atom. The Aufbau principle dictates that the subshells $(n\ell)$ be filled in order of increasing energy, the energy being determined in part by screening arguments. This principle is most easily understood in the context of a discussion of the ground states of multielectron atoms.

9.3 GROUND STATES OF N-ELECTRON ATOMS[4]

Consider an N-electron atom. The ground state of this atom is simply the state with the lowest possible total energy. Since the single-particle Hamiltonians in the central field approximation do not single out a unique direction in space, the energy of the state is independent of the quantum numbers m_{ℓ_i}, $i = 1, 2, \ldots, N$. Similarly, it is independent of m_{s_i}, $i = 1, 2, \ldots, N$.

Hence an energy level of the system may be specified by the $2N$ quantum numbers n_i, ℓ_i for $i = 1, 2, \ldots, N$. The *electronic configuration* of a state of the atom is a statement of the quantum numbers n_i and ℓ_i for all electrons. It also indicates how the electrons fill the shells and subshells of the atom. For example, the electronic configuration of the ground state of hydrogen is $1s$, of helium $1s^2$, of lithium $1s^2 2s$. The superscript 2 on the configuration of helium indicates that there are two electrons in the $1s$ shell.

Notice that we did not write $1s^3$ for the electronic configuration of lithium. The reason is that the Pauli exclusion principle forbids more than two electrons from occupying the same s subshell. To see this we need only recall that electrons in an s subshell have quantum numbers $\ell = 0$, $m_\ell = 0$. Thus their spin quantum numbers must differ. There are only two possibilities, $m_s = \pm\frac{1}{2}$, so only two electrons can occupy the s subshell.

The shells of the atom are sometimes labeled by the letters $K, L, M, \ldots$ corresponding to principal quantum numbers $1, 2, 3, \ldots$. Each shell consists of a number of subshells.[5]

The *Aufbau principle* states that the electrons are to be placed in subshells in accordance with the Pauli exclusion principle. The most natural ordering of the subshells would seem to be

$$\boxed{1s,\ 2s,\ 2p,\ 3s,\ 3p,\ 3d,\ 4s,\ \ldots,} \qquad (9.14)$$

where the energy increases from left to right. This ordering seems reasonable. Penetration arguments like those in Sec. 9.2 indicate that subshells of a particular shell are ordered in energy as $s, p, d, \ldots$, and we know that the energy of a shell increases with its principal quantum number.

As stated earlier, the number of electrons that can occupy a particular subshell is determined by the Pauli exclusion principle. Thus no more than two electrons can occupy an s $(\ell = 0)$ subshell (e.g., $1s$, $2s$, $3s$, ...), and in each subshell the electrons must be oppositely paired. Six electrons can occupy a p subshell $(\ell = 1)$, two with $m_{\ell_i} = -1$, two with $m_{\ell_i} = 0$, and two with $m_{\ell_i} = +1$. Similar arguments show that 10 electrons fill a d subshell, 14 fill an f subshell, and so on.

A shell that contains the full complement of electrons allowed by the exclusion principle is called a *closed shell* (or *filled shell*). Obviously, a shell that is not closed is *open* (or *partially filled*). If an atom consists of a number of closed shells and subshells plus one or more electrons in a partially filled shell, these electrons are called *valence electrons*. In lithium, $1s^2 2s$, for example, the $2s$ electron is the valence electron.

The Aufbau principle determines much of the shape and form of the periodic table of the elements. The chemical properties of various elements are largely determined by the number of valence electrons. It is chiefly these electrons that participate in bonding and chemical reactions. Because of the Aufbau principle, certain patterns in electronic configurations reappear periodically as the number of electrons increases. Thus carbon $(1s^2\,2s^2\,2p^2)$ and silicon $(1s^2\,2s^2\,2p^6\,3s^2\,3p^2)$ each have two p valence electrons; this fact implies that some of their chemical properties will be similar, and experiments indicate that such is indeed the case.[6]

Unfortunately, the simple ordering given in (9.14) breaks down in the $n = 3$ shell. For example, if the configuration of an atom consists of partially occupied $3d$ and $4s$ subshells, then, contrary to the ordering of (9.14), the $4s$ level fills before the $3d$ level. And the electronic configuration of potassium is $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s$, not $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d$. Qualitatively, this ordering can be understood by referring to probability densities. The small amount of probability density of the $4s$ orbital near the nucleus is enough to pull its energy level below that of the $3d$ orbital, which penetrates very little into the region of small r (see Fig. 3.4). In fact, the simple ordering of (9.14) is observed to break down in several regions of the periodic table—for example, for neutral and singly ionized transition metal ions, alkaline earths, and alkalies. The more highly ionized species tend to follow the ordering of (9.14). The details are too involved to go into here (see the Suggested Readings for this chapter).

