The hydrogen atom

Although solution of the Schrödinger equation for the hydrogen atom is not overly difficult, we shall not go into the problem here since we are more interested in the results than in the method. It may be pointed out, however, that the method is not unlike that used previously for a particle in a box. In the case of the hydrogen atom, the “box” is a sphere with sloping rather than vertical potential “walls.” As with the particle-in-a-box solution, constraints or boundary conditions are imposed which make possible the solution of the wave equation. These conditions are:

1. The wave function must be single-valued.
2. The wave function must be continuous.
3. The wave function must go to zero at infinity. This is a necessary condition so that the atom be finite.

4. The probability of finding the electron summed over all space must be one, that is, the wave function must be normalized.

It is found that the solution for the hydrogen atom contains three quantum numbers (as expected for a three-dimensional system), \( n, l, \) and \( m_l. \) The allowed values for these quantum numbers are discussed below. Each solution found for a different set of \( n, l, m_l \) is called an eigenfunction and represents an orbital in the hydrogen atom.

In order to plot the complete wave functions, one would in general require a four-dimensional graph with coordinates for each of the three spatial dimensions \( (x, y, z) \) or \( r, \theta, \phi) \) and a fourth value of the wave function.

In order to circumvent this problem and also to make it easier to visualize the actual distribution of electrons within the atom, it is common to break down the wave function, \( \Psi \), into three parts, each of which is a function of but a single variable. It is most convenient to use polar coordinates, so one obtains:

\[
\Psi(r, \theta, \phi) = R(r) \cdot \Theta(\theta) \cdot \Phi(\phi)
\]

where \( R(r) \) gives the dependence of \( \Psi \) upon distance from the nucleus and \( \Theta \) and \( \Phi \) give the angular dependence.

The radial wave function, \( R \)
The radial functions for the first three orbitals\(^7\) in the hydrogen atom are:

\[
n = 1, \quad l = 0, \quad m_l = 0 \quad R = \left( \frac{2}{a_0} \right)^{3/2} e^{-Zr/a_0} \quad 1s \text{ orbital}
\]

\[
n = 2, \quad l = 0, \quad m_l = 0 \quad R = \left( \frac{\sqrt{2}}{2a_0} \right)^{3/2} \left( 1 - \frac{2Zr}{a_0} \right) e^{-Zr/2a_0} \quad 2s \text{ orbital}
\]

\[
n = 2, \quad l = 1, \quad m_l = 0 \quad R = \left( \frac{\sqrt{3}}{2a_0} \right)^{3/2} e^{-Zr/2a_0} \quad 2p \text{ orbital}
\]

\(^7\) The general formula for radial eigenfunctions is in terms of the quantum numbers \( n \) and \( l \) is given by L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N.Y., 1960, and by D. J. Rorer, "Bonding Theory," McGraw-Hill, New York, 1968. The complete wave functions including both radial and angular parts through the 16th level are given by Pauling (\( n = 6 \)), Rorer (\( n = 3 \)), and also by F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Wiley, New York, 1966 (\( n = 3 \)).

where \( Z \) is the nuclear charge, \( e \) is the base of natural logarithms, and \( a_0 = h^2/4\pi\alpha^2 \) (see page 14), 0.529 Å. In hydrogen, \( Z = 1 \), but similar orbitals may be constructed where \( Z > 1 \) for other elements. For many-electron atoms, exact solutions of the wave equation are impossible to obtain, and these \( " \) hydrogen-like \( " \) orbitals are often used.

Although the radial functions may appear formidable, the important aspects may be made apparent by grouping the constants. For a given atom, \( Z \) will be constant and may be combined with the other constants resulting in considerable simplification:

\[
n = 1, \quad l = 0, \quad m_l = 0 \quad R = K_1 e^{-Zr/a_0} \quad 1s \text{ orbital}
\]

\[
n = 2, \quad l = 0, \quad m_l = 0 \quad R = K_2 \left( 2 - \frac{Zr}{a_0} \right) e^{-Zr/2a_0} \quad 2s \text{ orbital}
\]

\[
n = 2, l = 1, m_l = 0 \quad R = K_3 e^{-Zr/a_0} \quad 2p \text{ orbital}
\]

The most apparent feature of the radial wave functions is that they all represent an exponential “decay” (mathematically similar in form to the radioactive decay of radioisotopes), and that for \( n = 2 \) the decay is slower than for \( n = 1 \). This may be generalized for all radial functions: They decay as \( e^{-Zr/a_0} \). For this reason, the radius of the various orbitals (actually, the most probable radius) increases with increasing \( n \). A second feature is the presence of a node in the 2\( s \) radial function. At \( r = 2a_0 \), \( Z = 0 \) and the value of the radial function changes from positive to negative. Again, this may be generalized: s orbitals have \( n - 1 \) nodes, p orbitals have \( n - 2 \) nodes, etc. The radial functions for the hydrogen 1\( s \), 2\( s \), and 2\( p \) orbitals are shown in Fig. 2.8.

Since we are principally interested in the probability of finding electrons at various points in space, we shall be more concerned with the square of the radial functions than with the functions themselves. A useful way of looking at the problem is to consider the atom to be composed of “layers” much like an onion and to examine the probability of finding the electron in the “layer” which extends from \( r \) to \( r + \Delta r \) as shown in Fig. 2.9. The volume of the thin shell may be considered to be \( 4\pi r^2 \Delta r \). Now the volume of the sphere is:

\[
V = \frac{4\pi r^3}{3}
\]

\[
dV = 4\pi r^2 \, dr
\]

\[
R^2 \, dV = 4\pi r^2 R^2 \, dr
\]

Consider the radial portion of the wave function for the 1\( s \) orbital as plotted in Fig. 2.8. When it is squared and multiplied by \( 4\pi r^2 \), we obtain the probability function shown in Fig. 2.10. The essential features of this function may be obtained qualitatively as follows:

1. At \( r = 0 \), \( 4\pi r^2 R^2 = 0 \), hence the value at the nucleus must be zero.
2. At large values of \( r \), \( R \) approaches zero and hence \( 4\pi r^2 R^2 \) must approach zero.
3. In between, \( r \) and \( R \) both have finite values, so there is a maximum in the plot of probability \( (4\pi r^2 R^2) \) as a function of \( r \). It is interesting to note that this maximum occurs at \( r = a_0 \), the value of the Bohr radius. The wave-mechanical picture of the atom differs from the Bohr picture in that the electron is most probably to be found at a distance of 0.529 Å for \( n = 1 \) in the hydrogen atom.

Similar probability functions (including the factor \( 4\pi r^2 \)) for the 2\( s \), 2\( p \), 3\( s \), 3\( p \), and
Fig. 2.9 Volume of shell of thickness \( dr \).

