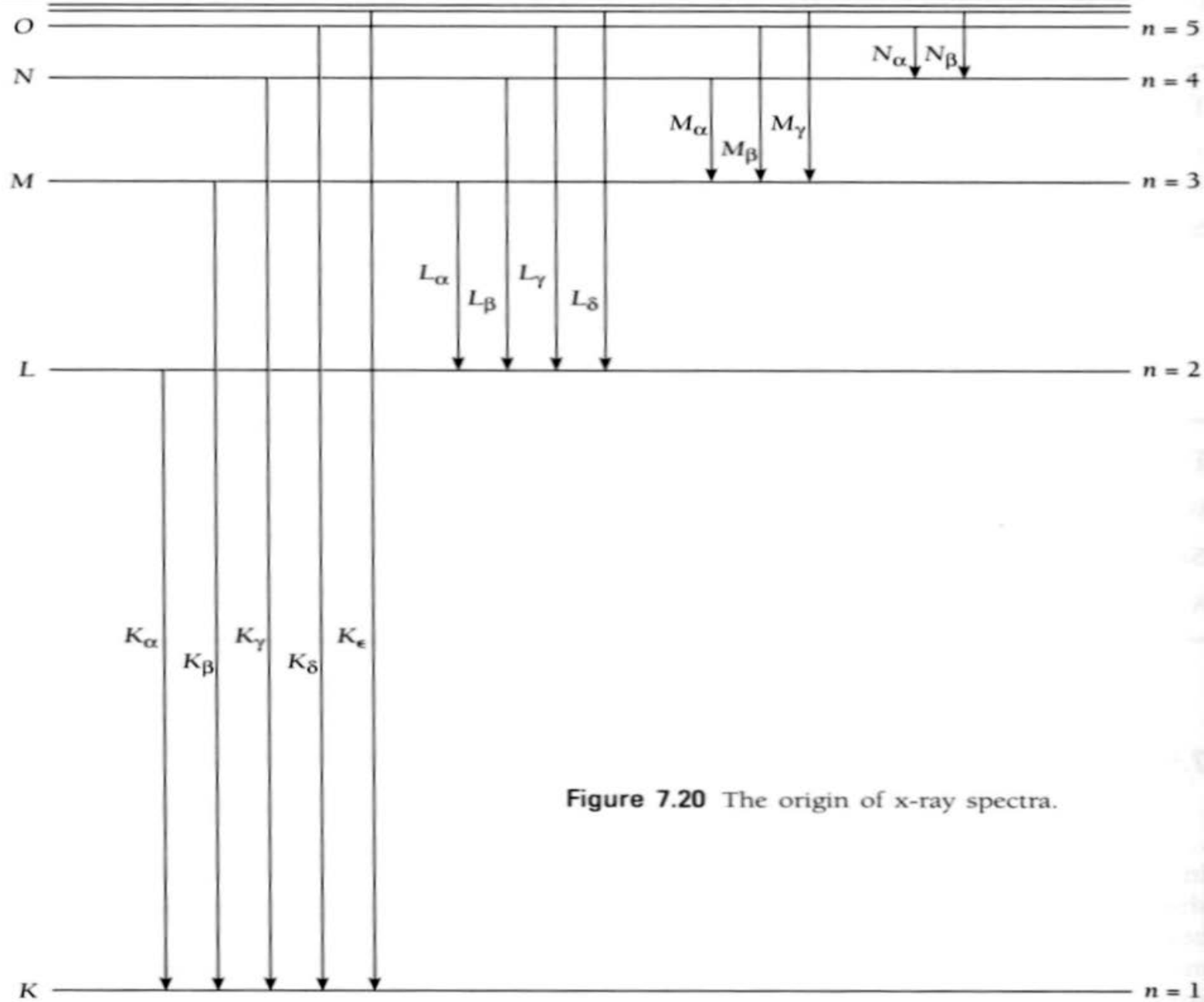


Figure 7.20 The origin of x-ray spectra.

