

CHAPTER 5

The Structure of Atoms

The last chapter gave us a comprehensive picture of the nature of the hydrogen atom, or of any atom containing a single electron. However, most of our world (though not most of the universe) is made up of atoms containing more than one electron. It is the purpose of this chapter to describe these more complex atoms.

How might we construct a many-electron atom? We naturally begin with a nucleus with the desired positive charge $+Ze$. We know from Chapter 4 what is obtained when we add a single electron to the nucleus: a species whose radial wave functions and energy levels differ from those of hydrogen only by scale factors. The natural step is to add a second electron, then a third, and so on until Z electrons have been added to give a neutral atom. But what rules govern the addition of these electrons? Each interacts not only with the nucleus, but with all the other electrons. These interactions involve not only the electrostatic forces but the magnetic properties of electrons as well. An accurate description of a many-electron atom must thus be quite complex. Fortunately, in many cases one can construct a useful approximation by assigning each electron its own set of quantum numbers, its own corresponding constants of motion, and its own wave function, or orbital, analogous to the wave functions of the hydrogen atom. We must determine the sequence of energies of these functions, which dictates the order in which these orbitals are "occupied." This sequence is governed by the Pauli exclusion principle, which says that each orbital has only a limited capacity to contain electrons. In fact, no two electrons can have the same values of the one-electron quantum numbers n , l , m , and m_s , where m_s is a quantum number for a property we shall introduce in the next section, called the electron spin.

Given the basic concepts of atomic structure, we go on to discuss several effects that influence the details of electron configurations and energies in individual atoms. Finally, we begin to explain how chemical behavior can be interpreted in terms of the microscopic structure of atoms.

5.1 Electron Spin; Magnetic Phenomena

Until now we have treated electrons as though they were simple charged mass points. This is an oversimplification. In reality, electrons (and other particles) behave in some ways as though they are spinning about their own axes. We shall examine some of the evidence for this conclusion, but first let us explain what it means by comparing spin and orbital motion.

We designate the spin angular momentum by the vector \mathbf{S} , just as we use \mathbf{L} to represent the electron's orbital angular momentum about the atomic nucleus. The spin angular momentum behaves in most ways like other angular momenta. Its magnitude $|\mathbf{S}|$ for a single electron is given by

$$|\mathbf{S}|^2 = s(s+1)\hbar^2, \quad (5.1)$$

where s is a quantum number; this is completely analogous to the relation $|\mathbf{L}|^2 = l(l+1)\hbar^2$ for the orbital angular momentum (Section 3.11). Thus $|\mathbf{S}|^2$ is an eigenvalue of an operator \mathbf{S}^2 , which we shall not discuss further. As with the other quantum numbers, we use the lowercase s for a single electron and the capital letter S for the total spin of an atom. Equations 5.1 and 3.162 still apply to the total atom, with S , L replacing s , l . (Note that we must now write the magnitudes of the angular momenta as $|\mathbf{S}|$, $|\mathbf{L}|$, because S , L are reserved for the quantum numbers.) One major difference between the spin and orbital angular momenta is in the values that the quantum numbers may have. For a single electron, s always has the value $\frac{1}{2}$, whereas you will recall that l may be any non-negative integer. When a system contains two or more electrons, the total spin (or orbital) angular momentum is the *vector* sum of the individual electronic angular momenta; we shall return later to this point.

The components of the spin angular momentum are also analogous to those of the orbital angular momentum. Only one component is a constant of the motion, characterized by a quantum number; as usual, we define this as the z component. Its value is given by

$$S_z = m_s \hbar, \quad (5.2)$$

analogous to Eq. 3.156, with the quantum number m_s (or M_s). Usually m_s is called the *spin quantum number* and s simply the *spin* ("the electron has spin $\frac{1}{2}$ "). The magnetic quantum number that we called m in the hydrogen atom can be designated as m_l (or M_l) for uniformity. Just as m_l can range from $+l$ to $-l$ in integral steps, the values allowed for m_s are $s, s-1, \dots, -s+1, -s$. Hence, for a single electron, the only possible values are $m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$; the corresponding values of S_z are $+\hbar/2$ and $-\hbar/2$.

The total angular momentum is designated as $\mathbf{J} \equiv \mathbf{L} + \mathbf{S}$, with quantum numbers j, m_j (or J, M_j). We postpone a full discussion of \mathbf{J} until Section 5.7.

Being charged, any spinning or orbiting electron constitutes an electric current moving in a loop; like any such loop current (as in a solenoid), it acts as a bar magnet or magnetic dipole. From this magnetic behavior, the existence of spin or orbital angular momentum can be deduced. In the presence of an external magnetic field \mathbf{B} , the potential energy of a microscopic magnetic dipole is given by

$$V_{\text{dipole-field}} = -\boldsymbol{\mu}_m \cdot \mathbf{B} = -\mu_m B \cos \theta, \quad (5.3)$$

where $\boldsymbol{\mu}_m$ is the *magnetic dipole moment*, analogous to the electric dipole moment $\boldsymbol{\mu}_e$ of Eq. 4.30. The potential energy thus has its minimum when $\boldsymbol{\mu}_m$ and \mathbf{B} are parallel; since $\boldsymbol{\mu}_m$ by definition is directed from the "south" to the "north" (north-seeking) pole of the magnet, this occurs when the north pole points in the direction of the external field.

Both the electron's orbital motion and its spin about its own axis produce magnetic dipole moments. The orbital moment $\boldsymbol{\mu}_l$ in the Bohr model is given by

$$\boldsymbol{\mu}_l = -\frac{e}{2m_e} \mathbf{L}, \quad (5.4)$$

from the classical equation for a current moving in a circular loop. Let us take our z axis in the direction of \mathbf{B} . The component of $\boldsymbol{\mu}_l$ in the direction of the magnetic field is then

$$(\mu_l)_z = \mu_l \cos \theta = -\frac{e}{2m_e} L_z = -\frac{e\hbar}{2m_e} m_l. \quad (5.5)$$

The quantized unit of $(\mu_l)_z$ is thus

$$\mu_B \equiv \frac{e\hbar}{2m_e} = 9.274009 \times 10^{-24} \text{ J/T} \quad (5.6)$$

(T = tesla), known as the *Bohr magneton*.¹ Equation 5.5 is not exactly correct, because m_e should be replaced by the reduced mass and there is a slight interaction with the spin moment.

The spin magnetic dipole moment $\boldsymbol{\mu}_s$ does not obey the classical Eq. 5.4, but rather, an equation with an additional factor:

$$\boldsymbol{\mu}_s = g_s \left(\frac{-e}{2m_e} \right) \mathbf{S}, \quad (5.7)$$

where g_s (the *Landé g factor*) is approximately 2. The actual value of g_s for the electron is 2.002319, differing from exactly 2 because of relativistic and radiative effects. By reasoning like that leading to Eq. 5.5, the component of $\boldsymbol{\mu}_s$ in the direction of the external field must equal $-g_s m_s$ Bohr magnetons; since $m_s = \pm \frac{1}{2}$, we have $(\mu_s)_z \approx \pm \mu_B$. If the electron were literally a charged particle spinning about its axis, the spin magnetic dipole moment and spin angular momentum would be related by the equivalent of Eq. 5.4; that is, g_s would have to be 1. The fact that this is not so shows that the electron spin is an essentially quantum mechanical phenomenon. Strictly, one can say only that the electron somehow has an intrinsic angular momentum \mathbf{S} ; the idea of "spin" is meaningful only as a convenient visualization, but the language has stuck.

We can now see why m_l is called the "magnetic" quantum number. In the absence of a magnetic field, all states with the same n and l have the same energy (except for fine-structure splitting). Once we apply an external field \mathbf{B} , however, the energy of each state changes by the amount given by Eq. 5.3. The total energy of an atom in a given state is thus shifted by an amount

$$\begin{aligned} E - E_0 &= -(\boldsymbol{\mu}_L + \boldsymbol{\mu}_S) \cdot \mathbf{B} = -(\mu_L + \mu_S)_z B \\ &= -\mu_B (M_L + g_s M_S) B; \end{aligned} \quad (5.8)$$

the splitting of spectral lines due to this process is called the *Zeeman effect*.² In the "normal Zeeman effect," for atoms with $S = 0$ (and thus $M_S = 0$), the adjacent energy levels are separated by an amount $\mu_B B$. In a moderately large field of 1 T (10^4 G), this splitting is about 9.3×10^{-24} J (or 5.8×10^{-5} eV), equivalent to less than 0.5 cm^{-1} . For nonzero spin the spectrum is more complicated ("anomalous Zeeman effect"), and spin-orbit interactions produce splitting even with no external field. It was to account for this behavior that George Uhlenbeck and Samuel Goudsmit (1925) proposed the hypothesis of electron spin.

¹ In Gaussian units one writes $\mu_l = -(e/2m_e c) \mathbf{L}$, and the Bohr magneton is $eh/2m_e c = 9.27410 \times 10^{-21} \text{ erg/G}$ (G = gauss). The SI unit can be written as either joules per tesla or ampere meters².

² An external electric field produces a similar splitting known as the *Stark effect*.

The electron is not the only particle with spin. In particular, both the proton and the neutron also have spin $\frac{1}{2}$. The total nuclear spin I is the vector sum of the individual nucleon spins; I is seldom large, and often is zero. Nuclear magnetic moments are far smaller than those of electrons, being measured in terms of the *nuclear magneton*,

$$\begin{aligned}\mu_N &\equiv \frac{e\hbar}{2m_p} = \mu_B \left(\frac{m_e}{m_p} \right) \\ &= \frac{\mu_B}{1836.15} = 5.050783 \times 10^{-27} \text{ J/T.}\end{aligned}\quad (5.9)$$

The proton and neutron have moments $\mu_p = 2.793\mu_N$ and $\mu_n = 1.913\mu_N$, respectively. The energy-level splitting of these particles in a magnetic field is correspondingly small, about 10^{-3} of that for an electron; heavier nuclei have even smaller splittings.

In spite of the minuscule size of these energy shifts, one can measure them quite accurately by the method of *nuclear magnetic resonance (nmr)*. One places the system in a strong magnetic field (≈ 1 T), passes a radiofrequency (rf) signal through it ($\nu \approx 100$ MHz), and varies B slowly until ΔE for some magnetic transition is equal to $h\nu$; the energy difference is then in *resonance* with the applied radiation, and absorption occurs. In the original approach, still occasionally used, the operator swept the field strength $|B|$ and recorded the absorption of rf power, thus producing a *magnetic resonance* spectrum. Now, more sophisticated methods use pulses of rf power, singly or in sequences, producing a time response in the system that can, in effect, be “decoded” to yield the spectrum of resonant energy intervals.³ Nuclear

magnetic moments observed this way can act as probes to tell us a good deal about the structure of atoms and molecules. This is possible because a nucleus is not merely acted upon by an external field, but is affected in a delicate and sensitive way by the fields of all the other particles (nuclei and electrons) in its vicinity. For example, a proton in an —OH group is in a slightly different field than a proton in a —CH₃ group, and protons in these two environments have slightly different spacings of their energy levels. Hence they exhibit resonances at slightly different magnetic field strengths in an oscillating field of fixed frequency. The *chemical shifts* of lines in the magnetic resonance spectrum are very small indeed, of the order of 10^{-6} of the total energy-level splitting, but they can be measured accurately. The detailed shape of the absorption spectrum can be interpreted to reveal much information about the environment of the nucleus studied, whether it is a proton or a heavier, more complex nucleus.

One can, of course, observe similar effects in the energy-level splittings due to electron spin. These are studied by the method of *electron spin resonance (esr)*, which gives information mainly on the electron distribution in molecules. Because of the larger magnetic moment of the electron, the esr transitions occur at higher frequencies, mainly in the microwave region. However, atoms or molecules with net electron spins different from zero are relatively uncommon, whereas nonzero nuclear magnetic moments are ubiquitous.

Energy levels of magnetic systems and magnetic resonance spectra often serve as useful models because of a special simplicity they have: Such systems have only a finite number of states and energy levels. This is quite different from any of the systems we have examined previously; those all have infinite numbers of states and levels. The hydrogen atom, for example, has an infinite number of bound states and then, of course, has all its continuum levels. We shall see in Chapter 16 and especially in Chapter 20, how a particular concept, that of negative absolute temperature, can be developed consistently for systems with only a finite number of states.

The astute reader will have recognized by now that although we have introduced several kinds of magnetic moments into our model of the atom, associated with electron spin, electron orbital motion, and nuclear spin, we have said little about the obvious problem that such magnetic moments must interact with one another. Indeed they do, but their interactions are weak and need not concern us in detail at this point. The interaction of electron spin and orbital moments, called *spin-orbit interaction*, is important for the energy levels of heavy atoms, and is measurable but relatively unimportant for the chemical properties of light atoms. Spin-orbit interaction is discussed in Section 5.7. The interactions among nuclear moments and between nuclear and electron moments are crucial for the use of nuclear and electron spin magnetic resonance as analytic and diagnostic tools; the identification of lines in nuclear resonance spectra

³ The method of “decoding” is called *Fourier analysis*. Any smooth function can be constructed (or expressed) by adding, with suitable amplitudes, sines and cosines. If the function lies within a finite interval, then that sum of sines and cosines is a discrete sum. Thus, for example, if we want to describe a function $f(t)$ in the interval from $t = 0$ to $t = 1$, then we may write $f(t) = \sum_{j=0}^{\infty} [a_j \sin(2\pi jt) + b_j \cos(2\pi jt)]$. If the interval is not that from 0 to 1, then we must just rescale the arguments of the sines and cosines by dividing t by the length of the interval and, if necessary, by shifting the origin so that the new variable lies in the interval from 0 to 1. If the variable t may range to ∞ , then the sum must be replaced by an integral, and the discrete index j , by a continuous index with the dimension of $[t]^{-1}$, i.e., a frequency ν . Thus, $f(t) = \int_0^{\infty} [a(\nu) \sin(2\pi \nu t) + b(\nu) \cos(2\pi \nu t)] d\nu$. To carry out a modern analysis of a magnetic resonance spectrum, one applies a magnetic field as an intense pulse for which the coefficients $a(\nu)$ and $b(\nu)$ are known—that is, a pulse whose time dependence is known. One measures the response, the changes of that applied pulse that produce an outgoing signal. The changes occur only at the frequencies ν , at which the system can exhibit a resonant response. Thus, the decoding process is one of finding those frequencies for which $a(\nu)$ and $b(\nu)$ change because the system under study responds to the applied pulse. These pulses may have durations as short as milliseconds or microseconds, they may be applied repetitively as a sample is moved, and may be focused to particular locations in space. These qualities have made magnetic resonance, especially nuclear magnetic resonance, a powerful tool for studying objects as complex as the human body, notably in the form known as *magnetic resonance imaging (MRI)*.

generally depends on knowing how one nuclear magnetic moment interacts with those of its neighbors.

Something should be said here about the origins of *macroscopic* magnetism. All the individual electrons in a material are tiny magnets, but ordinarily they are aligned at random and, in large numbers, cancel one another on average. An external magnetic field, however, tends to align the microscopic magnets; the net effect is to make \mathbf{B} slightly higher within the material than in a vacuum.⁴ This phenomenon is called *paramagnetism*. Both orbital and spin magnetic moments can contribute to paramagnetism. However, because the orbital moments are largely fixed in space by the molecular structure, it is mainly the spin moments that change their alignment in the presence of a field. Paramagnetism is thus rarely found in substances whose total molecular spin is zero, that is, for which the spin magnets cancel out within the molecule; such substances are called *diamagnetic*. In diamagnetic materials \mathbf{B} is actually a little less than in a vacuum because the field interferes with the orbital motions, but the effect is much smaller than it is in paramagnetism. Paramagnetic substances are weakly attracted, diamagnetic substances weakly repelled, by a magnet. As for the very large permanent magnetism that can be induced in metals like iron (*ferromagnetism*), this results from a cooperative interaction among spins on different atoms: For certain substances the electron spins are thus aligned in parallel over large regions or *domains*, appreciably reducing the total energy of the crystal.

We have introduced electron spin primarily because it is an important property in its own right: The total state of an electron is specified only when its spin is added to all the other properties characterized by quantum numbers. Moreover, it must be introduced to provide a full basis for the exclusion principle, which, in turn, underlies atomic structure. Spin is one of the properties that could not have been predicted from classical mechanics. It is illustrated by one of the most famous and fundamental experiments on which quantum theory rests, the Stern–Gerlach experiment. Appendix 5A describes this experiment.

5.2 The Pauli Exclusion Principle; the Aufbau Principle

The set of quantum numbers n , l , m_l , and m_s , and the physical attributes to which they correspond, give us the basis for

our first approach to the structure of complex atoms. In this section we shall see how electrons fit together to give each atom a sort of shell-like structure; this will lead us to a systematic interpretation of the periodic table. The model we discuss here is only approximate. In subsequent sections, we shall consider the validity of our approximations and the refinements necessary for a detailed explanation of atomic structure.

Consider first an ion made up of a nucleus with charge $+Ze$ ($Z > 1$) and a single electron bound to that nucleus. This is a hydrogenlike ion of the type discussed in Chapter 4, where we characterized the electron by the quantum numbers n , l , m (or m_l). We must now add the spin quantum number m_s to give a complete description of the state of the electron. Let us denote these four quantum numbers of the first electron by n_1 , l_1 , m_{l1} , m_{s1} , because we shall add another $Z - 1$ electron, one by one, to neutralize the total nuclear charge.

Suppose that we add a second electron to the ion, and that there are states in which both electrons are bound to the nucleus. To a first approximation, known as the *central field approximation*, the second electron can be treated as though it moves in the field of the nucleus and the *average* field produced by the first electron. In other words, we pretend that the second electron sees only a smeared-out charge cloud equivalent to the average spatial distribution of the first electron. Carrying the approximation a bit further, we also assume that the first electron responds to the *average* field of the second, rather than to its field at each instant.

The central field approximation permits us to assign to the second electron a one-electron wave function with a set of quantum numbers n_2 , l_2 , m_{l2} , m_{s2} . The energy levels and the shapes of the spatial wave functions or orbitals for the atom or ion with two electrons are somewhat different from those of the one-electron ion, for reasons we shall see very shortly. However, the quantum numbers retain the same basic meaning in both situations. The principal quantum number n is one more than the number of radial nodes in the one-electron wave function, and is the first guide to the energy; l specifies the electron's orbital angular momentum, and gives the number of angular nodes; m_l specifies the orientation of the electron's orbital angular momentum \mathbf{L} ; and m_s specifies the orientation of its spin angular momentum \mathbf{S} .

Suppose that the two-electron species, for example, the helium atom with $Z = 2$, is in its state of lowest energy. It would be natural to assume that both electrons then have the same quantum numbers, presumably those of the lowest state in the one-electron atom. This is correct for the quantum numbers n , l , and m_l , which for both electrons have the values $n = 1$, $l = 0$, and $m_l = 0$. (Remember that $n = 1, 2, \dots$, whereas $0 \leq l \leq n - 1$ and $|m_l| \leq l$.) However, both electrons cannot have the same value of m_s : One has $m_s = +\frac{1}{2}$, the other $m_s = -\frac{1}{2}$, and the total electron spin is zero. Here is a point where our classical intuition fails us, and we must introduce a quantum mechanical postulate to describe the way in which electrons behave. It is found that any two electrons in a single atom with the same values of n , l , and m_l

⁴ In a vacuum we have $\mathbf{B} = \mu_0(1 + \chi)\mathbf{H}$, where \mathbf{H} is the magnetic field strength (see footnote 8, p. 12, Chapter 1); \mathbf{H} is determined only by the external field source and any permanent magnetic movements of the matter in the field. Within a material we write $\mathbf{B} = \mu_0(1 + \chi)\mathbf{H}$, defining the *magnetic susceptibility* χ ; χ is positive in paramagnetic substances, negative in diamagnetic substances. One usually tabulates the molar susceptibility $\chi_M = \chi M/\rho$ (where M is molecular weight and ρ is density); a typical value for a paramagnetic metal would be about 10^{-10} m³/mol. We shall discuss magnetic susceptibility in greater detail in Section 9.6.

always have different values of m_s . More generally, in any atom or ion, *no two electrons ever share the same four quantum numbers*. This rule, proposed empirically by Wolfgang Pauli in 1925, is known as the *Pauli exclusion principle*. For the time being we shall take the exclusion principle as a postulate in its own right; in Section 6.7 we shall give a more general rule from which it can be derived.

