

Many-Electron Atoms

5-1 The Independent Electron Approximation

In previous chapters we have dealt with the motion of a single particle in various potential fields. When we deal with more than one particle, new problems arise and new techniques are needed. Some of these are discussed in this chapter.

In constructing the hamiltonian operator for a many electron atom, we shall assume a fixed nucleus and ignore the minor error introduced by using electron mass rather than reduced mass. There will be a kinetic energy operator for each electron and potential terms for the various electrostatic attractions and repulsions in the system. Assuming n electrons and an atomic number of Z , the hamiltonian operator is (in atomic units)

$$H(1, 2, 3, \dots, n) = -\frac{1}{2} \sum_{i=1}^n \nabla_i^2 - \sum_{i=1}^n (Z/r_i) + \sum_{i=1}^{n-1} \sum_{j=i+1}^n \frac{1}{r_{ij}} \quad (5-1)$$

The numbers in parentheses on the left-hand side of Eq. (5-1) symbolize the spatial coordinates of each of the n electrons. Thus, 1 stands for x_1, y_1, z_1 , or r_1, θ_1, ϕ_1 , etc. We shall use this notation frequently throughout this book. Since we are not here concerned with the quantum-mechanical description of the translational motion of the atom, there is no kinetic energy operator for the nucleus in Eq. (5-1). The index i refers to the electrons, so we see that Eq. (5-1) provides us with the desired kinetic energy operator for each electron, a nuclear electronic attraction term for each electron, and an interelectronic repulsion term for each *distinct* electron pair. (The summation indices guarantee that $1/r_{12}$ and $1/r_{21}$ will not *both* appear in H . This prevents counting the same physical interaction twice. The indices also prevent nonphysical self-repulsion terms, such as $1/r_{22}$, from occurring.) Frequently used alternative notations for the double summation in Eq. (5-1) are $\frac{1}{2} \sum_{i \neq j}^n 1/r_{ij}$, which counts each interaction twice and divides by two, and $\sum_{i < j}^n$ or $\sum'_{i, j}$ which is merely a shorthand symbol for the expression in Eq. (5-1). In each of these alternative notations, the summation is still over two indices, but the second \sum symbol is “understood.”

For the helium atom, Eq. (5-1) becomes (see Figure 5-1)

$$H(1, 2) = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - (2/r_1) - (2/r_2) + (1/r_{12}) \quad (5-2)$$

The helium hamiltonian (5-2) can be rewritten as

$$H(1, 2) = h(1) + h(2) + 1/r_{12} \quad (5-3)$$

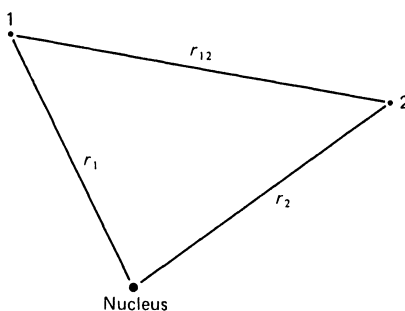


Figure 5-1 ▶ Interparticle coordinates for a three-particle system consisting of two electrons and a nucleus.

where

$$h(i) = -\frac{1}{2}\nabla_i^2 - 2/r_i \quad (5-4)$$

In Eq. (5-3) we have merely grouped H into two one-electron operators and one two-electron operator. There is no way to separate this hamiltonian *completely* into a sum of one-electron operators without loss of rigor. However, if we wish to *approximate* the hamiltonian for helium in such a way that it becomes separable, we might try simply ignoring the interelectronic repulsion term:

$$H_{\text{approx}} = h(1) + h(2) \quad (5-5)$$

If we do this, our approximate hamiltonian H_{approx} treats the kinetic and potential energies of each electron *completely independently* of the motion or position of the other. For this reason, such a treatment falls within the category of “independent electron approximations.”

Notice that each individual one-electron hamiltonian (5-4) is just the hamiltonian for a hydrogenlike ion, so it has as eigenfunctions the 1s, 2s, 2p, etc., functions of Chapter 4 with $Z = 2$. Such one-electron functions are referred to as *atomic orbitals*.¹ Representing them with the symbol ϕ_i (e.g., $\phi_1 = 1s$, $\phi_2 = 2s$, $\phi_3 = 2p_x$, $\phi_4 = 2p_y$, etc.) we have, then,

$$h(1)\phi_i(1) = \epsilon_i\phi_i(1) \quad (5-6)$$

where ϵ_i is referred to as the *orbital energy*, or *one-electron energy* for atomic orbital ϕ_i . As we saw in Chapter 4, ϵ_i is given in atomic units by

$$\epsilon_i = -\frac{1}{2}Z^2/n^2 \quad (5-7)$$

where n is the principal quantum number for ϕ_i , and Z is the nuclear charge. The “1” in Eq. (5-6) indicates that $\phi_i(1)$ is a function whose variable is the position of electron 1.

We will now show that *products of the atomic orbitals ϕ are eigenfunctions of H_{approx}* . Let the general product of atomic orbitals for helium be written $\phi_i(1)\phi_j(2)$. Then

$$H_{\text{approx}}\phi_i(1)\phi_j(2) = (h(1) + h(2))\phi_i(1)\phi_j(2) \quad (5-8)$$

$$= h(1)\phi_i(1)\phi_j(2) + h(2)\phi_i(1)\phi_j(2) \quad (5-9)$$

¹The term “atomic orbital” is used for any one-electron function used to describe the electronic distribution about an atom.

But $h(1)$ does not contain any of the variables in $\phi_j(2)$, and so they commute. Similarly, $h(2)$ and $\phi_i(1)$ commute, and

$$\begin{aligned} H_{\text{approx}}\phi_i(1)\phi_j(2) &= \phi_j(2)h(1)\phi_i(1) + \phi_i(1)h(2)\phi_j(2) \\ &= \phi_j(2)\epsilon_i\phi_i(1) + \phi_i(1)\epsilon_j\phi_j(2) \quad [\text{from Eq. (5-6)}] \\ &= (\epsilon_i + \epsilon_j)\phi_i(1)\phi_j(2) = E\phi_i(1)\phi_j(2). \end{aligned} \quad (5-10)$$

Thus, $\phi_i(1)\phi_j(2)$ is an eigenfunction of H_{approx} , and the eigenvalue E is equal to the sum of the orbital energies. These results are yet another example of the general rules stated in Section 2-7 for separable hamiltonians. Indeed, once we recognized that H_{approx} is separable, we could have written these results down at once.

Since the above terminology and results are so important for understanding many quantum-chemical calculations, we will summarize them here:

1. The hamiltonian for a multielectron system cannot be separated into one-electron parts without making some approximation.
2. Ignoring interelectron repulsion operators is one way to allow separability.
3. The one-electron operators in the resulting approximate hamiltonian for an atom are hydrogenlike ion hamiltonians. Their eigenfunctions are called *atomic orbitals*.
4. Simple products of atomic orbitals are eigenfunctions for the approximate hamiltonian.
5. *In this approximation* the total energy is equal to the sum of the one-electron energies.

EXAMPLE 5-1 What electronic energy is predicted by the above approximation for the lithium atom in its ground state? What is the experimental value for the total electronic energy, given that the first and second ionization energies are 0.198 a.u. and 2.778 a.u.?

SOLUTION ► The ground state configuration for lithium is $1s^22s$, so $E_{\text{approx}} = 2\epsilon_{1s} + \epsilon_{2s} = 2(-\frac{1}{2} \cdot \frac{3^2}{1^2} \text{ a.u.}) + (-\frac{1}{2} \cdot \frac{3^2}{2^2} \text{ a.u.}) = -10.125 \text{ a.u.}$ The experimental value of E equals minus the sum of all three ionization energies. The first two values are given, and the third can be calculated using the formula for one-electron ions: $IE_3 = -E_{Li^{2+}} = -(-\frac{1}{2} \cdot \frac{3^2}{1^2}) = 4.500 \text{ a.u.}$ Therefore, $E_{\text{exp}} = -(0.198 + 2.778 + 4.500) \text{ a.u.} = -7.476 \text{ a.u.}$ Clearly, the approximate hamiltonian predicts an electronic energy that is much lower than the experimental value. ◀

5-2 Simple Products and Electron Exchange Symmetry

In the independent particle model just described, the wavefunction for the lowest-energy state for helium is $1s(1)1s(2)$ since this has the lowest possible sum of one-electron energies. The *electronic configuration* for this state is symbolized $1s^2$, the superscript telling us how many electrons are in $1s$ orbitals. What might we expect for the electronic configuration of the lowest excited state? The answer is $1s2s$ (superscript “ones” are implicit). (At this point there is no reason for preferring this configuration to, say,

$1s2p_x$, but we shall show later that, in multielectronic systems, the $2s$ orbital has a lower energy than does a $2p$ orbital, even though they have the same principal quantum number.) Thus, we might write

$$\psi(1, 2) = 1s(1)2s(2) \equiv \underbrace{\sqrt{8/\pi} \exp(-2r_1)}_{\text{He}^+ 1s} \underbrace{\sqrt{1/\pi} (1 - r_2) \exp(-r_2)}_{\text{He}^+ 2s} \quad (5-11)$$

If one were to calculate \bar{r}_1 , the average distance from the nucleus for electron 1, using this wavefunction, one would obtain a value of $\frac{3}{4}$ a.u., consistent with the $1s$ state of a helium ion. For electron 2 one would find an average value, \bar{r}_2 , of 3 a.u., characteristic of the $2s$ state (Problem 5-2). How does this correspond to what we would find experimentally?

Before answering this question, we must recall that there are special problems associated with measuring the properties of an atomic system. The process of “seeing” electrons in atoms well enough to pinpoint their positions perturbs an atom so strongly that it cannot be assumed to be in the same state after the measurement. To get around this problem, we can assume that we have a very large number of identically prepared helium atoms, and that a single measurement of electronic positions will be made on each atom. It is assumed that the average of the instantaneous r values for a billion systems is identical to the average r value for a billion instants in a single undisturbed system.

When we consider the measurement of average values for r_1 and r_2 in helium, we immediately encounter another problem. Say we can effect a simultaneous measurement of the two electronic distances in the first He atom. We call these r_1 and r_2 and tabulate them for future averaging. Then we move on to a new helium atom and measure r_1 and r_2 for it. But we clearly have no way of identifying a particular one of these electrons with a particular one of the earlier pair. There is no connection between r_1 for one atom and r_1 for the next since all electrons are identical. If we want to know \bar{r} , we can only average them all together and leave it at that.

Thus, the wavefunction (5-11) does not seem to be entirely satisfactory since it enables us to calculate $\bar{r}_1 \neq \bar{r}_2$, something that is *in principle* impossible to measure. We need to modify the wavefunction so that it yields an average value for r_1 and r_2 (or for any quantity) that is independent of our choice of electron labels. This means that the electron density itself, given by $\psi(1, 2)^2$, must be independent of our electron labeling scheme.

In a two-electron system like helium, there are only two ways to arrange the labels “1” and “2” in a single product function. For example, the product $1s2s$ can be written

$$1s(1)2s(2) \quad \text{or} \quad 2s(1)1s(2) \quad (5-12)$$

Squaring these gives two different functions, namely,

$$\begin{aligned} 1s^2(1)2s^2(2) &= (8/\pi) \exp(-4r_1)(1/\pi)(1 - 2r_2 + r_2^2) \exp(-2r_2) \\ 2s^2(1)1s^2(2) &= (8/\pi) \exp(-4r_2)(1/\pi)(1 - 2r_1 + r_1^2) \exp(-2r_1) \end{aligned} \quad (5-13)$$

These are different since they predict, for instance, different distributions for electron 1. The functions (5-12) are said to differ by an interchange of electron indices, or coordinates. (Since electron labels denote position coordinates, interchange of labels in the mathematical formula corresponds to interchanging positions of electrons in the physical model.) For ψ^2 to be invariant under such an interchange, it is necessary that

ψ itself be either symmetric or antisymmetric under the interchange. That is, if P is an interchange operator such that $Pf(1, 2) = f(2, 1)$ then we need a ψ such that

$$P\psi = \pm\psi \quad (5-14)$$

since then

$$P(\psi^2) = (P\psi)^2 = (\pm\psi)^2 = \psi^2$$

One such wavefunction is given by the *sum* of eigenfunctions (5-12),

$$\psi_s = (1/\sqrt{2})[1s(1)2s(2) + 2s(1)1s(2)] \quad (5-15)$$

since

$$P\psi_s = (1/\sqrt{2})[1s(2)2s(1) + 2s(2)1s(1)] = \psi_s$$

(the factor $1/\sqrt{2}$ keeps the wavefunction normalized). Wavefunction (5-15) is thus symmetric under electron interchange. Is Eq. (5-15) still an eigenfunction for H_{approx} ? Yes, because the eigenfunctions (5-12) are degenerate (both have $E = \epsilon_{1s} + \epsilon_{2s}$) and can therefore be mixed together in any way we choose and still be eigenfunctions. The antisymmetric combination is

$$\psi_a = (1/\sqrt{2})[1s(1)2s(2) - 2s(1)1s(2)] \quad (5-16)$$

Thus far we have shown that simple products of atomic orbitals give us two degenerate eigenfunctions of H_{approx} for the configuration $1s2s$ and that these eigenfunctions fail to have the required symmetry properties for interchange of electron coordinates. But we have shown that, by taking the sum and difference of these simple products, we can form new eigenfunctions of H_{approx} that are respectively symmetric and antisymmetric with respect to the interchange of electron coordinates, so that ψ^2 is invariant to electron interchange.

There is another way we can demonstrate that the helium atom eigenfunctions ought to be symmetric or antisymmetric for electron exchange: We can examine the hamiltonian operator. We have shown in Chapter 2 that nondegenerate eigenfunctions must be symmetric or antisymmetric for any operation that leaves the hamiltonian unchanged and that degenerate eigenfunctions may always be mixed together in some combination so that they too are symmetric or antisymmetric. This suggests that, for the case under discussion (the helium atom), the hamiltonian operator might be unchanged by an exchange of electrons. First we examine H_{approx} :

$$PH_{\text{approx}} = P[h(1) + h(2)] = h(2) + h(1) = H_{\text{approx}} \quad (5-17)$$

Our approximate hamiltonian is invariant to electron exchange, so any *nondegenerate* eigenfunctions must be symmetric or antisymmetric for interchange of electron labels (or positions). Only because the $1s2s$ configuration leads to *degenerate* eigenfunctions were we able to find unsymmetric² eigenfunctions like Eq. (5-12). This situation is reminiscent of the particle-in-a-ring system discussed in Chapter 2, where degenerate,

²A function is unsymmetric for any operation that produces neither plus nor minus that function; i.e., if $Pf = y$ and $y \neq \pm f$, then f is unsymmetric under the operation P .

symmetric exponential eigenfunctions could be mixed to form degenerate unsymmetric trigonometric eigenfunctions. Let us now examine the *full* hamiltonian H :

$$PH(1, 2) = P[h(1) + h(2) + 1/r_{12}] = h(2) + h(1) + 1/r_{21} = H(1, 2) \quad (5-18)$$

Since r_{12} and r_{21} are the same distance, it is evident that the exact H is likewise invariant to interchange of electron labels. Thus, we see that appeal either to physical argument or to the invariance of H and of H_{approx} to exchange of electrons leads us to recognize the need to impose symmetry conditions on the wavefunctions.