Fig. 2.10 Radial probability functions for \( n = 1, 2, 3 \) for the hydrogen atom. The function gives the probability of finding the electron in a spherical shell of thickness \( dr \) at a distance \( r \) from the nucleus. [From "Atomic Spectra and Atomic Structure," by Gerhard Herzberg, Dover Publications, Inc., New York, 1944. Reprinted through permission of the publisher.]

3d orbitals are also shown in Fig. 2.10. Note that although the radial function for the 2s orbital is both positive (\( r < 2a_0/Z \)) and negative (\( r > 2a_0/Z \)), the probability function is everywhere positive (as of course it must be to have any physical meaning) as a result of the squaring operation.

The presence of a node in the wave function indicates a point in space at which the probability of finding the electron has gone to zero. This raises the interesting question "How does the electron get from one side of the node to the other if it can never be found exactly at the node?" This is probably not a valid question, since it presupposes our macroscopically prejudiced view that the electron is a particle. If we consider the electron to be a standing wave, no problem arises because it can simultaneously exist on both sides of a node. Consider a vibrating string on an instrument such as a guitar. If the string is fretted at the twelfth fret the note will go up one octave because the wavelength has been shortened by one-half.
Although it is experimentally difficult (a finger is not an infinitesimally small point), it is possible to sound the same note on either half of the octave-fretted string. This vibration can be continuous through the node at the fret. In fact, on the open string overtones occur at the higher harmonics such that nodes occur at various points along the string. Nodes are quite common to wave behavior and conceptual problems arise only when we try to think of the electron as a "hard" particle with a definite position.

Dirac* has provided a relativistic treatment that differs from the "standard" theory in a number of ways: (1) There are no nodes, either radial or angular in a Dirac atom. However, there are regions in which the electron density becomes very small. (2) Electron "spin" is shown to be a natural consequence of electron movement within the atom. (3) The electrons of given value of $l$ (see page 29) are not exactly degenerate, but differ slightly in energy. (4) The usual treatment of spin-orbit interactions is shown to be artificial. Nevertheless, almost all of the current discussions in quantum mechanics are in nonrelativistic terms because of mathematical simplicity and because the errors incurred are small. A strongly dissenting opinion on this practice, however, has been presented by Powell.**

The presence of one or more nodes causes small maxima in electron density between the nucleus and the largest maximum. It is often stated that these nodes and maxima have no chemical effect, but this is slightly misleading. There are two ways in which these nodes and maxima could affect bonding. (1) In a covalent bond, as we shall see later, we shall be very concerned with total overlap of the atomic orbitals which combine to form the bond. Regions of space where there are low electron densities, and especially where the sign of the wave function is changing, are not conducive to good overlap. Conceivably, if the node in an orbital wave function fell at the appropriate place it could seriously weaken a covalent bond. Prior to the suggestion of the perturbative ion such a radial node in the 4d orbitals was suggested as a possible reason for its apparent nonexistence. The subsequent synthesis of BrO$_4$ eliminates the necessity for such an explanation, and in every case in which careful calculations have been made it is found that the nodes lie too close to the nucleus to affect the bonding. (2) The fact that electrons in $s$ orbitals spend a small fraction of their time very close to the nucleus is extremely important in determining the energy of the orbitals. The ionization energies of $s$ electrons are always higher than those of corresponding $p$ electrons (and the trend continues to $d$ and $f$ electrons) because the $s$ orbitals are more penetrating, i.e., they have considerable electron density in the region of the nucleus. This is the fundamental reason responsible for the ordering of the energy levels: 1$s$, 2$s$, 3$s$, etc. (see pages 31 and 41).

**Angular wave functions**

The angular part of the wave function determines the spatial arrangement of the electron cloud and varies depending upon the type of orbital involved, i.e., $s$, $p$, $d$, or $f$, and its orientation in space. However, for a given type of orbital such as $s$ or $p$, the angular wave function is independent of the principal quantum number or energy level.

Some typical angular functions are:

$$l = 0, m_l = 0 \quad \Theta \Phi = (\frac{1}{\pi})^{1/2}$$

$s$ orbital

$$l = 1, m_l = 0 \quad \Theta \Phi = (2\pi)^{1/2} \cos \theta$$

$p$ orbital

$$l = 2, m_l = 0 \quad \Theta \Phi = (\frac{1}{3\pi})^{1/2} (3 \cos^2 \theta - 1)$$

$d$ orbital

---

by contours of equal electron density (Figs. 2.14 and 2.15), only the latter method is quantitatively accurate.\(^{13}\)

Since \(\Theta^2\Phi^2\) is termed an angular probability function, the question may properly be asked what its true meaning is, if not a "picture" of electron distribution. It, like any other graph, simply plots the value of a function \(6\Theta^2\Phi^2\) vs. the variable \(\theta\) or \(\phi\). If one chooses an angle \(\phi\), the probability that the electron will be found in that direction (summed over all distances) is proportional to the magnitude of the vector connecting the origin with the functional plot at that angle.

---

The allowed values of \( l \) range from zero to \( n - 1 \):
\[
l = 0, 1, 2, 3, \ldots, n - 1
\]

The quantum number \( l \) is a measure of the orbital angular momentum of the electron and determines the shape of the orbital. The types of orbitals are designated by the letters \( s, p, d, f, \ldots \), corresponding to the values of \( l = 0, 1, 2, 3, 4, \ldots \). The first four letters originate in spectroscopic notation (see page 35) and the remainder follow alphabetically. In the previous section we have seen the various angular wave functions and the resulting distribution of electrons. The nature of the angular wave function is determined by the value of the quantum number \( l \).

For orbitals with \( l > 0 \), there are a number \((2l + 1)\) of equivalent ways in which the orbitals may be oriented in space. In the absence of an electric or magnetic field, these orientations are degenerate; i.e., they are identical in energy. Consider, for example, the \( p \) orbital. It is possible to have a \( p \) orbital in which the maximum electron density lies on the \( z \) axis and the \( xy \) plane is a nodal plane. Equivalent orientations have the maximum electron density along the \( x \) or \( y \) axis. Application of a magnetic field splits the degeneracy of the set of three \( p \) orbitals. The magnetic quantum number, \( m_\ell \), is related to the component of angular momentum along a chosen axis, for example, the \( z \) axis, and determines the orientation of the orbital in space. Values of \( m_\ell \) range from \(-l\) to \(+l\):
\[
m_\ell = -l, -l + 1, \ldots, -1, 0, +1, +2, \ldots, +l
\]

Thus for \( l = 1 \), \( m_\ell = -1, 0, +1 \), and there are three \( p \) orbitals possible, \( p_x \), \( p_y \), and \( p_z \). Similarly, for \( l = 2 \) the \( d \) orbitals, \( m_\ell = -2, -1, 0, +1, +2 \), and for \( l = 3 \) the \( f \) orbitals, \( m_\ell = -3, -2, -1, 0, +1, +2, +3 \).