The exclusion principle imposes strict conditions on the assignment of quantum numbers. We have assigned $n = 1$, $l = 0$, $m_l = 0$ to the first two electrons, which must have $m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$, respectively. Now suppose that $Z \geq 3$, and we add a third electron, as, for example, in Li with $Z = 3$. There is no way to assign this electron to a state with $n = 1$, because all the possible combinations of n , l , m_l , and m_s correspond to states already occupied. We must thus assign the third electron a quantum number n_3 greater than 1. If we set $n_3 = 2$, then we may have $l_3 = 0$ or $l_3 = 1$. If $l_3 = 0$, then m_{l3} is necessarily 0; if $l_3 = 1$, then m_{l3} may be 0, +1, or -1; whatever values we assign l_3 and m_{l3} , the quantum number m_{s3} may be either $+\frac{1}{2}$ or $-\frac{1}{2}$. Which of all these states will the electron occupy? It may occupy any of them, but the most stable state is that of lowest energy, the ground state. To begin with, the energy nearly always increases with the value of n ; an electron will thus ordinarily take the lowest available value of n , in this case 2. Among states with the same value of n , the states with $l = 0$ normally have energies lower than those with $l = 1$, and so forth; the energies increase with increasing l . In the absence of external fields, and with internal electron-electron interactions neglected, states with the same n and l but different m_l or m_s differ only in orientation, and therefore must have the same energy.

In the hydrogen atom, whose electron moves in the Coulomb field of a single proton, the energy depends only on the principal quantum number n ; it makes no difference energetically what value we assign to l . This is a special property of two particles interacting through a Coulomb field. In more complex atoms, the field felt by each electron is a combination of the field of the nucleus and the fields of the other electrons, which have probability distributions extending over considerable regions of space. The effect of the other electrons is really twofold. First, each of them exerts a Coulomb force of the classical type; second, the mere presence of an electron at a point \mathbf{r} reduces the probability that another electron of the same spin be in the vicinity of \mathbf{r} . The latter is a purely quantum mechanical phenomenon, with no classical equivalent; it is a direct result of the exclusion principle. The net effect is as if there were an additional repulsive force (sometimes called *exchange force*) added to the Coulomb repulsion between electrons of the same spin. This is not a real force, represented by a term in the Hamiltonian; rather, we introduce the effect as a constraint on the form of the wave function, which has the effect of changing the charge distribution from that of the unconstrained wave function. As a result of these interactions the field on each electron is significantly different from that of

a simple, central Coulomb field. Because of the more complex field in a many-electron atom, the electron's energy depends on its angular momentum; thus the energies of states with the same n but different l are separated (split). In general, as we said previously, for a given n the energy increases with l . The reason should be clear from Fig. 4.5: The higher the value of l , the less likely an electron is to be found near the nucleus.

At this point we must say something about the word "orbital." We introduced this term in Section 4.3 to refer to a single-electron eigenfunction, but it is also loosely used for the corresponding state: One says that an electron is *in* a given orbital. By referring to one-electron states as orbitals, one can maintain a clear distinction between the true state of the entire atom, a concept that need imply no approximations, and the state of an individual electron, a concept associated with a particular approximate description of nature and therefore limited in its precision and applicability.

The complete wave function of an electron must include the spin as well as the spatial coordinates; we might write it as $\psi(r, \theta, \phi; m_s)$. To a very good approximation, however, the spin-orbit interaction can be neglected, and the Hamiltonian is separable into spatial and spin terms. We can then as usual factor the wave function, say, as $\psi(r, \theta, \phi)\alpha(m_s)$. It is the spatial part of the eigenfunction that is ordinarily called an "orbital." Two electrons with the same values of n , l , m_l have the same spatial wave function, and are thus said to occupy the same orbital.⁵ Every orbital can thus contain two electrons, which by the exclusion principle must have different values of m_s . An orbital is characterized by its values of n , l , m_l , but usual notation ignores m_l (which, to the extent that the simple orbital picture is valid, does not affect the energy) and uses the s , p , d , . . . notation to identify l . The first two electrons in an atom are thus said to be in a $1s$ ($n = 1$, $l = 0$) orbital, and the third should go into a $2s$ ($n = 2$, $l = 0$) orbital, which has a lower energy than a $2p$ ($n = 2$, $l = 1$) orbital.

The conditions imposed by the exclusion principle, together with our knowledge about energy levels, provide us with a rather accurate guide for describing the structure of atoms of any complexity in their ground states. This guide is a way of assigning quantum numbers, and implicitly wave functions, to each electron in the atom. In effect, we build up the atom by assigning one electron at a time to the available orbital of lowest energy. This is called the *Aufbau* (building-up) *principle*. The method is rather like adding marbles, one at a time, to a conical cup. The first marble goes to the bottom (the state of lowest energy in the earth's gravitational field), and successive marbles pile up as they can, each in the lowest place where there is room.

⁵ The wave function including spin is called a *spin orbital*, and this is restricted to a single electron. In this text we do not consider the nature of the function $\alpha(m_s)$ or the corresponding operator, for which a relativistic theory must be used.

We have already considered the ground states of the first few atoms. Now we shall extend this analysis to the entire periodic table.

5.3 Electronic Configurations of Atoms

For most purposes one can classify any state of an atom by giving the principal quantum number n and the angular momentum quantum number l for each of the electrons in the atom. It is these quantum numbers that largely determine the atom's energy and chemical behavior; varying the value of m_l or m_s makes only a very slight difference, which in first approximation we neglect altogether. A given assignment of n and l to all the electrons in an atom is called a *configuration*. Although it is not strictly correct to say that any atomic state is identical with a particular configuration, it is accurate to say that almost all known atomic states can be characterized by, and exhibit properties dominated by single configurations.

For an example of a configuration, let us consider the ground state of the nitrogen atom, which can be built up by adding seven electrons, one at a time, to a nucleus of charge $+7e$. As before, the first two electrons go into a $1s$ orbital. The third electron goes into a $2s$ orbital, with $n = 2$, $l = 0$, $m_l = 0$, and $m_s = \pm \frac{1}{2}$. The fourth can go into the same orbital, with the same values of n , l , m_l , and whichever value of m_s is not yet taken by the third electron. The next higher energy level is that with $n = 2$, $l = 1$, the $2p$ level, which can hold six electrons in three orbitals (with $m_l = +1, 0, -1$, respectively). The fifth, sixth, and seventh nitrogen electrons can thus all go into $2p$ orbitals. Later we shall have to consider which $2p$ orbitals they enter, but we do not need to know this here. Having said this much, we have specified the ground-state configuration of the nitrogen atom: There are two electrons in a $1s$ orbital, two in a $2s$ orbital, and three in $2p$ orbitals. The shorthand representation for this configuration is $1s^2 2s^2 2p^3$. In this notation each large number specifies the value of n , and the letter following it the value of l for a particular electronic state; the superscript gives the number of electrons with those values of n and l .

If one neglects electron-electron interactions and fine-structure effects, all the orbitals with the same values of n and l but different m_l have the same energy (in the absence of external fields). They differ only in the orientation of the electron's angular momentum with respect to an arbitrarily chosen axis. As in the hydrogen atom, their probability densities differ in orientation but not in radial distribution. The energies of the np , nd , . . . orbitals are moderately close to that of the ns orbital, but not equal to it except in the hydrogen atom. The radial distributions of the np , nd , . . . orbitals are also somewhat similar to that of the corresponding ns orbital at fairly large radii (cf. Fig. 4.5). Because of this similarity in both size and energy, one frequently refers to all the orbitals with the same n as a *shell*, and to those

with the same n and l as a *subshell*; this is the "shell model" of the atom. The shells with $n = 1, 2, 3, \dots$ are also referred to as the K, L, M, \dots shells. This terminology derives from x-ray spectroscopy (Section 2.3): The K series of emission lines are produced by electrons dropping into vacancies in the K or innermost shell, and so forth.

When all the quantum numbers available for a given shell or subshell have been assigned to electrons, it is said to be *filled* or *closed*. In the ground-state configuration of the nitrogen atom, the $n = 1$ or K shell (consisting of only the $1s$ subshell) is filled, the $2s$ subshell is filled, but the $2p$ subshell is only half-filled. There are still three vacancies in the $2p$ subshell, no matter how we assign the quantum numbers m_l and m_s , provided that we satisfy the exclusion principle. These vacancies are filled as we add more electrons, until in the neon atom ($Z = 10$) the shells with $n = 1$ and $n = 2$ are both completely filled.

To proceed any further we must know the sequence of orbital energy levels. The next section describes some of the ways these are derived; for the present, we can examine the levels as they turn out. One might assume that the energy increases in order from one shell to the next, and in the order s, p, d, \dots within each shell. This would give the sequence $1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f, 5s, \dots$. This scheme is valid through the $3p$ subshell, which is filled in the ground state of the argon atom ($Z = 18$). In the potassium atom ($Z = 19$), however, the nineteenth electron goes into a $4s$ rather than a $3d$ orbital. What happens is this: As the number of electrons increases, the energy difference between orbitals in the same shell becomes greater than the average energy difference between shells—in other words, the energy ranges spanned by the shells begin to overlap. One thus ought to know just how the energy levels vary as a function of Z , and we shall discuss this in the next section.

Fortunately, this detailed knowledge is not necessary to obtain a good approximation to the electronic configuration. The sequence in which orbitals are filled in the ground states of the elements is given with remarkable accuracy by the simple mnemonic device shown in Fig. 5.1. One need only remember that any subshell with angular momentum quan-

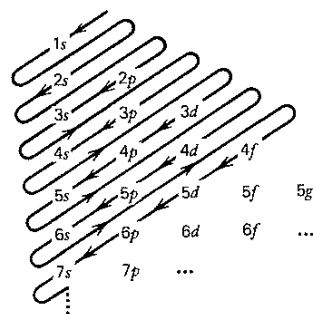


Figure 5.1 Approximate filling order of orbitals for the ground states of the elements.

turn number l can hold up to $2(2l + 1)$ electrons ($2l + 1$ possible values of m_l , each with two possible values of m_s): two in s subshells, six in p subshells, 10 in d subshells, and so forth. Given this information, and filling orbitals in the sequence indicated in Fig. 5.1, one can predict the ground-state configuration for any number of electrons.

The actual ground-state electronic configurations of the elements through Element 106, so far as they are now known, are given in Table 5.1. The configurations are obtained by analyses of electronic spectra, and in some cases (where two or more subshells are very close in energy) they are uncertain. Table 5.1 shows that the sequence predicted by Fig. 5.1

Table 5.1 Electronic Configurations of the Elements in Their Ground States

The configurations that differ from those predicted by Fig. 5.1 are indicated by a star (*). The symbol [(rare gas)] is an abbreviation for the inner electrons in the configuration of the ground state of the particular rare gas atom.

Z	Element	Configuration	Z	Element	Configuration	Z	Element	Configuration
1	H	$1s$	36	Kr	$[\text{Ar}]3d^{10}4s^24p^6$	71	Lu	$[\text{Xe}]4f^{14}5d^6s^2$
2	He	$1s^2$	37	Rb	$[\text{Kr}]5s$	72	Hf	$[\text{Xe}]4f^{14}5d^26s^2$
3	Li	$1s^22s$	38	Sr	$[\text{Kr}]5s^2$	73	Ta	$[\text{Xe}]4f^{14}5d^36s^2$
4	Be	$1s^22s^2$	39	Y	$[\text{Kr}]4d5s^2$	74	W	$[\text{Xe}]4f^{14}5d^46s^2$
5	B	$1s^22s^22p$	40	Zr	$[\text{Kr}]4d^25s^2$	75	Re	$[\text{Xe}]4f^{14}5d^56s^2$
6	C	$1s^22s^22p^2$	41	Nb	$[\text{Kr}]4d^45s^*$	76	Os	$[\text{Xe}]4f^{14}5d^66s^2$
7	N	$1s^22s^22p^3$	42	Mo	$[\text{Kr}]4d^55s^*$	77	Ir	$[\text{Xe}]4f^{14}5d^76s^2$
8	O	$1s^22s^22p^4$	43	Tc	$[\text{Kr}]4d^55s^2$	78	Pt	$[\text{Xe}]4f^{14}5d^96s^*$
9	F	$1s^22s^22p^5$	44	Ru	$[\text{Kr}]4d^75s^*$	79	Au	$[\text{Xe}]4f^{14}5d^{10}6s^*$
10	Ne	$1s^22s^22p^6$	45	Rh	$[\text{Kr}]4d^85s^*$	80	Hg	$[\text{Xe}]4f^{14}5d^{10}6s^2$
			46	Pd	$[\text{Kr}]4d^{10}*$	81	Tl	$[\text{Xe}]4f^{14}5d^{10}6s^26p$
11	Na	$[\text{Ne}]3s$	47	Ag	$[\text{Kr}]4d^{10}5s^*$	82	Pb	$[\text{Xe}]4f^{14}5d^{10}6s^26p^2$
12	Mg	$[\text{Ne}]3s^2$	48	Cd	$[\text{Kr}]4d^{10}5s^2$	83	Bi	$[\text{Xe}]4f^{14}5d^{10}6s^26p^3$
13	Al	$[\text{Ne}]3s^23p$	49	In	$[\text{Kr}]4d^{10}5s^25p$	84	Po	$[\text{Xe}]4f^{14}5d^{10}6s^26p^4$
14	Si	$[\text{Ne}]3s^23p^2$	50	Sn	$[\text{Kr}]4d^{10}5s^25p^2$	85	At	$[\text{Xe}]4f^{14}5d^{10}6s^26p^5$
15	P	$[\text{Ne}]3s^23p^3$	51	Sb	$[\text{Kr}]4d^{10}5s^25p^3$	86	Rn	$[\text{Xe}]4f^{14}5d^{10}6s^26p^6$
16	S	$[\text{Ne}]3s^23p^4$	52	Te	$[\text{Kr}]4d^{10}5s^25p^4$	87	Fr	$[\text{Rn}]7s$
17	Cl	$[\text{Ne}]3s^23p^5$	53	I	$[\text{Kr}]4d^{10}5s^25p^5$	88	Ra	$[\text{Rn}]7s^2$
18	Ar	$[\text{Ne}]3s^23p^6$	54	Xe	$[\text{Kr}]4d^{10}5s^25p^6$	89	Ac	$[\text{Rn}]6d7s^2*$
						90	Th	$[\text{Rn}]6d^27s^2*$
19	K	$[\text{Ar}]4s$	55	Cs	$[\text{Xe}]6s$	91	Pa	$[\text{Rn}]5f^26d^27s^2*$
20	Ca	$[\text{Ar}]4s^2$	56	Ba	$[\text{Xe}]6s^2$	92	U	$[\text{Rn}]5f^36d7s^2*$
21	Sc	$[\text{Ar}]3d4s^2$	57	La	$[\text{Xe}]5d6s^2*$	93	Np	$[\text{Rn}]5f^46d7s^2*$
22	Ti	$[\text{Ar}]3d^24s^2$	58	Ce	$[\text{Xe}]4f^5d6s^2*$ (or $4f^26s^2$)	94	Pu	$[\text{Rn}]5f^67s^2$
23	V	$[\text{Ar}]3d^34s^2$	59	Pr	$[\text{Xe}]4f^36s^2$	95	Am	$[\text{Rn}]5f^77s^2$
24	Cr	$[\text{Ar}]3d^54s^*$	60	Nd	$[\text{Xe}]4f^46s^2$	96	Cm	$[\text{Rn}]5f^76d7s^2*$
25	Mn	$[\text{Ar}]3d^54s^2$	61	Pm	$[\text{Xe}]4f^56s^2$	97	Bk	$[\text{Rn}]5f^86d7s^2*$ (or $5f^97s^2$)
26	Fe	$[\text{Ar}]3d^64s^2$	62	Sm	$[\text{Xe}]4f^66s^2$	98	Cf	$[\text{Rn}]5f^96d7s^2*$ (or $5f^{10}7s^2$)
27	Co	$[\text{Ar}]3d^74s^2$	63	Eu	$[\text{Xe}]4f^76s^2$	99	Es	$[\text{Rn}]5f^{10}6d7s^2*$ (or $5f^{11}7s^2$)
28	Ni	$[\text{Ar}]3d^84s^2$ (or $3d^94s^*$)	64	Gd	$[\text{Xe}]4f^75d6s^2*$	100	Fm	$[\text{Rn}]5f^{11}6d7s^2*$ (or $5f^{12}7s^2$)
29	Cu	$[\text{Ar}]3d^{10}4s^*$	65	Tb	$[\text{Xe}]4f^85d6s^2*$ (or $4f^96s^2$)	101	Md	$[\text{Rn}]5f^{12}6d7s^2*$ (or $5f^{13}7s^2$)
30	Zn	$[\text{Ar}]3d^{10}4s^2$	66	Dy	$[\text{Xe}]4f^{10}6s^2$	102	No	$[\text{Rn}]5f^{13}6d7s^2*$ (or $5f^{14}7s^2$)
31	Ga	$[\text{Ar}]3d^{10}4s^24p$	67	Ho	$[\text{Xe}]4f^{11}6s^2$	103	Lr	$[\text{Rn}]5f^{14}6d7s^2$
32	Ge	$[\text{Ar}]3d^{10}4s^24p^2$	68	Er	$[\text{Xe}]4f^{12}6s^2$	104	Rf	$[\text{Rn}]5f^{14}6d^27s^2$
33	As	$[\text{Ar}]3d^{10}4s^24p^3$	69	Tm	$[\text{Xe}]4f^{13}6s^2$	105	Db	$[\text{Rn}]5f^{14}6d^37s^2$
34	Se	$[\text{Ar}]3d^{10}4s^24p^4$	70	Yb	$[\text{Xe}]4f^{14}6s^2$	106	Sg	$[\text{Rn}]5f^{14}6d^47s^2$
35	Cl	$[\text{Ar}]3d^{10}4s^24p^5$						

is indeed quite reliable. The exceptions (marked by \star) are those cases in which detailed interactions override the gross features of the shell model; we shall examine these effects later. But already we have essentially explained the form of the periodic table (Table 1.3). The first two columns contain those elements in which s subshells are being filled; the last six columns correspond to the filling of p subshells; the 10 short columns in the middle (transition metals) to d subshells; and the lanthanide and actinide series to f subshells.