We now summarize the points we have tried to convey in this section.

1. A simple product function of the type $1s(1)2s(2)$ enables one to calculate different values of \bar{r} for electrons 1 and 2. This makes no physical sense since the electrons are *identical particles* and hence are not physically distinguishable.
2. Wavefunctions that overcome this difficulty must be either symmetric or antisymmetric with respect to exchange of electron labels (coordinates).
3. The fact that this kind of “exchange symmetry” must be present is also (or alternatively) seen from the fact that H (and also H_{approx}) is invariant under such an exchange operation.

EXAMPLE 5-2 Given the functions $f(x_1) = x_1^2$ and $g(x_2) = \exp(x_2)$, show that, for $x_1 = 1, x_2 = 2$, $f(x_1)g(x_2)$ is unsymmetric for exchange of the two x positions, $f(x_1)g(x_2) + g(x_1)f(x_2)$ is symmetric, and $f(x_1)g(x_2) - g(x_1)f(x_2)$ is antisymmetric.

SOLUTION ► For fg , we are examining what happens when $x_1^2 \exp(x_2)$ turns into $x_2^2 \exp(x_1)$. That is, we are comparing $1^2 \exp(2)$ to $2^2 \exp(1)$. The resulting values are 7.389 and 10.873—obviously neither plus or minus times each other. $fg + gf$ equals $1^2 \exp(2) + 2^2 \exp(1)$, or $7.389 + 10.873$. After switching positions, we get $10.873 + 7.389$, which is obviously the same thing. $fg - gf$ gives $7.389 - 10.873$. After switching, it gives $10.873 - 7.389$, which is obviously minus one times the first value. ◀

5-3 Electron Spin and the Exclusion Principle

Chemical and spectral evidence indicates that metals in Groups IA and IB of the periodic table are reasonably well represented by an electron configuration wherein one loosely held “valence” electron occupies an s orbital and all other electrons occur in pairs in orbitals of lower principal quantum number. Thus, lithium has a ground-state electronic structure approximated by the configuration $1s^2 2s$, sodium by $1s^2 2s^2 2p^6 3s$, copper by $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s$, etc. (A configuration indicating that all orbitals of given n and l are doubly occupied, leaving no other electrons, is often called a *closed shell*. Thus, the above-cited examples each consist of a closed shell plus one s valence electron.) The observation that each atomic orbital in such configurations is occupied by no more than two electrons was without a theoretical explanation for some time.

When an atom like sodium is placed in an external magnetic field, what should be the magnetic moment of the atom due to orbital motion of the electrons? The s electrons should contribute nothing since, by definition of s, $l = 0$ and hence the magnetic quantum number $m = 0$ for such electrons. An electron in a p orbital may have an orbital magnetic moment, but if all p levels ($l = 1, m = +1, 0, -1$) are equally occupied, the net magnetic moment should be zero. It is clear, then, that we might expect atoms in Groups IA and IB to possess no magnetic moment due to electron orbital motion. Nevertheless, Gerlach and Stern [1, 2] found that, when a beam of unexcited silver atoms is passed through an inhomogeneous magnetic field, it splits into two components as though each silver atom possesses a small magnetic moment capable of taking on either of two orientations in the applied field. (In a *homogeneous* magnetic field, the north and south poles of a magnetic dipole experience equal but oppositely directed forces, causing the dipole to become *oriented*. An example is a magnetic compass in the magnetic field of the earth. In an *inhomogeneous* magnetic field the poles experience opposite but unequal forces, causing the entire dipole to be *accelerated through space* in addition to being oriented.) Uhlenbeck and Goudsmit [3] and Bichowsky and Urey [4] independently suggested that the electron behaves as though it were a particle of finite radius spinning about its center of mass. Such a spinning particle would classically have angular momentum and, since it is charged, an accompanying magnetic moment.³

If we accept the model of electron spin, then we can rationalize our experimental facts if we assume each electron is capable of being in one of but two possible states of opposite spin. This is done in the following way. If we attribute *opposite* spins to the two 1s electrons in, say, silver, their spin moments should cancel. Similarly, all other orbital-sharing electrons would contribute nothing if their spins were opposed. Only the outermost (5s) electron would have an uncanceled spin moment. Its two possible orientations would cause the beam to split into two components as is observed.⁴

The evident need for the introduction of the concept of electron spin means that our wavefunctions of earlier sections are incomplete. We need a wavefunction that tells us not only the probability that an electron will be found at given r, θ, ϕ coordinates in three-dimensional space, but also the probability that it will be in one or the other spin state. Rather than seeking detailed mathematical descriptions of spin state functions, we will simply symbolize them α and β . Then the symbol $\phi(1)\alpha(1)$ will mean that electron number 1 is in a spatial distribution corresponding to space orbital ϕ , and that it has spin α . In the independent electron scheme, then, we could write the *spin orbital* (includes space and spin parts) for the valence electron of silver either as $5s(1)\alpha(1)$ or $5s(1)\beta(1)$. These two possibilities both occur in the atomic beam and interact differently with the inhomogeneous magnetic field.

We now focus on the manner in which spin considerations affect wavefunction symmetry. The electrons are still identical particles, so our particle distribution must be

³This classical model, developed in the 1920s, is pedagogically useful and is responsible for the term *spin*, which is still employed to describe the fourth quantum number. However, it was not until 1948 and 1967 that mathematical studies of the properties of linearized equivalents of the Schrödinger equation revealed the mathematical connection to this quantum number. For an entry to the literature, see Roman [10].

⁴Actually, other experimental evidence, such as splitting of atomic spectral lines due to applied magnetic fields, was also available. Furthermore, experience with the quantum theory of orbital angular momentum played a role in the treatment of electron spin. The reader should not think that the historical development of quantum theory of spin was as naive or simple as we make it appear here.

insensitive to our choice of labels. This last statement is equivalent to saying that ψ must be symmetric or antisymmetric for interchange of electron *space and spin coordinates*. Let us examine this situation in the case of ground state helium and lithium atoms.

In the independent electron approximation, the lowest-energy configuration for helium is $1s^2$. Let us write the various conceivable spin combinations for this configuration. They are

$$\left. \begin{array}{l} 1s(1)\alpha(1)1s(2)\alpha(2) \\ 1s(1)\alpha(1)1s(2)\beta(2) \\ 1s(1)\beta(1)1s(2)\alpha(2) \\ 1s(1)\beta(1)1s(2)\beta(2) \end{array} \right\} = 1s(1)1s(2) \left\{ \begin{array}{l} \alpha(1)\alpha(2) \\ \alpha(1)\beta(2) \\ \beta(1)\alpha(2) \\ \beta(1)\beta(2) \end{array} \right. \quad \begin{array}{l} (5-19) \\ (5-20) \\ (5-21) \\ (5-22) \end{array}$$

It is easy to see that the common space term $1s(1)1s(2)$ is symmetric for electron interchange. Likewise, $\alpha(1)\alpha(2)$ and $\beta(1)\beta(2)$ are each symmetric, so Eqs. (5-19) and (5-22) are totally symmetric wavefunctions. The spin parts of Eqs. (5-20) and (5-21) are unsymmetric (not antisymmetric) for interchange, so these wavefunctions are not satisfactory. However, we can take the sum and difference of Eqs. (5-20) and (5-21) to obtain

$$1s(1)1s(2) \left\{ \begin{array}{l} (1/\sqrt{2})[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \\ (1/\sqrt{2})[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \end{array} \right. \quad \begin{array}{l} (5-23) \\ (5-24) \end{array}$$

The $2^{-1/2}$ serves to maintain normality if we assume α and β to be orthonormal:

$$\int \alpha^*(1)\alpha(1)d\omega(1) = \int \beta^*(1)\beta(1)d\omega(1) = 1 \quad (5-25)$$

$$\int \alpha^*(1)\beta(1)d\omega(1) = \int \beta^*(1)\alpha(1)d\omega(1) = 0 \quad (5-26)$$

Here we use integrals and a differential element $d\omega$ in a “spin coordinate ω .” This is notationally convenient but not, for our purposes, worth delving into. We can interpret integration over ω to be in effect equivalent to summing over the possible electron indices. If, for a particular electron index, the spins agree, then the integral equals unity. If they disagree, the integral vanishes. Wavefunction (5-23) consists of symmetric space and spin parts, so it is overall symmetric. Wavefunction (5-24) contains a symmetric space part times an antisymmetric spin part, so it is overall antisymmetric. We have succeeded, then, in writing down four wavefunctions for the configuration $1s^2$ having proper symmetry for electron interchange. Three of these, Eqs. (5-19), (5-22), (5-23), are symmetric and one, Eq. (5-24), is antisymmetric. Experimentally, we know that the ground state of helium is a *singlet*, that is, there is but one such state. *This suggests that the wavefunction must be antisymmetric for exchange of electron space and spin coordinates.*

EXAMPLE 5-3 We have just shown four wavefunctions resulting from four spin functions times a symmetric space part ($1s^2$). Can we manipulate the $1s^2$ configuration to obtain an **antisymmetric** space part, as we did for the $1s2s$ configuration?

SOLUTION ► We can try to produce an antisymmetric space function by taking the product difference $1s(1)1s(2)-1s(2)1s(1)$. Since these two products are really the same, this combination equals zero. Thus, whereas two different orbitals can be arranged in two product combinations, one symmetric and the other antisymmetric, we find that a single orbital, doubly occupied, can appear only in one simple product, which must be symmetric for electron exchange. ◀

Now let us try lithium. The lowest-energy configuration should be $1s^3$, and we can write eight unique space-spin orbital products:

$$1s(1)1s(2)1s(3) \left\{ \begin{array}{l} \alpha(1)\alpha(2)\alpha(3) \quad (5-27) \\ \alpha(1)\alpha(2)\beta(3) \quad (5-28) \\ \alpha(1)\beta(2)\alpha(3) \quad (5-29) \\ \beta(1)\alpha(2)\alpha(3) \quad (5-30) \\ \alpha(1)\beta(2)\beta(3) \quad (5-31) \\ \beta(1)\alpha(2)\beta(3) \quad (5-32) \\ \beta(1)\beta(2)\alpha(3) \quad (5-33) \\ \beta(1)\beta(2)\beta(3) \quad (5-34) \end{array} \right.$$

Of these, the first and last are totally symmetric for all electron interchanges. The remaining six are unsymmetric for two out of three possible interchanges. Can we make appropriate linear combinations of these as we did for helium? Let us try. The problem is simplified by recognizing that, if we start with, say, two α 's and one β , we still have that number of α 's and β 's after interchange of electron labels. Hence, we mix together only functions that agree in total numbers of α 's and β 's, i.e., (5-28), (5-29), (5-30) with each other, or (5-31), (5-32), (5-33) with each other. Let us try the sum of (5-28), (5-29), and (5-30). Ignoring normalization, this gives the spin function

$$\alpha(1)\alpha(2)\beta(3) + \alpha(1)\beta(2)\alpha(3) + \beta(1)\alpha(2)\alpha(3) \quad (5-35)$$

Interchanging electron spin coordinates 1 and 2 gives

$$\alpha(2)\alpha(1)\beta(3) + \alpha(2)\beta(1)\alpha(3) + \beta(2)\alpha(1)\alpha(3)$$

which, upon reordering each product, is easily seen to be identical to (5-35). The same result arises from interchanging 1 and 3 or 2 and 3, and so (5-35) is symmetric for all interchanges. The sum of (5-31), (5-32), and (5-33) is likewise symmetric. Can we find any combinations that are totally antisymmetric? A few attempts with pencil and paper should convince one that it is impossible to find a combination that is antisymmetric for all interchanges. Experimentally, we know that no state of lithium corresponds to a $1s^3$ configuration.

To summarize, we have found that for the configuration $1s^2$ we can write three wavefunctions that are symmetric and one that is antisymmetric under exchange of electron space and spin coordinates, while for the configuration $1s^3$ we can construct symmetric or unsymmetric wavefunctions, but no antisymmetric ones. The physical observation

is that atoms exist in only *one* state having an electronic structure approximately represented by the configuration $1s^2$, but that there are no atoms having any state represented by $1s^3$. This and other physical evidence has led to the recognition of the *exclusion principle*: Wavefunctions must be *antisymmetric* with respect to simultaneous interchange of space *and* spin coordinates of electrons.⁵ In invoking the exclusion principle, we exclude all of the $1s^3$ wavefunctions and three out of the four wavefunctions we were able to construct for the ground state of helium, leaving (5-24) as the only acceptable wave-function.

We have seen that the ground state configuration of lithium cannot be $1s^3$. Can we satisfy the exclusion principle with the next-lowest energy configuration $1s^22s$? We will try to find a satisfactory solution, but our manipulations will be simplified if we streamline our notation. We will write a function such as $1s(1)1s(2)2s(3)\alpha(1)\beta(2)\alpha(3)$ as $1s1s2s\alpha\beta\alpha$, allowing *position* in the sequence to stand for the electron label. Interchanging electrons 1 and 2 is then represented by switching the order of space functions in positions 1 and 2 and spin functions in positions 1 and 2 thus

$$1s1s2s\alpha\beta\alpha \xrightarrow{1\leftrightarrow 2} 1s1s2s\beta\alpha\alpha \quad (5-36)$$

This interchange produced a new function rather than merely reversing the sign of our starting function. But if we take the difference between the two products in Eq. (5-36), we will have a function that is antisymmetric to 1, 2 interchange: $1s1s2s(\alpha\beta\alpha - \beta\alpha\alpha)$. Now we subject this to a 1, 3 interchange and the new products produced are subtracted to give a function that is antisymmetric to 1, 3 interchange: $1s1s2s(\alpha\beta\alpha - \beta\alpha\alpha) - 2s1s1s(\alpha\beta\alpha - \alpha\alpha\beta)$. The first pair of terms is still not antisymmetric to 2, 3 interchange, and the second pair is not antisymmetric to 1, 2 interchange. We can use either one of these interchanges to produce two new terms to subtract. Either way, the resulting wavefunction, antisymmetric for all interchanges, is

$$\frac{1}{\sqrt{6}}[1s1s2s(\alpha\beta\alpha - \beta\alpha\alpha) + 1s2s1s(\beta\alpha\alpha - \alpha\alpha\beta) + 2s1s1s(\alpha\alpha\beta - \alpha\beta\alpha)] \quad (5-37)$$

The factor $6^{-1/2}$ normalizes (5-37) since all of the six space-spin products are normalized and orthogonal to each other product by virtue of either space-orbital or spin-orbital disagreement, or both. Note that, whereas the two-electron wavefunction for helium was separable into a single space function times a spin function, the lithium wavefunction must be written as a linear combination of such products. This is usually true when we deal with more than two electrons.