It is an interesting fact that just as the single \( s \) orbital is spherically symmetric, the summation of a set of three \( p \) orbitals, five \( d \) orbitals, or seven \( f \) orbitals is also spherically symmetric. Thus, although it might appear as though an atom such as neon with a filled set of \( s \) and \( p \) orbitals would have a "lumpy" electron cloud, the total probability distribution is perfectly spherical (see Problem 2.13).

From the above rules we may obtain the allowed values of \( n, l, \) and \( m_\ell \). We have seen previously (page 20) that a set of particular values for these three quantum numbers determines an eigenfunction or orbital for the hydrogen atom. The possible orbitals are therefore:

- \( n = 1 \):
  - \( l = 0 \): \( m_\ell = 0 \) - 1s orbital
- \( n = 2 \):
  - \( l = 0 \): \( m_\ell = 0 \) - 2s orbital
  - \( l = 1 \): \( m_\ell = -1, 0, +1 \) - 2p\(_{x,y,z}\) orbitals
- \( n = 3 \):
  - \( l = 0 \): \( m_\ell = 0 \) - 3s orbital
  - \( l = 1 \): \( m_\ell = -1, 0, +1 \) - 3p\(_{x,y,z}\) orbitals
  - \( l = 2 \): \( m_\ell = -2, -1, 0, +1, +2 \) - 3d\(_{xy, xz, yz}\) orbitals
- \( n = 4 \):
  - \( l = 0 \): \( m_\ell = 0 \) - 4s orbital

---


15 This statement is true only for the nonrelativistic treatment. If relativistic effects are included, a small dependence on \( l \) is also found. This should not be confused with the much larger differences in orbital energies that result from electron-electron interactions in polyatomic molecules.

16 Although the \( p \) and \( d \) orbitals correspond to \( m = 0 \), there is no similar one-to-one correspondence for the other orbitals and other values of \( n \). See J. C. Davis, Jr., "Advanced Physical Chemistry," Ronald, New York, 1965, pp. 170-171, or B. N. Figgis, "Introduction to Ligand Fields," Wiley, New York, 1966, pp. 9-15.

17 These orbitals are sketched and discussed further in Chapter 8.
We can now summarize the relation between the quantum numbers \( n, l, \) and \( m_l \), and the physical pictures of electron distribution in orbitals by a few simple rules. It should be emphasized that these rules are no substitute for a thorough understanding of the previous discussion, but merely serve as handy guides to recall some of the relations.

1. Within a given atom, the lower the value of \( n \), the more stable (lower in energy) will be the orbital.

2. There are \( n \) types of orbitals in the \( n \)th energy level (i.e., the third energy level has \( s, p, \) and \( d \) orbitals).

3. There are \( 2l + 1 \) orbitals of each type (i.e., one \( s \), three \( p \), five \( d \), and seven \( f \)). This is also equal to the number of values which \( m_l \) may assume for a given \( l \) value.

4. There are \( n - l - 1 \) nodes in the radial distribution functions of all orbitals (e.g., the 3s orbital has two nodes, the 4d orbitals have each one). There are \( l \) nodal surfaces in the angular distribution function of all orbitals (e.g., 3s orbitals have none, \( d \) orbitals have two).

The **pseudoelectronic atom**

Everything which has been discussed thus far deals only with the hydrogen atom, the only atom for which the Schrödinger wave equation has been solved exactly. It can be extended readily to one-electron ions isoelectronic with hydrogen such as \( \text{He}^+ \), \( \text{Li}^{2+} \), \( \text{Be}^{3+} \), etc., by using the appropriate value of the nuclear charge, \( Z \). The next simplest atom, helium, consists of a nucleus and two electrons. We thus have three interactions, the attraction of electron 1 for the nucleus, the attraction of electron 2 for the nucleus, and the repulsion between electrons 1 and 2. This is an example of the classic three-body problem in physics and cannot be solved exactly. We can, however, approximate a solution to a high degree of accuracy using successive approximations. For simple atoms such as helium this is not too difficult, but for heavier atoms the number of interactions which must be considered rises at an alarming rate and the calculations become extremely laborious. There are a number of methods of approximation which have been used and we shall not explore them here beyond describing in conceptual terms one of the more accurate methods. It is referred to as the Hartree-Fock method after the men who developed it, or the self-consistent field (SCF) method. It consists of (1) assuming a reasonable wave function for each of the electrons in an atom except one, (2) calculating the effect which the field of the nucleus and the remainder of the electrons exert on the chosen electron, and (3) calculating a wave function for the last electron, including the effects of the field of the other electrons. A different electron is then chosen and using the field resulting from the other electrons (including the contribution from the improved wave function of the formerly chosen electron), an improved wave function is calculated. This process is continued until the wave functions for all of the electrons have been improved and the cycle is then started over to improve further the wave function of the first electron in terms of the field resulting from the improved wave functions of the other electrons. The cycle is repeated as many times as necessary until a negligible change takes place in improving the wave functions. At this point it may be said that the wave functions are self-consistent and are a reasonably accurate description of the atom.

Calculations such as the above indicated that orbitals in atoms other than hydrogen do not differ in any radical way from the hydrogen orbitals previously discussed. The principal difference lies in the consequence of the increased nuclear charge—all of the orbitals are somewhat contracted. It is common to call such orbitals which have been adjusted by an appropriate nuclear charge hydrogen-like orbitals. Within a given major energy level it is found that the energy of these orbitals increases in the order \( s < p < d < f \). For the higher energy levels these differences are sufficiently pronounced that a staggering of orbitals may result, for example: \( 6s < 5d < 4f < 6p \). The energy of a given orbital depends on the nuclear charge (atomic number) and different types of orbitals are affected to different degrees. Thus there is no single ordering of energies of orbitals which will be universally correct for all elements. Nevertheless, the following order: \( 1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 5d < 4f < 6p < 7s < 6d < 5f \) is found to be extremely useful. This complete order is correct for no single element, yet paradoxically, with respect to placement of the outermost or valence electron it is remarkably accurate for all elements. For example, the valence electron in potassium must come between the 3d and 4s orbitals, and, as predicted by this series, it is found in the 4s orbital. The above ordering should be assumed to be only a rough guide to the filling of energy levels (see "Aufbau Principle," page 32). In many cases the orbitals are very similar in energy and small changes in atomic structure can invert two levels and change the order of filling. Nevertheless, the above series is a useful guide to the building up of electronic structure if it is realized that exceptions may occur. A useful mnemonic diagram has been suggested by Moeller (Fig. 2.17). To recall the order of filling, one merely follows the arrows and the numbers from one orbital to the next.