[4] See Prob. 9.1 for excited states.

[5] The subshells are denoted by spectroscopists as $K, L_1, L_2, M_1, M_2, \ldots$ corresponding to $1s, 2s, 2p, 3s, 3p, \ldots$, respectively. Thus you may see the shell structure of an atom indicated by notation like $K, L(L_1, L_2), M(M_1, M_2, M_3), \ldots$.

[6] In fact, silicon-based life has been proposed as a possible alternative to the carbon-based life of which we are so fond. See Carl Sagan, *The Cosmic Connection* (New York: Anchor Press, 1973), p. 47.

The actual ordering of orbitals for neutral atoms is better described by the following convenient table.

Shell n	Increasing energy →
$n = 1, 2, 3$	$1s$ $2s$ $2p$ $3s$ $3p$ · $3d$
$n = 4$	$4s$ $4p$ · $4d$ · · $4f$ · ·
$n = 5$	$5s$ $5p$ · $5d$ ·
$n = 6$	$6s$ $6p$

(9.15)

A list of the ground-state configurations of all atoms appears in Appendix 5.

Wave Functions

Summarizing, we see that, in order to construct the ground-state configuration of a multielectron atom, we assign electrons to subshells according to (9.15) and the Pauli principle, beginning with the subshell of lowest energy. The corresponding ground-state wave function can be written down from Eq. (9.8). For example, the eigenfunction for the ground state of an atom with N even is

$$\psi_\tau = |\psi_{1s}(\mathbf{r}_1)\alpha(1) \quad \psi_{1s}(\mathbf{r}_2)\beta(2) \quad \psi_{2s}(\mathbf{r}_3)\alpha(3) \cdots \psi_{n\ell m_\ell}(\mathbf{r}_{N-1})\alpha(N-1) \; \psi_{n\ell m_\ell}(\mathbf{r}_N)\beta(N)|, \tag{9.16}$$

where the functions $\psi_{(n\ell m_\ell)_i}(\mathbf{r}_i)$ are single-particle orbitals obtained by solving the Schroedinger equation for the ith particle in the isolated electron approximation or the central field approximation. Using a bar to denote spin "down," we can abbreviate Eq. (9.16) as

$$\psi_\tau = |1s(1) \quad \overline{1s(2)} \quad 2s(3) \quad \overline{2s(4)} \quad \cdots \quad n\ell m_\ell(N-1) \quad \overline{n\ell m_\ell(N)}|. \tag{9.17}$$

The energy is simply the sum of the energies of each electron.

Example 9.1
Ground State of Neon

For neon ($N = 10$), the ground-state configuration is (by the Aufbau principle) $1s^2 2s^2 2p^6$. Therefore the ground-state wave function is

$$\psi_1 = |1s(1)\,\overline{1s(2)}\,2s(3)\,\overline{2s(4)}\,2p_0(5)\,\overline{2p_0(6)}\,2p_{-1}(7)\,\overline{2p_{-1}(8)}\,2p_1(9)\,\overline{2p_1(10)}|. \tag{9.18}$$

The ground state of neon is a singlet (why?).