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 $(Z - 1)^2 e^4$. This gives

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

K_α x-rays

$$\nu = \frac{3cR(Z-1)^2}{4} \tag{7.21}$$

where $R = me^4/8\epsilon_0^2 ch^3 = 1.097 \times 10^7\ \mathrm{m}^{-1}$ 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

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

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In 1913–1914 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 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. 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.

Summary for this Chapter (things you need to know)

Spin

•Why do we have to introduce Spin? What is the spin quantum number? What is the spin angular momentum? What is the z-component of spin angular momentum? (What is the z-component of spin magnetic moment?)

•What did the Stern-Gerlach experiment confirm?

•How many quantum numbers we need to determine a quantum state of an electron? What the quantity does each of the quantum numbers determine?

Many Electron Atoms

•What is Pauli Exclusion Principle?

•What is the origin of the periodic table?

•What are the shell and subshell capacities?

•What is the Hund's Rule?

•What is the Spin-Orbit coupling?

•What is the LS coupling?

•How does X-ray arise from? What do the K-series, L-series, etc mean?

TABLE 6.2 Atomic Electron States

	$l = 0$	$l = 1$	$l = 2$	$l = 3$	$l = 4$	$l = 5$
$n = 1$	1s					
$n = 2$	2s	2p				
$n = 3$	3s	3p	3d			
$n = 4$	4s	4p	4d	4f		
$n = 5$	5s	5p	5d	5f	5g	
$n = 6$	6s	6p	6d	6f	6g	6h