**Electron spin and the Pauli principle**

As expected from our experience with a particle in a box, three quantum numbers are necessary to describe the spatial distribution of electrons in atoms. To describe an electron in an atom completely, a fourth quantum number, \( m_s \), called the spin quantum number, must be specified. This is because every electron has associated with it a magnetic moment which is quantized in one of two possible orientations: parallel with or opposed to an applied magnetic field. The magnitude of the magnetic moment is given by the expression:

\[
\mu = 2.00 \sqrt{s(s + 1)}
\]

(2.50)

where the moment (\( \mu \)) is expressed in Bohr magnetons (eb/Ampere) and \( s = |m_s| \). The allowed values of the spin quantum number are \( \pm \frac{1}{2} \). For an atom with two electrons, the spins may be either parallel (\( s = 1 \)) or opposed and thus cancel (\( s = 0 \)). In the latter situation the electrons are referred to as paired. Atoms having only paired electrons (\( s = 0 \)) are repelled slightly when placed in a magnetic field and are termed diamagnetic. Atoms having one or more unpaired electrons (\( s \neq 0 \)) are attracted strongly by a magnetic field and are termed paramagnetic.

Electrons having the same spin are strongly repulsive and tend to occupy different regions of space. This is a result of a fundamental law of nature known as the Pauli exclusion principle. 18

---


20 In the Dirac relativistic treatment, mentioned previously, electron "spin" follows naturally as the fourth quantum number necessary to define electron behavior.
The exclusion principle. It states that total wave functions (including spin) must change their signs on exchange of any pair of electrons in the system. Briefly, this means that if two electrons have the same spin they must have different spatial wave functions (i.e., different orbitals) and if they occupy the same orbital they must have paired spins. The Pauli principle and the so-called Pauli repulsive forces\(^{21}\) have far-reaching consequences in chemistry but for our present discussion it may be stated as follows: In a given atom, no two electrons may have all four quantum numbers identical. This means that in a given orbital specified by \(n, l,\) and \(m_s\), a maximum of two electrons may exist (\(m_s = \pm \frac{1}{2}\) and \(m_s = \mp \frac{1}{2}\)).

The Aufbau principle

The electron configuration or distribution of electrons among orbitals may be determined by application of the Pauli principle and the ordering of energy levels suggested above. The method of determining the appropriate electron configuration of minimum energy (the ground state) makes use of the aufbau principle, or “building up” of atoms one step at a time. Protons are added to the nucleus and electrons are added to orbitals to build up the desired atom. It should be emphasized that this is only a formalism for arriving at the desired electron configuration, but an exceedingly useful one.

The quantum numbers \(n, l,\) and \(m_s\) in various permutations describe the possible orbitals of an atom. These may be arranged according to their energies. The ground state for the hydrogen atom will be the one with the electron in the lowest orbital, the \(1s\). The spin of the electron may be of either orientation with neither preferred. We would thus expect a random distribution of spins and indeed if a stream of hydrogen atoms were introduced into a magnetic field, half would be deflected in one direction, the other half in the opposite direction. Thus the four quantum numbers for a hydrogen atom are \((1, 0, 0, \pm \frac{1}{2})\). For the helium atom we can start with a hydrogen atom and add a proton to the nucleus and a second electron. This second electron will have the first three quantum numbers identical to those from a hydrogen atom (i.e., the electron will also seek the lowest possible energy, the \(1s\) orbital) but the spin must be opposed to that of the first electron. So the quantum numbers for the two electrons in helium are \((1, 0, 0, + \frac{1}{2})\) and \((1, 0, 0, - \frac{1}{2})\). This fills the \(1s\) orbital and the addition of a third electron to form a lithium atom requires that the \(2s\) orbital, the next lowest in energy, must be used. The electron configuration of the first three elements together with the quantum numbers of the last electron are\(^{22}\):

- \(\text{H} = 1s^1\) \(1, 0, 0, \pm \frac{1}{2}\)
- \(\text{He} = 1s^2\) \(1, 0, 0, \pm \frac{1}{2}\)
- \(\text{Li} = 1s^22s^1\) \(2, 0, 0, \pm 
- \(\text{Be} = 1s^22s^2\) \(2, 0, 0, \pm \frac{1}{2}\)
- \(\text{B} = 1s^22s^22p^1\) \(2, 1, 1, \pm \frac{1}{2}\)

This procedure may be continued, one electron at a time, until the entire list of elements has been covered. A complete list of electron configurations of the elements is given in Table 2.2. It will be seen that there are only a few differences between these configurations which are obtained experimentally and a similar table which might be constructed on the basis of the aufbau principle. In every case in which an exception occurs the energy levels involved are exceedingly close together and factors not accounted for in the above discussion invert the energy levels. For example, the \((n = 1)\) and \(ns\) levels tend to lie very close together when these levels are filling, with the latter slightly lower in energy. If some special stability arises such as a filled or half-filled subshell (see pages 37 and 45), the most stable arrangement may not be \(ns^l (n - 1)d^0\). In Cr and Cu, the extra stability associated with half-filled and filled subshells is apparently sufficient to make the ground state configuration of the isolated atoms \(3d^54s^1\) and \(3d^{10}4s^2\) instead of \(3d^44s^2\) and \(3d^84s^2\), respectively. Too much importance should not be placed on this type of deviation, however. Its effect on the chemistry of these two elements is minimal. It is true that copper has a reasonably stable \(+1\) oxidation state (corresponding to \(3d^{10}4s^2\)) but the \(+2\) state is even more stable. For chromium, the most stable ion

\(^{21}\) The Pauli “force” corresponds to no classical interaction but results from the nature of quantum mechanics. Although it is common in chemistry to speak of “repulsions” and “stabilizing energies” resulting from the Pauli principle, these do not arise directly from the energetics of spin-spin interactions but from the electrostatic energies resulting from the spatial distribution of electrons as a result of the requirements of the Pauli exclusion principle. See W. J. Kauffman, “Quantum Chemistry,” Academic, New York, 1957, pp. 319-320; F. A. Matsen, J. Amer. Chem. Soc., 92, 3553 (1970).