Neon was a particularly fortunate choice for our illustration; because its configuration is that of a closed shell, in which all the electrons are paired, we could write down a unique Slater determinant as in Eq. (9.18). If the configuration of an atom corresponds to an open shell, there will be some ambiguity about the assignment of quantum numbers to electrons. For example, the ground-state configuration of lithium is $1s^2 2s$, and the $2s$ electron can have $m_s = +\frac{1}{2}$ or $m_s = -\frac{1}{2}$. The two resulting wave functions are degenerate. Similarly, for carbon, with configuration $1s^2 2s^2 2p^2$, we can write several Slater determinants corresponding to the same energy. The $2p$ subshell contains two *equivalent electrons*, so called because their principal and orbital angular momentum quantum numbers are the same. The electronic configuration and energy depend only on the quantum numbers n_i and ℓ_i for each electron, but a wave function depends on n_i, ℓ_i, m_{ℓ_i}, and m_{s_i}, $i = 1, 2, \ldots, N$.

> **Exercise 9.1** Write the 15 different degenerate wave functions corresponding to the ground-state configuration of carbon. What is the ground-state energy of these functions in the isolated electron approximation?

Thus the presence of equivalent electrons in a partially filled shell gives rise to degenerate wave functions. As in the one-electron atom, some of this degeneracy is lifted when previously ignored interactions are considered (e.g., the spin-orbit interaction).

9.4 ANGULAR MOMENTUM COUPLING IN MULTIELECTRON ATOMS

A number of interactions have been omitted from the Hamiltonian in Eq. (9.3). The N electrons each have a spin magnetic moment and an orbital magnetic moment associated with them. All these magnetic moments can interact in various ways. The mutual coulomb repulsion of the electrons, which is related to forces that are directed not toward the nucleus but along lines between electrons, influences the individual orbital angular momenta $\mathbf{L}_i$ in such a way that they couple. Although each individual angular momentum operator does not commute with $\mathcal{H}$ (if these potential energy terms are included) and so is not a constant of the motion, the resultant total orbital

angular momentum is a constant of the motion. The individual spins can also be coupled together to form a total spin angular momentum.

We see, therefore, that *electrostatic interactions* tend to couple all the orbital angular momenta and all the spin angular momenta. In addition, there are the spin-orbit interaction and other *magnetic interactions* (spin-spin, spin-other-orbit). The spin-orbit interaction gives rise to terms proportional to $\mathbf{L}_i \cdot \mathbf{S}_i$ and acts to couple the orbital angular momentum of the ith electron to its spin angular momentum so as to form a total $\mathbf{J}_i$.

Both types of interaction, electrostatic and magnetic, are present in any particular atom. However, the magnetic interactions are usually weaker. For example, in light atoms, the electrostatic repulsions are of the order of ~ 1 eV, whereas the spin-orbit potential energy is of the order of $\sim 10^{-4}$ to $\sim 10^{-3}$ eV. Hence the angular momentum coupling in a light atom is as follows:

1. The orbital angular momenta $\mathbf{L}_i$, $i = 1, 2, \ldots, N$, couple to form a total orbital angular momentum

$$\mathbf{L} = \sum_{i=1}^{N} \mathbf{L}_i, \tag{9.19}$$

and the spin angular momenta $\mathbf{S}_i$ couple to form the total spin angular momentum

$$\mathbf{S} = \sum_{i=1}^{N} \mathbf{S}_i. \tag{9.20}$$

This coupling is established at the level where only the electrostatic interactions are included in the Hamiltonian.

2. The weaker magnetic interactions act to couple $\mathbf{L}$ to $\mathbf{S}$ so as to form the total angular momentum of the atom

$$\mathbf{J} = \mathbf{L} + \mathbf{S}. \tag{9.21}$$

This particular coupling scheme, in which the electrostatic interactions dominate the magnetic interactions and are thereby included in the Hamiltonian first, is called *Russell-Saunders coupling*.[7]

In heavy atoms, the electrostatic repulsion terms are of the order of $\sim 10^3$ eV for the inner electrons and the magnetic or spin-orbit terms are of the order of $\sim 10^4$ eV. Thus an alternate coupling scheme is more appropriate:

1. Each electron's $\mathbf{L}_i$ and $\mathbf{S}_i$ couple via the magnetic interactions to yield

$$\mathbf{J}_i = \mathbf{L}_i + \mathbf{S}_i, \qquad i = 1, 2, \ldots, N. \tag{9.22}$$

[7]Some authors refer to this process as *LS* coupling.