Thus far we have considered only ground states. Although highly excited states sometimes require more elaborate descriptions, the concept of electronic configuration still gives a satisfactory representation of many excited states. For example, one can obtain a very good representation of the first excited state of helium by assigning one electron to the $1s$ orbital and the other to the $2s$, the next orbital on the energy ladder. The configuration is then $\text{He}^*(1s2s)$, where the asterisk indicates an excited state. At a slightly higher energy one finds the configuration $\text{He}^*(1s2p)$. One can proceed all the way up the series of configurations in which one electron is excited to the normally empty orbitals with any values of n and l . Finally, at the limit of the series, sufficient energy removes the electron from the atom altogether; one then has $\text{He}^+(1s) + e^-$, a helium ion in its ground state plus a free electron.⁶

To obtain an excited configuration, of course, one need not excite just a single electron. For example, if we excite a helium atom by giving it enough energy to put one electron in the $2s$ orbital and the other electron in the $2p$ orbital, we have the doubly excited configuration $\text{He}^*(2s2p)$; or both could be excited to the $2s$ orbital (with opposite spins), giving $\text{He}^*(2s^2)$. Such states are actually known experimentally, but their energies are very high indeed compared with states having only one excited electron. We might expect this, particularly for a small atom like helium, because we know that in the hydrogen atom the states with $n = 2$ are three-quarters of the way up from the ground state to the ionization limit. This should be roughly true for helium also, and in fact the first excited state of He is about 80% of the way from the ground state to the energy of $\text{He}^+ + e^-$. Therefore the energy required to excite two electrons from the K shell to the L shell would be over one and one-half times the energy required to remove a single electron from the atom, leaving the other in its lowest state. This is indeed the case: A doubly excited helium atom has more than enough total energy to become a helium positive ion and a free electron. However, much of the time, the energy is divided between the two electrons and is not readily available to just one for purposes of ionization. As a result, when doubly excited helium atoms are produced, it takes some time (corresponding to many Bohr periods of revolution in the $n = 2$ orbit) for an average doubly excited atom to convert itself into a singly charged helium ion and a free electron.

Transitions between one electronic configuration and another are responsible for most of the lines in the emission and absorption spectra of atoms. Generally speaking, transitions involving the outer (valence) electrons lie in the visible and adjacent regions. (The highest atomic ionization energy for removal of one outer electron—or *first ionization potential*—is that of helium, corresponding to $\lambda = 504 \text{ \AA}$.) The more tightly bound inner-shell electrons give rise to the x-ray spectrum. Tens of thousands of assignments of atomic spectral lines have been made, meaning that their initial and final states have been determined. Much of modern science and technology could hardly exist without these assignments. (Some examples: The design of lasers requires a knowledge of the specific states of individual atoms and the selection rules governing transitions among them. The industrial analysis of steel uses atomic spectroscopy for the quantitative determination of trace materials.)

5.4 Calculation of Atomic Structures

Now we shall briefly survey the methods used to determine energy levels, quantum states, and wave functions for complex atoms. Unlike those for the hydrogen atom, however, the results obtained are only approximate (though of high accuracy for light atoms).

To describe the state of any quantum mechanical system, one need “simply” write down the Hamiltonian and solve the Schrödinger equation for the wave function. But let us look at such a Hamiltonian. For an atom with N electrons we have the operator

$$H = \sum_{i=1}^N \left(\frac{\mathbf{p}_i^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r_i} \right) + \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N \frac{e^2}{4\pi\epsilon_0 r_{ij}} + \text{magnetic moment interactions}, \quad (5.10)$$

where r_i is the distance of the i th electron from the nucleus and r_{ij} is the distance between the i th and j th electrons. The factor $\frac{1}{2}$ is to prevent counting each interaction twice. Even in classical mechanics one cannot solve exactly the equations of motion for the three-body problem; here we have an $(N + 1)$ -body problem, and an exact solution of the Schrödinger equation is clearly impossible. One must therefore resort to approximate methods.

One of the most important ways of obtaining approximate solutions is the *variation method*. Suppose that one guesses a trial wave function ψ , which can be any well-behaved and normalized function of the coordinates. One can show that, for any such ψ ,

$$E' \equiv \int \cdots \int \psi^* H \psi dq_1 \cdots dq_N \geq E_0, \quad (5.11)$$

where H is the Hamiltonian operator of the system and E_0 is its lowest eigenvalue. The equality, of course, holds only when ψ is the true ground-state wave function of the system. The more closely ψ resembles this true wave function,

⁶ The energy levels of the helium atom are plotted in Fig. 5.10.

the closer the integral E' will come to the value E_0 . If ψ contains one or more adjustable parameters, it is a straightforward calculation to find the values of these parameters that minimize E' . By either trial-and-error or systematic procedures, one can obtain functions that give lower and lower values of E' ; when no further improvement can be made, ψ is presumably the best possible approximation to the true wave function within whatever restrictions one has put on one's calculations.⁷ There are ways to extend the method to excited states.

To see how the variation method works, let us consider the ground state of the helium atom. If the two electrons did not interact with each other at all, each would independently be in a hydrogenlike $1s$ orbital; since the $1s$ wave function is proportional to e^{-Zr/a_0} , the total wave function for the helium atom would then be of the form

$$\psi^{(1)} = Ae^{-Zr_1/a_0} e^{-Zr_2/a_0}, \quad (5.12)$$

with $Z = 2$. (When the Hamiltonian is separable, the wave function is a product of functions of the individual coordinates.) If $\psi^{(1)}$ is taken as a trial wave function and the operator of Eq. 5.10 as the Hamiltonian (with the magnetic terms omitted), then the integral Eq. 5.11 gives $E' = -74.83$ eV. The actual ground-state energy (E_0) is known from spectroscopic data to be -78.99 eV (and the last figure is, at worst, ± 1), so the wave function needs considerable improvement if we want accuracy consistent with our ability to measure this quantity. Since each helium electron is partially screened from the nucleus by the other electron, it is logical to try replacing Z by an adjustable parameter Z' :

$$\psi^{(2)} = Ae^{-Z'r_1/a_0} e^{-Z'r_2/a_0}. \quad (5.13)$$

Varying the value of Z' , one finds the integral Eq. 5.11 to be minimized when $Z' = \frac{27}{16}$, yielding the value $E' = -77.49$ eV; the error in energy is only one-third as much as before.

⁷ The variational principle follows from a generalization of the expansion of a function in Fourier series; i.e., in a series of sines and cosines of the form $\sum_n [A_n \sin n\theta + B_n \cos n\theta]$. (This form is appropriate when the range for which the expansion is desired has been scaled to the interval from 0 to 2π .) The generalization is the fact that many sets of functions, notably the complete sets of solutions of any of a very large set of differential equations, including the Schrödinger equation, can also be used to express any arbitrary (not-too-discontinuous) function by using them in a series like the Fourier expansion. If the series expansion is *exact* for the lowest-energy state, ψ_0 , then whatever the actual series may be that one uses, we recognize that the series would consist of only one term if the exact solutions of the Schrödinger equation were being used. Operating on ψ_0 with H simply multiplies ψ_0 by the lowest-energy eigenvalue E_0 . If we have only achieved an approximation ϕ_{approx} to the exact solution, as is usually the case, the series expressed in terms of the exact solutions would contain some of the lowest-energy eigenfunction and some of other, higher-energy eigenfunctions. Hence, when we operate on this approximate function $\phi_{\text{approx}} = a_0\psi_0 + \sum_{j=1} a_j\psi_j$ with the Hamiltonian H and compute the expectation value of the energy, we obtain contributions to that value from not only E_0 but from higher energies as well. Consequently, the approximations to the exact lowest-energy value all lie higher than the exact value, and the exact energy is the greatest lower bound of all such approximations.

The next step carries us beyond the simple configurational wave function, by introducing a term that takes explicit account of the repulsion between the electrons. One way is to use a wave function with terms containing the interelectronic distance r_{12} , for example,

$$\psi^{(3)} A(1 + cr_{12})e^{-Z'r_1/a_0} e^{-Z'r_2/a_0}, \quad (5.14)$$

with $c > 0$, which grows larger as the electrons move farther apart; varying both Z' and c , one obtains $E' = -78.66$ eV, only 0.33 eV higher than the experimental value. The function of Eq. 5.14 cannot be labeled by a single configuration as 5.12 or 5.13 can be. Obviously one can carry this process as far as one wants, by using more and more complicated polynomials in the r 's. With enough adjustable parameters—and enough computer time—one can get arbitrarily close to E_0 . Calculations have in fact been made with ψ 's containing over 1000 adjustable parameters, giving an E' that not only agrees with E_0 within experimental accuracy, but is indeed far more precise (and presumably accurate) than experiment. With 26 parameters, one can determine E' to within about 1 part in 10^7 . Such results are, for all practical purposes, equivalent to an exact solution. Later in this section we shall give a physical interpretation to the complex wave functions needed to obtain such accuracy.

Because we can compute very accurate wave functions for two-electron atoms, we can construct very reliable pictures of the electron distributions in these atoms. Figure 5.2 shows several such distributions. Note that the atoms and ions in their ground states have very high concentrations of charge density near their nuclei. The total charge at distances far from a nucleus is significant, but in the figures showing the charge density itself (without a weighting factor of r^2), the charge density away from the nucleus is quite small. The total charge at about the distance r is spread out over the entire spherical shell with volume $4\pi r^2 dr$, so the amount at any point may be quite small although the amount in the entire shell is not.

Executing such elaborate and accurate computations has become feasible, even inexpensive, for the lighter atoms. When one goes beyond the first or second row of the Periodic Table, even the largest computers do not have the capacity to do the job with the same accuracy with which we can compute, for example, the wave function and energy of the helium atom in its ground or even its excited states. But whether one chooses or is limited by available methods, one may go far without achieving spectroscopic accuracy for the total wave function and energy; it is possible to get useful approximations in terms of the central field model and one-electron orbitals.

This method was introduced by D. R. Hartree. The basic assumption is that the wave function can be well represented as a product of one-electron orbitals,

$$\psi = \phi_1 \phi_2 \cdots \phi_N, \quad (5.15)$$

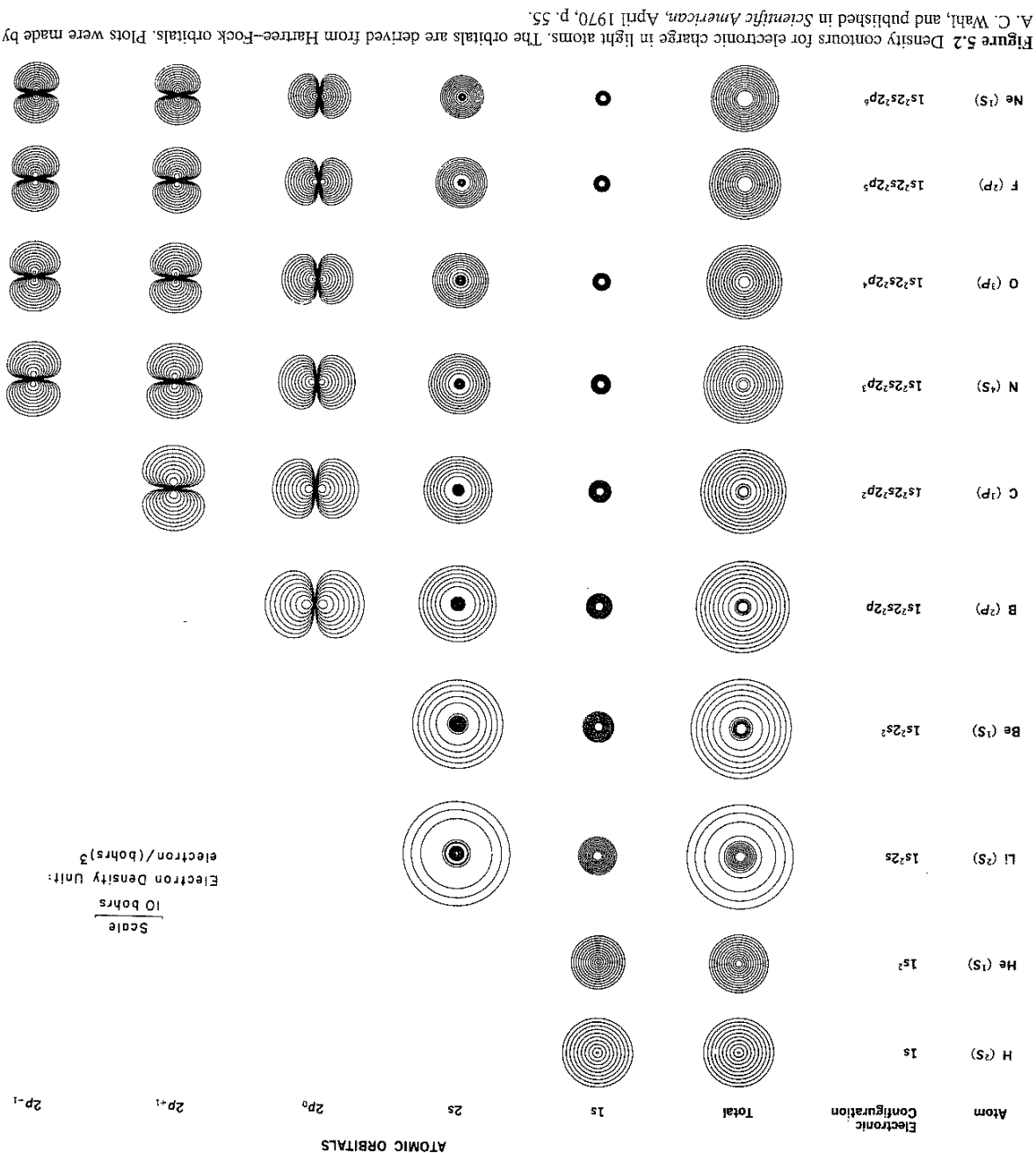


Figure 5.2 Density contours for electronic charge in light atoms. The orbitals are derived from Hartree-Fock orbitals. Plots were made by A. C. Wahl, and published in *Scientific American*, April 1970, p. 55.

where each of the φ_i is a function of the coordinates of the i th electron only. Suppose that this wave function is substituted in Eq. 5.11, using the Hamiltonian 5.10 without the magnetic terms; one can show that the lowest possible value of E' is then obtained when each of the φ_i is a solution of the equation

$$H_i \varphi_i = \epsilon_i \varphi_i, \quad (5.16)$$

$$H_i \varphi_i = \left(\frac{\mathbf{p}_i^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r_i} + \sum_{j \neq i} \int |\varphi_j|^2 \frac{e^2}{4\pi\epsilon_0 r_{ij}} dV_j \right) \varphi_i$$

where $dV_i \equiv r_i^2 \sin \theta_i d\theta_i d\phi_i$, and ϵ_i is the orbital energy eigenvalue. Hartree's approximation is thus equivalent to the central field approximation. The instantaneous electron-electron repulsions appearing in Eq. 5.10 are replaced by integrals giving the *average* repulsion over all possible positions of the other electrons (since $|\phi_j|^2 dV_j$ is the probability of finding the j th electron in the volume element dV_j).

It is still necessary to solve simultaneously N equations of the form of Eqs. 5.16; this is done by successive approximation. One starts with a trial set of orbitals $\phi_i^{(1)}$. These could be hydrogenlike orbitals, for example, although other functions are known that lead to more rapid convergence; the angular part of each orbital, of course, is always taken to be a spherical harmonic. In each of the N Eqs. 5.16 one substitutes the $\phi_j^{(1)}$ (for $j \neq i$) and solves to obtain a new function $\phi_i^{(2)}$ (which in general can be expressed only in numerical form). These are again substituted in Eqs. 5.16 and the equations solved to obtain a set of $\phi_i^{(3)}$. The process is repeated until no further change occurs, that is, until the $\phi_i^{(n)}$ differ negligibly from the $\phi_i^{(n-1)}$. In this limit the orbitals consistently reproduce the average field in which each electron moves, and are thus called *self-consistent field (SCF)* orbitals.

The initial set of trial orbitals must correspond to the desired electronic configuration of the atom. For example, in the nitrogen atom, two of the ϕ_i must be 1s-type functions, two 2s-type, and three 2p-type. (What is a "1s-type" orbital? As in any other spherically symmetric problem, the wave function with quantum numbers n, l must have l angular nodes and $n - l - 1$ radial nodes.) If one carries out such SCF calculations for a variety of possible configurations, the configuration of the atomic ground state should be the one that gives the lowest total energy. Although the calculations are in fact too approximate to reproduce all the observed sequences of electronic states, they do give the gross features of the orbital-filling sequence.

The Hartree approximation still does not take full account of the interaction between electrons. It includes the average Coulombic repulsion in the $e^2/4\pi\epsilon_0 r_{ij}$ integrals (which we will sometimes abbreviate as e^2/r_{ij}) of Eqs. 5.16, but ignores the *exchange interaction* associated with the exclusion principle. As we shall see in the next chapter, to obtain a wave function that satisfies the exclusion principle, one must replace the simple product of Eq. 5.15 with a determinant, containing all the possible permutations of the electrons among the orbitals. We shall wait until Chapter 6 to go into the details of this approach. One still applies the iterative procedures of the self-consistent field method, leading to what are called *Hartree-Fock SCF* orbitals.

Hartree-Fock SCF calculations have been carried out for all the elements, leading to the results summarized in Fig. 5.3. The quantity plotted is the Hartree-Fock orbital energy ϵ_i , corresponding to the Hartree ϵ_i of Eqs. 5.16. (We need not distinguish one-electron energies, so long as we recognize the Hamiltonian to which they refer.) To the extent that the orbital approximation is valid, ϵ_i should equal the energy required to remove (ionize) one electron from the i th orbital

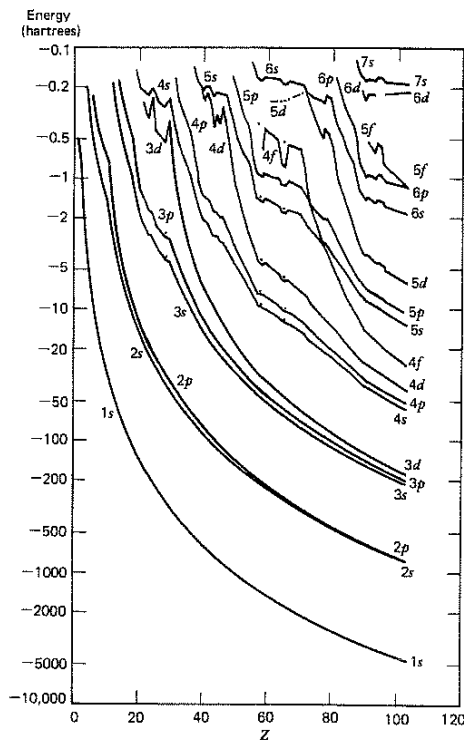


Figure 5.3 Hartree-Fock orbital energies of the elements. The energies plotted are those calculated by F. Herman and R. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N.J., 1963), for the configurations listed in Table 5.1. Spin-orbit splitting (Section 5.7) is neglected, but relativistic corrections are included. The energy units (hartrees) are defined at the end of Section 5.4.

(*Koopmans' theorem*). Such orbital binding energies can be measured by spectroscopic or electron-scattering techniques. (See especially Section 7.10 for a description of photoelectron spectroscopy, the most direct way to measure orbital binding energies.) The calculated ϵ_i 's of Fig. 5.2 generally agree with experimental values to within a few percent. Some typical atomic charge distributions, both for individual orbitals and for total charge distributions, are shown in Fig. 5.3.

The Hartree-Fock calculations also give the approximate orbital-filling sequence, but there are certain anomalies. For example, the 3d orbital energy is consistently lower than the 4s energy, indicating correctly that a 4s electron is more easily ionized. The predicted ground states of Sc and Sc⁺ are, respectively, $\dots 3d4s^2$ and $\dots 3d4s$. In spite of this, the 4s orbital is filled first, because the *total* energy of the atom is lower in the $3d4s^2$ configuration. For Sc again, the configurations $\dots 3d^24s$ and $\dots 3d^3$ are, respectively, 2.11 eV and 4.19 eV above the ground state. These anomalies, like those in Table 5.1, show that one cannot completely explain atomic structure in terms of single-orbital energies.

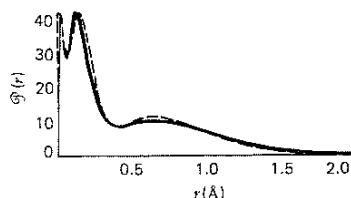


Figure 5.4 Radial distribution of electrons in the argon atom, according to Hartree SCF calculations (---) and electron-diffraction measurements (—).