Since $1s^22s$ is the lowest-energy configuration for which we can write an antisymmetrized wavefunction, this is the ground state configuration for lithium in this independent-electron approximation.

In summary, phenomenological evidence suggests that an electron can exist in either of two "spin states" in the presence of a magnetic field. Writing wavefunctions including spin functions and comparing these with experimental facts indicates that states exist only for wavefunctions that satisfy the exclusion principle.

⁵A broader statement is: Wavefunctions must be antisymmetric (symmetric) with respect to simultaneous interchange of space and spin coordinates of fermions (bosons). A fermion is characterized by half-integral spin quantum number; a boson is characterized by integral spin quantum number. Electrons have spin quantum number $\frac{1}{2}$ and are therefore fermions.

5-4 Slater Determinants and the Pauli Principle

It was pointed out by Slater [5] that there is a simple way to write wavefunctions guaranteeing that they will be antisymmetric for interchange of electronic space and spin coordinates: one writes the wavefunction as a determinant. For the $1s^2 2s$ configuration of lithium, one would write

$$\psi = \frac{1}{\sqrt{6}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(2)\alpha(2) & 1s(3)\alpha(3) \\ 1s(1)\beta(1) & 1s(2)\beta(2) & 1s(3)\beta(3) \\ 2s(1)\alpha(1) & 2s(2)\alpha(2) & 2s(3)\alpha(3) \end{vmatrix} \quad (5-38)$$

Expanding this according to the usual rules governing determinants (see Appendix 2) gives

$$\begin{aligned} \psi = \frac{1}{\sqrt{6}} [& 1s(1)\alpha(1)1s(2)\beta(2)2s(3)\alpha(3) + 2s(1)\alpha(1)1s(2)\alpha(2)1s(3)\beta(3) \\ & + 1s(1)\beta(1)2s(2)\alpha(2)1s(3)\alpha(3) - 2s(1)\alpha(1)1s(2)\beta(2)1s(3)\alpha(3) \\ & - 1s(1)\beta(1)1s(2)\alpha(2)2s(3)\alpha(3) - 1s(1)\alpha(1)2s(2)\alpha(2)1s(3)\beta(3)] \end{aligned} \quad (5-39)$$

This can be factored and shown to be identical to wavefunction (5-37) of the preceding section.

A simplifying notation in common usage is to delete the α , β symbols of the spin-orbitals and to let a bar over the space orbital signify β spin, absence of a bar being understood to signify α spin. In this notation, Eq. (5-38) would be written

$$\psi = \frac{1}{\sqrt{6}} \begin{vmatrix} 1s(1) & 1s(2) & 1s(3) \\ 1\bar{s}(1) & 1\bar{s}(2) & 1\bar{s}(3) \\ 2s(1) & 2s(2) & 2s(3) \end{vmatrix} \quad (5-40)$$

The general prescription to follow in writing a Slater determinantal wavefunction is very simple:

1. Choose the configuration to be represented. $1s1\bar{s}2s$ was used above. (Here we write $1s1\bar{s}2s$ rather than $1s^2 2s$ to emphasize that the two $1s$ electrons occupy different spin-orbitals.) For our general example, we will let U_i stand for a general spin-orbital and take a four-electron example of configuration $U_1 U_2 U_3 U_4$.
2. For n electrons, set up an $n \times n$ determinant with $(n!)^{-1/2}$ as normalizing factor. Every position in the first row should be occupied by the first spin-orbital of the configuration; every position in the second row by the second spin-orbital, etc. Now put in electron indices so that all positions in *column* 1 are occupied by electron 1, column 2 by electron 2, etc.

In the case of our four-electron configuration, the recipe gives

$$\psi = \frac{1}{\sqrt{4!}} \begin{vmatrix} U_1(1) & U_1(2) & U_1(3) & U_1(4) \\ U_2(1) & U_2(2) & U_2(3) & U_2(4) \\ U_3(1) & U_3(2) & U_3(3) & U_3(4) \\ U_4(1) & U_4(2) & U_4(3) & U_4(4) \end{vmatrix} \quad (5-41)$$

Notice that the principal diagonal (top left to bottom right) contains our original configuration $U_1U_2U_3U_4$. Often, the Slater determinant is represented in a space-saving way by simply writing the principal diagonal between short vertical bars. The normalizing factor is deleted. Thus, Eq. (5-41) would be symbolized as $|U_1(1)U_2(2)U_3(3)U_4(4)|$.

We have indicated the general recipe for writing down a Slater determinant, and we have seen that, for the configuration $1s\bar{1}s2s$, this gives an antisymmetric wavefunction. Now we will give a general proof of the antisymmetry of such wavefunctions for exchange of electrons. We have already seen that interchanging the space and spin coordinates of electrons 1 and 2 corresponds to going through the wavefunction and changing all the $1s$ to $2s$ and vice versa; i.e., electron *labels* denote coordinates. In a Slater determinant, interchanging electron labels 1 and 2 is the same thing as interchanging columns 1 and 2 of the determinant. [See Eq. (5-41) and note that columns 1 and 2 differ only in electron index.] But a determinant reverses sign upon interchange of two rows or columns. (See Appendix 2 for a summary of the properties of determinants.) Hence, any Slater determinant reverses sign (i.e., is antisymmetric) upon the interchange of space and spin coordinates of any two electrons.

Suppose we tried to put two electrons into the same space-orbital with the same spin. This would require that the same spin-orbital be written twice in the configuration, causing two rows of the Slater determinant to be identical. [If both $1s$ electrons in Eq. (5-40) had α spin, the bars would be absent from row 2.] We just stated that the determinant must reverse sign upon interchange of two rows. If we interchange two *identical* rows, we change nothing yet the sign must reverse: the determinant must be equal to zero. Thus, the determinantal wavefunction vanishes when we try to put more than one electron into the same spin-orbital, indicating that this is not a physically allowed situation. This is a generalization of our earlier discovery that no $1s^3$ configuration is allowed by the exclusion principle, such a configuration requiring at least two electrons to have the same space and spin functions.

This restriction on allowable electronic configurations is more familiar to chemists as the Pauli principle: *In assigning electrons to atomic orbitals in the independent electron scheme, no two electrons are allowed to have all four quantum numbers ($n, l, m, spin$) the same.* The Pauli principle is a restatement of the exclusion principle as it applies in the special case of an orbital approximation to the wavefunction.

5-5 Singlet and Triplet States for the $1s2s$ Configuration of Helium

We showed in Section 5-2 that two *space* functions having proper space symmetry could be written for the configuration $1s2s$. One was symmetric (Eq. 5-15) and one was antisymmetric (Eq. 5-16). Now we find that spin functions must be included in our wavefunctions, and in a way that makes the final result antisymmetric when space and spin coordinates are interchanged. We can accomplish this by multiplying the symmetric space function by an antisymmetric spin function, calling the result $\psi_{s,a}$. Thus,

$$\psi_{s,a}(1, 2) = (1/\sqrt{2})[1s(1)2s(2) + 2s(1)1s(2)](1/\sqrt{2})[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad (5-42)$$

Alternatively, we can multiply the antisymmetric space term by any one of the three possible symmetric spin terms:

$$\psi_{a,s}(1, 2) = (1/\sqrt{2})[1s(1)2s(2) - 2s(1)1s(2)] \begin{cases} \alpha(1)\alpha(2) & (5-43a) \\ (1/\sqrt{2})[\alpha(1)\beta(2) + \beta(1)\alpha(2)] & (5-43b) \\ \beta(1)\beta(2) & (5-43c) \end{cases}$$

All four of these wavefunctions satisfy the exclusion principle and each is linearly independent of the others, indicating that four distinct physical states arise from the configuration 1s2s.

There are a number of important points that can be illustrated using these wavefunctions. The first has to do with Slater determinants. Let us write down a Slater determinantal expression corresponding to wavefunction (5-43a). The configuration is 1s(1) α (1)2s(2) α (2), giving the Slater determinant (where absence of a bar indicates α spin)

$$\psi_{a,s}(1, 2) = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1) & 1s(2) \\ 2s(1) & 2s(2) \end{vmatrix} \quad (5-44)$$

which, upon expansion, gives us Eq. (5-43a). If we attempt the same process to obtain Eq. (5-43b), we encounter a difficulty. The configuration 1s(1) α (1)2s(2) β (2) leads to a 2×2 determinant, which, upon expansion, gives two product terms, whereas Eq. (5-43b) involves four product terms. The Slater determinantal functions corresponding to Eqs. (5-42) and (5-43b) are, in fact,

$$\psi_{a,s}^{s,a}(1, 2) = \frac{1}{\sqrt{2}} \left\{ \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1) & 1s(2) \\ 2\bar{s}(1) & 2\bar{s}(2) \end{vmatrix} \mp \frac{1}{\sqrt{2}} \begin{vmatrix} 1\bar{s}(1) & 1\bar{s}(2) \\ 2s(1) & 2s(2) \end{vmatrix} \right\} \quad (5-45)$$

The lesson to be gained from this is that a *single Slater determinant does not always display all of the symmetry possessed by the correct wavefunction*. (In this particular case, a single determinant restricts one of the AOs to α spin and the other to β , which is an artificial limitation.)

Next we will investigate the energies of the states as they are described by these wavefunctions. We have already pointed out that they are degenerate eigenfunctions of H_{approx} , but we will now examine their interactions with the full hamiltonian (5-2). Since our wavefunctions are not eigenfunctions of this hamiltonian, we cannot compare eigenvalues. Instead we must calculate the average values of the energy for each wavefunction, using the formula

$$\bar{E} = \frac{\int \psi^* H \psi d\tau}{\int \psi^* \psi d\tau} \quad (5-46)$$

The symbol “ $d\tau$ ” stands for integration over space and spin coordinates of the electrons: $d\tau = dv d\omega$. Since both space and spin parts of our wavefunctions are normalized [cf. Eqs. (5-25) and (5-26)], the denominator of Eq. (5-46) is unity and may be ignored. The energy thus is given by the expression

$$\bar{E} = \int \psi^* \left[-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - (2/r_1) - (2/r_2) + (1/r_{12}) \right] \psi d\tau \quad (5-47)$$

Notice that the energy operator H contains no terms that would interact with spin functions α and β . (Such terms do arise at higher levels of refinement, but we ignore them for now.) Hence, the spin terms of ψ can be integrated separately, and, since all spin factors in Eqs. (5-42) and (5-43) are normalized, this gives a factor of unity in all four cases. This means that the average energies will be entirely determined by the space parts of the wavefunctions. This, in turn, means that all three states (5-43), which have the same space term, will have the same energy but that the state approximated by the function (5-42) may have a different energy. If our approximate representation of the exact eigenfunctions is physically realistic, we expect helium to display two excited state energies in the energy range consistent with a $1s2s$ configuration. Furthermore, we expect one of these state energies to be triply degenerate.

Which of these two state energies should be higher? To determine this requires that we expand our energy expression (5-47) for each of the two space functions (5-42) and (5-43).

$$\begin{aligned} \bar{E}_3 = \frac{1}{2} \iint [1s^*(1)2s^*(2) \pm 2s^*(1)1s^*(2)] & \left[-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - (2/r_1) \right. \\ & \left. - (2/r_2) + (1/r_{12}) \right] [1s(1)2s(2) \pm 2s(1)1s(2)] dv(1)dv(2) \quad (5-48) \end{aligned}$$

(The subscript on \bar{E} refers to the degeneracy of whichever energy level we are considering.) This expands into a large number of terms. Integrals over one-electron operators may be written as products of two integrals, each over a different electron.⁶ Thus, the expansion over the kinetic energy operators gives

$$\begin{aligned} & \frac{1}{2} \left\{ \int 1s^*(1) \left[-\frac{1}{2}\nabla_1^2 \right] 1s(1) dv(1) \int \cancel{2s^*(2)2s(2)} dv(2) \right. \\ & + \int 2s^*(2) \left[-\frac{1}{2}\nabla_2^2 \right] 2s(2) dv(2) \int \cancel{1s^*(1)1s(1)} dv(1) \\ & + \int 2s^*(1) \left[-\frac{1}{2}\nabla_1^2 \right] 2s(1) dv(1) \int \cancel{1s^*(2)1s(2)} dv(2) \\ & + \int 1s^*(2) \left[-\frac{1}{2}\nabla_2^2 \right] 1s(2) dv(2) \int \cancel{2s^*(1)2s(1)} dv(1) \\ & \pm \int 1s^*(1) \left[-\frac{1}{2}\nabla_1^2 \right] 2s(1) dv(1) \int \cancel{2s^*(2)1s(2)} dv(2) \\ & \pm \int 2s^*(2) \left[-\frac{1}{2}\nabla_2^2 \right] 1s(2) dv(2) \int \cancel{1s^*(1)2s(1)} dv(1) \\ & \pm \int 2s^*(1) \left[-\frac{1}{2}\nabla_1^2 \right] 1s(1) dv(1) \int \cancel{1s^*(2)2s(2)} dv(2) \\ & \left. \pm \int 1s^*(2) \left[-\frac{1}{2}\nabla_2^2 \right] 2s(2) dv(2) \int \cancel{2s^*(1)1s(1)} dv(1) \right\} \quad (5-49) \end{aligned}$$

⁶We have already shown that, if the $1/r_{12}$ term is absent, the energy is equal to $E_{1s} + E_{2s}$, for He^+ , which is equal to -2.5 a.u. Therefore, the detailed breakdown leading to Eqs. (5-49)–(5-51) is not necessary. However, we will present it in detail in the belief that some students will benefit from another specific example of integration of two-electron products over one-electron operators.