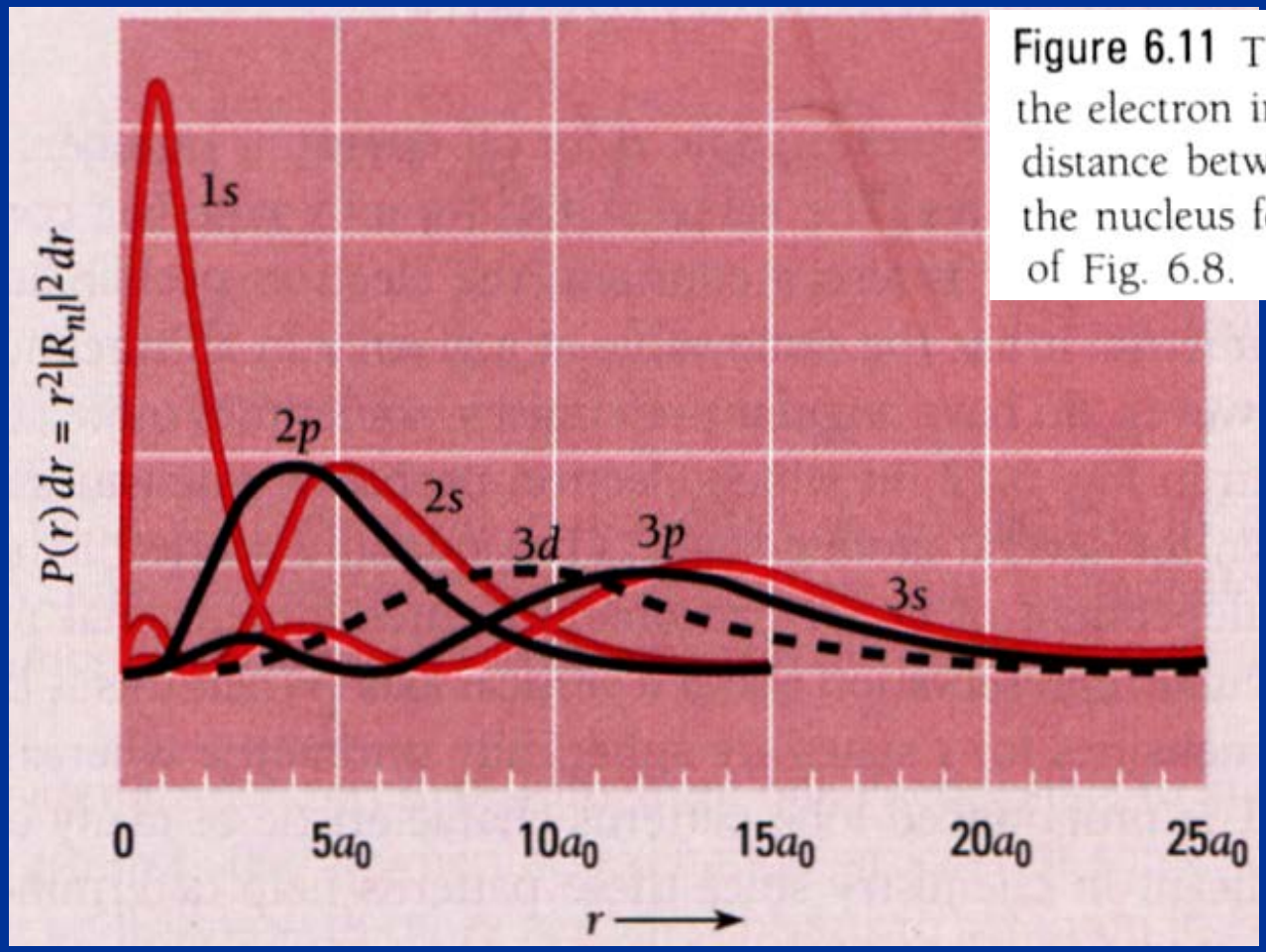
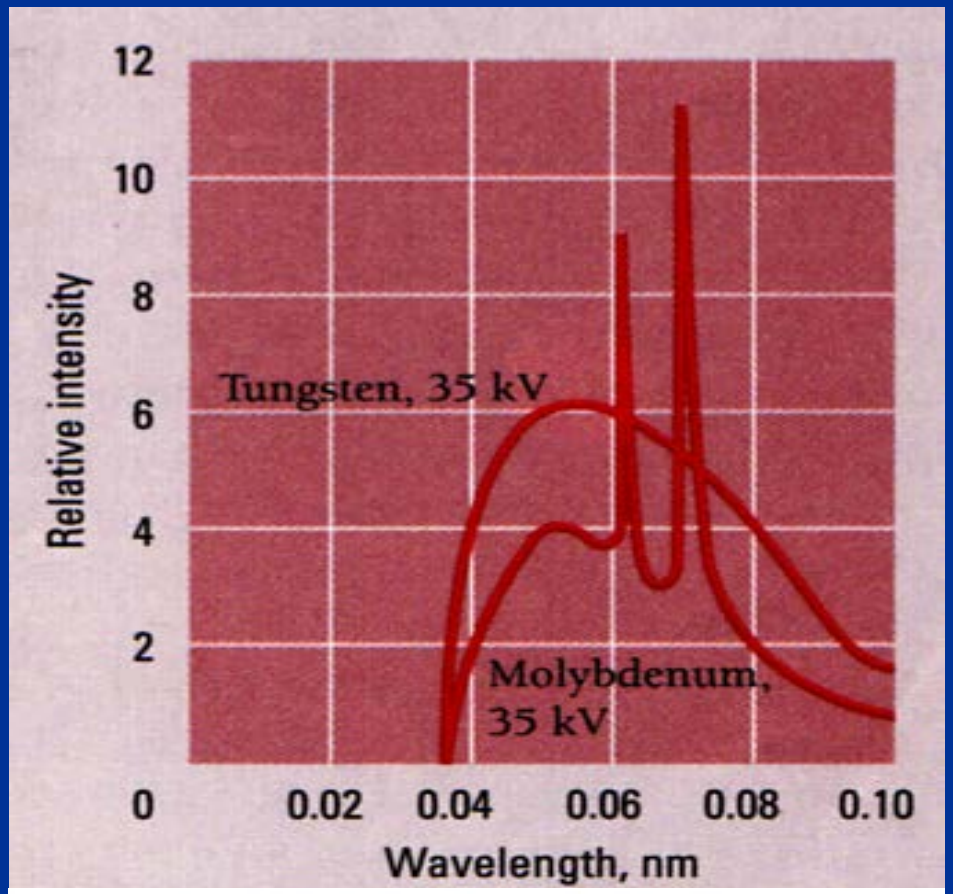


Figure 6.11 The probability of finding the electron in a hydrogen atom at a distance between r and $r + dr$ from the nucleus for the quantum states of Fig. 6.8.