Another way to check the SCF calculations is in terms of the spatial distribution of electrons. Adding together the squared orbital functions $|\phi_i|^2$ and integrating over angles, one can obtain the total electron density as a function of r . In Fig. 5.4 the results of such a calculation are compared with an experimental radial distribution function derived from electron-diffraction measurements. The quantity plotted is the probability of finding an electron in the shell between r and $r + dr$. The agreement of the two curves is reasonably good, and in both one can clearly see the shell structure of the atom.

The Hartree–Fock method gives the best possible wave functions describing the motion of each electron in the *mean* potential field of all the other electrons. In mathematical terms, these are the best functions that can be obtained within the central field, one-electron orbital model. But now we must remember that this is only an approximation. At any given instant the field felt by each electron is *not* the spherically symmetrical mean field, but depends on the instantaneous positions of the other electrons. There must be some degree of *correlation* among the positions of the electrons which cannot be simply treated in terms of separate orbitals. Some of this is due to the magnetic moment interactions, which we take up in a later section. The main contribution, however, is from the instantaneous Coulomb and exchange (exclusion-principle) repulsions between electrons; the electrons in a real atom must thus be able to avoid one another more effectively than the central field model would allow. The effect of correlation can be illustrated with our earlier discussion of the helium atom. The trial function 5.13 is a Hartree product of two identical one-electron orbitals; in Eq. 5.14 multiplication by the correlation function $1 + cr_{12}$ gives a better value for the energy, but the wave function can no longer be factored into orbitals.

Figure 5.5 illustrates the effect of correlation in the helium atom, for which it is possible to construct a graphic representation of the phenomenon. We start with the six-dimensional probability density $\mathcal{P}(\mathbf{r}_1, \mathbf{r}_2) = |\psi(\mathbf{r}_1, \mathbf{r}_2)|^2$; one can integrate over three of the variables and obtain a three-dimensional probability density $\rho(r_1, r_2, \theta_{12})$ that depends only on the distances r_1 and r_2 of electrons 1 and 2 from the nucleus, and on θ_{12} , the angle between the vectors

\mathbf{r}_1 and \mathbf{r}_2 . From this function of three variables, one can construct the *conditional* probability density for finding electron 2 at r_2 and on θ_{12} , with r_1 at a chosen value r'_1 . This conditional probability is the function

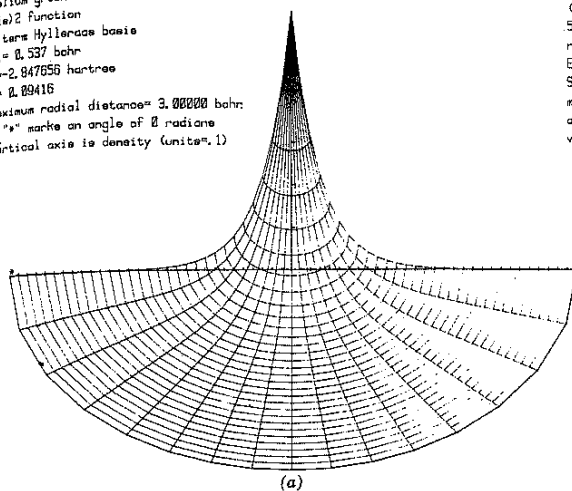
$$d(r_2, \theta_{12} | r'_1) = \frac{\rho(r'_1, r_2, \theta_{12})}{\rho(r'_1)}, \quad (5.17)$$

where $\rho(r'_1)$ is the probability density for finding r_1 at r'_1 whatever r_2 and θ_{12} may be. By constructing graphs of $d(r_2, \theta_{12} | r'_1)$ for various values of r'_1 and—more important in our present context—for wave functions of different levels of refinement, we can learn how the distribution of probability for one electron is affected by the position of another, and how different wave functions represent the effects of spatial correlation. Figure 5.5a shows the conditional probability $d(r_2, \theta_{12} | r'_1)$ for the ground state of helium according to a wave function based on a $1s^2$ configuration; Fig. 5.5c is the conditional probability for the same atom and for the same value of r'_1 but based on a very accurate wave function.

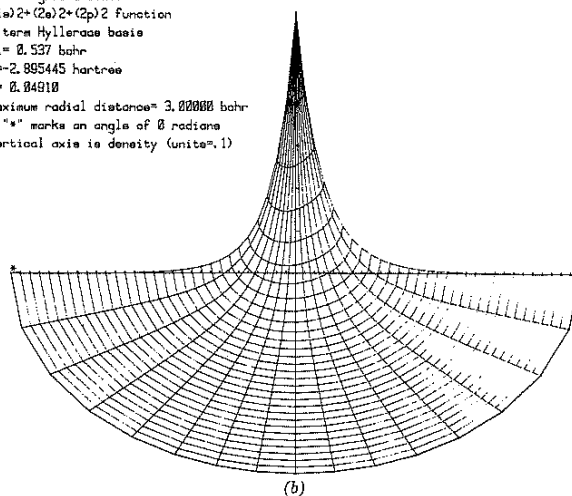
Another way to improve wave functions beyond the level of single-configuration representations is to write them as sums of terms, in which each term corresponds to a different configuration. This method, called configuration interaction, will be discussed in detail in Chapter 6, in connection with the H_2 molecule. For the present, we note only that a wave function composed mostly of a $1s^2$ term, but with a bit of $2s^2$ configuration, is a better representation of the ground state of He than the pure $1s^2$ function, and that addition of some $2p^2$ configuration makes it better still; Fig. 5.5b shows the conditional probability for such a function, which is still not as accurate as the 26-term function used for Fig. 5.5c. The one rule restricting what functions may be included in such sums is that they all must correspond to the same quantum numbers and constants of motion. For example, to represent the ground state of helium, all the functions in the sum must have total spin $S = 0$ and a total orbital angular momentum quantum number $L = 0$, since S and L are good quantum numbers for the ground state (and all the other states we know) of helium.

The difference between the total Hartree–Fock energy of an atom and the true energy in a given state is defined as the *correlation energy*; the Hartree–Fock method always gives an energy higher than the true value, in accordance with Eq. 5.11. The correlation energy is usually of the order of 1 eV per electron pair; this is of about the same magnitude as chemical bond energies, and thus cannot be neglected if one wishes to proceed accurately from atomic to molecular properties. Various methods exist for estimating correlation energies. To a good approximation, the total correlation energy can be taken as a sum of two-electron correlation energies, which can be calculated by methods like those used in the helium atom; most of the effect seems to be due to the interaction of electron pairs in the same orbital. In Chapter 14 we shall see how this approximation can be used

CONDITIONAL PROBABILITY DENSITY
Helium ground state
(1s)² function
1 term Hylleraas basis
 $r_1 = 0.537$ bohr
 $E = -2.947656$ hartree
 $S = 0.09416$
maximum radial distance = 3.00000 bohr
a "s" marks an angle of 0 radians
vertical axis is density (units = 1)



CONDITIONAL PROBABILITY DENSITY
Helium ground state
(1s)² + (2s)² + (2p)² function
5 term Hylleraas basis
 $r_1 = 0.537$ bohr
 $E = -2.985445$ hartree
 $S = 0.04918$
maximum radial distance = 3.00000 bohr
a "s" marks an angle of 0 radians
vertical axis is density (units = 1)



CONDITIONAL PROBABILITY DENSITY
Helium ground state
26 term Hylleraas-Kinoshita basis
 $r_1 = 0.537$ bohr
 $E = -2.983722$ hartree
 $S = 0.06451$
maximum radial distance = 3.00000 bohr
a "s" marks an angle of 0 radians
vertical axis is density (units = 1)

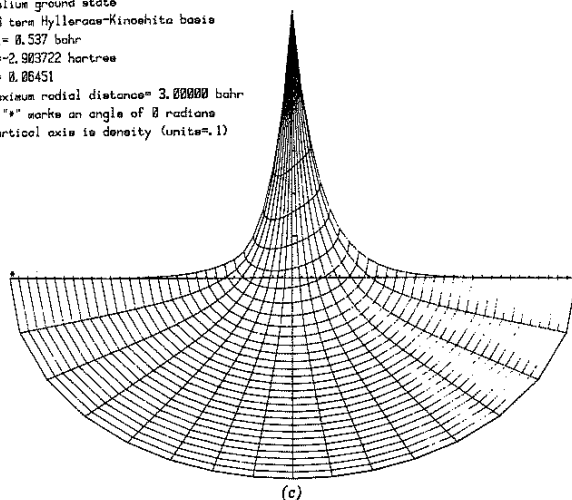


Figure 5.5 Conditional probability densities for the ground state of helium, for three wave functions. (a) Probability density for finding electron 2 at any point in space when electron 1 is 0.537 bohr to the left of the nucleus, based on a simple, single-configuration $1s^2$ wave function. (b) The corresponding conditional probability density based on a best superposition of $1s^2$, $2s^2$, and $2p^2$ configurations. (c) The corresponding conditional probability density based on an accurate (26-term) wave function. The nucleus is located where the distribution peaks; the distance 0.537 bohr is the most probable distance of electron 1 from the nucleus. Note from the tilt of the contours of constant radius that there is no angular correlation in (a), some in (b), and more in (c). Graphs supplied by Paul Rehms.

to estimate *molecular* correlation energies from thermochemical data.

An additional shortcoming in the Hartree-Fock method as just described arises from the effects of relativity. In atoms with fairly large Z , the inner electrons have such high kinetic energies that their velocities approach the speed of light; their masses thus become significantly larger than the mass of a stationary electron. This results in a shrinkage of the electrons' orbits and an increase in their binding energy.

Although Hartree-Fock calculations can include this effect in only an approximate way,⁸ the relativistic energy correction is known to be larger than the nonrelativistic correlation

⁸ A completely relativistic quantum mechanics requires the revision of the Schrödinger equation itself. In this theory (originated by Dirac), the electron spin appears automatically in the solution of the wave equation; the spin is thus inherently not only a quantum mechanical, but also a relativistic, phenomenon.

energy for heavy atoms. For light atoms this is of little significance. For heavy atoms, the relativistic shrinkage of *s* and *p* shells makes them especially effective screens of the nuclear charge for *d* and *f* shells, which thus enlarge. Closed subshell atoms such as Hg become somewhat inert.⁹

The Hartree or independent-particle approach is not the only way to make a first approximation to the behavior of atomic electrons, particularly valence electrons. It is possible to start with a model in which the electrons move collectively, much as the atoms of small polyatomic molecules do. We shall examine such molecules in Chapters 8 and 9. In many respects, collective motions of valence electrons seem to correspond more closely to conserved quantities than motions of individual electrons. For example, electrons can exchange angular momenta rather readily by collisions within an atom. In terms of practical computations, however, no approach has yet been developed with the power of the Hartree method and its subsequent refinements to approach accurate, if elaborate and complex, representations of real atoms.

In Fig. 5.3 we expressed the energies in *hartrees*. This unit, named for D. R. Hartree, is defined as

$$1 \text{ hartree} \equiv 2 \text{ rydbergs} \equiv 2hcR_{\infty} \equiv \frac{e^4 m_e}{4\epsilon_0^2 \hbar^2} \\ = 4.359743 \times 10^{-18} \text{ J} = 27.21138 \text{ eV}.$$

The ground-state energy of the hydrogen atom is thus -0.5 hartree. Published calculations on atoms and molecules most commonly give energy in hartrees and distance in Bohr radii ($a_0 = 0.5292 \text{ \AA}$), a combination known as *atomic units*.¹⁰ The utility of such units is obvious: The ubiquitous $e^2/4\pi\epsilon_0 r$ in hartrees is numerically equal to a_0/r . Similarly, m_e is the atomic unit of mass, e of charge, and \hbar of angular momentum. The constants are usually suppressed, leading to equations like $V = -1/r$; this is certainly convenient for making calculations, but is not recommended unless you know just what is missing. In this text we write all such equations out in full.

5.5 Atomic Structure and Periodic Behavior

The physical and chemical properties of the elements vary systematically with atomic number, in a way best summarized by the periodic table. We may now relate this behavior to atomic structure. To do this, at least for light elements, we do not need refinements such as term splitting (Sec. 5.6). The

gross features of the periodic table can be explained quite simply in terms of electron configurations and shell structure. In this section we shall look briefly at the chemical behavior of the various families of elements, and at a number of physical properties associated with individual atoms.

The most strikingly similar group of elements is probably the so-called inert gases (rare gases, noble gases): helium, neon, argon, krypton, xenon, and radon. Until 1962 these elements were thought to form no compounds whatsoever; now krypton, xenon, and radon are known to form a limited number of compounds with fluorine and oxygen. Still, they remain by far the most unreactive family of elements. Even the forces between their monatomic molecules are very weak, so that they have very low melting and boiling temperatures. (Radon, the heaviest, boils at -62°C .) Usually one glibly attributes the inertness of these elements to their "closed-shell structure." In fact they have only closed subshells; all but helium have outer shells with the configuration $\dots ns^2 np^6$, and all their occupied inner subshells are filled. But other atoms have closed-subshell structures also, yet are hardly in the same category chemically. Palladium, for example, has the configuration $\dots 4s^2 4p^6 4d^{10}$, and is clearly not inert; even more reactive are the alkaline earth metals, with $\dots ns^2$ outside an inert-gas configuration, and the family of zinc, cadmium, and mercury. What, then, is really responsible for the inertness?

For a closed-shell atom to form a chemical bond, the outer shell must be "cracked open" in some way. One indication of the difficulty of doing this is the energy of the lowest excited state, in which one electron has been promoted to the lowest empty orbital. In the alkaline earths and the zinc group this excitation is simply $ns \rightarrow np$, between two orbitals that lie quite close together in energy. But for the inert gases the lowest excitation is $np \rightarrow (n+1)s$, all the way to the next higher shell, and the energy required is much greater (cf. Fig. 5.10). To illustrate this point, here are the first excitation energies (in electron volts):

He	19.8	Ne	16.6	Ar	11.5	Kr	9.9	Xe	8.3	Rn	6.8
Be	2.7	Mg	2.7	Ca	1.9	Sr	1.8	Ba	1.1	Ra	1.6
		Zn	4.0	Cd	3.7	Hg	4.7				

(As for palladium, the excitation is $4d \rightarrow 5s$ and takes only 0.8 eV .) The energy gained by forming a chemical bond is usually in the range $2\text{--}6 \text{ eV}$, which clearly is enough to "crack the shell" in all but the inert gases.

Another way for an atom to undergo chemical reaction is ionization, in which one electron is removed from the atom altogether. The energy required to remove one electron from a neutral atom is usually called the first *ionization potential*.¹¹

⁹ For relativistic effects, see P. Pyykko and J. P. Desclaux, *Acc. Chem. Res.* **12**, 276 (1979) and K. Pitzer *ibid.*, 282. For a more detailed discussion of atomic orbitals see R. S. Berry, *J. Chem. Educ.* **43**, 293 (1966).

¹⁰ Often written as "a.u." with no further explanation, or not specified at all. This can be confusing, especially since some people use rydbergs instead of hartrees.

¹¹ Strictly, "potential" implies electric potential or voltage. But for a single electron the ionization potential in volts is numerically the same as the ionization energy in electron volts, and the two terms are often used interchangeably.

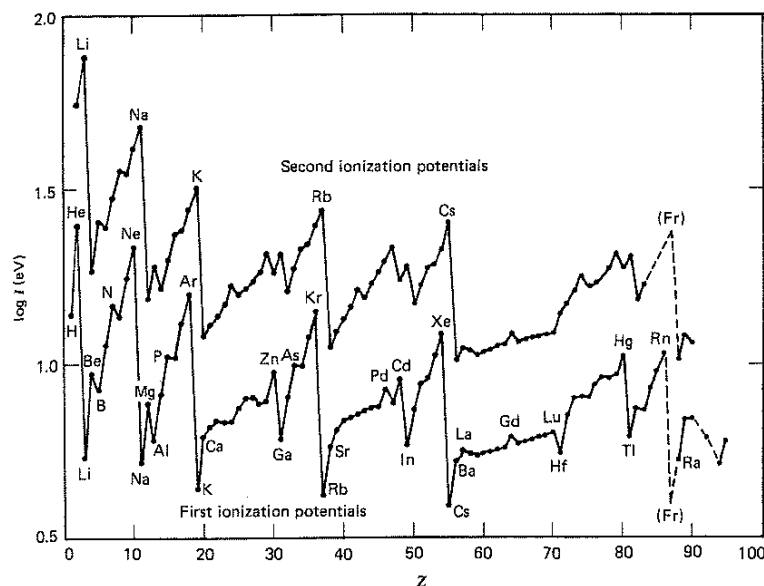


Figure 5.6 First and second ionization potentials of the elements. A number of the more significant peaks in the lower curve have been identified. The broken lines (---) give the probable behavior of the curves where no data are available.

(I or I_1); the second ionization potential (I_2) is the energy of removing a second electron, and so forth. The ionization potential is among the properties that show the most clearly periodic behavior, as can be seen in Fig. 5.6. Note that the second ionization potential is always higher than the first (since there is a greater net positive charge holding the second electron) and has its peaks shifted one unit to higher Z .

Let us examine the structure of the first-ionization-potential curve. The inert gases, as we might expect, have the highest first ionization potentials: It is very hard to remove an electron from a closed p subshell. (There are small peaks for such other closed-shell atoms as the zinc family and palladium.) The lowest values are those for the alkali metals (Li, Na, K, Rb, Cs, Fr), with one loosely bound s electron outside a closed shell; similarly, the next most prominent minima in the curve are for those atoms with a single outer p electron (B, Al, Ga, In, Tl). The small peaks for the lighter $\cdots np^3$ atoms (N, P, As) illustrate the stability of a half-filled subshell. All these details are superimposed on two grosser features, the overall downward trend of the ionization potential with Z and the upward trend within each period; these effects are closely associated with the variation in atomic size, which we shall discuss shortly.

Figure 5.6 can help us to understand a good deal about chemical behavior. After the inert gases, the most clearly defined family of elements is that of the alkali metals. Their ionization potentials are all about 4–5 eV, comparable to the energies normally available in chemical reactions. The result is that these atoms readily lose one electron to form the M^+ ions, and their chemistry is primarily the chemistry of these ions. However, the alkali metals have the *highest* second ionization potentials (ca. 25–75 eV), so that one virtually never sees alkali M^{2+} ions in chemical systems. This is again a matter of closed-shell structure: The alkali M^+ ions are iso-

electronic¹² with the inert gas atoms, with the outer electrons even more tightly bound.

The alkaline earth metals (Be, Mg, Ca, Sr, Ba, Ra) have closed-subshell configurations, but we have already shown that this does not lead to inertness. On the contrary, the outer s electrons are relatively weakly bound (the alkaline earths have the lowest second ionization potentials), and the atom readily gives both up to form the M^{2+} ion. Beryllium is an exception: Having the highest ionization potentials of the family, it forms mainly covalent compounds. The elements of the zinc family, with the configurations $\cdots (n-1)d^{10}ns^2$, also generally form M^{2+} ions; however, the ionization potentials are relatively high, and the metals are much less reactive than the alkaline earths.

Since it is easier to remove one electron than two, why do we never see compounds containing ions like Ca^+ ? The principal reason is the intense Coulomb field of the M^{2+} ion, which is of course twice as strong as that of an M^+ ion at the same distance. This field makes the lattice (bonding) energy of, say, solid $CaCl_2$ much greater than that of $CaCl$ would be—enough greater to outweigh a second ionization potential of more than 10 eV. Similar considerations apply to the hydration energy in solution, where we again find only M^{2+} alkaline-earth ions. We shall consider the energy balance of processes such as these in Chapter 14. One *can* obtain the M^+ ions by applying energy to isolated atoms, as in electrical discharges or very hot gases; in such environments, we

¹² Two atoms or ions are *isoelectronic* if they have the same number of electrons. Isoelectronic systems usually have the same configuration and certain similarities in physical properties. But their chemical behavior is quite different—compare the reactivity of Ar and K^+ —because of the dominant effect of the ionic charge and its Coulomb field.