The orthogonality of the 1s and 2s orbitals causes the terms preceded by \pm to vanish. Furthermore, integrals that differ only in the variable label [such as those in the second and third terms of (5-49)] are equal, so that this expansion becomes

$$\int 1s^*(1) \left[-\frac{1}{2} \nabla_1^2 \right] 1s(1) dv(1) + \int 2s^*(1) \left[-\frac{1}{2} \nabla_1^2 \right] 2s(1) dv(1) \quad (5-50)$$

Expansion of Eq. (5-48) over $(-2/r_1 - 2/r_2)$ proceeds analogously to give

$$\int 1s^*(1)(-2/r_1)1s(1) dv(1) + \int 2s^*(1)(-2/r_1)2s(1) dv(1) \quad (5-51)$$

The final term in the hamiltonian, $1/r_{12}$, occurs in four two-electron integrals:

$$\begin{aligned} & \frac{1}{2} \left\{ \iint 1s^*(1)2s^*(2)(1/r_{12})1s(1)2s(2) dv(1) dv(2) \right. \\ & + \iint 2s^*(1)1s^*(2)(1/r_{12})2s(1)1s(2) dv(1) dv(2) \\ & \pm \iint 1s^*(1)2s^*(2)(1/r_{12})2s(1)1s(2) dv(1) dv(2) \\ & \left. \pm \iint 2s^*(1)1s^*(2)(1/r_{12})1s(1)2s(2) dv(1) dv(2) \right\} \quad (5-52) \end{aligned}$$

The first two integrals of (5-52) differ only by an interchange of labels "1" and "2," and so they are equal to each other. The same is true of the second pair. Thus, the average value of the energy is

$$\begin{aligned} \bar{E}_3 = & \left\{ \int 1s^*(1) \left[-\frac{1}{2} \nabla_1^2 \right] 1s(1) dv(1) + \int 1s^*(1) [-2/r_1] 1s(1) dv(1) \right. \\ & + \int 2s^*(1) \left[-\frac{1}{2} \nabla_1^2 \right] 2s(1) dv(1) + \int 2s^*(1) [-2/r_1] 2s(1) dv(1) \\ & + \iint 1s^*(1)2s^*(2)(1/r_{12})1s(1)2s(2) dv(1) dv(2) \\ & \left. \pm \iint 1s^*(1)2s^*(2)(1/r_{12})2s(1)1s(2) dv(1) dv(2) \right\} \quad (5-53) \end{aligned}$$

Notice that, since $-\frac{1}{2}\nabla^2 - 2/r$ is the hamiltonian for He^+ , the first two integrals of Eq. (5-33) combine to give the average energy of He^+ in its 1s state. The second pair gives the energy for He^+ in the 2s state. Thus, Eq. (5-53) can be written

$$\bar{E}_3 = E_{1s} + E_{2s} + J \pm K \quad (5-54)$$

where J and K represent the last two integrals in Eq. (5-53). No bars appear on E_{1s} or E_{2s} because these "average energies" are identical to the eigenvalues for the He^+ hamiltonian (Problem 5-15).

The integral J denotes electrons 1 and 2 as being in "charge clouds" described by $1s^*1s$ and $2s^*2s$, respectively. The operator $1/r_{12}$ gives the electrostatic repulsion energy between these two charge clouds. Since these charge clouds are everywhere negatively charged, all the interactions are repulsive, and it is necessary that this "coulomb

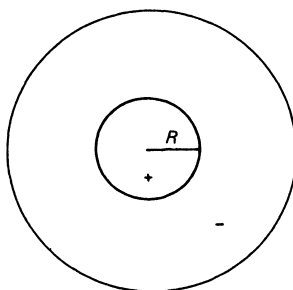


Figure 5-2 ► The function produced by multiplying together hydrogenlike 1s and 2s orbitals. R is the radius of the spherical nodal surface.

integral” J be positive. Alternatively, we can argue that the functions $1s^*1s$, $2s^*2s$, and $1/r_{12}$ are everywhere positive, so the integrand of J is everywhere positive and J must be positive.

The integral K is called an “exchange integral” because the two product functions in the integrand differ by an exchange of electrons. This integral gives the net interaction between an electron “distribution” described by $1s^*2s$, and another electron in the same distribution. (These distributions are mathematical functions, not physically realizable electron distributions.) The $1s2s$ function is sketched in Fig. 5-2. Because the $2s$ orbital has a radial node, the $1s2s$ function (which is the same as $1s^*2s$ since the $1s$ function is real) also has a radial node. Now the function $1s(1)2s(1)1s(2)2s(2)$ will be positive whenever r_1 and r_2 are either both smaller or both larger than the radial node distance (R in Figure 5-2). But when one r value is smaller than R and the other is greater, corresponding to the electrons being on opposite sides of the nodal surface, the product $1s(1)2s(1)1s(2)2s(2)$ is negative. These positive and negative contributions to K are weighted by the function $1/r_{12}$, which is always positive and hence unable to affect the sign of the integrand. But $1/r_{12}$ is smallest when the electrons are far apart. This means that $1/r_{12}$ tends to reduce the contributions where the electrons are on opposite sides of the node (i.e., the negative contributions), and so the value of K turns out to be positive (although not as large in magnitude as J , which has no negative contribution at all).

Since the integral K is positive, we can see from Eq. (5-54) that the *triply degenerate energy level lies below the singly degenerate one, the separation between them being $2K$* . (We note in passing that these independent-electron wavefunction energies are not simply the sum of one-electron energies as was the case when we used H_{approx} , thereby ignoring interelectronic repulsion.)

The experimental observation agrees qualitatively with these results. There are two state energies associated with the $1s2s$ configuration. When the atom is placed in an external magnetic field, the lower-state-energy-level splits into three levels. The state having the higher energy has a “multiplicity” of one and is called a singlet. The lower-energy with multiplicity three is called a triplet. (The reference to a “triplet state” should not be construed to mean that this is one state. It is a triplet of states.)

It is possible to use vector arguments similar to those presented in Chapter 4 to understand why the triply degenerate level splits into three different levels in the presence of a homogeneous magnetic field. Let us first consider the case of a single electron. We have already indicated that two spin states are possible, which we have labeled α and β .

In a magnetic field the angular momentum vectors precess about the field axis z , as depicted in Figure 5-3. The z components of the angular momentum vectors are constant but the x and y components are not. Because the *allowed* z components must in general differ by one atomic unit (stated but not proved in Chapter 4), and because there are but two allowed values (inferred from observations such as the splitting of a beam of silver atoms into two components), and because the two kinds of state are *oppositely* affected by magnetic fields, it is concluded that the z components of angular momentum (labeled m_s) are equal to $+\frac{1}{2}$ and $-\frac{1}{2}$ a.u. for α and β , respectively. Following through using orbital angular momentum relations as a model, we postulate an electron spin quantum number s equal to the maximum z -component of spin angular momentum in a.u., $\frac{1}{2}$, and a spin angular momentum vector s having length $\sqrt{s(s+1)}$ a.u. The degeneracy, $g_s = 2s + 1$, equals 2, in agreement with the two orientations in Fig. 5-3.

As noted in Chapter 4, half-integer quantum numbers correspond to eigenfunctions that cannot be expressed as spherical harmonics. We will not pursue the question of detailed expressions for α and β here. (However, see the problems at the end of Chapter 9.)

Now let us turn to the two-electron system. We will assume that the magnetic moments of the two electrons interact independently with the external field. This ignores the fact that each electron senses a small contribution to the magnetic field resulting from the magnetic moment of the other electron.

Another factor that could affect the magnetic field sensed by the spin moment is the magnetic moment resulting from the *orbital* motions of the electrons, although this is not present if both electrons are taken to be in s atomic orbitals (AOs). For two electrons, we can imagine four situations: $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$, and $\beta\beta$. We pointed out earlier (Section 4-5) that, for a system composed of several moving parts, the total angular momentum is the sum of the individual angular momenta, and the z component is the sum of the individual z components. For the four spin situations listed above, this means that the net z components of spin angular momentum (labeled M_s) are $+1$, 0 , 0 , and -1 a.u., respectively. The spin combinations $\alpha\beta + \beta\alpha$ [from the triplet (5-43b)] and $\alpha\beta - \beta\alpha$

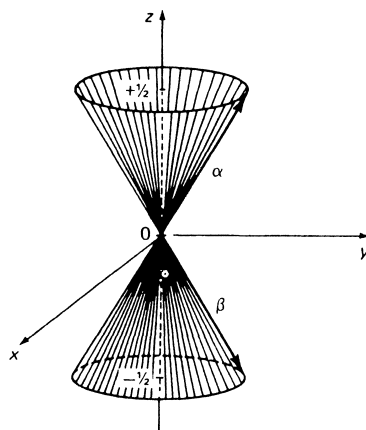


Figure 5-3 ► The angular momentum vectors for α and β precess around the magnetic field axis z . The z components of these vectors are constant and have values of $+\frac{1}{2}$ and $-\frac{1}{2}$ a.u. respectively.

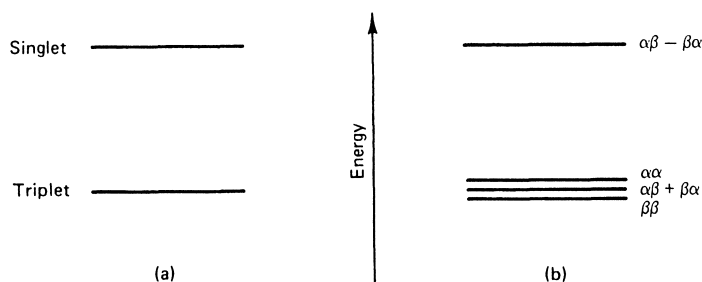


Figure 5-4 ► Energy levels for singlet and triplet levels of $1s2s$ helium in (a) absence, and (b) presence of an external magnetic field.

[from the singlet (5-42)] are linear combinations of $\alpha\beta$ and $\beta\alpha$. However, since these two functions have the same value for the z component of angular momentum (zero), their linear combinations will also have that value. It follows that the z components of the spin angular momenta of the triplet of states (5-43) are $+1$, 0 , and -1 a.u., and for the singlet (5-42) it is zero. Because the electrons are charged, these spin angular momenta correspond to spin magnetic moments, which interact differently with the applied magnetic field to give splitting of the triplet (see Figure 5-4). It is customary to refer to all three spin states in (5-43) as having *parallel* spins even though the vector diagram for the (5-43b) state is not particularly in accord with this terminology. For the singlet state, the spins are said to be *opposed*, or *antiparallel*.

5-6 The Self-Consistent Field, Slater-Type Orbitals, and the Aufbau Principle

Up to now we have used wavefunctions that, while not being eigenfunctions of the hamiltonian, are eigenfunctions of an “effective hamiltonian” obtained by ignoring the interelectronic repulsion operator $1/r_{ij}$. That is, these wavefunctions would be exactly correct if the electrons in helium were attracted by the nucleus, but did not repel each other. For this reason, we have referred to this as an independent electron approximation. Because we have neglected interelectronic repulsion, we cannot expect such a wavefunction to give very good numerical predictions of charge density or energy. We can compare the energy of He in the $1s^2$ (ground) state as predicted by our independent electron wavefunction and H_{approx} (-108.84 eV) with the experimental value (-79.0143 eV). (See Table 5-1.) This shows that the predicted energy is much too low, which is understandable since we have neglected an important repulsive (hence positive) interaction energy. But we can account for much of this neglected energy by calculating the *average* value of the energy using H (with $1/r_{12}$ included) instead of H_{approx} . This gives a value of -74.83 eV—much better, though now too high by more than 4 eV. Even though we have now accounted for interelectronic repulsion, there is still a problem: Because we ignored interelectronic repulsion in arriving at these wavefunctions, they predict electron densities that are too large near the nucleus. In reality, interelectronic repulsion prevents so much build-up of charge density. Methods have been devised that partially overcome this problem by retaining the convenient form of orbital products but modifying the formulas for the orbitals themselves to make them more diffuse.

TABLE 5-1 ► Average Values for Energy Calculated from Helium Atom Ground State Approximate Wavefunctions^a

Wavefunction description	\bar{E} (eV)
1) Product of He ⁺ orbitals	-74.83
2) Product of hydrogenlike orbitals with ζ fixed by SCF method	-77.48
3) Best product-type wavefunction	-77.870917
4) Nonorbital wavefunction of Pekeris [9]. This wavefunction uses functions of r_1 , r_2 and r_{12} as coordinates and has the form of an exponential times a linear combination of 1078 terms	-79.00946912

^a $\bar{E} = \int \psi^* H \psi d\tau / \int \psi^* \psi d\tau$, where H is given by Eq. (5-2).

Let the ground state of helium be our example. We take the ordinary independent-electron wavefunction as our initial approximation:

$$1s(1)1s(2) \equiv \sqrt{8/\pi} \exp(-2r_1) \sqrt{8/\pi} \exp(-2r_2) \quad (5-55)$$

These atomic orbitals are correct only if electrons 1 and 2 do not “see” each other *via* a repulsive interaction. They really do repel each other, and we can *approximate* this repulsion by saying that electron 2 “sees” electron 1 as a smeared out, time-averaged charge cloud rather than the rapidly moving point charge that is actually present. The initial description for this charge cloud is just the absolute square of the initial atomic orbital occupied by electron 2: $[1s(2)]^2$. Our approximation now has electron 1 moving in the field of a positive nucleus embedded in a spherical cloud of negative charge. Thus, for electron 1, the positive nuclear charge is “shielded” or “screened” by electron 2. Hence, electron 1 should occupy an orbital that is less contracted about the nucleus. Let us write this new orbital in the form

$$1s'(1) = \sqrt{\zeta^3/\pi} \exp(-\zeta r_1) \quad (5-56)$$

where ζ is related to the screened nuclear charge seen by electron 1. The mathematical methods used to evaluate ζ will be described later in this book.