2. The influence of the electrostatic interactions then couples the $\mathbf{J}_i$ together to form

$$\mathbf{J} = \sum_{i=1}^{N} \mathbf{J}_i. \tag{9.23}$$

This scheme is called *j-j coupling* and is generally less common than Russell-Saunders coupling.

Regardless of which scheme is used, the vector coupling proceeds according to the familiar rules of Chapter 7. If both electrostatic and magnetic interactions are taken into account, the individual ℓ_i, m_{ℓ_i}, m_{s_i}, j_i, m_{j_i}, L, M_L, S, and M_S are no longer good quantum numbers. Only J and M_J, corresponding to the magnitude of the total angular momentum of the atom and its projection along the $\hat{z}$ axis, are good quantum numbers of the system. The important point is that the question of which quantum numbers are good quantum numbers can be answered only in the context of a particular form of the orbital approximation. For example, in the isolated electron approximation, where each electron completely ignores its fellow electrons, L_i^2, S_i^2, $(L_z)_i$, $(S_z)_i$, J_i and $(J_z)_i$, $i = 1, 2, \ldots, N$, all commute with the Hamiltonian; therefore ℓ_i, m_{ℓ_i}, s_i, m_{s_i}, j_i, and m_{j_i} are all perfectly good quantum numbers and can be used to label states of the atom.

Exercise 9.2 Show that $(L_z)_i$ does not commute with $V'(\mathbf{r}_i - \mathbf{r}_j) = e^2/r_{ij}$ and thus does not commute with the Hamiltonian $\mathcal{H}$ of Eq. (9.3). Show also that $(L_z)_i + (L_z)_j$ does commute with $V'(\mathbf{r}_i - \mathbf{r}_j)$ so that $L_z = \sum_{i=1}^{N} (L_z)_i$ commutes with $\mathcal{H}$.

Because it is more frequently encountered, let us consider Russell-Saunders coupling in some detail.

9.5 RUSSELL-SAUNDERS COUPLING

In this case, the relevant equations are (9.19) to (9.21). The quantum numbers associated with the operators L^2, S^2, J^2, L_z, S_z, and J_z are L, S, J, M_L, M_S, and M_J, respectively.

Exercise 9.3 Draw a set of vector diagrams like the one in Fig. 7.1, illustrating Russell-Saunders coupling for a two-electron atom.

In the approximation in which spin-orbit coupling terms are neglected, eigenfunctions can be labeled by the quantum numbers $\{n, L, S, M_L, \text{and } M_S\}$ or by $\{n, L, S, J, M_J\}$. In improved approximations, in which spin-orbit interactions are included in the Hamiltonian, we must use the latter set—for M_L and M_S are no longer good quantum numbers—and in the vector model

we picture the "precession of **L** and **S** about **J**" (see Prob. 9.4). Thus the appropriate set depends on two interrelated factors: (a) the strength of the spin-orbit interaction tending to couple **L** and **S** and (b) the accuracy to which we wish to treat the system.

How can we determine the new quantum numbers, given the assigned values of n_i, ℓ_i, m_{ℓ_i}, and m_{s_i} for each electron? The relationships are familiar from the treatment of angular momentum coupling in Sec. 7.3 and the one-dimensional model of Sec. 8.4. For example, the allowed values of M_L and M_S are given by

$$M_L = \sum_{i=1}^{N} m_{\ell_i} \tag{9.24}$$

$$M_S = \sum_{i=1}^{N} m_{s_i}, \tag{9.25}$$

and the eigenfunctions ψ_γ in the orbital approximation satisfy

$$L_z\psi_\gamma = M_L\hbar\psi_\gamma, \tag{9.26}$$

$$S_z\psi_\gamma = M_S\hbar\psi_\gamma. \tag{9.27}$$

Similarly, it is easy to determine the allowed values of L and S for, say, a two-electron atom. Generalizing the rules of vector coupling in Chapter 7, we have

$$L = |\ell_1 - \ell_2|, \ldots, \ell_1 + \ell_2 \tag{9.28}$$

and

$$S = 0, 1, \tag{9.29}$$

where we have assumed that $(n_1\ell_1) \neq (n_2\ell_2)$.[8] Of course, for a given L and S, M_L and M_S are given by

$$M_L = -L, \ldots, L, \tag{9.30}$$

$$M_S = -S, \ldots, S. \tag{9.31}$$

These relations are consistent with Eqs. (9.24) and (9.25). Given values for L and S, the allowed values of J and M_J are

$$J = |L - S|, \ldots, L + S, \tag{9.32}$$

$$M_J = -J, \ldots, J. \tag{9.33}$$

Notice that

$$M_J = M_L + M_S. \tag{9.34}$$

Exercise 9.4 Prove that the only allowed values of L and S for a closed-shell configuration are $L = 0$ and $S = 0$.