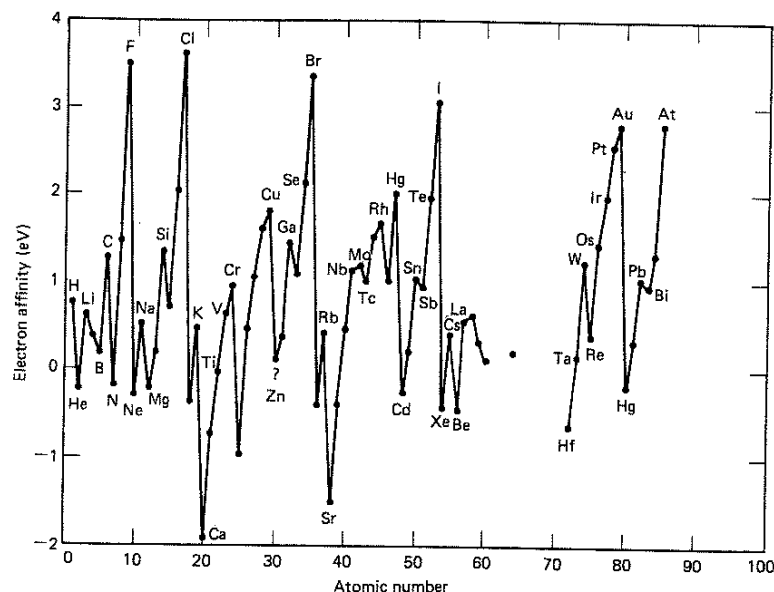


Figure 5.7 Electron affinities of the elements. The values are those selected in the review by H. Hotop and W. C. Lineberger, *J. Phys. Chem. Ref. Data* 4, 539 (1975); others are those of R. J. Zollweg, *J. Chem. Phys.* 50, 4251 (1969).

can also observe compounds such as CaCl_2 , which are quite unstable under ordinary, ambient conditions.

Now let us look at the other side of the periodic table, where most of the nonmetallic elements are found. Here the atoms have vacancies in nearly filled p subshells, and can attain more stable configurations by *adding* electrons to form negative ions. The *electron affinity* (A) of a given atom is the energy gained when one electron is added. The electron affinity of X is thus the same as the first ionization potential of X^- , and a plot of electron affinities should resemble the lower curve in Fig. 5.6 but shifted one unit *lower* in Z . Such a plot is given in Fig. 5.7. Note that even the highest atomic electron affinities are less than the lowest atomic ionization potentials. The periodic pattern is clear.

As expected, the highest electron affinities are those of the halogens (F, Cl, Br, I, At), which readily add electrons to form the familiar X^- (halide) ions. Most of the elements near the right side of the periodic table have relatively large electron affinities, and can generally be regarded as electron-accepting species. These elements complement the electron-donating tendency of the alkali and alkaline earth metals, with which they form ionic compounds. The second-highest peaks, surprisingly, are the coinage metals (Cu, Ag, Au), but these form negative ions only in hot gases, in which these materials exist as isolated atoms,¹³ and, in the case of Au, in binary, salt-like compounds with the alkali metals, e.g., as NaAu , which behaves like Na^+Au^- in its crystalline form. At the other extreme, many elements actually have *negative* electron affinities—that is, force would be required to make

an electron stick to the neutral atom. The dips in the curve are mainly those atoms with exceptionally stable configurations, having either closed subshells (inert gases, alkaline earths, Zn family) or *half-filled* outer subshells ($\dots np^3$; N, P, etc.; $\dots nd^3$; Mn, Re).

Unlike the case of the ionization potentials, no atoms have positive second electron affinities. The Coulomb repulsion between an X^- ion and an additional electron is so great that no stable X^{2-} ion is known to exist in isolation. Nevertheless, species such as O^{2-} and S^{2-} do appear to exist in ionic crystals, where they are stabilized by the high lattice energy; all these compounds hydrolyze readily in aqueous solution, forming more stable covalently bonded species (OH^- , HS^- , etc.).

Whereas the alkali and alkaline earth metals form almost exclusively ionic compounds, this is not true of the elements at the other side of the periodic table. Besides adding electrons to form negative ions, they can also share their outer electrons to form covalent bonds. In most simple compounds this results in the equivalent of an inert-gas configuration around each atom, as illustrated by the familiar Lewis formulas in which dots represent the outer-shell electrons (e.g., $2\text{H} \cdot + \cdot \ddot{\text{O}} \cdot = \text{H} : \ddot{\text{O}} : \text{H}$). We shall see in the next few chapters that such electron-sharing can be described in terms of orbitals extending over more than one atom. Covalent bonding occurs primarily between atoms not too different in *electronegativity*. The latter is a rather vague concept, defined by Pauling as “the power of an atom in a molecule to attract electrons to itself.” Electronegativity is roughly equivalent to “nonmetallic character,” and generally increases toward the upper right of the periodic table. Since atomic ionization potentials and electron affinities both tend to increase in the same direction, one method of defining

¹³ However, the bonding in CsAu (and perhaps RbAu) is largely ionic.

numerical electronegativities takes the average of these two quantities. We shall look at this and other methods in Section 7.7, where electronegativities will be found in Table 7.7.

We can now account for the most obvious division of the periodic table, that between metals and nonmetals. Basically, a metallic element is one whose atom has one or more loosely bound valence (outer-shell) electrons; this description fits all the elements whose outermost subshell is ns ($n > 1$), as well as many with partially filled p subshells. The valence electrons are easily removed to form positive ions, as we have seen in the alkalis and alkaline earths. Metals ordinarily exist as solids in which these electrons are relatively free to move throughout the crystal; the mobility of the electrons accounts for the high electrical and thermal conductivity characteristic of metals. (We shall have more to say about the structure of metals in Chapter 11.) By contrast, the typical nonmetals have nearly full p subshells, and can form closed-shell configurations by sharing only a few electrons in small, covalently bonded molecules (Cl_2 , O_2 , P_4 , etc.). The bonding forces within these molecules are strong, but (as in the inert gases) the forces between them are quite weak, so that many of the nonmetals are gases at ordinary temperatures. Along the borderline between metals and nonmetals, the elements often exist in solid forms containing infinite networks of covalent bonds; the best-known examples are the diamond and graphite forms of carbon. The great majority of the elements are metals, since all the transition elements (in which d or f subshells are being filled) have ns^2 or ns outer shells.

The trends in physical and chemical properties across the periodic table can best be understood by considering atomic sizes. The size of an atom cannot have a precise meaning, since at large distances the electron density merely trails off exponentially. However, fairly self-consistent sets of "atomic radii" can be defined for various purposes. In principle, the radii should be such that $r_A + r_B$ gives the actual internuclear distance in a bond between atoms A and B. Unfortunately, there exists no set of radii that can reproduce all bond lengths with experimental accuracy. In Table 5.2 we list *covalent radii*, which should add to give the lengths of single (two-electron) bonds between atoms not too different in electronegativity. These values are most easily obtained by halving the lengths of homonuclear single bonds (e.g., r_{Cl} is half the bond length in Cl_2). In many cases they reproduce other bond lengths within a few percent. A graph of covalent radii would closely resemble the atomic volume graph of Fig. 1.7, except that those elements made up of distinct molecules (most of the nonmetals) have relatively large volumes.

However, there are also many bond lengths quite different from what Table 5.2 predicts; let us digress to consider some of the reasons. A drastic shortening occurs when more than two electrons are shared, that is, in multiple bonds ($\text{C}-\text{C}$, 1.54 Å; $\text{C}=\text{C}$, 1.34 Å; $\text{C}\equiv\text{C}$, 1.20 Å); we shall see that this results from an increase in bonding energy. There is also a shortening associated with any degree of ionic

character (electronegativity difference) of the bond; for example, the $\text{C}-\text{O}$ single bond is 1.43 Å rather than 1.51 Å ($r_{\text{C}} + r_{\text{O}}$). For crystals essentially composed of ions rather than neutral atoms—the alkali halides, for example—one can derive an altogether different set of *ionic radii*, as we shall see in Chapter 11; the ionic radii depend strongly on charge, positive ions being smaller and negative ions larger than the neutral atoms. Finally, the effective radius of an atom increases with its *coordination number*, the number of atoms to which it is bonded. Since an atom in a solid metal usually has 6 to 12 nearest neighbors, the interatomic distances in metals are typically about 10% more than the naively-expected value of twice the covalent radii. With corrections for all these effects, one can reproduce most bond lengths with reasonable accuracy.¹⁴

Regardless of all these reservations, Table 5.2 is quite adequate for studying the relative sizes of atoms. To a rough approximation, the atomic radius corresponds to the outermost peak in the electron radial distribution (Fig. 5.4), that is, to the most probable radius of the valence electrons. Since this radius increases with n , the atomic size increases with each period in most families of the periodic table.

In an alkali metal atom we have a single outer-shell electron; if it were completely outside the closed-shell core, it would simply feel the Coulomb field of a net +1 charge, its most probable radius would be that of a hydrogen ns orbital, $r_n = n^2 a_0$, and we could predict the sizes of the alkali atoms from the quantum number n of their single valence-shell electrons and the radius of the hydrogen ns orbital with the same principal quantum number n . The actual increase in radius with Z is of course much slower: The 6s electron in cesium has its outermost peak at about 2.7 Å, compared with 26 Å for a hydrogen 6s electron. The reason is that even the outermost electron has much of its charge density within the electron core (cf. Fig. 4.5), and is thus not perfectly "shielded" from the nucleus. The binding force on each electron thus increases steadily with the nuclear charge Z , as we already know from Fig. 5.2. The 6s electron in cesium ($Z = 55$) is bound almost as tightly as the 5s electron in rubidium ($Z = 37$), and the atomic size is only slightly larger.

We can now understand the trend across each period. One might expect that adding a second ns electron would increase the atomic size, because of the repulsion between the two valence electrons. In fact, the increase of Z by 1 has a much greater effect, and the alkaline earth atoms are uniformly smaller than their alkali neighbors. Electrons in an open shell generally shield one another from the nucleus quite poorly, since they tend to be in different regions of space (for two electrons, on opposite sides of the nucleus).

¹⁴ For detailed discussions of the various kinds of atomic radii, see L. Pauling, *The Nature of the Chemical Bond*, 3rd ed. (Cornell University Press, Ithaca, N.Y., 1960), and J. C. Slater, *Quantum Theory of Molecules and Solids*, Vol. 2 (McGraw-Hill, New York, 1965).

H 0.30	Li 1.34	Na 1.54	K 1.96	Rb 2.10	Cs 2.29	Fr 2.42
	Be 0.89	Mg 1.36	Ca 1.74	Sr 1.92	Ba 1.98	Ra 2.10
	B 0.79	Al 1.25	Sc 1.44	Y 1.62	La 1.69	Ac 1.84
	C 0.77	Si 1.18	Ti 1.32	Zr 1.45	Ce 1.65	Th 1.65
	N 0.74	P 1.10	V 1.22	Nb 1.34	Pr 1.64	Pa 1.50
	O 0.74	S 1.02	Cr 1.18	Mo 1.30	Nd 1.64	U 1.42
	F 0.71	Cl 0.99	Mn 1.17	Tc 1.27	Pm 1.63	Np
He (0.5)	Ne (0.7)	Ar (0.95)	Fe 1.16	Ru 1.25	Sm 1.62	Pu
			Co 1.16	Rh 1.25	Eu 1.85	Am
			Ni 1.15	Pd 1.28	Gd 1.62	Cm
			Cu 1.17	Ag 1.34	Tb 1.61	Bk
			Zn 1.25	Cd 1.41	Dy 1.60	Cf
			Ga 1.24	In 1.43	Ho 1.58	Es
			Ge 1.22	Sn 1.40	Er 1.58	Fm
			As 1.22	Sb 1.41	Tm 1.58	Md
			Se 1.17	Te 1.37	Yb 1.70	No
			Br 1.14	I 1.33	Lu 1.56	Lr
			Kr 1.10	Xe 1.30	Hf 1.44	Rf
					Ta 1.34	Db
					W 1.30	Sg
					Re 1.28	Bh
					Os 1.26	Hs
					Ir 1.26	Mt
					Pt 1.30	
					Au 1.34	
					Hg 1.44	
					Tl 1.55	
					Pb 1.54	
					Bi 1.52	
					Po 1.53	
					At (1.50)	
					Rn (1.45)	

There are some exceptions to this trend. As we move up the series of the transition metals in the Periodic Table, the $(n-1)d$ subshell is being filled, whereas the outer shell remains virtually unchanged at ns^2 . Since inner-shell electrons shield one another poorly, these atoms are relatively small, and a slight size increase accompanies the resumption of outer-shell filling. The shrinkage due to poor shielding is even more marked for the lanthanides, in which the $4f$ sub-

The trends in atomic size are directly correlated with those in ionization potential and electron affinity. Both the latter increase across each period, as the atomic size shrinks and the outer-shell electrons become more tightly bound.

¹⁵ Note the anomalously large sizes of $\text{Eu}(\cdot \cdot \cdot 4f^{16}6s^2)$ and $\text{Yb}(\cdot \cdot \cdot 4f^{14}6s^2)$, with their exceptionally stable configurations.

They decrease sharply at the beginning of a new period, as a larger, more weakly bound outer shell is begun. And each period has values lower than the preceding, since the binding energy decreases with distance from the nucleus. This effect too is less than it would be with perfect shielding: Cesium has $I_1 = 3.89$ eV, compared with the 0.38 eV ($= 13.6 \text{ eV}/n^2$) required to ionize a 6s hydrogen electron; the effective nuclear charge seen by the valence electron in its ground state is thus $Z^* = (3.89/0.38)^{1/2} = +3.2$, rather than the +1 of perfect shielding.¹⁶

We have not yet discussed the chemical behavior of the transition metals. Although these elements have only two outer-shell *ns* electrons, the partially filled $(n-1)d$ subshell is quite near the “surface” of the atom and relatively loosely bound. As a result, transition metals ordinarily form compounds in which both the *s* and the *d* electrons are involved in bonding, with a wide variety of possible oxidation states. For example, manganese ($\cdots 3d^5 4s^2$) and oxygen form the species MnO , Mn_2O_3 , MnO_2 , and MnO_4^{2-} , and MnO_4^- . Even the unoccupied orbitals close to the outer shell can accept electrons from other species (*ligands*), giving rise to the complexes typical of the transition elements, such as $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$. These complexes usually have low-lying excited states resulting from the splitting of *d*-orbital levels; since the energy differences often correspond to visible radiation, most such complexes are colored. We shall have much to say about these species in Chapter 9. Unlike the $(n-1)d$ subshells, the lanthanide 4*f* subshell is fairly deep within the atom, and the M^{3+} ions that dominate these elements’ chemistry involve the loss of only one 4*f* electron. The actinide 5*f* electrons are not as deeply buried, and the lower actinides (especially uranium) commonly have high oxidation states. Since the binding energies of both *d* and *f* electrons increase with *Z* more rapidly than those of outer-shell electrons (cf. Fig. 5.2), the lower oxidation states again predominate toward the high-*Z* ends of the transition and actinide series.

As was mentioned in Section 5.1, paramagnetism occurs primarily in substances with unpaired electron spins. In most compounds of the nontransition elements, either ionization or the formation of covalent bonds leaves all the electrons paired. This is not true of the transition metals, in which some or all of the *d* electrons often remain unpaired; thus many transition metal compounds are paramagnetic. We shall discuss this behavior (with special reference to complex ions) in Section 9.6. The most intense paramagnetism is found among the lanthanides, with their many unpaired *f* electrons.¹⁷

We could look at other properties of the elements, nearly all showing some periodic behavior, but our point has been made. A vast amount of “chemistry”—that is, the observed differences between chemical substances—can be well understood in terms of a simple description of atomic structure. We have only scratched the surface of this subject, and further details can be found in advanced texts on inorganic chemistry. We turn in the next two sections to more detailed interactions that determine the states of atoms, in order to complete the groundwork we need to see how atoms are put together to form molecules. Then we shall devote the next four chapters to this latter task.

5.6 Term Splitting and the Vector Model

We have gone far by assuming that the electronic configuration of an atom dominates its energy and other properties. We have examined some aspects of correlation, for which the configuration model is inadequate, but this is nonetheless a very good representation of atoms with closed shells, and a good first approximation for many other real atoms as well. The set of closed-shell species includes the ground states of helium ($1s^2$), the other inert gases ($\cdots ns^2 np^6$), and the alkaline earths ($\cdots ns^2$); these configurations are distinguished by having all the occupied subshells filled. Another group that is well represented by single configurations includes hydrogen and the alkalis in their ground states ($\cdots ns$), in which the atom has a single *s* electron outside a closed-shell structure, and the halogens ($\cdots np^5$), with only a single vacancy in an otherwise closed shell. In all these cases the electron configuration corresponds to only a single state or energy level of the atom.

In most atoms, however, a single configuration may describe several different states. These are real, physically distinguishable states, which can differ from one another by as much as several electron volts in energy. One speaks of the splitting of the configuration into *terms*;¹⁸ in this context a “term” is equivalent to a state or group of states. The basic difference between terms of the same configuration lies in the angular momentum of the atom. The configuration defines the magnitudes of the vectors **L** and **S** for each electron, but not their orientations. There is thus more than one possible way to couple (add) these vectors to give the total angular momentum. These different ways of coupling correspond to different assignments of the quantum numbers m_l

¹⁶ For the alkali metal atoms we have $Z^* = n/n^*$, in terms of the effective quantum numbers of Eq. 2.12.

¹⁷ Some typical room-temperature molar susceptibilities (χ_M) in $10^{-12} \text{ m}^3/\text{mol}$: nontransition metals, Na 16, Zn -11; transition metals, Ti 153, Mn 529; lanthanides, Pr 5010, Er 44300; nonmetals, S -15, Xe -44. These values are for the elements in their normal states; higher values are often found in compounds (e.g., MnCl_2 14350).

¹⁸ This language derives from spectroscopy: For a transition between states 1 and 2, the frequency of the absorbed or emitted radiation is given by

$$\nu = \left| \frac{E_2}{h} - \frac{E_1}{h} \right|,$$

the difference of two *terms* characteristic of the two states.

and m_s , hence to different spatial distributions of the electrons. Since the spatial relationships of the electrons are different, the terms must differ in energy.

We can describe this term splitting most simply with the *vector model of the atom*. This is a method for organizing the possible states of an atom into terms, by selecting only the most important of the many types of interaction. It also serves as a bookkeeping device for counting and classifying the terms corresponding to a given configuration. The essence of the vector model lies in the ways of adding angular momentum vectors, the topic we postponed discussing in Section 5.1.

In contrast to vector addition in classical physics, the addition of quantum mechanical angular momenta cannot be carried out by determining the x , y , and z components of the individual vectors and adding these separately. This is because the uncertainty principle forbids us to know more about any angular momentum vector than its magnitude and one of its components, usually defined as the z component. Knowing only the lengths and the z components, however, is sufficient to define the quantum states we need. For any quantized angular momentum vector, say \mathbf{J} , the two are related by the usual space-quantization rules: The magnitude of \mathbf{J} is given by an equation of the form of Eq. 5.1,

$$|\mathbf{J}| = [J(J+1)]^{1/2} \hbar, \quad (5.18)$$

and the z component by an equation of the form of Eq. 5.2,

$$J_z = M_J \hbar \quad (M_J = J, J-1, \dots, -J+1, -J), \quad (5.19)$$

with appropriate quantum numbers J and M_J .