Next we turn to electron 2, which we now take to be moving in the field of the nucleus shielded by the charge cloud *due to electron 1, now in its expanded orbital*. Just as before, we find a new orbital of form (5-56) for electron 2. The value of ζ that we calculate for electron 2, however, will be different from what we found for electron 1 because the shielding of the nucleus by electron 1 is different from what it was by electron 2 in our previous step. We now have a new distribution for electron 2, but this means that we must recalculate the orbital for electron 1 since this orbital was appropriate for the screening due to electron 2 in its old orbital. After revising the orbital for electron 1, we must revise the orbital for electron 2. This procedure is continued back and forth between electrons 1 and 2 until the value of ζ converges to an unchanging value (under the constraint that electrons 1 and 2 ultimately occupy orbitals having the same value of ζ). Then the orbital for each electron is consistent

with the potential due to the nucleus and the charge cloud for the other electron: the electrons move in a “self-consistent field” (SCF).

The result of such a calculation is a wavefunction in much closer accord with the actual charge density distributions of atoms than that given by the complete neglect of interelectron repulsion.⁷ A plot of the electron density distribution in helium as given by wavefunction (5-55) and by a similar wavefunction with optimized ζ is given in Fig. 5-5. Because each electron senses only the time-averaged charge cloud of the other in this approximation, it is still an independent-electron treatment. The hallmark of the independent electron treatment is a wavefunction containing only a product of one-electron functions. It will not contain functions of, say, r_{12} , which would make ψ depend on the instantaneous distance between electrons 1 and 2.

Atomic orbitals that are eigenfunctions for the one-electron hydrogenlike ion (for integral or nonintegral Z) are called *hydrogenlike orbitals*. In Chapter 4 we noted that many hydrogenlike orbitals have radial nodes. In actual practice, this mathematical aspect causes increased complexity in solving integrals in quantum chemical calculations. Much more convenient are a class of modified orbitals called *Slater-type orbitals* (STOs). These differ from their hydrogenlike counterparts in that they have no radial nodes. Angular terms are identical in the two types of orbital. The unnormalized radial term for an STO is

$$R(n, Z, s) = r^{(n-1)} \exp[-(Z - s)r/n] \quad (5-57)$$

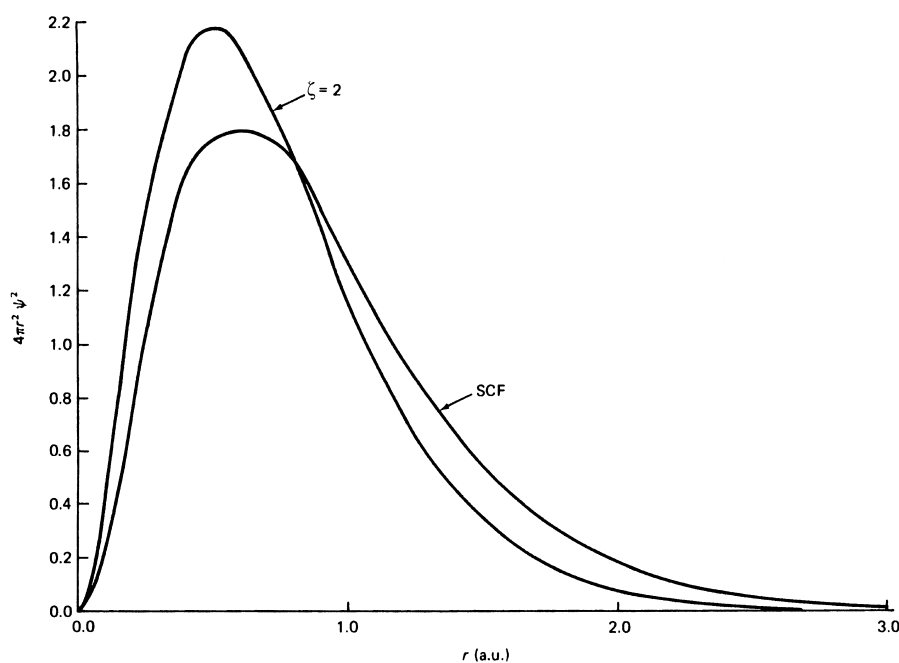


Figure 5-5 ► Electron distribution in helium as given by SCF and unshielded independent electron approximations.

⁷In practice, mathematical techniques have been found that lead to a self-consistent solution without explicit iteration between evolving AOs that converge to some final optimized ζ . Examples are described in Chapters 7 and 12. A thorough discussion of the SCF and related methods is given in Chapter 11.

where Z is the nuclear charge in atomic units, n is the principal quantum number, and s is a “screening constant” which has the function of reducing the nuclear charge Z “seen” by an electron. Slater [7] constructed rules for determining the values of s that will produce STOs in close agreement with those one would obtain by an SCF calculation. These rules, appropriate for electrons up to the 3d level, are

1. The electrons in the atom are divided up into the following groups: 1s|2s,2p|3s, 3p|3d.
2. The shielding constant s for an orbital associated with any of the above groups is the sum of the following contributions:
 - a) Nothing from any electrons in groups to the right (in the above list) of the group under consideration
 - b) 0.35 from each other electron in the group under consideration (except 0.30 in the 1s group)
 - c) If the orbital under consideration is an s or p orbital, 0.85 for each electron with principal quantum number less by 1, and 1.00 for each electron still “farther in”; for a d orbital, 1.00 for all electrons farther in

For example, nitrogen, with ground state configuration $1s^2 2s^2 2p^3$, would have the same radial part for the 2s and 2p STOs. This would be given by the formula ($n = 2$, $Z = 7$, $s = 4 \times 0.35 + 2 \times 0.85 = 3.1$)

$$R_{2s,2p}(2, 7, 3.1) = r^{(2-1)} \exp[-(7 - 3.1)r/2] = r \exp(-1.95r)$$

For the 1s level, $n = 1$, $Z = 7$, $s = 0.30$, and

$$R_{1s} = \exp(-6.7r)$$

Comparing orbital exponents, we see that the 1s charge cloud is compressed much more tightly around the nucleus than are the 2s and 2p “valence orbital” charge clouds. Slater-type orbitals are very frequently used in quantum chemistry because they provide us with very good approximations to self-consistent field atomic orbitals (SCF-AOs) with almost no effort.

Clementi and Raimondi [8] have published a refined list of rules for the shielding constant, which extends to the 4p level. Their rules include contributions to shielding due to the presence of electrons in shells outside the orbital under consideration. Such contributions are not large, and, up to the 3d level, there is reasonably good agreement between these two sets of rules.

The fact that STOs have no radial nodes results in some loss of orthogonality. Angular terms still give orthogonality between orbitals having different l or m quantum numbers, but STOs differing only in their n quantum number are nonorthogonal. Thus, 1s, 2s, 3s, ... are nonorthogonal. Similarly $2p_z, 3p_z, \dots$ or $3d_{xz}, 4d_{xy}, \dots$ are nonorthogonal. In practice, this feature is handled easily. The only real problem arises if one *forgets* about this nonorthogonality when making certain calculations.

When carrying out SCF calculations on multielectronic atoms, one finds that the orbital energies for 2s and 2p functions are not the same. Similarly, 3s 3p, and 3d orbitals are nondegenerate. Yet these orbitals were degenerate in the one-electron hydrogenlike

system in which energy was a function of n but not of l or m . Why are these orbital energies nondegenerate in the many-electron calculation? A reasonable explanation can be found by considering the comparative effectiveness with which a pair of 1s electrons screen the nucleus from a 3s or a 3p electron. Comparing the 3s, 3p, and 3d hydrogenlike orbital formulas in Table 4-2 shows that the 3s orbital is finite at the nucleus, decreasing proportionally to r for small r . The 3p orbitals vanish at the nucleus but grow as r for small r . The 3d orbitals vanish at the nucleus but grow as r^2 for small r . The result of all this is that an s electron spends a larger amount of its time near the nucleus than a p electron of the same principal quantum number, the p electron spending more time near the nucleus than the d, etc. Hence, the s electron penetrates the “underlying” charge clouds more effectively and is therefore less effectively shielded from the nucleus. Since the s electron sees a greater effective nuclear charge, its energy is lower than that of the p electron. (This effect is not obvious in STOs since the 3s and 3p STOs have the same radial function which vanishes at the nucleus. However, the STO for 3d does reflect the nondegeneracy since Slater’s rules give it a different screening constant from 3s or 3p.)

The tendency for higher l values to be associated with higher orbital energies leads to the following orbital ordering:

$$1s\ 2s\ 2p\ 3s\ 3p\ 4s\ 3d\ 4p\ 5s\ 4d\ 5p\ 6s\ 5d\ 4f\ 6p\ 7s\ 6d\ 5f\ \dots \quad (5-58)$$

When we get to principal quantum numbers of 3 and higher, the energy differences between different l values for the same n become comparable to the differences between different n levels. Thus, in some atoms, the 4s level is almost the same as the 3d level, etc.

In compiling data on ground states of atoms, Hund noticed that *greatest stability results if the AOs in a degenerate set are half-filled with electrons before any of them are filled*. This generalization, called *Hund’s rule*, is sometimes stated in an alternative form: *Of the states associated with the ground state configuration of an atom or ion, those with greatest spin multiplicity lie deepest in energy*. Chemists generally find the former version to be more convenient, spectroscopists the latter. The reason for the equivalence of these statements will emerge later in this chapter.

EXAMPLE 5-4 An unexcited Fe atom has an electronic configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$. What is its spin multiplicity?

SOLUTION ► All electrons below $3d^6$ are spin-paired in orbitals, hence contribute nothing to M_S . In $3d^6$, we have 4 electrons that can each occupy a 3d AO alone. If we follow Hund’s rule and seek maximum spin multiplicity, we make all their spins the same (α). Then maximum, $M_S = 4 \cdot \frac{1}{2} = 2$, so $S = 2$, and spin multiplicity is $2S + 1 = 5$. The atom has a quintet ground “state” (really five states). ◀

The energy-ordering scheme (5-58) coupled with the Pauli or exclusion principle and Hund’s rule leads us to a simple prescription for “building up” the electronic configurations of atoms. This *aufbau* principle is familiar to chemists and leads naturally to a correlation between electronic structure and the periodic table. The procedure is to place all the electrons of the atom into atomic orbitals, two to an orbital, starting at the

low-energy end of the list (5-58) and working up in energy. In addition, when filling a set of degenerate levels like the five 3d levels, one half-fills all the levels with electrons of parallel spin before filling any of them. This prescription enables one to guess the electronic configuration of any atom, once its atomic number is known, unless it happens to put us into a region of ambiguity, where different levels have almost the same energy. (Electronic configurations for such atoms are deduced from experimentally determined chemical, spectral, and physical properties.) The configuration for carbon (atomic number 6) would be $1s^2 2s^2 2p^2$, with the understanding that p electrons occupy *different* p orbitals and have parallel spins. (Recall that we expect the most stable of all the states arising from the configuration $1s^2 2s^2 2p^2$ to be the one of highest multiplicity. The 2p electrons can produce either a singlet or a triplet state just as could the two electrons in the 1s2s configuration of helium. The triplet should be the ground state and this corresponds to parallel spins, which *requires* different p orbitals by the exclusion principle.)

It is important to realize that the orbital ordering (5-58) used in the *aufbau* process is not fixed, but depends on the atomic number Z . The ordering in (5-58) cannot be blindly followed in all cases. For instance, the ordering shows that 5s fills before 4d. It is true that element 38, strontium, has a $\dots 4p^6 5s^2 4d^0$ configuration. But a later element, palladium, number 46, has $\dots 4p^6 4d^{10} 5s^0$ as its ground state configuration. The effect of adding more protons and electrons has been to depress the 4d level more than the 5s level.

5-7 Electron Angular Momentum in Atoms

Most of our attention thus far has been with wavefunction symmetry and energy. However, understanding atomic spectroscopy or interatomic interactions (in reactions or scattering) requires close attention to angular momentum due to electronic orbital motion and “spin.” In this section we will see what possibilities exist for the total electronic angular momenta of atoms and how these various states are distinguished symbolically.

We encountered earlier (Section 4-5) the notion that the total angular momentum for a classical system is the vector sum of the angular momenta of its parts. If the system interacts with a z -directed field, the total angular momentum vector precesses about the z axis, so the z component continues to be conserved and continues to be equal to the sum of z components of the system’s parts. Since quantum hydrogenlike systems obey angular momentum relations analogous to a *precessing* classical system, it is this z -axis behavior that we focus on as we seek to construct the nature of the total angular momentum from the orbital and spin parts we already understand.

Because it is the *total* angular momentum that is conserved in a multicomponent classical system, it is the total angular momentum that obeys the quantum rules we have previously described for separate spin and orbital components. If we consider a one-electron system, the combined spin-orbital angular momentum can be associated with a quantum number symbolized by j (analogous to s and l). Then we can immediately say that the allowed z components of total angular momentum are, in a.u., $m_j = \pm j, \pm(j-1), \dots$ and that the length of the vector is $\sqrt{j(j+1)}$ a.u.

The implication of accepting total angular momentum as the fundamental quantized quantity is that the spin and orbital angular momenta do not individually obey the

quantum rules we have so far applied to them— s and l are not “good” quantum numbers. However, for atoms of low atomic number they are in fact quite good, especially for low-energy states, and we can continue to refer to the s and l quantum numbers in such cases with some confidence. (Classically, this corresponds to cases where there is little transfer of angular momentum between modes.)

5-7.A Combined Spin-Orbital Angular Momentum for One-Electron Ions

The key to understanding the following discussion is to remember that a quantum number l , s , or j really tells us *three* things:

1. It equals the *maximum* value of m_l , m_s , or m_j . If $l = 2$, the maximum allowed value of m_l is 2, and the maximum z component of orbital angular momentum is 2 a.u.
2. It allows us to know the *length* of the related angular momentum vector, \mathbf{l} , \mathbf{s} , or \mathbf{j} , in a.u. For j , this is given by $\sqrt{j(j+1)}$. If $j = 2$, the length of the total angular momentum vector \mathbf{j} is $\sqrt{6}$ a.u.
3. It allows us to know the *degeneracy*, g , of the energy level due to states having this angular momentum. For s , this is $2s + 1$. If $s = 1/2$, $g_s = 2$. The corresponding l degeneracies produce the s, p, d, f degeneracies of 1, 3, 5, 7.

Using the hydrogen atom as our example, let us consider what the *total* electronic angular momentum is in the ground (1s) state. For an s AO, $l = 0$, and so there is no orbital angular momentum. This means that the *total* angular momentum is the same as the spin angular momentum, so $j = s = 1/2$, $m_j = \pm 1/2$. The diagram for the vector \mathbf{j} , then, looks just like that for \mathbf{s} (Fig. 5-3).