[8]More complicated cases are treated similarly. See Prob. 9.2.

In addition to labeling states of the system, these quantum numbers provide useful labels for the energy levels of the atom.

Atomic Terms

We expect the energy of a particular level to depend on L and S (and J if spin-orbit interactions are not ignored) but not on M_L, M_S (or M_J). Therefore we may label the levels by their *atomic terms*, which are written ${}^{2S+1}L$, where we use letters S, P, D, ... for $L = 0, 1, 2, \ldots$, The superscript $2S + 1$ is called the *multiplicity* of the level; that is, singlet, doublet, triplet, and so on. For example, states with $S = 0$ and $L = 2$, arising from the same configuration, are collectively referred to as the ${}^1D$ term. In the approximation where spin-orbit effects are ignored, all states of a given term are degenerate. In general, a term ${}^{2S+1}L$ is $(2S + 1)(2L + 1)$-fold degenerate. For example, the ${}^3P$ term of carbon $(1s^22s^22p^2)$ is ninefold degenerate.

In the Russell-Saunders coupling scheme, the subscript J can be appended to the term designation to indicate one of the allowed values $J = |L - S|, \ldots, L + S$. For example, for $L = 1$, $S = 1$—a ${}^3P$ term—we have ${}^3P_0$, ${}^3P_1$, ${}^3P_2$. We may refer to these as *sublevels*; they are degenerate as long as the spin-orbit interaction is ignored. We shall return to this point in our discussion of Hund's rules. Each sublevel ${}^{2S+1}L_J$ is $(2J + 1)$-fold degenerate, and obviously the sum of the degeneracies of all sublevels must equal the degeneracy of the corresponding term. For example, the sublevels ${}^3P_0$, ${}^3P_1$, ${}^3P_2$ are one-, three-, and five-fold degenerate, respectively, for a total nine-fold degeneracy as required. Of course, when the spin-orbit interactions are considered, the degeneracy between different J sublevels is lifted. However, the $(2J + 1)$-fold degeneracy of *each* sublevel remains. This degeneracy can be removed by application of an external magnetic field; this is the Zeeman effect again (see Prob. 9.5).

Implied Terms[9]

It might seem a trivial matter to determine the terms for, say, the ground state of a particular atom. We merely write down the quantum numbers of the equivalent electrons in partially filled shells and couple them according to the rules of Eqs. (9.28) to (9.33). (Note that closed shells and subshells contribute nothing; see Exercise 9.4.) Doing so for carbon, which has two equivalent $2p$ electrons, we obtain the terms shown in Table 9.1. However, we have completely neglected the Pauli exclusion principle, which restricts the quantum numbers of the electrons in the atom and forces us to discard some of the terms in the table.

[9]The method outlined in this subsection follows closely the discussion in Peter O'D. Offenhartz, *Atomic and Molecular Orbital Theory* (New York: McGraw-Hill, 1970), Chap. 6.

Table 9.1
Atomic terms and sublevels obtained by applying Russell-Saunders coupling to the carbon atom. Only $^1S_0$, $^1D_2$, $^3P_1$, and $^3P_0$ remain after the Pauli exclusion principle has been taken into consideration.

L	S	J	Term	Sublevels
0	0	0	^1S	$^1S_0$
1	0	1	^1P	$^1P_1$
2	0	2	^1D	$^1D_2$
0	1	1	^3S	$^3S_1$
1	1	2, 1, 0	^3P	$^3P_2$, $^3P_1$, $^3P_0$
2	1	3, 2, 1	^3D	$^3D_3$, $^3D_2$, $^3D_1$

Table 9.2
Values of m_{ℓ_1}, m_{ℓ_2}, m_{s_1}, and m_{s_2} allowed by the Pauli exclusion principle for carbon ($1s^2 2s^2 2p^2$) and resulting values of M_L and M_S.