X-ray spectra of tungsten and molybdenum at 35 kV accelerating potential.

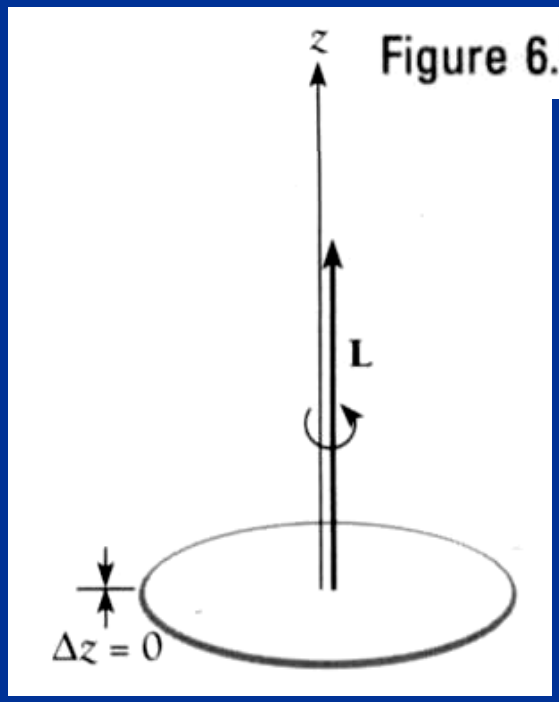


Figure 6.5 (*a*)

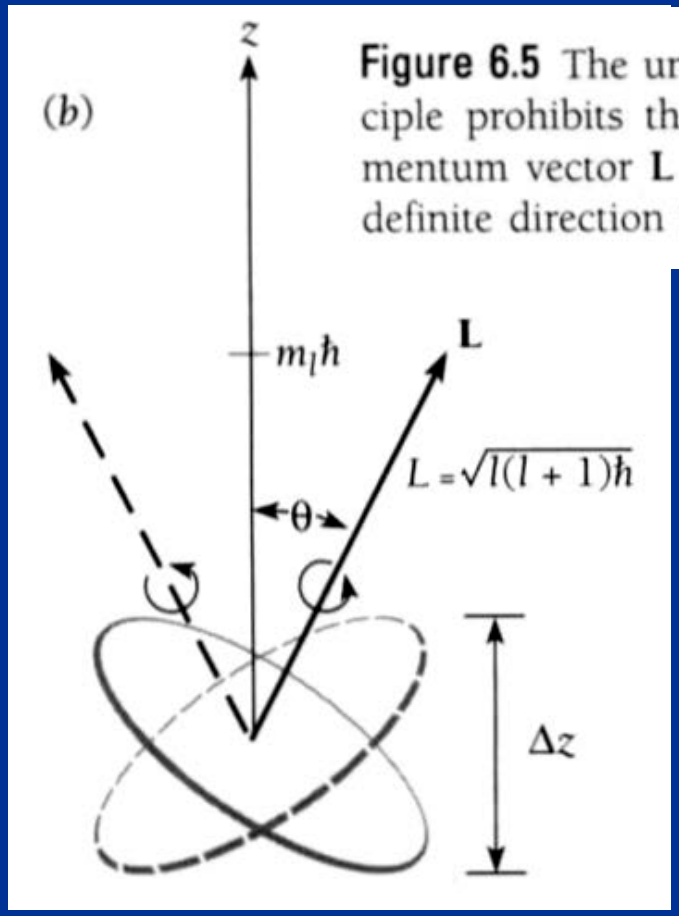


Figure 6.5 The uncertainty principle prohibits the angular momentum vector **L** from having a definite direction in space.

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