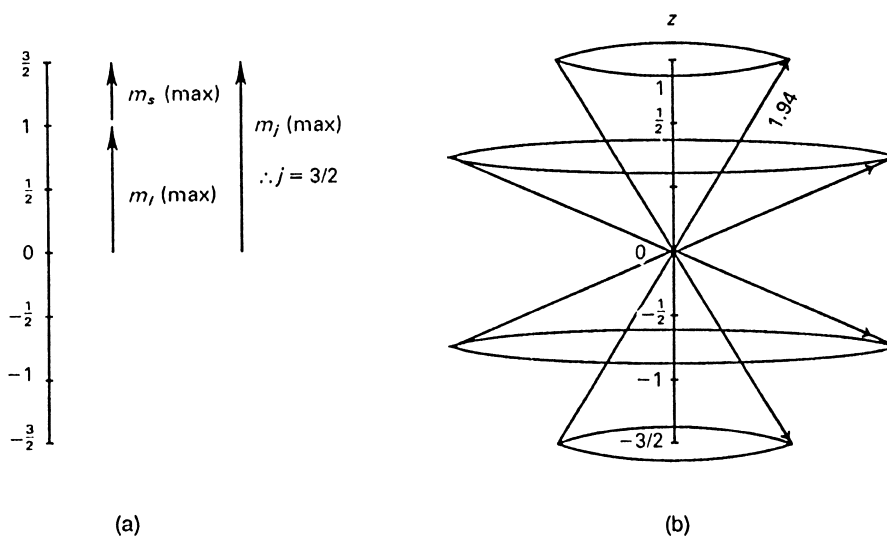


Figure 5-6 ► (a) Maximum z components of orbital and spin angular momenta for a p electron leading to a *total* z component of $3/2$. (b) The four states corresponding to the $j = 3/2$ vector assuming its possible z intercepts ($3/2, 1/2, -1/2, -3/2$).

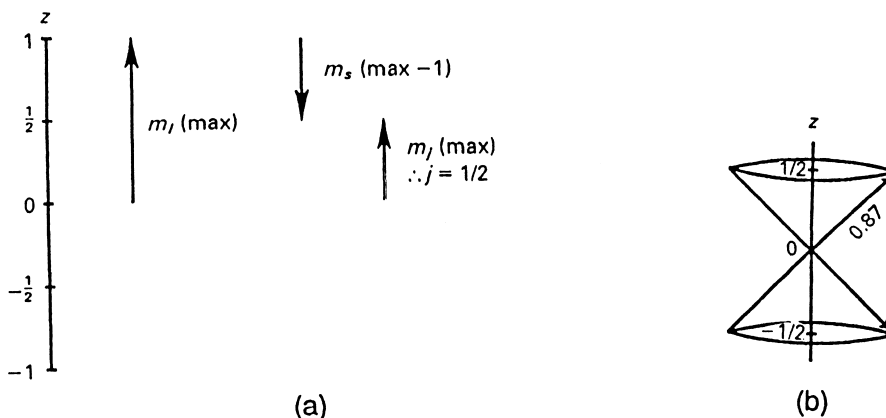


Figure 5-7 ► (a) $j = 1/2$, resulting when l is oriented with its maximum z intercept and s is oriented in its other orientation (other than as in Fig. 5-6). (b) The two states corresponding to the $J = 1/2$ vector assuming its possible z intercepts ($1/2, -1/2$).

More interesting is an excited state, say $2p$. Now $l = 1$ and $s = 1/2$. From $l = 1$ we can say that the maximum orbital z component of angular momentum is 1 a.u. $s = 1/2$ tells us that there is an additional maximum spin z component of $1/2$. The maximum sum, then, is $3/2$ for the z component of \mathbf{j} . But, if this is the maximum m_j , then j itself must be $3/2$ and the length of \mathbf{j} must be $\sqrt{(3/2)(5/2)} = 1.94$ a.u. There must be $2j + 1 = 4$ allowed orientations of \mathbf{j} , with z intercepts at $3/2, 1/2, -1/2, -3/2$ in a.u. (Fig. 5-6).

We are not yet finished with the $2p$ possibilities. The total angular momentum is the sum of its orbital and spin parts, and we have so far found the way they combine to give the *maximum* z component. But this is not the *only* way they can combine. It is possible to have $m_l = 1$ and $m_s = -1/2$. Then the maximum $m_j = 1/2$, so $j = 1/2$, giving us a vector \mathbf{j} of length $\sqrt{(1/2)(3/2)}$ a.u. and two orientations (Fig. 5-7).

So far we have identified six states, four with $j = 3/2$ and two with $j = 1/2$. This is all we should expect since we have three $2p$ AOs and two spins, giving a total of six combinations. It seems, though, that we could generate some more states by now letting $m_l = 0$ or -1 and combining these with $m_s = \pm 1/2$. However, these possibilities are already implicitly accounted for in the multiplicity of states we recognize to be associated with the $j = 3/2, 1/2$ cases already found. This illustrates the general approach to be taken when combining two vectors: Orient the larger vector to give maximum z projection, and combine this projection with *each* of the allowed z components of the smaller vector. This gives all of the possible $m_j(\text{max})$ values, hence all of the j values. In other words, it gives us all of the allowed vectors, \mathbf{j} , each oriented with maximum z component, and it remains only to recognize that these can have certain other orientations corresponding to z intercepts of $m_j - 1, m_j - 2, \dots, -m_j$.

States can be *labeled* to reflect all of the angular momentum parts they possess. The main symbol is simply s, p, d, f, g, etc. depending on the l value as usual. A superscript at left gives spin multiplicity ($2s + 1$) for the states. A subscript at right tells the j quantum number for the states. If an individual member of the group of states having the same j value is to be cited, it is identified by placing its m_j value at upper right.

Thus, all six of the states discussed above can be referred to as 2p states. The two groups having different total angular momentum are distinguished as ${}^2p_{3/2}$ and ${}^2p_{1/2}$. One of the four states in the former group is the ${}^2p_{3/2}^{-1/2}$ state.

The general form of the symbol is ${}^{2s+1}l_j^{m_j}$. Such symbols are normally called *term symbols*, and the collection of states they refer to is called a *term* (except when an *individual* state is denoted by inclusion of the m_j value).

The reason for distinguishing between the ${}^2p_{3/2}$ and ${}^2p_{1/2}$ terms is that they occur at slightly different energies. This results from the different energies of interaction between the magnetic moments due to spin and orbital motions. For instance, if l and s are coupled so as to give the maximum j , their associated magnetic moments are oriented like two bar magnets side by side with north poles adjacent. This is a higher-energy arrangement than the other extreme, where l and s couple to give minimum j , acting as a pair of parallel bar magnets with the north pole of each next to the south pole of the other. So ${}^2p_{1/2}$ should be lower in energy than ${}^2p_{3/2}$ for hydrogen.

EXAMPLE 5-5 For a hydrogen atom having $n = 3, l = 2$, what are the possible j values, and how many states are possible? Indicate the lengths of the j vectors in a.u. What term symbols apply?

SOLUTION ► If $l = 2$ (d states), there are five AOs and two possible spins, so we expect a total of ten possible states. The maximum possible values of the z -component of angular momentum for orbital and spin respectively are 2 and 1/2. So the maximum value is 5/2 giving a vector length of $\sqrt{35}/4$ a.u. and six possible z projections, hence six states. The term symbol is ${}^2d_{5/2}$. The remaining possible j value is $2 - 1/2 = 3/2$, accounting for four more states and giving a vector length of $\sqrt{15}/4$ a.u. and a term symbol of ${}^2d_{3/2}$. ◀

5-7.B Spin-Orbital Angular Momentum for Many-Electron Atoms

Much of what we have seen for one-electron ions continues to hold for many-electron atoms or ions. All the symbolism is the same, except that capital letters replace lowercase: The quantum numbers are L, S , and J , and the main symbol becomes S, P, D, F, G, etc. There is a total orbital angular momentum vector \mathbf{L} with quantum number L that equals the maximum value of M_L . The length of \mathbf{L} is $\sqrt{L(L+1)}$ a.u., and it has $2L + 1$ orientations. Vectors \mathbf{S} and \mathbf{J} behave analogously. When constructing the vectors \mathbf{J} , we continue to place the larger of \mathbf{L} and \mathbf{S} to give maximum z intercept, and add to this the possible z intercepts of the smaller vector. The situation, then, is just as before except that we need to figure out the possible values for M_L and M_S by combining the allowed values of $m_l(1), m_l(2), \dots$ and $m_s(1), m_s(2), \dots$.⁸

⁸This procedure of first combining individual orbital contributions to find \mathbf{L} and spin contributions to find \mathbf{S} and then combining these to get \mathbf{J} is referred to as “ L - S coupling,” or “Russell-Saunders coupling.” The other extreme is to first combine \mathbf{l} and \mathbf{s} for the first electron to give $\mathbf{j}(1)$, \mathbf{l} and \mathbf{s} for the second electron to give $\mathbf{j}(2)$, \dots and then combine these individual-electron \mathbf{j} 's to give \mathbf{J} . This is more appropriate for atoms having high atomic number (in which electrons move at relativistic speeds in the vicinity of the nucleus), and is referred to as “ j - j coupling.” We will not describe j - j coupling in this text. The reader should consult Herzberg [6] for a fuller treatment.

For example, if we have found that $M_L(\max) = 2$ (which means $L = 2$) and $M_S(\max) = 1$ (which means $S = 1$), we have that $M_J(\max)$ can be $2 + 1$, $2 + 0$, and $2 + (-1)$, or 3 , 2 , and 1 . This means that the possible values of J are 3 , 2 , 1 , giving three different \mathbf{J} vectors. Since $L = 2$ and $S = 1$, the term symbols for these three J cases are 3D_3 , 3D_2 , and 3D_1 . Notice that the multiplicities of these three terms— 7 , 5 , and 3 , respectively, obtained from $2J + 1$ —total 15 states, which is just what we should expect for the 3D symbol (spin multiplicity of 3 , orbital multiplicity of 5). The 15 triplet-D states are found in three closely spaced levels, differing in energy because of different spin-orbital magnetic interactions.

The problem remains, how do we find the M_L and M_S values that allow us to construct term symbols? There are two situations to distinguish in this context, and a different approach is taken for each.

1. Nonequivalent Electrons. The first situation is exemplified by carbon in its $1s^2 2s^2 2p 3p$ configuration. It is not difficult to show that the electrons in the $1s$ and $2s$ AOs contribute no net angular momentum and can be ignored: The spins of *paired* electrons are opposed, hence cancel, and the s -type AOs have no angular momentum, hence cannot contribute. However, even p , d , etc. sets of AOs cannot contribute *if they are filled* because then any orbital momentum having z intercept m_l is canceled by one with $-m_l$. The important result is that *filled subshells do not contribute to orbital or spin angular momentum*. The remaining $2p$ and $3p$ electrons occupy different sets of AOs, hence are called *nonequivalent* electrons.

Since these electrons are never in the same AO, they are not restricted to have opposite spins at any time—their AO and spin assignments are independent. There are three AO choices (p_1 , p_0 , p_{-1}) and two spin choices—six possibilities—for *each* electron, hence 36 unique possibilities. We should expect, therefore, 36 states to be included in our final set of terms.

We first find the possible L values. m_l for each electron is 1 , 0 , or -1 . We orient the larger of the \mathbf{l} vectors to give the maximum $m_l(1) = +1$ and orient the second \mathbf{l} in all possible ways, giving $m_l(2) = +1, 0, -1$. (Since the vectors have equal length in this case there is no “larger–smaller” choice to make.) The net M_L values are $+2, +1, 0$, and this tells us that the possible L values are $2, 1, 0$.

Treating m_s values similarly gives $M_S = 1, 0$, so $S = 1, 0$.

Thus, we have three \mathbf{L} vectors and two \mathbf{S} vectors. We now combine every one of the \mathbf{L} , \mathbf{S} pairs. In each case, we again take the longer in its position of greatest z overlap and combine it with the shorter in *all* of its orientations. This gives the J values shown in Table 5-2. The appropriate term symbols follow from L , S , and J in each case. Thus, our term symbols are ${}^3D_3, {}^3D_2, {}^3D_1, {}^1D_2, {}^3P_2, {}^3P_1, {}^3P_0, {}^1P_1, {}^3S_1$ and 1S_0 for a total of $7 + 5 + 3 + 5 + 5 + 3 + 1 + 3 + 3 + 1 = 36$ states.

In the absence of external fields, these 36 states occur in 10 energy levels, one for each term. These lie at different energies for several reasons. We have already seen, in our discussion of $1s2s$ helium states, that different spin multiplicities are associated with different symmetries of the spin wavefunction, meaning that the space part of the wavefunctions also differ in symmetry. This has a significant effect on energy, so 1S and 3S , for example, have rather different energies. Different L values amount to different occupancies of AOs, which also has an effect on the spatial wavefunctions, so 3P and 3S have different energies. Finally, we have already seen that different J values correspond to different relative orientations of orbital and spin angular momentum

TABLE 5-2 ▶ L and S Values for Two Nonequivalent Electrons and Resulting J Values and Term Symbols

L	S	J	Term
2	1	3	3D_3
		2	3D_2
		1	3D_1
2	0	2	1D_2
		1	1
1	3P_1		
0	3P_0		
1	0	1	1P_1
0	1	1	3S_1
0	0	0	1S_0

vectors, hence of magnetic moments. For light atoms, this is a relatively small effect, so 3P_2 , 3P_1 , and 3P_0 have only slightly different energies. The resulting energies for states of carbon in $1s^22s^22p^2$, $1s^22s^22p3p$, and $1s^22s^22p4p$ configurations are shown in Fig. 5-8. Only the major term-energy differences are distinguishable on the scale of the figure. The line for 3D is really three very closely spaced lines corresponding to 3D_3 , 3D_2 , and 3D_1 terms.

2. Zeeman Effect. It was pointed out in Section 4-6 that the orbital energies of a hydrogen atom corresponding to the same n but different m_l undergo splitting when a magnetic field is imposed. Now we have seen that spin angular momentum is also present. Therefore, a proper treatment of the Zeeman effect requires that we focus on *total* angular momentum, not just the orbital component. Since there are $2J + 1$ states with different M_J values in a given term, we expect each term to split into $2J + 1$ evenly separated energies in the presence of a magnetic field, and this is indeed what is seen to happen (through its effects on lines in the spectrum). For example, a 3P_2 term splits into five closely spaced energies, corresponding to $M_J = 2, 1, 0, -1, -2$, and a 1P_1 term splits into three energies.