Entry	m_ℓ			M_L	M_S
	−1	0	+1		
1	↑ ↓			−2	0
2		↑ ↓		0	0
3			↑ ↓	2	0
4	↑	↑		−1	1
5	↑	↓		−1	0
6	↓	↑		−1	0
7	↓	↓		−1	−1
8	↑		↑	0	1
9	↑		↓	0	0
10	↓		↑	0	0
11	↓		↓	0	−1
12		↑	↑	1	1
13		↑	↓	1	0
14		↓	↑	1	0
15		↓	↓	1	−1

To illustrate, we begin by listing the allowed values of m_{ℓ_1} and m_{s_1} (valence electrons only) and the resultant values of M_L and M_S for carbon in Table 9.2. Since Exercise 9.1 showed that there are 15 degenerate Slater determinants for the ground state of carbon, we expect to find 15 entries in the table. Each entry in this table corresponds to one allowed state of the system. We now list the number of states with a particular M_L and M_S in Table 9.3a, which is

Table 9.3a
First Implied-Terms Table

M_L \ M_S	1	0	−1
2	0	1	0
1	1	2	1
0	1	3	1
−1	1	2	1
−2	0	1	0

called an *implied terms table*. We shall use it to determine the allowed terms for carbon.

First, consider the largest possible values of L and S: $L = 2$ and $S = 1$. These values give rise to the ^3D term in Table 9.1. If they were allowed, entries corresponding to $M_L = 2$ and $M_S = 1$ would have to appear in Table 9.2. A glance at the table shows that they do not. We must discard the ^3D term and the sublevels $^3D_3$, $^3D_2$, and $^3D_1$ as disallowed by the Pauli principle.

Now we turn to the next largest values: $L = 2$, $S = 0$. This is the ^1D term. Since there are entries in Table 9.2 with $M_L = 2$, $M_S = 0$, we know that this term is allowed. The ^1D term corresponds to five states, depending on whether $M_L = -2, -1, 0, 1, 2$. Each state is a singlet and has one of $M_L = -2, -1, 0, 1, 2$. Consequently, we have determined the nature of five of the states in Table 9.3a. Subtracting these states from the table yields Table 9.3b (we subtract 1 from each element in the second column). We look next at $L = 1$, $S = 1$—that is, the ^3P terms. Entries with $M_L = -1, 0, +1$ and $M_S = -1, 0, 1$ remain in Table 9.3b, so the $^3P_2$, $^3P_1$, and $^3P_0$ sublevels are allowed. They correspond to nine states altogether. Substracting them from Table 9.3b, we obtain Table 9.3c. But only one state is left in Table 9.3c. It

Table 9.3b
Second Implied-Terms Table

M_L \ M_S	1	0	−1
2	0	0	0
1	1	1	1
0	1	2	1
−1	1	1	1
−2	0	0	0

Table 9.3c
Final Implied-Terms Table

M_L \ M_S	1	0	−1
2	0	0	0
1	0	0	0
0	0	1	0
−1	0	0	0
−2	0	0	0

has $M_L = 0$, $M_S = 0$ and gives the ^1S term. Thus this term is allowed; and since no more states remain, the terms ^3S and ^1P are forbidden. We have shown that of all the atomic terms that might be generated by Russell-Saunders coupling for carbon, only the terms ^1S, ^3P, and ^1D are allowed by the Pauli exclusion principle.

Precisely the same analysis holds for any atom with two equivalent p electrons outside closed subshells. The implied-terms method is a convenient bookkeeping procedure and can be applied to any configuration (see Prob. 9.2).

To complete our picture of the quantum mechanics of multielectron atoms, we must know how the terms obtained above are ordered in energy. This is the subject of Sec. 9.6. Also unresolved at this point is the question of precisely which of the many degenerate Slater determinants constitute a particular wave function for state $\gamma = (S, L, M_L, M_S)$. To answer, we must actually construct the eigenfunction of interest. This topic is discussed in Prob. 9.3.