We can approach the classification of atomic states by a series of approximations. The first, of course, is the central field approximation, in which the energy of the atom depends only on the configuration—that is, on the values of n and l (and thus $|\mathbf{L}|$) for each of the electrons, but not on the values of m_l and m_s . This would be valid only if each electron moved in a spherically symmetric field; in the real atom, the electron–electron interactions split up each configuration into many states of somewhat different energies. The next approximation rests on the fact that some kinds of interactions are much stronger than others. For the lighter atoms, all states with the same values of the quantum numbers L and S (for the entire atom) have nearly the same energy, whereas states with different values of L or S are appreciably different in energy. One can thus group together all states with the same L, S as a single term; when this is a good approximation, one speaks of *LS coupling*.¹⁹

Why is the energy so strongly dependent on the values of L and S ? The reasons are those we introduced when discussing the exclusion principle: the Coulomb and exchange

interactions between electrons. The quantum number L defines the total orbital angular momentum of the atom; as in the hydrogen atom, the value of L governs the symmetry of the atomic wave function. States with different L obviously have different charge distributions, and thus different electron–electron interaction energies. The effect of the spin quantum number S is more indirect. Each value of S corresponds to a particular combination of the electronic m_s 's, which by the exclusion principle can be combined only with particular values of m_l (e.g., if two electrons in a given subshell have the same m_s , their values of m_l must differ). Thus a change in S also implies a change in the charge distribution and energy.

The total angular momentum vectors for an atom can be obtained by adding together (*coupling*) the vectors for the individual electrons:

$$\mathbf{L} = \sum_i \mathbf{L}_i \quad \text{and} \quad \mathbf{S} = \sum_i \mathbf{S}_i. \quad (5.20)$$

The z components of \mathbf{L} and \mathbf{S} are then given by

$$L_z = M_L \hbar \quad \left(M_L = \sum_i m_{li} \right) \quad \text{and} \quad S_z = M_S \hbar \quad \left(M_S = \sum_i m_{si} \right). \quad (5.21)$$

One can readily show that both \mathbf{L} and \mathbf{S} sum to zero over any closed subshell;²⁰ thus only those electrons outside closed subshells ("open-shell electrons") need to be taken into account. For example, the inert gases and alkaline earths have $\mathbf{L} = \mathbf{S} = 0$, and can thus have only a single term with $L = S = 0$. The alkalis have one s electron outside a closed shell and therefore have $L = 0$, $S = \frac{1}{2}$. Group III elements boron, aluminum, etc., with one p electron outside a closed s^2 subshell, can have only $L = 1$, $S = \frac{1}{2}$, and also show no term splitting. The same is true for the halogens, with only one vacancy in a subshell: Again we have $L = 1$, $S = \frac{1}{2}$, because m_l and m_s cancel out for all but one of the electrons. It is only in configurations with more than one unpaired electron²¹ that things get more complicated and term splitting appears.

The simplest atom for which these complications appear in the ground state is that of carbon, with the configuration $1s^2 2s^2 2p^2$. We need consider only the two open-shell

²⁰ From Table 3.1 one can see that $\sum_{m_l} |Y_{l,m_l}(\theta, \phi)|^2$ for any l is independent of θ and ϕ . That is, the total electron distribution for a closed subshell is spherically symmetric, and thus has no orbital angular momentum. It is also clear that the z components of \mathbf{L} and \mathbf{S} must vanish, since positive and negative values of m_l and m_s cancel.

²¹ That is, in which at least one subshell contains more than one electron and more than one vacancy.

¹⁹ Also known as *Russell-Saunders coupling*.

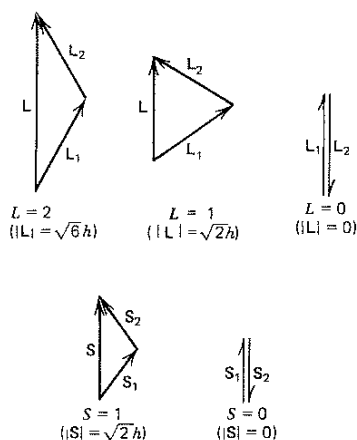


Figure 5.8 Possible ways of coupling angular momentum vectors for two p electrons: $\mathbf{L} = \mathbf{L}_1 + \mathbf{L}_2$, $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$. Each electron has $l = 1$, $s = \frac{1}{2}$, so that

$$|\mathbf{L}_1| = |\mathbf{L}_2| = [l(l+1)]^{1/2} \hbar = \sqrt{2} \hbar,$$

$$|\mathbf{S}_1| = |\mathbf{S}_2| = [s(s+1)]^{1/2} \hbar = \frac{\sqrt{3}}{2} \hbar.$$

The diagrams show the only ways of adding these vectors consistent with

$$|\mathbf{L}| = [L(L+1)]^{1/2} \hbar, \quad |\mathbf{S}| = [S(S+1)]^{1/2} \hbar.$$

The vectors are drawn in their own plane; the z axis is in general not in this plane, but must be at an angle such that $L_{zi} = m_{li}\hbar$, $L_z = M_L\hbar$, $S_{zi} = m_{si}\hbar$, $S_z = M_S\hbar$. There are six possible combinations of L and S , but for equivalent electrons (same n , l) the exclusion principle allows only $L = 1$, $S = 1$; $L = 2$, $S = 0$; and $L = 0$, $S = 0$.

$2p$ electrons. A single $2p$ electron has $n = 2$, $l = 1$, three possible choices of m_l , and two possible choices of m_s , a total of six possible sets of quantum numbers; because of the exclusion principle, only five of these are available to a second electron. There are thus $(6 \times 5)/2 = 15$ possible assignments of the two electrons. (Division by 2 is required because the electrons are indistinguishable, and we cannot tell which is counted first.) Not all of these 15 assignments are physically distinguishable; to see how many separate terms they give rise to, we must determine what values of L and S can correspond to each assignment.

In Fig. 5.8 we show the possible ways in which the angular momentum vectors of two p electrons can be added to give different values of L and S . The value of L for an atom, like that of L for an electron, must be a positive integer or zero ($L = 0, 1, 2, \dots$); the value of S is integral ($S = 0, 1, 2, \dots$) for an even number of electrons, half-integral ($S = \frac{1}{2}, \frac{3}{2}, \dots$) for an odd number. In the LS -coupling approximation, each physically distinct state (term) of the atom corresponds to a specific combination of L and S . These terms can be found in several ways, but the most straightforward method is sufficient for our purposes.

For an electron with given quantum numbers l_i , m_{li} , m_{si} we know both the magnitudes and the z components of the vectors \mathbf{L}_i , \mathbf{S}_i . Although these vectors can add to give several different atomic values of L or S , there is no ambiguity in the addition of the z components:

$$M_L = \sum_i m_{li}, \quad M_S = \sum_i m_{si}. \quad (5.22)$$

One can thus make a preliminary classification of atomic states according to the values of M_L and M_S . This is done by tabulating all the possible assignments of m_l and m_s for the open-shell electrons, then obtaining the sums of Eq. 5.22 for each such assignment. In Table 5.3 we have illustrated how this is done for the carbon atom (or any other np^2 configuration). In order to satisfy the exclusion principle, any state in which both electrons have the same m_l must have $m_{s1} \neq m_{s2}$. Since the two electrons are equivalent, two assignments that differ only by interchange of the subscripts "1" and "2" correspond to the same state, which we list only once.²² We thus obtain the predicted 15 assignments.

Next we decide which values of L and S go with each of these assignments. Since for any state we must have $M_L \leq L$, the existence of states with $M_L = \pm 2$ implies that there must be a term with $L = 2$, that is, a D term. This term must also include states with the other possible orientations of \mathbf{L} relative to the z axis—that is, it includes one each of the states with $M_L = 1, 0, -1$ in Table 5.3. We do not need to specify which states these are, and within the scope of this text one cannot make such a specification. Finally, since the states with $M_L = \pm 2$ have only $M_S = 0$, we conclude that S must be zero for the D term. To sum up, five of the states in Table 5.3 belong to a term with $L = 2$, $S = 0$. We designate any atomic term by a capital letter corresponding to the value of L , with a left superscript equal to $2S + 1$ (called the *multiplicity*); in the present case the term is 1D , read "singlet D ."

That is one term accounted for. There are no other states with $M_L = 2$, and thus no other terms with $L = 2$. Three states each remain unassigned with $M_L = 1, -1$; these must belong to a term (or terms) with $L = 1$, a P term. Each of these groups of three (triplets) is made up of states with $M_S = 1, 0, -1$, which correspond to the possible orientations of \mathbf{S} for $S = 1$. The term containing these states thus has $L = 1$, $S = 1$, with the designation²³ 3P ("triplet P "). To complete

²² Thus $m_{l1} = 1$, $m_{l2} = 1$, $m_{s1} = \frac{1}{2}$, $m_{s2} = -\frac{1}{2}$ is the same state as $m_{l1} = 1$, $m_{l2} = 1$, $m_{s1} = -\frac{1}{2}$, $m_{s2} = \frac{1}{2}$. But $m_{l1} = 1$, $m_{l2} = 0$, $m_{s1} = \frac{1}{2}$, $m_{s2} = -\frac{1}{2}$ and $m_{l1} = 1$, $m_{l2} = 0$, $m_{s1} = -\frac{1}{2}$, $m_{s2} = \frac{1}{2}$ are different states, since only the m_s 's are interchanged. In Chapter 6 we shall designate the spin states of individual electrons by the *Pauli spin functions*: If electron 1 has $m_s = +\frac{1}{2}$, we write $\alpha(1)$ as its spin function; if electron j has $m_s = -\frac{1}{2}$, we write its spin function as $\beta(j)$.

²³ The multiplicity $2S + 1$ gives the number of possible quantized orientations of the vector \mathbf{S} . Terms with $2S + 1 = 1, 2, 3, 4, \dots$ are called *singlets*, *doublets*, *triplets*, *quartets*, etc.

Table 5.3 Addition of z Components of Angular Momenta for Two Equivalent p Electrons (as in the Carbon Atom, $1s^2 2s^2 2p^2$): $l_1 = l_2 = 1$

m_{l_1}	m_{l_2}	$M_L = \sum_i m_{li}$	m_{s_1}	m_{s_2}	$M_S = \sum_i m_{si}$	Term
1	1	2	$\frac{1}{2}$	$-\frac{1}{2}$	0	1D
1	0	1	$\frac{1}{2}$	$\frac{1}{2}$	1	3P
			$\frac{1}{2}$	$-\frac{1}{2}$	0	$^1D, ^3P$
			$-\frac{1}{2}$	$\frac{1}{2}$	0	3P
1	-1	0	$-\frac{1}{2}$	$-\frac{1}{2}$	-1	3P
			$\frac{1}{2}$	$\frac{1}{2}$	1	3P
			$-\frac{1}{2}$	$-\frac{1}{2}$	-1	3P
0	0	0	$\frac{1}{2}$	$-\frac{1}{2}$	0	$^1D, ^3P, ^1S$
			$-\frac{1}{2}$	$\frac{1}{2}$	0	
			$\frac{1}{2}$	$-\frac{1}{2}$	0	
0	-1	-1	$\frac{1}{2}$	$\frac{1}{2}$	1	3P
			$\frac{1}{2}$	$-\frac{1}{2}$	0	$^1D, ^3P$
			$-\frac{1}{2}$	$\frac{1}{2}$	0	
-1	-1	-2	$-\frac{1}{2}$	$-\frac{1}{2}$	-1	3P
			$\frac{1}{2}$	$-\frac{1}{2}$	0	1D

NUMBER OF ASSIGNMENTS			
M_L	M_S		
	1	0	-1
2		1	
1	1	2	1
0	1	3	1
-1	1	2	1
-2		1	

the possible orientations of \mathbf{L} , the 3P term must also include a set of states with $M_L = 0$ and $M_S = 1, 0, -1$; these account for three of the as-yet-unassigned states with $M_L = 0$. The 3P term thus comprises a total of nine states, and only one of the original 15 states remains unassigned, one of the states with $M_L = 0, M_S = 0$. This state can only be the single component of a term with $L = 0, S = 0$, a 1S ("singlet S") term.

We have thus shown that the ground-state configuration of the carbon atom contains three terms: 1D , 3P , and 1S . (Note that three of the geometrically possible L, S combinations in Fig. 5.8 do not exist; they are ruled out by the exclusion principle.) Among them these terms account for all 15 possible assignments of quantum numbers: nine states in the 3P term, five in the 1D , one in the 1S . For seven of these 15 states, however, we cannot tell which assignment goes with which term (see Table 5.3); in these states we cannot assign a complete set of quantum numbers to the individual electrons. For example, there are two states with $M_L = 1, M_S = 0$, one in the 1D term and one in the 3P term; but there is no way to specify in which of these the electron with

$m_l = 1$ has $m_s = \frac{1}{2}$. In cases such as this, the orientations of \mathbf{L}_i and \mathbf{S}_i for each electron are not fixed, and the z components of \mathbf{L}_i and \mathbf{S}_i ($m_l\hbar$ and $m_s\hbar$) are not constants of the motion. We say that m_l and m_s are no longer "good quantum numbers." One can interpret this by saying that the electrons interact in such a way as to exert torques on one another, changing the orientation of each electron's angular momentum. This picture explains why we speak of "coupled" angular momenta. What the LS -coupling model assumes is that the total angular momenta \mathbf{L} and \mathbf{S} are conserved, so that L, M_L, S , and M_S are good quantum numbers.

If the electrons do not have definite quantum numbers, how does one set up the wave function for an atom in a given term? In the orbital model the atomic wave function, Eq. 5.15, is a product (or a determinant) of the orbital wave functions ϕ_i , each of which involves the quantum numbers of a particular electron. What one must do is to obtain such a product, call it $\psi^{(j)}$, for each of the possible assignments in the term; the atomic wave function is then a linear combination of these products, $\sum_j c_j \psi^{(j)}$. The problem, which we shall not go into, is to obtain the c_j such that the resulting wave function gives the correct values of L and S , i.e., is an eigenfunction of the operators L^2 and S^2 .

The three terms in the carbon atom's ground configuration are physically distinct, each with its own energy, electron distribution, and magnetic properties. The terms 3P and 1D , however, are *multiplets*, consisting of nine and five states, respectively. In the LS -coupling approximation the states within a given term are degenerate, all having the same energy. In reality there is a further fine-structure splitting, for reasons we shall discuss in the next section.

One can obtain from spectroscopic data the energy levels corresponding to the various terms. In the carbon atom the 3P term is lowest in energy, the 1D next, and the 1S highest (cf. Fig. 5.9). For most ground-state configurations, the order of term energies is conveniently given by *Hund's rules*:

1. Within a given configuration, the term energies increase as S decreases.
2. Among terms with the same S , the term energies increase as L decreases.

This ordering implies that the differences in electron-electron interactions associated with different values of S affect the energy more strongly than the corresponding differences associated with L ; this is indeed true when the LS -coupling approximation applies. Since the energy is lowest when S has its maximum value, the ground states of open-shell atoms usually have as many electrons as possible with unpaired spins.

It was long believed that the physical basis for Hund's first rule is a simple effect: that the Pauli exclusion principle keeps two electrons of the same spin far enough away from each other to make their repulsive Coulomb interaction

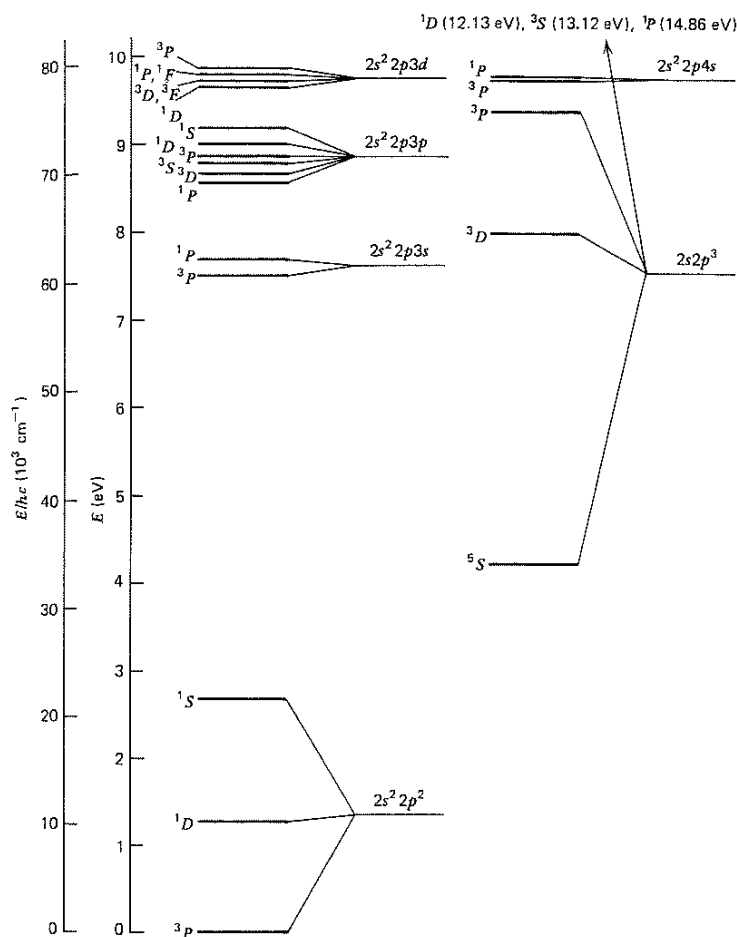


Figure 5.9 Low-lying energy levels of the carbon atom, with term designations. The terms belonging to each configuration have been bracketed together. The energy is measured above the ground state.

smaller than it is in a corresponding singlet, where the exclusion principle does not affect the spatial correlation. Careful studies²⁴ made it clear that the interelectronic energy of Coulomb repulsion is *larger* in triplet states of simple atoms and molecules than it is in the corresponding singlets based on the same configurations. The reason the energies of the triplets are lower and Hund's first rule holds is that the larger electron–electron repulsion of the triplet is accompanied by an attractive electron–nuclear attraction that more than compensates for the electron–electron repulsion. The electrons in the triplets have larger average values of r_{12}^{-1} , by coming closer, on average, to their nuclei and thus to one another.

The method we have developed for the carbon atom can be applied to other atoms as well. Reviewing the single-term configurations, we see that the closed-shell atoms, with $L = 0$, $S = 0$, have only $1S$ terms; the alkalis ($\cdots ns$, $L = 0$, $S = \frac{1}{2}$) only $2S$ terms; and the boron–aluminum group ($\cdots np$, $L = 1$, $S = \frac{1}{2}$) only $2P$ terms. If a subshell is more than half-filled, it is simpler to work with the vacancies (“holes”) in the subshell as if they were electrons; one can show that the values of L and S are the same when calculated either way. For example, the ground state of the oxygen atom, $1s^2 2s^2 2p^4$, with two holes in the $2p$ subshell, can be treated as a case of $2p^2$. The oxygen atom thus has the same three terms as the carbon atom, as do the other $\cdots np^2$ and $\cdots np^4$ elements. Similarly, the halogens ($\cdots np^5$) have only $2P$ terms like the boron group. The only nontransition elements remaining are the nitrogen group ($\cdots np^3$), for which the ground state must have $S = \frac{3}{2}$ by Hund's first rule; the rest of the term analysis is left as a problem. (Note that the filling sequence ns^2 , $ns^2 np$, \dots , $ns^2 np^6$ has the ground-state multiplicities 1, 2, 3, 4, 3, 2, 1.)

²⁴ See, for example, E. R. Davidson, *J. Chem. Phys.* **42**, 4199 (1965); J. P. Colpa and R. E. Brown, *Mol. Phys.* **26**, 1453 (1973); E. A. Colbourn, *J. Phys. B* **8**, 1926 (1975); J. Katriel and R. Pauncz, *Adv. Quantum Chem.* **10**, 145 (1977).