A surprising feature of this phenomenon is that the amount of splitting is not the same for all terms, despite the fact that adjacent members of any term always differ by ± 1 unit of angular momentum on the z axis. For instance, the spacing between adjacent members of the 3P_2 term mentioned above is 1.50 times greater than that in the 1P_1 term. It was recognized that terms wherein $S = 0$, so that J is entirely due to orbital angular momentum ($J = L$), undergo “normal splitting”—i.e., equal to what classical physics would predict for the amount of angular momentum and charge involved. On the other hand, terms wherein J is entirely due to spin ($L = 0$, so $J = S$) undergo *twice* the splitting predicted from classical considerations. [This extra factor of two (actually 2.0023) was without theoretical explanation until Dirac’s relativistic treatment of quantum mechanics.]

Terms wherein J contains contributions from both L and S have Zeeman splittings other than one or two times the normal value, depending on the details of the way L and

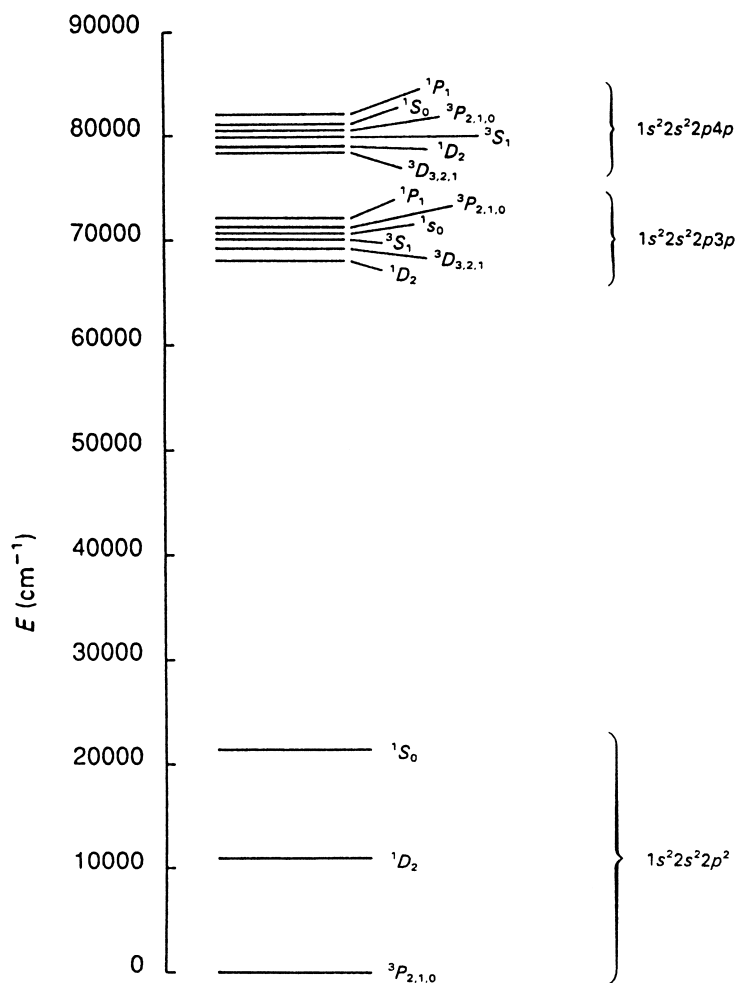


Figure 5-8 ▶ Energy levels for carbon atom terms resulting from configurations $1s^22s^22p^2$, $1s^22s^22p3p$, and $1s^22s^22p4p$.

S are combined. The extent to which a term member's energy is shifted by a magnetic field of strength B is

$$\Delta E = g\beta_e M_j B \quad (5-59)$$

where β_e is the Bohr magneton (Appendix 10) and g is the Landé g factor, which accounts for the different effects of L and S on magnetic moment that we have been discussing:

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad (5-60)$$

It is not difficult to see that this formula equals one when $S=0$, $J=L$, and equals two when $L=0$, $J=S$. For the 3P_2 term, $S=1$, $L=1$, $J=2$, and g equals 1.5, indicating that, in this state, half of the z -component of angular momentum is due to orbital

motion, and half is due to spin (which is double-weighted in its effect on magnetic moment).

3. Equivalent Electrons. Observe that the energy-level diagram for carbon (Fig. 5-8) shows the 10 expected terms for the excited $2p3p$ and $2p4p$ configurations, but not for the ground $2p^2$ configuration. There are no new terms for the latter case, but some of the terms present for $2p3p$ or $2p4p$ are gone, namely 3D , 3S , and 1P . The remaining terms account for 15 states. Evidently 21 states that are possible for a pair of nonequivalent p electrons are not allowed for a pair of *equivalent* electrons in a p^2 configuration. We will see that some of the states that are different for nonequivalent electrons become one and the same for equivalent electrons and must be excluded. Others are excluded by the Pauli exclusion principle because they would require two electrons to be in the same AO with the same spin.

We now demonstrate the method for discovering the terms that exist for equivalent electrons. This is more difficult than for nonequivalent electrons, even though there are fewer terms. We first list all the orbital-spin combinations (called microstates), strike out those that are redundant or that violate the Pauli exclusion principle, and then infer from the remaining microstates what terms exist.

Taking the p^2 case for illustration, we begin with the 36 microstates listed in Table 5-3. Some of these microstates are equivalent to others. For instance, $2p_1(1)2p_1(2)\alpha(1)\beta(2)$ is not a different state from $2p_1(1)2p_1(2)\beta(1)\alpha(2)$. These both correspond to a pair of electrons in the same pair of spin orbitals, $2p_1$ and $\overline{2p_1}$. Since electrons are indistinguishable, we cannot expect wavefunctions differing only in the order of electron labels to correspond to different physical states. [The single state that does exist would be accurately represented by $2p_1(1)2p_1(2)(\alpha(1)\beta(2) - \beta(1)\alpha(2))$, which is a linear combination of the microstates. But we do not need to go to this level of detail when finding terms. We only need to recognize that there is but one state here and omit one of the microstates as superfluous.] Accordingly, we strike out rows 3, 19, and 35 from Table 5-3, labeling them “R” for redundant.

Another way to recognize this equivalence is to observe that the microstates deemed redundant differ only by an interchange of a pair of electrons. This reveals that the set of four microstates with $2p_1(1)2p_0(2)$ is equivalent to the set with $2p_0(1)2p_1(2)$. Therefore, we can strike out rows 13–16. A similar argument removes rows 25–32. Already we have removed 15 microstates.

Next we look for violations of the Pauli exclusion principle. This leads us to strike out rows 1, 4, 17, 20, 33, and 36, labeling them “P” for Pauli. Our remaining microstates number 15 and are reassembled in Table 5-4, along with values of the quantum numbers for z components of the relevant angular momentum vectors for individual electrons as well as for their sum.

At this stage of the argument, the final column of Table 5-4 (the term symbols) is not yet known. We are about to fill out this column by making use of a simple rule that is based on the diagrammatic device described earlier—placing the larger vector so that it has the maximum z extension and then placing the shorter vector in all its allowed orientations. It is not difficult to see that the maximum resultant z component (M_J) can be achieved in one and only one way, namely when *both* vectors give their maximum z projection. This means that the maximum- M_J -member of a given set of states in the same term should be recognized as corresponding to one and only one microstate, because there is only one way to achieve this orientation. So we look for this maximum

TABLE 5-3 ► Unrestricted List of Space-Spin Combinations for a Pair of Electrons (Same Subshell). R = "Redundant," P = "Pauli"

Row number	Electron number				Comment
	1	2	1	2	
1	p ₁	p ₁	α	α	P
2	p ₁	p ₁	α	β	
3	p ₁	p ₁	β	α	R
4	p ₁	p ₁	β	β	P
5	p ₁	p ₀	α	α	
6	p ₁	p ₀	α	β	
7	p ₁	p ₀	β	α	
8	p ₁	p ₀	β	β	
9	p ₁	p ₋₁	α	α	
10	p ₁	p ₋₁	α	β	
11	p ₁	p ₋₁	β	α	
12	p ₁	p ₋₁	β	β	
13	p ₀	p ₁	α	α	R
14	p ₀	p ₁	α	β	R
15	p ₀	p ₁	β	α	R
16	p ₀	p ₁	β	β	R
17	p ₀	p ₀	α	α	P
18	p ₀	p ₀	α	β	
19	p ₀	p ₀	β	α	R
20	p ₀	p ₀	β	β	P
21	p ₀	p ₋₁	α	α	
22	p ₀	p ₋₁	α	β	
23	p ₀	p ₋₁	β	α	
24	p ₀	p ₋₁	β	β	
25	p ₋₁	p ₁	α	α	R
26	p ₋₁	p ₁	α	β	R
27	p ₋₁	p ₁	β	α	R
28	p ₋₁	p ₁	β	β	R
29	p ₋₁	p ₀	α	α	R
30	p ₋₁	p ₀	α	β	R
31	p ₋₁	p ₀	β	α	R
32	p ₋₁	p ₀	β	β	R
33	p ₋₁	p ₋₁	α	α	P
34	p ₋₁	p ₋₁	α	β	
35	p ₋₁	p ₋₁	β	α	R
36	p ₋₁	p ₋₁	β	β	P

TABLE 5-4 ► Allowed Space-Spin Combinations and M Quantum Numbers for a Pair of p Electrons (Same Subshell)

Microstate	$m_l(1)$	$m_l(2)$	$m_s(1)$	$m_s(2)$	M_L	M_S	M_J	State term
$p_1p_1\alpha\beta$	1	1	1/2	-1/2	2	0	2	${}^1D_2^2$
$p_1p_0\alpha\alpha$	1	0	1/2	1/2	1	1	2	${}^3P_2^2$
$p_1p_0\alpha\beta$	1	0	1/2	-1/2	1	0	1	$({}^1D_2^1)$
$p_1p_0\beta\alpha$	1	0	-1/2	1/2	1	0	1	$({}^3P_2^1)$
$p_1p_0\beta\beta$	1	0	-1/2	-1/2	1	-1	0	$({}^3P_2^0)$
$p_1p_{-1}\alpha\alpha$	1	-1	1/2	1/2	0	1	1	$({}^3P_1^1)$
$p_1p_{-1}\alpha\beta$	1	-1	1/2	-1/2	0	0	0	$({}^1D_2^0)$
$p_1p_{-1}\beta\alpha$	1	-1	-1/2	1/2	0	0	0	$({}^3P_1^0)$
$p_1p_{-1}\beta\beta$	1	-1	-1/2	-1/2	0	-1	-1	$({}^3P_2^{-1})$
$p_0p_0\alpha\beta$	0	0	1/2	-1/2	0	0	0	${}^1S_0^0$
$p_0p_{-1}\alpha\alpha$	0	-1	1/2	1/2	-1	1	0	$({}^3P_0^0)$
$p_0p_{-1}\alpha\beta$	0	-1	1/2	-1/2	-1	0	-1	$({}^1D_2^{-1})$
$p_0p_{-1}\beta\alpha$	0	-1	-1/2	1/2	-1	0	-1	$({}^3P_1^{-1})$
$p_0p_{-1}\beta\beta$	0	-1	-1/2	-1/2	-1	-1	-2	$({}^3P_2^{-2})$
$p_{-1}p_{-1}\alpha\beta$	-1	-1	1/2	-1/2	-2	0	-2	$({}^1D_2^{-2})$

M_J and, from its microstate, get the L and S values that go with it. That gives us the information we need to establish the term symbol.

We start, then, by seeking the maximum M_J value in Table 5-4. This is $M_J = 2$, and it occurs twice (in the first two rows). The first of these goes with $M_L = 2$, $M_S = 0$. Since these result when \mathbf{L} and \mathbf{S} are giving their maximum z component, we conclude that $L = 2$, $S = 0$. This, then, is a member of the 1D_2 term. (It is the ${}^1D_2^2$ member of that term, since $M_J = 2$.) We label this row ${}^1D_2^2$ and proceed to select microstates that can account for the other four members of this term. Our choice is controlled by the requirements that (1) the M_J values for the other members must be 1, 0, -1, -2, and (2) we cannot have an $|M_S|$ value larger than zero or an $|M_L|$ value larger than 2. (That would be impossible for states resulting from vectors having $L = 2$ and $S = 0$.) Our selections are indicated in Table 5-4, with parentheses to indicate that these assignments follow from recognition of the leading member ${}^1D_2^2$. (All are symbolized as 1D_2 .)

There is some arbitrariness in selecting the "inner" members, for which $|M_J| < J$: The parenthetical term ${}^1D_2^2$ could just as easily be assigned to $p_1p_0\beta\alpha$ as $p_1p_0\alpha\beta$. (Actually, neither of these microstates is a correct wavefunction for ${}^1D_2^2$. A linear combination of them is. But, if we only wish to designate term symbols, we need not worry about this.)

We have accomplished already the identification of a term 1D_2 and the elimination of five microstates from our list. The other microstate having $M_J = 2$ has $M_L = M_J = 1$, so we know this goes with $L = 1$, $S = 1$ and has the symbol ${}^3P_2^2$. Again, four other members exist down the table, and we select them, being careful that $|M_L|$ and $|M_S|$ do not exceed 1, while $M_J = 1, 0, -1, -2$.

At this point, we must recognize that we are not through with the 3P family. The existence of the 3P part of the symbol implies the existence of nine states, but 3P_2

accounts for only five of them. The others come from 3P_1 and 3P_0 , resulting from $M_L = 1$ with $M_S = 0, -1$. (We did not worry about this for the 1D_2 term because only five states are implied by 1D .) So we seek the microstates associated with these terms and label them as shown in the table.

Only one microstate remains. For this $M_L = M_S = 0$, so this is a state labeled ${}^1S_0^0$.

The term symbols for the p^2 configuration, then, are ${}^1D_2, {}^3P_2, {}^3P_1, {}^3P_0, {}^1S_0$, for a total of 15 states. The energies for these terms are shown in Fig. 5-8. The five terms fall into three energy groups, since the 3P terms are found to be very close in energy. High resolution spectra can be used to see the slight energy differences between terms that appear to be at the same level at the energy scale used in Fig. 5-8. Delving further, the degenerate energies of microstates in the same term can be made to separate by imposing a magnetic field (Zeeman effect).

Based on spectroscopic assignments of energy levels for large numbers of atoms, Hund proposed a set of rules enabling one to predict the energy ordering for terms associated with *equivalent* electrons. These rules are, in order of decreasing influence:

1. Terms having greater spin multiplicity lie lower in energy.
2. Within each spin multiplicity, terms having greater L lie lower.
3. Within the same L and S , levels of different J behave oppositely, according to whether the subshell is more or less than half-filled: If less than half-filled, terms with lower J lie lower.