\(^{22}\) The \(m_s\) values for the unpaired electron in H, Li, and B are, of course, undefined and may be either \(\pm \frac{1}{2}\). It is merely necessary that the values for He and Be be opposite of those for H and Li. Likewise, the last electron in boron may enter the \(2p_x\), \(2p_y\), or \(2p_z\) orbital, all equal in energy, and so the \(m_s\) value given above is arbitrary.
<table>
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<th>Electron configuration</th>
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<td>He</td>
<td>1s²</td>
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<tr>
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<td>B</td>
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<td>[Ne]3s³</td>
</tr>
<tr>
<td>17</td>
<td>Cl</td>
<td>[Ne]3s³</td>
</tr>
<tr>
<td>18</td>
<td>Ar</td>
<td>[Ne]3s³</td>
</tr>
<tr>
<td>19</td>
<td>K</td>
<td>[Ar]4s¹</td>
</tr>
<tr>
<td>20</td>
<td>Ca</td>
<td>[Ar]4s¹</td>
</tr>
<tr>
<td>21</td>
<td>Sc</td>
<td>[Ar]4s¹</td>
</tr>
<tr>
<td>22</td>
<td>Ti</td>
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</tr>
<tr>
<td>23</td>
<td>V</td>
<td>[Ar]4s¹</td>
</tr>
<tr>
<td>24</td>
<td>Cr</td>
<td>[Ar]4s¹</td>
</tr>
<tr>
<td>25</td>
<td>Mn</td>
<td>[Ar]4s¹³</td>
</tr>
<tr>
<td>26</td>
<td>Fe</td>
<td>[Ar]4s¹³</td>
</tr>
<tr>
<td>27</td>
<td>Co</td>
<td>[Ar]4s¹³</td>
</tr>
<tr>
<td>28</td>
<td>Ni</td>
<td>[Ar]4s¹³</td>
</tr>
<tr>
<td>29</td>
<td>Cu</td>
<td>[Ar]4s¹³</td>
</tr>
<tr>
<td>30</td>
<td>Zn</td>
<td>[Ar]4s¹³</td>
</tr>
<tr>
<td>31</td>
<td>Ga</td>
<td>[Ar]4s¹³</td>
</tr>
<tr>
<td>32</td>
<td>Ge</td>
<td>[Ar]4s¹³</td>
</tr>
<tr>
<td>33</td>
<td>As</td>
<td>[Ar]4s¹³</td>
</tr>
<tr>
<td>34</td>
<td>Se</td>
<td>[Ar]4s¹³</td>
</tr>
<tr>
<td>35</td>
<td>Br</td>
<td>[Ar]4s¹³</td>
</tr>
<tr>
<td>36</td>
<td>Kr</td>
<td>[Ar]4s¹³</td>
</tr>
<tr>
<td>37</td>
<td>Rb</td>
<td>[K]5s¹</td>
</tr>
<tr>
<td>38</td>
<td>Sr</td>
<td>[K]5s¹</td>
</tr>
<tr>
<td>39</td>
<td>Y</td>
<td>[K]5s¹</td>
</tr>
<tr>
<td>40</td>
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<td>[K]5s¹</td>
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<tr>
<td>41</td>
<td>Nb</td>
<td>[K]5s¹</td>
</tr>
<tr>
<td>42</td>
<td>Mo</td>
<td>[K]5s¹</td>
</tr>
<tr>
<td>43</td>
<td>Tc</td>
<td>[K]5s¹</td>
</tr>
<tr>
<td>44</td>
<td>Ru</td>
<td>[K]5s¹</td>
</tr>
<tr>
<td>45</td>
<td>Rh</td>
<td>[K]5s¹</td>
</tr>
<tr>
<td>46</td>
<td>Pd</td>
<td>[K]5s¹</td>
</tr>
<tr>
<td>47</td>
<td>Ag</td>
<td>[K]5s¹</td>
</tr>
<tr>
<td>48</td>
<td>Cd</td>
<td>[K]5s¹</td>
</tr>
<tr>
<td>49</td>
<td>In</td>
<td>[K]5s¹</td>
</tr>
<tr>
<td>50</td>
<td>Sn</td>
<td>[K]5s¹</td>
</tr>
<tr>
<td>51</td>
<td>Sb</td>
<td>[K]5s¹</td>
</tr>
<tr>
<td>52</td>
<td>Te</td>
<td>[K]5s¹</td>
</tr>
</tbody>
</table>


The polyelectronic atom in aqueous solution is Cr⁺³, with the Cr⁺² ion and the Cr⁺⁰ oxidation state (as in CrO₂⁻) reasonably stable; the Cr⁵⁺ oxidation state is practically unknown. For both Cu⁺² and Cr⁺³ (as well as many other transition metal ions) ligand field effects in their complexes (see Chapter 8) are sufficient to permit the easy loss of d electrons.

In the case of the lanthanide elements (elements 57–71) and those immediately following, the 5d⁴ and 4f⁴ levels are exceedingly close. In lanthanum it appears that the 57th electron enters the 5d⁴ level rather than the 4f⁴. Thereafter the 4f⁴ level starts to fill, and lanthanides appear not to have any 5d⁴ electrons. Here again too much attention to details of the electron configuration is not rewarding from a chemist's point of view—indeed it may be quite misleading. The small difference in energy between a 5d⁴ 4f⁴ configuration and a 5d⁴ 4f⁵ configuration is very small. For mnemonic purposes, all lanthanide elements behave as though they had an electron configuration: 6s²⁵d⁴⁺5f⁴, i.e., the most stable oxidation state is always that corresponding to loss of three electrons (the 6s and 5d).

There are some other interesting "anomalies" in the electron configurations of various elements, but they are of minor importance from a chemical point of view.

Although the Aufbau principle and the ordering of orbitals given previously may be used reliably to determine electron configurations, it must again be emphasized that the device is a formalism and may lead to serious error if overextended. For example, in the atoms of the elements potassium, calcium, and scandium the 4s level is lower in energy than the 3d level. This is not true for heavier elements or for charged ions. The energies of the various orbitals are sensitive to changes in nuclear charge and to the occupancy of other orbitals by electrons (see "Shielding," page 40) and this prevents the designation of an absolute ordering of orbital energies. It happens that the ordering suggested by Fig. 2.19 is reasonably accurate when dealing with orbitals corresponding to the valence shell of an atom; that is, the energies 3d > 4s and 5p > 4d are correct for elements potassium and yttrium, for example, but not necessarily elsewhere.

Atomic states and term symbols

It is convenient to be able to specify the energy, angular momentum, and spin multiplicity of an atom by a symbolic representation. For example, in hydrogen we may define S, P, D, and F states depending upon whether the single electron occupies an s, p, d, or f orbital. The ground state of hydrogen, 1s¹, is a 1S state, etc.

The total angular momentum of an electron is the resultant of the orbital angular momentum vector and the electron spin angular momentum vector. Both of these are quantized and we can define a new quantum number, j:

\[ J = l + s, \ldots, |l - s| \]

We denote the value of j as a subscript appended to the symbol representing the state of the atom (term symbol). For example, for the ground state of hydrogen we have 1S₁/₂.

For the P state, j can have two values, l + s and l - s, resulting in 2P₁/₂ and 2P₃/₂. These are at slightly different energies, hence a doublet appears in the spectrum corresponding, for example, to \( P_{1/2} \rightarrow S_{1/2} \) and \( P_{3/2} \rightarrow S_{1/2} \). We denote that the P state is a...