9.6 HUND'S RULES

It is now possible to determine the allowed atomic terms corresponding to a particular electronic configuration. For example, in carbon we found ^1S, ^3P, and ^1D; each sublevel $^1S_0$, $^1D_2$, $^3P_2$, $^3P_1$, and $^3P_0$ arising from these terms has a different energy when spin-orbit interactions are included in the Hamiltonian. We would like to know these energies. However, Chapter 7 has demonstrated that actual calculation of the shift and ordering in energy of these levels can be a time-consuming and difficult process. Fortunately, a set of rules exists that enables us to avoid such calculations if qualitative rather than quantitative results are satisfactory. Called *Hund's rules*, they provide an estimate of the ordering in energy of the levels and sublevels for the case of equivalent electrons in the ground configuration.

RULE 1: The terms(s) arising from the ground configuration with the maximum multiplicity (2S + 1) *lies lowest in energy.*

Rule 1 can be understood by generalizing the spin-pairing arguments of Sec. 8.3 to three-dimensional multielectron atoms. Recall that in the two-electron case, we found that like spins (unpaired spins) "repel" and unlike spins (paired spins) "attract." In a multielectron atom, a state with high multiplicity contains a greater number of electrons with parallel spins than does one of low multiplicity. Since these electrons all "avoid one another", the energy of the state with high multiplicity lies below that of a state with low multiplicity.

RULE 2: Of several levels with the same multiplicity, the one with the maximum value of L *lies lowest in energy.*

Rule 2 can also be crudely understood as a consequence of the electrostatic repulsion of electrons. In a state of large orbital angular momentum quantum number L, the electrons can be thought of as orbiting "in the same direction." Such electrons can remain separated from one another at all times and so have a lower energy than do electrons "orbiting in the opposite direction," which must approach one another at some time.

RULE 3: Of several sublevels with the same multiplicity and total quantum number L*:*

(a) the sublevel with the minimum value of J *lies lowest in energy if the configuration has a shell that is less than half-filled;*

(b) the sublevel with the maximum value of J *lies lowest in energy if the configuration has a shell that is more than half-filled.*

Rule 3 is primarily a consequence of the spin-orbit interaction plus the fact that the electrostatic potential energy increases as r increases.[10] If we apply Hund's rules, together with our knowledge of the effects of electrostatic and magnetic interactions for Russell-Saunders coupling, to carbon, we obtain the energy level diagram of Fig. 9.1. (The splittings in this diagram are not exactly to scale.)

As with the Aufbau principle, Hund's rules provide a simple rule of thumb for determining features of atomic structure. They, too, break down in some cases. The reason for this breakdown lies at the very core of the orbital approximation. In writing an electronic configuration, all we must specify is how electrons are placed into subshells. The actual distribution of electrons in a particular quantum mechanical state is sometimes more accurately

[10] In case (a) the sublevels are called *regular multiplets;* in case (b) they are called *inverted multiplets.*

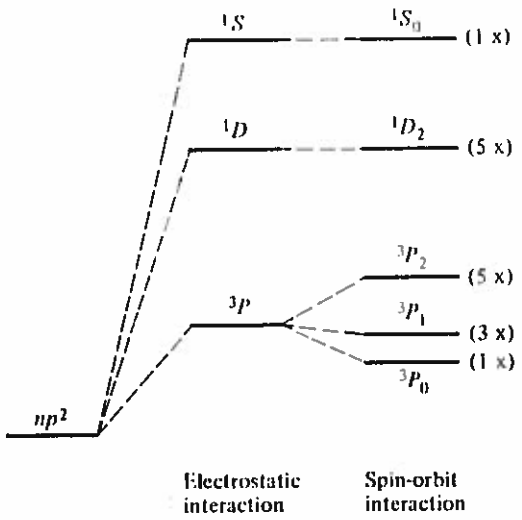

Figure 9.1 Schematic energy level diagram for the np^2 valence configuration (e.g., $n = 2$: carbon) showing the effects of electrostatic and spin-orbit interactions. Degeneracies are indicated to the side of each sublevel (Russell-Saunders coupling).

described by a mixture of more than one such configuration. A detailed discussion of this phenomenon, called "configuration interaction" (or configuration mixing), is beyond the scope of this book.