As for the transition elements, one can now see what is implied by most of the anomalies in those electron configurations marked by stars in Table 5.1. Consider the chromium atom ($Z = 24$), which one would expect to be $\cdots 3d^4 4s^2$. By Hund's first rule, the ground state would have $S = 2$, with four parallel spins. But the actual ground-state configuration is $\cdots 3d^5 4s$, which by Hund's rule should have six parallel spins ($S = 3$). Thus the effect of the increase in S on the energy must be greater than the very small difference between the $3d$ and $4s$ orbital energies. In the copper atom ($Z = 29$), the shift from $\cdots 3d^9 4s^2$ to $\cdots 3d^{10} 4s$ does not affect S ; however, the exchange interaction is particularly large for a filled (or half-filled) subshell, in which the electrons of each spin have a spherically symmetric charge density, and the resulting term splitting again outweighs the orbital energy difference. Nearly all the anomalous configurations contain (or at least tend toward) filled or half-filled d or f subshells, which are stabilized by these effects.

So far we have discussed only configurations with *equivalent* open-shell electrons, electrons in the same subshell. If the electrons are nonequivalent, there is a slight difference in the bookkeeping. Let us consider the $1s^2 2s^2 2p 3p$ excited state of carbon, in which the $2p$ and $3p$ electrons are nonequivalent. The table of quantum number assignments, Table 5.4, is now somewhat longer than in the equivalent-electron case.

Since the two p electrons have different values of n , the exclusion principle no longer limits the possible values of m_s , and all 36 of the possible combinations are distinct assignments. The smaller table shows how these assignments are distributed over the possible values of M_L and M_S . By reasoning like that we used before, it is not difficult to find the terms: These are 1D (5 states), 3D (15 states), 1P (3 states), 3P (9 states), 1S (1 state), and 3S (3 states), the number of states again adding up to 36. This time we have used all possible combinations of L and S (Fig. 5.8).

Other excited configurations can be similarly analyzed into their terms; Fig. 5.9 shows all the energy levels of the carbon atom up to 10 eV above the ground state, each with its configuration and term designation. In general, both the energy differences between configurations and those between terms of the same configuration tend to grow smaller with increasing excitation energy. This is apparent here in the sequence $2p^2$, $2p3s$, $2p3p$, $2p3d$, $2p4s$ (as usual, the $3d$ and $4s$ energies are practically the same): The more a given electron is excited, the greater is its average distance from the nucleus, the less it interacts with the inner electrons, and thus the smaller is the term splitting. In highly excited states, however, the configurations tend to overlap in energy, indicating that the differences between orbital energies in the central field decrease even more rapidly than the term splitting due to deviations from the central field.

For most atoms term assignments have been made for hundreds or even thousands of states, where energy differences are obtained from spectroscopic data. Yet only a frac-

Table 5.4 Addition of s Components of Angular Momenta for Two Nonequivalent p Electrons (as in $1s^2 2s^2 2p 3p$, the Excited State of Carbon): $l_1 = l_2 = 1$

m_{l1}	m_{l2}	$M_L = \sum_i m_{li}$	m_{s1}	m_{s2}	$M_S = \sum_i m_{si}$
1	1	2	$\frac{1}{2}, -\frac{1}{2}$	$\frac{1}{2}, -\frac{1}{2}$	1, 0, 0, -1
1	0	1	$\frac{1}{2}, -\frac{1}{2}$	$\frac{1}{2}, -\frac{1}{2}$	1, 0, 0, -1
1	-1	0	$\frac{1}{2}, -\frac{1}{2}$	$\frac{1}{2}, -\frac{1}{2}$	1, 0, 0, -1
0	1	1	$\frac{1}{2}, -\frac{1}{2}$	$\frac{1}{2}, -\frac{1}{2}$	1, 0, 0, -1
0	0	0	$\frac{1}{2}, -\frac{1}{2}$	$\frac{1}{2}, -\frac{1}{2}$	1, 0, 0, -1
0	-1	-1	$\frac{1}{2}, -\frac{1}{2}$	$\frac{1}{2}, -\frac{1}{2}$	1, 0, 0, -1
-1	1	0	$\frac{1}{2}, -\frac{1}{2}$	$\frac{1}{2}, -\frac{1}{2}$	1, 0, 0, -1
-1	0	-1	$\frac{1}{2}, -\frac{1}{2}$	$\frac{1}{2}, -\frac{1}{2}$	1, 0, 0, -1
-1	-1	-2	$\frac{1}{2}, -\frac{1}{2}$	$\frac{1}{2}, -\frac{1}{2}$	1, 0, 0, -1

NUMBER OF ASSIGNMENTS

$M_L \backslash M_S$	1	0	-1
2	1	2	1
1	2	4	2
0	3	6	3
-1	2	4	2
-2	1	2	1

Note: The tabulation of the m_s 's is condensed. For each combination of m_{l1} and m_{l2} , there are four possible assignments:

m_{s1}	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$
m_{s2}	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$
M_S	1	0	0	-1

tion of the conceivable transitions between states are observed, many transitions being "forbidden" for reasons outlined in Section 4.5. In the LS -coupling approximation the principal selection rules for allowed transitions can be shown to be

$$\begin{aligned} \Delta l &= \pm 1 && \text{(for an electron),} \\ \Delta L &= 0, \pm 1, && \Delta S = 0 && \text{(for the atom);} \end{aligned} \quad (5.23)$$

these rules hold quite well for the lighter atoms. They are illustrated for the helium atom by Fig. 5.10, which groups the energy levels by their term designations and shows the principal spectral lines. The most striking feature is that transitions between singlet and triplet states are forbidden, in accordance with the rule $\Delta S = 0$. (A line corresponding to $1s^2 1S - 1s2p^3 P$ does appear, but very weakly.) Both $1s2s$ excited states are metastable: Since they can decay to the ground state only by forbidden transitions, they have relatively long lifetimes. Note also how all the energy levels for a given n approach one another as $n \rightarrow \infty$; each series of terms converges to the same limit, the ground state of the He^+ ion.

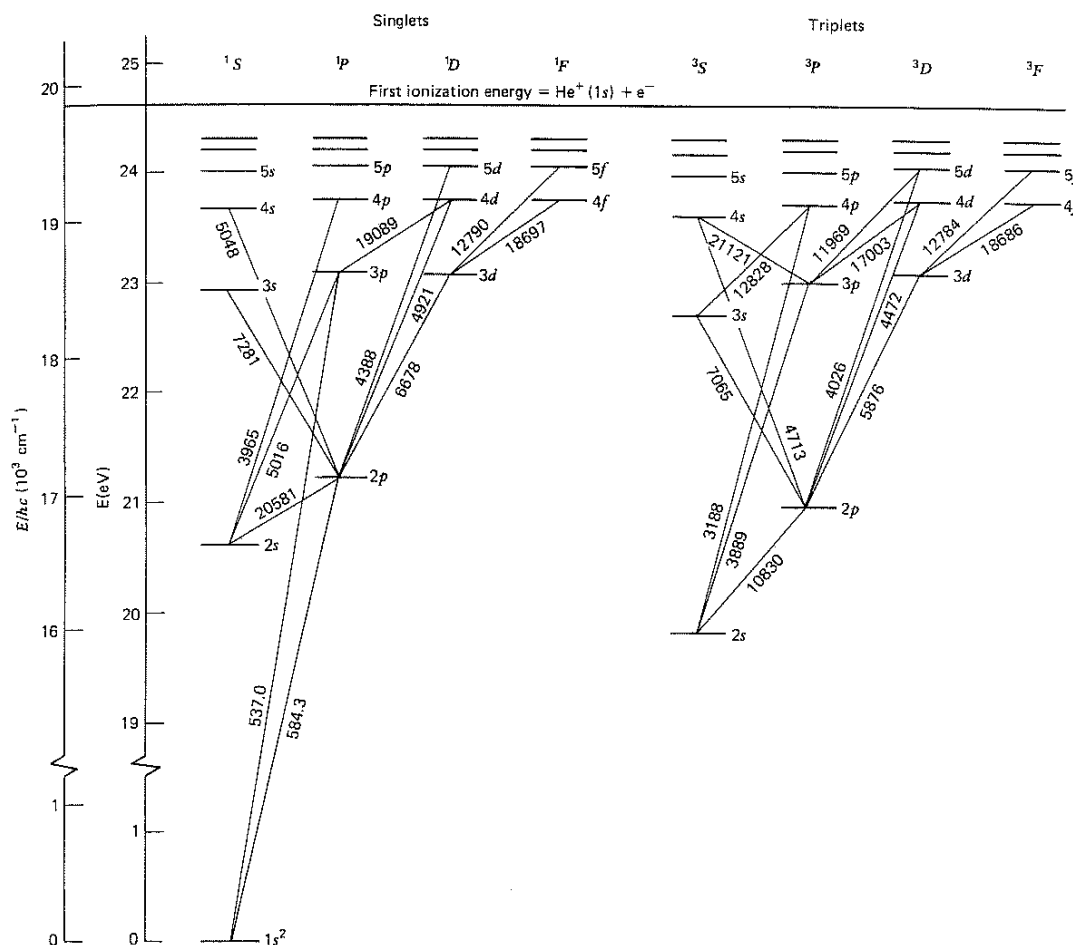


Figure 5.10 Energy levels of the helium atom, arranged by term designations. Except for the ground state, each level is identified by the configuration of only the excited electron. Some of the principal (most intense) spectral lines are shown, each with its wavelength in angstroms.

5.7 Fine Structure and Spin–Orbit Interaction

We still have not come to the end of our analysis of atomic energy levels. Not only do configurations split into terms, but the terms themselves often split into closely spaced levels. This is the fine structure of the energy spectrum, which we have already mentioned on several occasions. Some examples are illustrated in Fig. 5.11.

What is the cause of the fine-structure splitting? The term splitting is due to the nonspherical part of the electrostatic interactions between electrons. Reviewing the Hamiltonian of Eq. 5.10, we see that we still have not considered the magnetic moment interactions. Each electron has both an orbital magnetic moment and a spin magnetic moment, which interact with each other and with the moments of all the other electrons. Since it is precisely in the orientation of

\mathbf{L} and \mathbf{S} that the states within a given term differ from one another, the electrons in each of these states see a slightly different magnetic field. The states of a multiplet term are thus not really degenerate after all.

The interaction between the spin and orbital magnetic moments is ordinarily far greater than the spin–spin and orbital–orbital interactions. We can thus neglect the latter two and speak only of the *spin–orbit interaction*. The logical extension of the *LS*-coupling model is to assume that this interaction depends only on the total L and S for an atom. To a fairly high level of approximation, the interaction energy is given by

$$E_{so} = \zeta \mathbf{L} \cdot \mathbf{S} = \langle \zeta \mathbf{L} \cdot \mathbf{S} \rangle, \quad (5.24)$$

where the multiplier ζ is a function of the specific atomic state. The value of ζ is notably difficult to obtain from

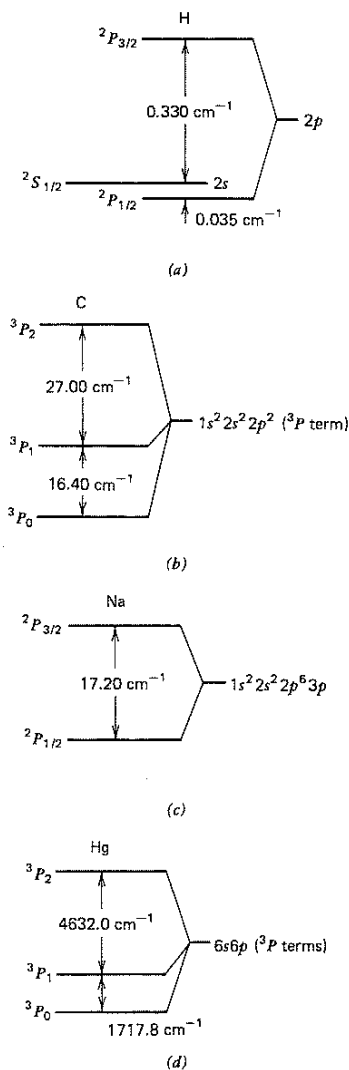


Figure 5.11 Some fine-structure splittings (not drawn to the same scale). Energy differences are expressed as $\Delta E/hc$ in cm^{-1} : $1 \text{ eV}/hc = 8066 \text{ cm}^{-1}$. (a) The $n = 2$ level of hydrogen. (b) The ground-state term of carbon (cf. Fig. 5.9). (c) The first excited state of sodium: Sodium-vapor lamps emit a doublet line at 5890 and 5896 Å, corresponding to the transitions $2p \ ^2P_{3/2} \rightarrow 2s \ ^2S_{1/2}$ and $2p \ ^2P_{1/2} \rightarrow 2s \ ^2S_{1/2}$. (d) The first excited state of mercury, showing the effect of large spin-orbit interaction in heavy atoms.

theory in any general way, and is often treated as an experimental parameter. Equation 5.24 then represents the fact that the interaction of two magnetic dipoles must involve their scalar product, in this case $\mu_L \cdot \mu_S$, which is proportional to $\mathbf{L} \cdot \mathbf{S}$. Leaving ζ as a parameter is often useful when one wishes to make spectral assignments or predict magnetic properties.

The spin-orbit energy can be put in more convenient form in terms of the total angular momentum \mathbf{J} , which is the vector sum of \mathbf{L} and \mathbf{S} :

$$\mathbf{J} \equiv \mathbf{L} + \mathbf{S}. \quad (5.25)$$

Since

$$\mathbf{J}^2 \equiv \mathbf{J} \cdot \mathbf{J} = \mathbf{L}^2 + \mathbf{S}^2 + 2\mathbf{L} \cdot \mathbf{S}, \quad (5.26)$$

substitution in Eq. 5.24 gives

$$E_{so} = \frac{\zeta}{2} (\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2). \quad (5.27)$$

All three of these squares of angular momenta are capable of being measured simultaneously. Hence it is no surprise that \mathbf{J}^2 for an atom is a constant of the motion, with eigenvalues given by

$$\mathbf{J}^2 = J(J+1)\hbar^2; \quad (5.28)$$

J is sometimes called the *inner quantum number*. Like S , J is integral for an even number of electrons, half-integral for an odd number. The z component of \mathbf{J} is

$$J_z = M_J \hbar \quad (M_J = J, J-1, \dots, -J), \quad (5.29)$$

so that for each J there are $2J+1$ possible space-quantized orientations of \mathbf{J} , giving Zeeman-effect splitting in an external field.

Just as in a given configuration the \mathbf{L}_i and \mathbf{S}_i can add to give various values of L and S (cf. Fig. 5.8), so in a given term \mathbf{L} and \mathbf{S} can add to give several values of J . The maximum value of the z component for given L , S is clearly

$$\begin{aligned} (J_z)_{\max} &= (L_z + S_z)_{\max} \\ &= (M_L + M_S)_{\max} \hbar = (L + S)\hbar, \end{aligned} \quad (5.30)$$

or $(M_J)_{\max} = L + S$; since M_J runs up to J , the maximum value of J is also $L + S$. One can similarly show that the minimum possible value of J is $|L - S|$, so that J can have the values $L + S, L + S - 1, \dots, |L - S|$. For example, in a 3D term ($L = 2, S = 1$) we have $J = 3, 2, 1$. The term thus splits into states of slightly different energy, designated by a right subscript giving the value of J : $^3D_3, ^3D_2, ^3D_1$. Note that no such splitting occurs if either L or S is zero, that is, in all S or singlet terms; this is why the inert gases (1S), alkalis (2S), and alkaline earths (1S) have no fine structure in their ground states. In the LS -coupling approximation the selection rules (Eq. 5.23) are supplemented by

$$\Delta J = 0, \pm 1 \quad (5.31)$$

(with $J = 0 \rightarrow J = 0$ forbidden); the various values of J in a given pair of initial and final terms give rise to what is called a spectral multiplet, several closely spaced lines. For light atoms the spin-orbit interactions lead to relatively small differences between the energies of states with the same L , S but different J . In the first row of the periodic table (Li to Ne), these energy differences are at most comparable to mean thermal energies at room temperature (ca. 0.04 eV/molecule). However, the interaction energy increases rapidly with nuclear charge, roughly as Z^4/n^3 . The halogen atoms offer a clear illustration of this effect. The ground configuration of a halogen atom is $\dots np^5$, giving only a 2P term ($L = 1$, $S = \frac{1}{2}$). This term may have either of two values of J , $\frac{1}{2}$ or $\frac{3}{2}$. The energy separations, $E(^2P_{1/2}) - E(^2P_{3/2})$, for fluorine, chlorine, bromine, and iodine are 0.05, 0.11, 0.46, and 0.94 eV, respectively. This means that both states are effectively part of the ground state in the fluorine atom at ordinary temperatures, but that the higher-energy $^2P_{1/2}$ states must really be considered as excited states for the other halogens. The upper state of iodine was used to store the energy in the first chemical laser, with the radiation due to the transition $^2P_{1/2} \rightarrow ^2P_{3/2}$. Some other typical spin-orbit splittings are shown in Fig. 5.11;²⁵ note that the effect occurs even in the hydrogen atom, breaking up the degeneracy of states with the same n .

The LS -coupling approximation assumes that all states of the same term have virtually the same energy, regardless of J , with the spin-orbit interaction only a minor perturbation. This clearly breaks down in the heavier atoms, where an approximation known as *jj coupling* is more useful. In this scheme the \mathbf{L}_i and \mathbf{S}_i of each electron are first coupled to form a \mathbf{J}_i (with quantum numbers j_i, m_{j_i}), and the \mathbf{J}_i are then coupled to form \mathbf{J} for the atom. Each set of j_i then gives a " j_i term," a group of closely spaced levels with the Coulomb-exchange interaction producing the fine structure. The selection rules for L and S break down and are replaced by $\Delta j = 0, \pm 1$ (for an electron). In the previous section we pointed out how the electronic interactions spoil the quantum numbers m_l and m_s , since each electron's angular momenta no longer have constant orientations. What the

spin-orbit interaction does is to make L and S no longer good atomic quantum numbers. Once \mathbf{L} and \mathbf{S} interact with each other, neither is separately conserved. In heavy atoms, the selection rule of Eq. 5.31 is the only one obeyed; violations of the rules of Eq. 5.23 are quite common. One example is the familiar bluish light of a mercury street lamp; the transition responsible for emission of this intense light would be forbidden by the rules of the LS -coupling scheme.

Strictly speaking, things are even worse than this. Once the electrons interact at all, the energy and total angular momentum of each electron cannot be conserved, which means that n and l are not really good quantum numbers either. The assignment of atoms to specific configurations (not to mention terms) is thus only an approximation, although for most purposes a very good one. In the most accurate calculations including electron correlation one must take the actual atomic wave function to be a linear combination ("mixture") of the wave functions corresponding to various configurations; this is an extension of the method we described earlier for the wave functions of individual terms. In such a rigorous approach one cannot meaningfully assign any quantum numbers or energies to individual electrons.

Why do we emphasize these limitations on our assumptions when one can get quite good results with the electron configuration model? Unfortunately, there are important quantities for which these results are not good enough, in particular those quantities that depend on small differences between very large numbers. The total electronic binding energy in a large atom may be some thousands of electron volts, but the energy *change* when two such atoms join to form a molecule—the bond energy—is typically of the order of 5 eV. The best Hartree-Fock calculations for atoms are no better than 0.1–0.2% in the energy. In molecules one cannot do even that well, since there is not spherical symmetry and interatomic forces spoil the configuration model still more. It is thus clear that one must use different techniques to obtain bond energies and other quantities of chemical interest for molecules. In the next chapter we shall begin to see how this is done.

The discussion thus far has neglected one other kind of angular momentum and magnetic moment that affects the energy levels of atoms and molecules, albeit on a scale of energies smaller than the spin-orbit and spin-spin interactions of electrons. This is the angular momentum of the nucleus, which produces a magnetic field of order 1/2000 of the field of the electron spin but whose effects are quite detectable in high-resolution spectra. The splittings of energy levels associated with the magnetic electron-nuclear interactions are called *hyperfine* interactions because of the small size of the effects. They have proved to be useful probes of how the electron penetrates the nucleus.