---

²² This is the reverse of the historical process: S, P, D, and F states were observed spectroscopically (and named after sharp, primary, diffuse, and fundamental characteristics of the spectra). Later the symbols s, p, d, and f were applied to orbitals.
doublet by a preceding superscript, \( ^3P \). Thus the term symbol is \( ^3P \) (pronounced "doubled \( P \)") for the \( P \) state and \( ^1P \) for the individual states.

For a polyelectronic atom we may define an atomic (as opposed to electronic) quantum number \( L \):

\[
L = l_1 + l_2 + l_3 + l_4 - 1, l_1 + l_2 - 2, \ldots, |l_1 - l_2|
\]

(2.52)

We can also define the component of the total angular momentum along a given axis:

\[
M_L = L, L - 1, L - 2, \ldots, 0, \ldots, -L
\]

(2.53)

The number of possible values of \( M_L \) is given by \( 2L + 1 \). \( M_S \) is also given by:

\[
M_S = m_s + m_{s_2} + \cdots + m_n
\]

(2.54)

Likewise we can define an atomic spin quantum number representing the total spin:

\[
S = \sum \frac{1}{2} j_i
\]

(2.55)

For a given value of \( S \), there will be \( 2S + 1 \) spin states characterized by \( M_S \):

\[
M_S = S, S - 1, S - 2, \ldots, -S
\]

(2.56)

or

\[
M_S = m_s + m_{s_2} + \cdots + m_n
\]

(2.57)

We can now couple the resultant orbital angular momentum (\( L \)) with the spin angular momentum (\( S \)). The new quantum number \( J \) is obtained:

\[
J = L + S, L + S - 1, L + S - 2, \ldots, |L - S|
\]

(2.58)

For a helium atom, \( L = 0, S = 0, J = 0 \), and the term symbol for the ground state is \( ^1S \). For lithium, we can make use of the fact that all closed shells and subshells (such as the He example just given) contribute nothing to the term symbol. Hence the 2s electron results in \( L = 0, S = \frac{1}{2}, J = \frac{1}{2} \), and the term symbol is \( ^1S \). The reader may verify that Be = \( ^1S \) and B = \( ^2P \). For carbon there are two \( p \) electrons. The spins may be paired or unpaired, so \( L = 2, 1, 0; S = 1, 0; \) and \( J = 3, 2, 1, 0 \). To work out the appropriate states for this system requires a systematic approach so the following specific steps may be taken:

1. Determine the possible values of \( M_L \). In the case of carbon with an electron configuration of \( 1s^22s^22p^2 \), \( L \) can have a maximum value of 2 and \( M_L \) can have values of \(-2, -1, 0, +1, +2\).

2. Determine the possible values of \( M_S \). In carbon the 1s and 2s represent filled subshells and so the spin is determined by the 2p electrons. \( M_S \) can thus have values of \(-1, 0, +1\) corresponding to paired \( S = 0 \) and unpaired \( S = 1 \) 2p electrons.

3. Set up a chart of microstates. Each combination of a value of \( m_l \) with a corresponding value of \( m_s \) is called a microstate. For example, the two 2p electrons could be paired \((m_l = +1)\) and \(-1\) with an \( m_s \) value of \(+1\) and \(-1\) each. This microstate may be symbolized as \( ^1P \), \( ^1P \) and has \( M_L \) and \( M_S \) values of \(+2\) and \( +1 \), respectively. The microstate \( ^1S \), \( ^1S \) is then entered in the table at \( M_L = 2 \) and \( M_S = 0 \). All possible combinations of \( m_l \) and \( m_s \) are listed in the table:

<table>
<thead>
<tr>
<th>( M_L )</th>
<th>( M_S )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td>-1</td>
<td>-1</td>
</tr>
</tbody>
</table>

Of the 21 microstates shown above, 6 are forbidden by the Pauli principle, and are therefore crossed out. For example, \(( -1, -1 )\) corresponds to a single \( p \) orbital (having \( m_s = -1 \)) containing two electrons, both with spin \( m_s = +1 \).

4. Resolve the chart of microstates into appropriate atomic states. An atomic state forms an array of microstates consisting of \( 2S + 1 \) columns and \( 2L + 1 \) rows. For example, a \( ^3P \) state requires a \( 3 \times 3 \) array of microstates. Inspection of the table indicates that it may be resolved into \( ^1D \) (a central column of five rows), a \( ^3P \) (a three by three array of nine microstates), and a \( ^1S \) (the remaining microstate at \( M_L = 0 \) and \( M_S = 0 \)). It is not necessary nor meaningful to attempt to ascribe individual microstates to one or another of the atomic states. It is merely necessary to account for all of the microstates.

The resulting states for the \( p^2 \) configuration are thus determined to be \( ^1S, ^3P \), and \( ^1D \). States for other electron configurations are listed in Table 2.3.

The ground state of an atom may be chosen by application of Hund's rules. Hund's first rule is that of maximum multiplicity. It states that the ground state will be that having the largest value of \( S \), in the case of carbon the \( ^3P \). Such a system having a maximum number of parallel spins will be stabilized by the exchange energy resulting from their more favorable spatial distribution compared with that of paired electrons (see Pauli principle, page 31).

The second rule states that if two states have the same multiplicity, the one with the higher value of \( L \) will lie lower in energy. Thus the \(^1D \) lies lower in energy than the \(^1S\). The greater stability of states in which the electrons are coupled to produce maximum angular momentum is also related to the spatial distribution and movement of the electrons.

The third rule states that for subshells that are less than half full, states with lower \( J \) are lower in energy; for subshells that are more than half full, states with higher \( J \) values are more stable. Applied to carbon, this rule predicts the ground state to be \(^3P_2\).

\(^3P_2\) Hund's rules are inviolate in predicting the correct ground state of an atom. There are occasional exceptions when the rules are used to predict the ordering of excited states.
Table 2.4 Multiple Terms of Various Electron Configurations

<table>
<thead>
<tr>
<th>Equivalent electrons</th>
<th>Non-equivalent electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>s, p, and d [^{10}]</td>
<td>[^{1}]S [^{1}]S</td>
</tr>
<tr>
<td>p and p</td>
<td>[^{1}]p [^{1}]p</td>
</tr>
<tr>
<td>p[^{1}] and p</td>
<td>[^{1}]P [^{1}]P</td>
</tr>
<tr>
<td>p[^{2}] and p</td>
<td>[^{1}]s [^{1}]D [^{1}]s [^{1}]P</td>
</tr>
<tr>
<td>d and d</td>
<td>[^{1}]D [^{1}]D</td>
</tr>
<tr>
<td>d[^{1}] and d</td>
<td>[^{1}]F [^{1}]p [^{1}]G [^{1}]D [^{1}]s [^{1}]S</td>
</tr>
</tbody>
</table>
| d\[^{2}\] and d  | \[^{1}\]D \[^{1}\]D \[^{1}\]G \[^{1}\]D \[^{1}\]F \[^{1}\]D \[^{1}\]D \[^{1}\]F \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1}\]D \[^{1}\]P \[^{1\}]