9.7 CONCLUDING REMARKS: *j-j* COUPLING

We suggested in Sec. 9.4 that Russell-Saunders coupling is not applicable to heavy atoms because the magnetic interactions, which tend to couple the spin and orbital angular momenta of the individual electrons to one another to form $\mathbf{J}_i = \mathbf{L}_i + \mathbf{S}_i$, become more important than the electrostatic interactions.

An alternative to Russell-Saunders coupling is *j-j coupling*; the relevant equations are (9.22) and (9.23). The quantum numbers of the individual electrons j_i and m_{j_i} are, for a given ℓ_i (≥ 1) and $s_i = \frac{1}{2}$,

$$j_i = \ell_i - \tfrac{1}{2}, \ell_i + \tfrac{1}{2}, \tag{9.35}$$

$$m_{j_i} = -j_i, \ldots, j_i. \tag{9.36}$$

The individual total angular momenta $\mathbf{J}_i$ then couple to give the total $\mathbf{J}$. For a two-electron atom, the quantum numbers J and M_J are simply

$$J = |j_1 - j_2|, \ldots, j_1 + j_2, \tag{9.37}$$

$$M_J = -J, \ldots, J. \tag{9.38}$$

The levels are labeled by J and (j_1, j_2) rather than by term designations as in Russell-Saunders coupling (see Prob. 9.6).

In general, the level corresponding to all electrons having the smallest values of j_i will lie lowest in energy. Thus in the case of lead (Pb), which has an np^2 valence configuration built on a closed shell (see Appendix 5), we find levels ordered as $(\frac{1}{2}, \frac{1}{2})$, $(\frac{3}{2}, \frac{1}{2})$, and $(\frac{3}{2}, \frac{3}{2})$. Usually the level with the lowest value of J for given j_1 and j_2 lies lowest in energy; however, this should not be taken as a strict rule.

Two final comments are necessary. First, for many medium-weight and heavy atoms, neither Russell-Saunders nor *j-j* coupling is precisely accurate; the electrostatic and magnetic interactions are of comparable magnitude. In such a case, a much more complicated scheme must be employed. Second, there is a relationship between the two schemes. This point is illustrated in Fig. 9.2, which shows schematically the transition from pure Russell-Saunders coupling in a light element of Group IV of the periodic table to nearly pure *j-j* coupling in the heaviest element in Group IV. Notice that all the atoms in Fig. 9.2 have the same valence configuration (np^2). The lines from left to right correlate the two extreme limits connecting levels of the same total angular momentum quantum number J.

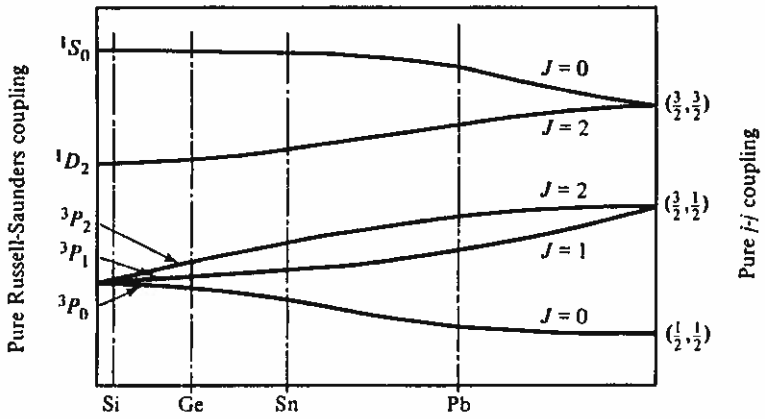

Figure 9.2 Illustration of the "correlation" of Russell-Saunders and *j-j* coupling schemes for Group IV atoms (electronic valence configuration: np^2). (From P. W. Atkins, *Molecular Quantum Mechanics*, Vol. 2. Oxford: The Clarendon Press, 1970.)

So ends our discussion of atomic structure. It would easily be possible to spend many more pages improving our understanding of atomic properties and exploring the oddities of the periodic table. We refer the interested reader to the references below instead.