²⁵ With sufficient resolution one can often observe even finer splittings, known as *hyperfine structure*; the difference between hyperfine levels is usually of the order of a few tenths of a cm^{-1} ($\Delta E/hc$). There are two principal causes: (1) each isotope of an element has a different nuclear mass. Thus the reduced masses of the electrons differ slightly among the isotopes, as do their energy levels; cf. Eq. 4.16 and footnote 5 of Chapter 4 for hydrogenlike atoms. (2) The spin magnetic moment of the nucleus interacts with the electron magnetic moments, with an effect similar to that of spin-orbit splitting. In the hydrogen atom both spins are $\frac{1}{2}$, giving rise to two states; the transition between them produces the famous 21 cm line used by radio astronomers to detect hydrogen.

The Stern–Gerlach Experiment

Among the experiments that illustrate the nature of quantization, perhaps the most vivid is the one first performed by O. Stern and W. Gerlach in 1921. This experiment clearly demonstrated that angular momenta (and the associated magnetic moments) are quantized, and that space quantization makes possible the physical separation of atoms or molecules in different quantum states. It also furnished the evidence from which the existence of electron spin was later deduced. The experiment could be done with atoms having either spin or orbital angular momentum; in fact, Stern and Gerlach worked with silver atoms, which have a spin of $\frac{1}{2}$ (the same as the electron) and zero orbital angular momentum.

In essence, the Stern–Gerlach experiment consists of passing a beam of atoms down a collimating axis and into an *inhomogeneous* magnetic field, whose field strength is greater on one side of the beam than on the other. Such a system is shown in Fig. 5A.1. A uniform field would merely tend to align the atomic magnets; the inhomogeneous field also exerts a net translational force on the atoms. The field as shown in the figure is stronger toward the north pole of the magnet. Any particle entering the region of the field with its own north pole toward the north pole of the field is thus repelled more by the north–north repulsion than by the south–south repulsion, and is driven toward the south pole of the field. Similarly, any particle entering with its own south pole toward the field's north pole is driven toward the north pole of the field. The extent of this deflection depends on the angle between the magnetic moment and the field, and on the field gradient.

If the atomic magnets were classical particles, their moments could initially be directed at any angle to the field. One would then observe a continuous and symmetrical distribution of deflected atoms leaving the region of the inhomogeneous field; some would be deflected toward the field's north pole, some toward the south pole, and some would be

undeflected. But what is actually observed is one group of atoms all deflected the same amount toward the north pole, and an equal number deflected the same amount toward the south pole. The distribution is discontinuous. The reason, as we now know, is that the spin moments are not randomly oriented. If the applied field vector defines the z axis, then for $S = \frac{1}{2}$ the z component of μ_z can only have the values $+\mu_B$ and $-\mu_B$. Atoms in each state are deflected by a characteristic fixed amount, and two distinct beams leave the region of the field. Each of these beams contains only one of the spin states.

Note that the experiment as described assumes no special preparation of the entering beam. One can prepare the beam in ways that affect the relative intensities of the two emerging beams, but one cannot increase the number of emerging beams²⁶ or produce a continuous distribution of emerging particles. One way of preparing the beam, however, is to select for the entering beam *one* of the beams emerging from an identical apparatus having the same spatial orientation. This choice amounts to selecting only those atoms in a particular quantum state, all with the same value of M_S , and passing only those into the second magnet. Since these atoms all have magnetic moments with the same orientation to the field (which again is directed along the z axis), only a single beam will emerge from the second apparatus. Figure 5A.2a illustrates this phenomenon.

The ability to separate particles in different quantum states has made the Stern–Gerlach experiment particularly important in providing a conceptual basis for quantum mechanics. With some kind of trap to remove the other beam

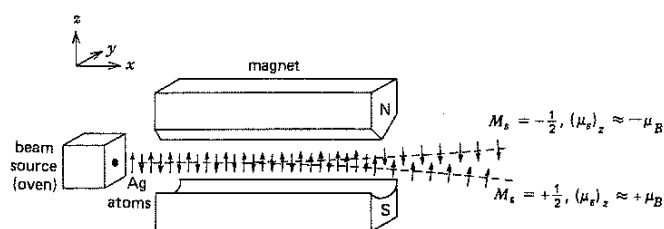


Figure 5A.1 Schematic diagram of the Stern–Gerlach apparatus. The magnetic field is stronger near the pointed north pole than near the smoothly curved south pole. The “atomic magnets” emerging from the oven are driven downward or upward according to whether the z components of the magnetic moments point up or down (as indicated by arrows). The two emerging beams are in distinct quantum states.

²⁶ For a given kind of atoms, that is. In general there will be one beam for each possible value of $M_J = M_L + M_S$; for the silver atom in its ground state we have $L = 0$ (S state), $M_L = 0$, $M_J = M_S = \pm \frac{1}{2}$.

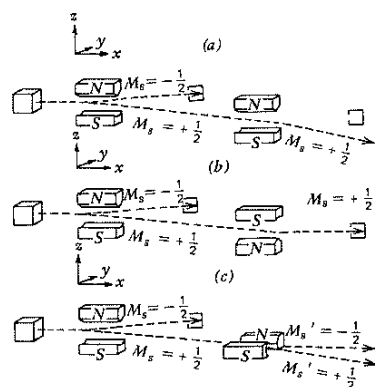


Figure 5A.2 Effects of successive Stern-Gerlach experiments. (a) Both apparatuses set to pass only atoms with $M_S = +\frac{1}{2}$: The first "filter" removes half of the original beam, the second "filter" passes all of the residual beam. (b) The first apparatus passes only $M_S = +\frac{1}{2}$, the second (with magnetic field reversed) passes only $M_S = -\frac{1}{2}$; none of the beam passes through the second "filter." (c) First apparatus selects for z component of spin, passing the beam with $S_z = +\frac{1}{2}\hbar$ (and S_y indeterminate); second apparatus selects for y component of spin, splitting that beam into two beams with $S_y = \pm\frac{1}{2}\hbar$ (and S_z indeterminate).

(or beams), the apparatus is like a filter that passes only those particles in one precisely known quantum state. Once selected, the particles remain in that state so long as they are undisturbed. A second filter that passes the same quantum state leaves the beam unaffected. On the other hand, suppose that the second filter is set to pass a different quantum state—for example, that the first filter passes only the state with $M_S = +\frac{1}{2}$ and the second only the state with $M_S = -\frac{1}{2}$ (both defined with respect to the same z axis). If the filters are so adjusted, then *none* of the beam atoms will get through the second filter. This is shown schematically in Fig. 5A.2b. The two possible quantum states, $M_S = +\frac{1}{2}$ and $M_S = -\frac{1}{2}$, are mutually exclusive; an atom in one state cannot be in the other. All this illustrates the distinct identity of quantum mechanical eigenstates, in this case eigenstates of the z component of angular momentum.

The Stern-Gerlach experiment yields a second kind of insight into the quantum nature of matter when one uses a second selector in another way. In our discussion so far, we have spoken about testing for the quantum state transmitted by the first filter, or for another of the quantum states distinguished by the apparatus. As we have described the experiment, these are states with different quantized values of the z component of spin angular momentum, $S_z = M_S\hbar$. The act of measuring S_z by applying an inhomogeneous magnetic field in the z direction forces the atoms to be in one or another of the eigenstates of S_z . But suppose that one uses a second apparatus to test for quantization relative to the x or y axis, perpendicular to the z axis defined by the first apparatus. Recall from our discussion of the quantum properties

of angular momentum that one *cannot* simultaneously know the components of angular momentum along two axes. To do so would violate the uncertainty principle. The knowledge that a particular beam emerging from the first apparatus has $M_S = +\frac{1}{2}$ (and thus $S_z = \frac{1}{2}\hbar$) with respect to the z axis is essentially complete knowledge. One might know less, but one can never have any more knowledge than this, about the orientation of the vector S .

Very well, suppose that the second apparatus is arranged to separate atoms according to their y components of angular momentum (in the same coordinate system), as shown in Fig. 5A.2c. This measurement must force the component S_y to take on one of its eigenvalues; relative to a field in the y direction, S_y has the possible values $M_S'\hbar$, where $M_S' = \pm\frac{1}{2}$, since Eq. 5.2 applies to the component of S in *any one* direction. But now what happens when one puts the beam with $S_z = \frac{1}{2}\hbar$ into this apparatus? For these atoms one has the maximum possible knowledge about the z component of spin angular momentum; one must therefore have the minimum possible knowledge about the x and y components. For a system that can assume only two states, a condition of minimum knowledge can mean only that the two states are equally probable. This in turn means that the beam with $S_z = \hbar/2$ ($M_S = \frac{1}{2}$) must split into two beams of equal intensity, corresponding to $S_y = \hbar/2$ ($M_S' = \frac{1}{2}$) and $S_y = -\hbar/2$ ($M_S' = -\frac{1}{2}$). But what is the value of S_z for these new beams? We cannot know this. The beam entering the second apparatus has a definite value of S_z , and thus is indeterminate in S_y ; the outgoing beams have definite values of S_y and are indeterminate in S_z . We have traded information about one kind of quantization for information about another kind of quantization, and the two kinds are mutually exclusive.

The uncertainty principle is particularly well illustrated by the experiment just described. A "complete" description of the system, within the constraints of this principle, consists of the specification of eigenvalues for as many variables as nature allows to be measured simultaneously. The classical notion, that one can simultaneously determine each and every property with unlimited accuracy, is simply invalid. Similar results should be obtained in any other experiment, real or conceptual, in which particles in different quantum states are physically separated.

• FURTHER READING

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● PROBLEMS

- A magnetic dipole with strength 1.2 Bohr magnetons is in a uniform magnetic field whose strength is 500 oersted. What is the difference in energy between the orientations of the dipole parallel (north-to-north) and antiparallel (north-to-south) to the applied magnetic field? Suppose the dipole has the low-energy orientation; the application of an oscillatory magnetic field at the appropriate frequency can induce absorption of energy and the eventual transition to the high-energy orientation. Sketch the system, indicating the dipole, the external field and the oscillatory field, at three specified times during a single cycle. Be careful to show the *directions* of all vectors. What is the resonant frequency of the dipole in the given field?
- Using a classical expression analogous to Eq. 5.4, compute the magnetic moment of a 500-g sphere of metal on a 1-m string, whirling at a rate of 1 revolution per second, and carrying an excess negative charge of 10^{-12} F. (One faraday, F, is 1 mol of electrons, or 96,485 C.) What is the energy of interaction of this magnetic dipole with the earth's magnetic dipole if the two are parallel?
- Compute the frequency of the electromagnetic radiation associated with a transition of an electron between the state with $m_s = +\frac{1}{2}$ and the state with $m_s = -\frac{1}{2}$, if the electron is in a field of 0.5 T (5000 gauss). Compute the corresponding frequency if the particle is a proton instead of an electron.
- A Stern–Gerlach experiment is conducted with silver atoms passing through a magnetic field whose gradient is 3×10^2 T/m. The length of the region of the field gradient is 0.05 m. The particles travel 0.5 m to their target surface after leaving the field with initial speed 10^5 m/s. How far apart are the points where the two emerging beams strike the target? (Recall the analysis of Thomson's experiment to determine e/m .)
- Sodium atoms are put through a Stern–Gerlach apparatus and separated into two beams of equal intensity as shown in Fig. 5A.2a. The beam corresponding to $M_S = +\frac{1}{2}$ is then put through a second pair of magnets whose orientation is rotated about the beam axis through an angle θ with respect to the first pair of magnets. Figures 5A.2b and 5A.2c correspond to special cases with $\theta = 180^\circ$ and $\theta = 90^\circ$, respectively. Calculate the relative intensities of the beams with $M'_S = +\frac{1}{2}$ and $M'_S = -\frac{1}{2}$ for arbitrary θ . Ignore the small nonzero angle at which the beam emerges from the first separating device.
- Explain, in terms of the symmetry of the forces exerted on an electron, why l and m are good quantum numbers for each electron in the central field model, but not in real atoms.
- The most probable value of each electron–nuclear distance in H^- is 1.178 bohr; the average value of the electron–nuclear distance is 2.707 bohr. What qualitative inferences can one make about the shape of the electron probability density from a comparison of these two numbers?
- Within a series of isoelectronic ions such as Li, Be^+ , B^{2+} , C^{3+} , and so on, the relative contribution of the correlation energy to the total energy of the system diminishes with increasing nuclear charge. Explain.
- Prove that $\frac{27}{16}$ is the value of the “effective nuclear charge” Z' of Eq. 5.13 that minimizes the expectation value E' of energy (Eq. 5.11) when $\psi^{(2)}(r_1, r_2)$ of Eq. 5.13 is used to evaluate E' .
- Put the entries in the following sets of configurations in order of increasing energy. Then check your intuition by comparing the results with the experimental results from atomic spectroscopy, as given, for example, by C. E. Moore, *Atomic Energy Levels* (National Bureau of Standards Circular 467).
 - Li, $1s^2 2s$
 $1s 2s^2$
 $1s 2s 2p$
 $1s^2 2p$
 - C, $1s^2 2s^2 2p^2$
 $1s^2 2s 2p^3$
 $1s 2s^2 2p^3$
 $1s^2 2s^2 2p 3s$
- Using the tables given by C. E. Moore in *Atomic Energy Levels* (National Bureau of Standards Circular 467),

compute the energies of the following atomic configurations by taking the appropriately weighted averages of the atomic state energies in the tables. (The configuration energies can be given relative to the ground state of the atom.)

- (a) C, $1s^2 2s^2 2p^2$;
 - (b) N, $1s^2 2s^2 2p^3$;
 - (c) N, $1s^2 2s^2 2p^2 3s$.
12. Explain why the second ionization potential of lithium, for the process $\text{Li}^+ \rightarrow \text{Li}^{2+} + e^-$, is less than that predicted for a hydrogenlike atom with $Z = 3$.
 13. Consider the effect of the nuclear charge on the importance of relativistic effects in atoms, first by estimating from a Bohr model the velocity of a $1s$ electron in an atom of lead. The effective mass of a particle with rest mass m and speed v is $m' = m/\sqrt{1 - (v^2/c^2)}$. What is v/c for a $1s$ electron of Pb? What is its effective mass, based on the simple expression above for m' ? What velocity v' does one obtain if one carries out the Bohr calculation with the above expression for m' , instead of a velocity-independent m ?
 14. The outer electron of an alkali atom may be treated in an approximate way, as if it were in a hydrogenic orbital. Suppose that one takes the quantum number for the outer electron to be 2, 3, 4, 5, and 6, respectively, for Li, Na, K, Rb, and Cs. What values must Z be given to account for the observed first ionization potentials of these atoms? Explain why they differ from unity.
 15. Use the Pauli exclusion principle and Hund's rules to find the number of unpaired electrons and the term of lowest energy for the following atoms:
 - (a) P
 - (b) S
 - (c) Ca
 - (d) Br
 - (e) Fe
 16. Hydrogen atoms are placed in a strong magnetic field and excited; their emission spectrum is recorded under conditions of moderately high resolution (0.1 cm^{-1} or better). What is the appearance of the portion of the spectrum due to $\text{H}(3p) \rightarrow \text{H}(2s)$ transitions, and how does it differ from the spectrum of the same transition in the absence of a magnetic field?
 17. Show that the lowest configuration of the nitrogen atom, $1s^2 2s^2 2p^3$, gives rise to the terms 2D , 2P , and 4S .
 18. Derive the terms of the configuration $1s^2 2s^2 2p^6 3s^2 3p^3 d$, of the silicon atom.
 19. Explain this observation: The energy difference between $1s^2 2s$, $^2S_{1/2}$ and $1s^2 2p$, $^2P_{1/2}$ states of Li is 14904 cm^{-1} , whereas that between the $2s$, $^2S_{1/2}$ and $2p^2$, $^3P_{1/2}$ states of Li^{2+} is only 2.4 cm^{-1} .
 20. The first excited state (and higher excited states as well) of He exhibits a positive electron affinity, although the electron affinity of He in its ground state is negative.
 - (a) What are the configuration and term designations of the first two excited states of the helium atom?
 - (b) What is the configuration and term designation of the lowest-energy bound state of the negative ion He^- ? Note that this cannot be the same as any state built by adding an electron to He in its ground state.
 - (c) Interpret why atoms in excited configurations generally have positive electron affinities, whereas atoms in closed-shell ground-state configurations seem to have only negative electron affinities.
 21. What are the lowest terms for the ions Ti^{2+} , Mn^{2+} , and Fe^{3+} , if the first two electrons to be lost by the corresponding neutrals are the two $4s$ electrons? What are the possible values of the quantum number J for each of these ions?
 22. What J values are possible for the 3P , 1D , and 1S states of the silicon atom? Look up the observed splittings of these states in C. E. Moore, *Atomic Energy Levels* (National Bureau of Standards Circular 467) and estimate the spin-orbit splitting parameter ζ for as many of these states as the data permit.
 23. Given the following data:

	Li	Na	K	Rb	Cs	Fr
Z	3	11	19	37	55	87
Atomic weight	6.94	23.00	39.10	85.47	132.91	?
Density (g/cm^3)	0.53	0.97	0.86	1.53	1.90	?
Atomic volume (cm^3)	13.0	23.7	45.5	55.9	70.0	?
Melting point ($^\circ\text{C}$)	186	97.5	62.3	38.5	26	?
Boiling point ($^\circ\text{C}$)	1200	880	760	700	670	?

Predict the numerical values for the atomic weight, density, atomic volume, melting and boiling points of francium, element number 87. What will be its characteristic chemical properties?
 24. Show from Eqs. 5.26 and 5.27 that the energy associated with spin-orbit interaction is

$$E_{so} = \frac{1}{2} \zeta \hbar^2 [J(J+1) - L(L+1) - S(S+1)].$$

25. (Difficult) Substitute $\psi^{(1)}$ of Eq. 5.12 and $\psi^{(2)}$ of Eq. 5.13 into the expression for the expectation value of the energy, Eq. 5.11, and show that the corresponding values given in the text, -74.83 eV and -77.49 eV, respectively, are correct.
26. Electronic structure calculations can be performed using readily available software packages. (One such package, available free of charge from Iowa State University, is GAMESS, Generalized Atomic and Molecular Electronic Structure System—see <http://www.msg.ameslab.gov/GAMESS/GAMESS.html>.) A popular calculational method is the Hartree–Fock Self-Consistent Field (HF–SCF) calculation with each atomic orbital being represented as a linear combination of Gaussian basis functions of the form e^{-r^2} . A variety of basis sets are available.
- (a) In a minimal basis STO– NG calculation, each atomic orbital is represented by one Slater type orbital of the form e^{-r} , which is itself composed of N Gaussians.
- (b) In an m – npG basis set calculation, each inner shell atomic orbital is represented as one linear combination of m Gaussians. Each valence shell atomic orbital is represented by two basis functions, a lin-

ear combination of n Gaussians and a linear combination of p Gaussians.

Compute the Hartree–Fock ground electronic state energy of atomic hydrogen using the following basis sets: (a) STO–3G; (b) 3–21G; (c) 6–31G. Note for hydrogen that there are no inner shell orbitals. Compare the computed orbital energy to the exact ionization energy of the hydrogen atom in its electronic ground state.

27. Compute the Hartree–Fock energy of the ground electronic state of the He atom using the (a) STO–3G, (b) 3–21G, and (c) 6–31G basis sets and the HF–SCF method. Compare these calculated energy values to the experimental value of -78.99 eV.
28. Repeat Problem 5.27 for the C atom in its ground electronic state, computing the 1–electron orbital energies (the eigenvalues corresponding to the α and β sets of eigenvectors reported by GAMESS). Compare the least-negative eigenvalue with the experimental first ionization energy (Koopman’s Theorem).
29. Repeat Problem 5.27 +2 for the O atom in its ground electronic state.