Although the complexity of determining the appropriate terms increases with the number of electrons and with higher \(L\) values,\(^{11}\) the method outlined above (known as Russell-Saunders coupling) may be applied to atoms with more electrons than the carbon atom in the foregoing example. Russell-Saunders coupling (also called \(LS\) coupling because it assumes that the individual values of \(j\) and \(s\) couple to form \(L\) and \(S\), respectively) is normally adequate, especially for lighter atoms. For heavier atoms with higher nuclear charges, coupling occurs between the spin and orbit for each electron \((j = l + s)\). The resultant coupling is known as \(jj\) coupling. In general, \(LS\) coupling is usually assumed and deviations are discussed in terms of the effects of spin-orbit interactions.

Periodicity of the elements

A natural result of the \textit{aufbau} principle and its relation to the quantum numbers \(n, l,\) and \(m_l\) is the periodic classification of the elements. In fact, the common long form of the periodic chart (Fig. 2.18) may be considered a graphic portrayal of the rules of atomic structure given previously. The vertical groups of the chart may be classified as follows: (1) Groups IA and IIA, the alkali and alkaline earth metals. These elements are characterized by an \(ns^1\) or \(ns^2\) electronic configuration. (2) The \("B"\) group elements,
the transition metals. In their ground states these elements are characterized by having their d orbitals in the process of being filled. For example, the first transition series proceeds from Sc (4d^1) to Zn (4d^10). (3) The lanthanide and actinide metals. These elements are characterized by the filling of a set of f orbitals. Each series starts with Ce (4f^1) and ends with Lu (4f^14) and Lr (5f^14). (4) The posttransition metals and nonmetals. Groups IIA to VIIIA. The classification here is imprecise, principally because the distinction between metal and nonmetal is somewhat arbitrary, but is usually associated with a "stepwise" division line running from boron to antimony. All of these elements (except He) share the feature of filling p orbitals, the noble gases representing a completely filled set of p orbitals.

It is possible to trace the Aufbau principle simply by following the periodic chart. Consider the elements from Cs (Z = 55) to Rn (Z = 86). In the elements Cs and Ba, the electrons enter (and fill) the 5s level. The next electron enters the 5p level and La (Z = 57) may be considered a transition element. In the elements Ce through Lu, the electrons are added to 4f levels and these elements are lanthanide or inner transition elements. After the 4f level is filled with Lu, the next electrons continue to fill the 6d orbitals (the transition elements Hf to Hg), and finally, the 5p level is filled in the elements Tl to Rn, in accord with Table 2.2. The periodic chart may thus be used to derive the electron configuration of an element as readily as use of the rules given above. It should be quite apparent, however, that the chart can give us back only the chemical knowledge that we have used in composing it; it is not a source of knowledge in itself. It is useful in portraying and correlating the information which has been obtained with regard to electron configurations and other atomic properties.

Shielding

As shown by Eq. (2.11) the energy of an electron in an atom is a function of \( Z^2 \rho^2 \). Since the nuclear charge (= atomic number) increases more rapidly than the principle quantum number, this might lead one to expect that the energy necessary to remove an electron from an atom would continually increase with increasing atomic number. This is not so, as can be shown by comparing hydrogen (\( Z = 1 \)) with lithium (\( Z = 3 \)). The ionization energies are 13.6 eV (H) and 5.4 eV (Li). The energy for lithium corresponds to a charge of one and two units. This corresponds to the nuclear charge which the valence electron actually "sees." The radial probability functions for hydrogen-like orbitals have been discussed previously (Fig. 2.10). The bulk of the electron density of the 1s orbital lies between the nucleus and the bulk of the 2s density. The laws of electrostatics state that when a test charge is outside of a "cage" of charge such as that represented by the 1s electrons, the potential is exactly the same as though the latter were located at the center (nucleus). In this case, the valence electron in the 2s orbital would experience a potential equivalent to a net nuclear charge of (2Z^2 = 1.0). A charge which penetrates the cage will be unshielded and would experience a potential equivalent to the full nuclear charge, Z^2 = 3.0. This is not meant to imply that the energy of the 2s electron varies as it penetrates the 1s orbital, but that the energy is determined by an effective nuclear charge, Z^*, which is somewhat less than the actual nuclear charge, Z:

\[
Z^* = Z - S
\]

(2.59)

where S is the shielding or screening constant.

As a result of the presence of one or more maxima near the nucleus, s orbitals are very penetrating and are somewhat less shielded by inner-shell electrons than are orbitals with higher values of l. In turn, they tend to shield somewhat better than other orbitals. Orbitals with high l values such as d and f orbitals are much less penetrating and are far poorer at shielding.

In a similar manner the radial distributions of 3s, 3p, and 3d orbitals may be compared (Fig. 2.10). Although the d orbitals are "smaller" in the sense that the most probable radius decreases in the order 3s > 3p > 3d, the presence of one node and an intranodal maximum in the 3p, and the presence of two nodes and one intranodal maxima in the 3s, cause them to be affected more by the nucleus. Hence the energies of these orbitals lie 3d > 3p > 3s as we have seen in filling the various energy levels previously.

In order to estimate the extent of shielding, a set of empirical rules has been proposed by Slater. It should be realized that these rules are simplified generalizations based upon the average behavior of the various electrons. Although the electronic energies estimated by Slater's rules are often not very accurate, they permit simple estimates to be made and will be found useful in related topics such as atomic size and electronegativity.

To calculate the shielding constant for an electron in an np or ns orbital:

1. Write out the electronic configuration of the element in the following order and groupings: (1s) (2s, 2p) (3s, 3p) (3d) (4s, 4p) (4d) (5s, 5p), etc.
2. Electrons in any group to the right of the (ns, np) group contribute nothing to the shielding constant.
3. All of the other electrons in the (ns, np) group shield the valence electron to an extent of 0.35 each.\(^{27}\)
4. All electrons in the n - 1 shell shield to an extent of 0.85 each.
5. All electrons n - 2 or lower shield completely, i.e., their contribution is 1.00 each.

When the electron being shielded is in a d or f orbital, the procedure is the same except that rules 4 and 5 become:

6. All electrons in groups lying to the left of the nd or nf group contribute 1.00.

**Examples**

1. Consider the valence electron in \( N = 1s^2 2s^2 2p^5 \). Grouping of the orbitals gives (1s)^2(2s)^2(2p)^5. \( S = (2 \times 0.85) + (4 \times 0.35) = 3.10 \). Z^* = Z - S = 7.0 - 3.1 = 3.9.