According to these rules, the five levels for carbon in its $1s^2 2s^2 2p^2$ configuration should be, in order of increasing energy, ${}^3P_0, {}^3P_1, {}^3P_2$ (closely spaced) followed by 1D_0 , followed by 1S_0 . The actual energies (in cm^{-1}) are, respectively, 0, 16.4, 43.5, 10194.8, 21647.7 (Fig. 5-8). The order of states for the excited $2p3p$ and $2p4p$ configurations is different. This is not a breakdown of Hund's rules because these are not equivalent-electron cases.

Hund's first rule is the source of the aufbau rule, cited earlier, that each AO of a subshell becomes half-filled before any of them become filled with electrons. The equivalence of these statements is easily demonstrated (Problem 5-30).

One can use Hund's rules to find the *lowest*-energy state term symbol without going through the tedious microstate process just described. For an atom having an outer subshell configuration of p^2 we would first recognize that we seek maximum S , so the electrons must have parallel spin, giving $S = 1$. (We use Hund's most influential rule first.) Subject to this constraint, we seek maximum L . Since the electrons cannot both be in p_1 with the same spin, $p_1 p_0$ is next best, giving maximum $M_L = 1$, so $L = 1$. $S = 1, L = 1$ gives $J = 2, 1, 0$, so we know the corresponding terms are ${}^3P_2, {}^3P_1, {}^3P_0$. Since the $2p$ subshell is less than half-filled, 3P_0 is the ground term.

5-8 Overview

This chapter describes the new features that appear when we deal with systems having more than one electron. One of these features, interelectron repulsion, is easy to understand in its manifestation as operators in the hamiltonian and as coulomb repulsion integrals, J , in the average energy expression. Another feature, antisymmetry for

electron exchange and the resulting existence of exchange integrals, K , is unfamiliar and unintuitive, without a classical counterpart, yet is enormously important in its effect on electronic structure.

In addition to these features, we have noted the importance of recognizing that atomic states conserve magnitude and z component of total angular momentum. Using this permits us to characterize states in terms of J , L , and S (even though the latter two are not “good” quantum numbers) for ground and excited configurations. This is essential in atomic spectroscopy (a topic we do not pursue in this book) and also allows one, with the assistance of Hund’s rules, to predict the energy order for states associated with the ground configuration of any atom.

In closing this chapter, we should emphasize again a point frequently forgotten by chemist. In the orbital approach to many-electron systems we have a convenient *approximation*. This is an imperfect but useful way to describe atomic structure. There are more accurate ways to approximate eigenfunctions of many-electron hamiltonians, but this usually involves more difficulty in interpretation. The orbital representation of ψ appears to be the best compromise between accuracy and convenience for most chemical purposes.

5-8.A Problems

- 5-1. Write down the hamiltonian operator for the lithium atom, in a.u.
- 5-2. Calculate the values of \bar{r}_1 and \bar{r}_2 consistent with the He wavefunction $\psi(1, 2) = 1s(1)2s(2) \dots$ (Eq. 5-11).
- 5-3. Calculate the energy in electron volts of a photon with associated wavelength 0.1 a.u. Compare this result with the ionization energy in electron volts of the hydrogen atom in its ground state. Why is this comparison relevant?
- 5-4. Show that the wavefunction (5-15) is normalized if the 1s and 2s orbitals are orthonormal.
- 5-5. Show that the wavefunction (5-16) is antisymmetric with respect to exchange of electron coordinates.
- 5-6. Show that the wavefunction (5-37) would vanish if 2s were replaced throughout by 1s, giving a $1s^3$ configuration.
- 5-7. Produce a totally antisymmetric wavefunction starting from the configuration $1s(1)\alpha(1)2p(2)\beta(2)1s(3)\beta(3)$. Use the method described for Eq. (5-37) and use a determinantal function as a check.
- 5-8. Set up the integral of the product between $(1s1s2s\alpha\beta\alpha)^*$ and $2s1s1s\alpha\alpha\beta$. (Use symbols rather than explicit atomic orbital formulas.) Factor the integral into a product of integrals over one-electron space functions and one-electron spin functions. Indicate the value of each of the resulting six integrals and of their product.
- 5-9. a) Write down the Slater determinantal wavefunction for the configuration $1s1\bar{s}2p_z$.

- b) Expand this determinant into a linear combination of products.
 c) Write down the nonzero part of expansion (b) when $r_3 = 0$, $r_1 = 1$ a.u., $r_2 = 2$ a.u. [Do not evaluate the expression; just use symbols like $1s$ ($r = 1$).] Also write down the nonzero part of (b) when $r_2 = 0$, $r_1 = 1$, $r_3 = 2$, and when $r_1 = 0$, $r_2 = 2$, $r_3 = 1$. Is there any physical difference between saying “electron 3 is at the nucleus” and saying “an electron is at the nucleus?” Explain.

5-10. Wavefunction (5-38) describes a member of a *doublet*. Write the wavefunction for the other member.

5-11. A particle is capable of being in any one of *three* spin states. Call them α , β , and γ . Suppose you have two such particles in a molecule.

- a) Write down all the spin functions you can that are symmetric for exchange of these two particles. (Do not worry about normalization.)
 b) Write down all the antisymmetric cases.

5-12. The following wavefunction is proposed for an excited state of the lithium atom

$$\psi = \frac{1}{\sqrt{6}} \begin{vmatrix} \overline{1s}(1) & \overline{1s}(2) & \overline{1s}(3) \\ \overline{2s}(1) & \overline{2s}(2) & \overline{2s}(3) \\ \overline{3s}(1) & \overline{3s}(2) & \overline{3s}(3) \end{vmatrix}$$

Here $1s$, $2s$, and $3s$ are eigenfunctions for the Li^{2+} hamiltonian.

- a) Does this wavefunction satisfy the Pauli exclusion principle? Explain.
 b) Write the exact H for the lithium *atom* in atomic units.
 c) Is ψ an eigenfunction for the exact hamiltonian?
 d) If interelectronic repulsion terms are neglected in H , what energy, in a.u., is associated with ψ ?
 e) What z component of spin and orbital angular momentum (in atomic units) would you expect for the atom in this state, ignoring any nuclear contribution?
- 5-13.** Write the normalized Slater determinantal wavefunction for beryllium in the $1s^2 2s^2$ configuration. Do *not* expand the determinant.
- 5-14.** Write down the ground state configuration for the fluorine atom. Use Slater’s rules to find the orbital exponents $\zeta = (Z - s)/n$ for $1s$ and $2s$, $2p$ orbitals.
- 5-15.** Show that the average value of an operator for a state described by an *eigenfunction* for that operator is identical to the eigenvalue associated with that eigenfunction.
- 5-16.** Explain briefly the observation that the energy difference between the $1s^2 2s^1 ({}^2S_{1/2})$ state and the $1s^2 2p^1 ({}^2P_{1/2})$ state for Li is $14,904 \text{ cm}^{-1}$, whereas for Li^{2+} the $2s^1 ({}^2S_{1/2})$ and $2p^1 ({}^2P_{1/2})$ states are essentially degenerate. (They differ by only 2.4 cm^{-1} .)
- 5-17.** In Chapter 4 it was stated that the magnitude of the square of the angular momentum is given by $l(l + 1)$ a.u., and that z components can be any of the values $-l, -l + 1, \dots, l - 1, l$ a.u. Similar relations hold for spin. From this fact plus

the knowledge that the possible z components of spin angular momentum are $\pm\frac{1}{2}$ a.u., calculate the length of the spin angular momentum vector.

- 5-18.** It has been shown that, for a single spinning electron, two spin states are possible having z components of spin angular momentum of $+1/2$ and $-1/2$ a.u. For two unpaired electrons, the state of greatest multiplicity is a triplet ($M_s = +1, 0, -1$). Show that, in general, the maximum spin multiplicity resulting from n unpaired electrons equals $n + 1$.
- 5-19.** You have been shown symbolically that $1s(1)2s(2) \pm 2s(1)1s(2)$ and $\alpha(1)\beta(2) \pm \beta(1)\alpha(2)$ are symmetric or antisymmetric for exchange of electron labels (electron coordinates). For a more concrete and familiar example, take two functions: $f(x) = \exp(x)$ and $g(y) = y^3$. Construct combinations of these functions that are symmetric and antisymmetric for exchange of x and y coordinates. Set $x = 1$ and $y = 2$ and evaluate each function. Now set $x = 2$ and $y = 1$ and evaluate again. Compare results.
- 5-20.** Give all the allowed term symbols for a hydrogen atom (a) in the $n = 1$ level, (b) in the $n = 2$ level. In each case, total up the states to see whether you have the expected number.
- 5-21.** Consider the following helium atom wavefunction:

$$\psi = 1s(1)3d_{+2}(2)\alpha(1)\alpha(2)$$

- Is this a satisfactory wavefunction in the sense of meeting general symmetry conditions resulting from particle indistinguishability and the exclusion principle? If not, how would you modify it to make it satisfactory?
 - Identify the term to which this state (modified if necessary) belongs.
- 5-22.** How many *states* exist for the configuration spd ?
- 5-23.** A group of related terms has the common symbol 2P . (This is called a term multiplet.)
- What are the full term symbols for this multiplet?
 - How many energy levels exist (in the absence of a magnetic field) for this multiplet?
 - Indicate into how many levels each member of the multiplet splits in the presence of an external magnetic field.
- 5-24.** Given the following space part of an approximate wavefunction for a Li^+ ion: $(1/\sqrt{2})[1s(1)2p_1(2) + 2p_1(1)1s(2)]$,
- Write a physically possible spin part for this wavefunction.
 - What energy would this state have (in a.u.) if the $1/r_{12}$ term in H did not exist?
 - What *average* energy (expressed in terms of symbols like J) would this state have using the correct H (including $1/r_{12}$)?
 - You have not been shown the rules for operating with S^2 , the operator for the square of total spin angular momentum, but you can nevertheless guess what the result would be if S^2 operates on this state function. What is your guess?

- 5-25.** A state in the term 3D_3 is described by the wavefunction ψ . What is the value of x in each of the expressions $\text{Op } \psi = x\psi$, where Op is as given below? (Assume L - S coupling to be valid. If more than one x is possible, list them all.) (a) L^2 (b) S^2 (c) J^2 (d) L_z (e) S_z (f) J_z .
- 5-26.** Carbon ($1s^22s^22p^2$) and oxygen ($1s^22s^22p^4$) have a “symmetrical” relation in their $2p$ occupancy: C has one electron *less* than a half-filled subshell, O has one electron *more*. Another way of stating this is to note that C has 2 electrons and 4 holes in its $2p$ shell, while O has 2 holes and 4 electrons.
- Show that this leads to the same lowest-energy family (or “multiplet”) of term symbols, ${}^3P_{2,0,1}$.
 - How do these atoms *differ* in the energy-ordering of these three terms?
 - Show that this agreement in lowest-energy multiplet terms holds in general for atoms having this symmetrical occupation relation.
- 5-27.** Predict the ground state term symbol for each of the following atoms.
- Na ($1s^22s^22p^63s$)
 - P ($1s^22s^22p^63s^23p^3$)
 - Ne ($1s^22s^22p^6$)
 - Ti ($1s^22s^22p^63s^23p^64s^23d^2$)
- 5-28.** Calcium atoms are excited to the $[\text{Ar}]4s4p$ configuration.
- How many states are there?
 - What are the term symbols?
- 5-29.** a) Find all the terms for boron in its ground configuration, $1s^22s^22p$, and order these terms according to energy.
b) Repeat for phosphorus, $[\text{Ne}]3s^23p^3$.
- 5-30.** Explain how Hund’s first rule is equivalent to the aufbau rule that degenerate AOs half-fill with electrons before any are filled, when forming the lowest-energy state(s).
- 5-31.** How many states exist for each of the following term multiplets?
- 3D
 - 5F
- 5-32.** For a given electron configuration, are all of the following terms possible? Explain your reasoning. ${}^2P_{3/2}$, ${}^2P_{1/2}$, 1S_0 .
- 5-33.** How many states exist for each of the following configurations? (a) sd (b) sp (c) s^2p (d) pd (e) dd (nonequivalent)
- 5-34.** a) How many states are associated with the 4F term multiplet?
b) Write down the term symbols included in this multiplet.
- 5-35.** By inspection, what is the term symbol with the maximum J value we can have for the configuration sd ? What other terms would be included in the same multiplet?

- 5-36. Derive a formula for the number of states that exist for two *equivalent* electrons in a subshell having degeneracy g . How many states does this predict for p^2 ? for d^2 ?
- 5-37. Evaluate the splitting between adjacent lines in Zeeman-split terms 3D_3 , 3D_2 , 3D_1 , 1D_2 , when B equals 1 tesla.

Multiple Choice Questions

(Try to answer these without referring to the text.)

- Which one of the following is an acceptable (unnormalized) approximate wavefunction for a state of the helium atom?
 - $[1s(1)1s(2) - 1s(1)1s(2)]\alpha(1)\alpha(2)$
 - $1s(1)1s(2)[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$
 - $[1s(1)2s(2) + 2s(1)1s(2)]\alpha(1)\alpha(2)$
 - $[1s(1)2s(2) + 2s(1)1s(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)]$
 - None of the above is acceptable.
- The spin multiplicity of an atom in its ground state and having the outer-shell configuration $4s^23d^7$ is
 - 19
 - 15
 - 7
 - 5
 - None of the above.
- Which one of the following statements is NOT true for the ground state of the helium atom?
 - The atom's size (measured by r_{av}) is larger than the size of He^+ in its 1s state.
 - The ground state is a singlet.
 - The energy of the $2p_0$ orbital is above that of the 2s orbital.
 - The effective nuclear charge seen by both electrons is less than 2.
 - The atom's electronic energy is equal to -108.8 eV.
- The crudest orbital model for the ground state of He uses the 1s atomic orbitals for He^+ , for which $Z = 2$. Which of the following statements describes correctly the situation that pertains to a change to a more appropriate value?
 - The improved Z value is larger than 2, and the orbitals become more contracted.
 - The improved Z value is larger than 2, and the orbitals become more expanded.
 - The improved Z value is smaller than 2, and the orbitals become more contracted.
 - The improved Z value is smaller than 2, and the orbitals become more expanded.
 - The improved Z value is smaller than 2, but this only affects the computed energy, and not orbital size.

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