2. Consider the valence (4d) electron in \( Z = 30 \). The grouped electron configuration is (1s)^2(2s)^2(2p)^6(3s)^1(3p)^6(3d)^10(4s)^2. \( S = (10 \times 1.00) + (18 \times 0.85) + (1 \times 0.35) = 25.65 \). Z^* = 4.35.

3. Consider a 3d electron in \( Z = 30 \). The grouping is as in Example 2, but the shielding is \( S = (18 \times 1.00) + (9 \times 0.35) = 21.15 \). Z^* = 8.85.

\(^{27}\) Except in the 1s orbital for which a value of 0.30 seems to work better.
It can be seen that the rules are an attempt to generalize and to quantify those aspects of the radial distributions discussed previously. For example, $d$ and $f$ electrons are screened more effectively ($S = 1.00$) than $s$ and $p$ electrons ($S = 0.85$) by the electrons lying immediately below them. On the other hand, Slater's rules assume that all electrons, $s$, $p$, $d$, or $f$, shield electrons lying above them equally well (in computing shielding the nature of the shielding electron is ignored). This is not quite true as we have seen above and will lead to some error. For example, in Ga, $s^3p^33d^14s^24p^1$, the rules imply that the $4p$ electron is shielded as effectively by the $3d$ electron as by the $3p$ orbital, contrary to Fig. 2.10.

Slater formulated these rules in proposing a set of orbitals for use in quantum-mechanical calculations. Slater orbitals are basically hydrogen-like but differ in two important respects:

1. They contain no nodes. This simplifies them considerably but of course makes them less accurate.
2. They make use of $Z^*$ in place of $Z$, and for heavier atoms, $n$ is replaced by $n^*$, where for $n = 4$, $n^* = 3.7$; $n = 5$, $n^* = 4.0$; $n = 6$, $n^* = 4.2$. The difference between $n$ and $n^*$ is referred to as the quantum defect.

In order to remove the difficulties and inaccuracies in the simplified Slater treatment of shielding, Clementi and Raimondi have obtained effective nuclear charges from self-consistent field wave functions for atoms from hydrogen to krypton and generalized these into a set of rules for calculating the shielding of any electron. The shielding which an electron in the $n$th energy level and $l$th orbital ($S_{n,l}$) experiences is given by:

$$S_{n,l} = 0.3(N_{n,l} - 1) + 0.0072(N_{n,l} + N_{2n,l}) + 0.0153(N_{n+1,l} + N_{3n,l})$$

$$S_{n,l} = 1.7208 + 0.3601(N_{n,l} - 1 + N_{2n,l}) + 0.2062(N_{n+1,l} + N_{3n,l})$$

$$S_{n,l} = 2.5787 + 0.3326(N_{n,l} - 1) - 0.0773N_{n,l} - 0.0161(N_{n+1,l} + N_{3n,l}) - 0.0489N_{n+1,l} + 0.0085N_{3n,l}$$

$$S_{n,l} = 8.4927 + 0.250(N_{n,l} + N_{2n,l}) + 0.0778N_{n,l} + 0.3382N_{2n,l} + 0.1978N_{3n,l}$$

$$S_{n,l} = 9.3435 + 0.380(N_{n,l} - 1) + 0.0526N_{n+l} - 0.3289N_{2n,l} + 0.1558N_{3n,l}$$

$$S_{n,l} = 10.505 + 0.097(N_{n+1,l} - 1) + 0.833N_{3n+1,l} + 0.0687N_{4n+1,l}$$

$$S_{n,l} = 13.5894 + 0.269(N_{n+1,l} - 1) - 0.1065N_{3n+1,l}$$

$$S_{n,l} = 24.7782 + 0.2905N_{3n+1,l} - 1)$$

where $N_n$ represents the number of electrons in the $n$th orbital. For the examples given above the effective nuclear charges obtained are $Z_n = 3.756$, $Z_{2n} = 5.965$, and $Z_{3n} = 13.987$. The shielding rules of Clementi and Raimondi explicitly account for penetration of outer orbital electrons. They are thus more accurate and realistic than Slater's rules, at the expense, however, of more complex computation with a larger number of parameters. If accuracy greater than that afforded by Slater's rules is necessary it would appear that direct application of the effective nuclear charges from the SCF wave functions not only is the most simple but also the most accurate. Such values are listed in Table 2.4.

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<th>3p</th>
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The size of atoms

Atomic size is at best a rather nebulous quantity since atoms have no well-defined boundary similar to that of a billiard ball. In order to answer the question, How big is an atom? one must first pose the questions, How are we going to measure the atom and how hard are we going to push? The latter is particularly important because measuring atoms is analogous to measuring an overripe grapefruit with a pair of calipers—the value we get depends on how hard we squeeze. For this reason, it is impossible to set up a single set of values called "atomic radii" applicable under all conditions. It is necessary to define the conditions under which the atom (or ion) exists and also our
method of measurement. These will be discussed later (see Chapter 5). Nevertheless, it
will be useful now to discuss trends in atomic sizes without becoming too specific at the
present time about the actual sizes involved.
As we have seen from the radial distribution functions, the most probable radius
tends to increase with increasing n. Countering this tendency is the effect of increasing
effective nuclear charge which tends to contract the orbitals. From these opposing
forces, we obtain the following results:
1. Atoms tend to increase in size from one period (h horizontal row of the periodic
chart) to the next. Because of shielding, \( Z^+ \) increases very slowly from one period to
the next. For example, using Slater's rules we obtain the following values for \( Z^+ \):
   - H = 1.0
   - Li = 1.1
   - Na = 2.2
   - K = 2.2
   - Rb = 2.2
   - Cs = 2.2
The result of the opposing tendencies of \( n \) and \( Z^+ \) is that atomic size increases as one
progresses down Group I. This is a general property of the periodic chart with but
few minor exceptions which will be discussed later.
2. Within a given series, the principle quantum number does not change. (Even in
the "long" series in which the filling may be in the order ns, \( n-1d \), np, the outermost
electrons are always in the \( n \)th level.) The effective nuclear charge increases steadily,
however, since electrons added to the valence shell shield each other very ineffectively.
For the second series:
   - Li = 1.3
   - Be = 1.95
   - B = 2.60
   - C = 3.25
   - N = 3.90
   - O = 4.55
   - F = 5.20
   - Ne = 5.85
As a result there is a steady contraction from left to right. The net effect of the top-to-
bottom and the left-to-right trends is a discontinuous variation in atomic size. There is
a steady contraction with increasing atomic number until there is an increase in the
principal quantum number. This causes an abrupt increase in size, followed by a further
decrease.

**Ionization energy**
The energy necessary to remove an electron from an atom is the ionization energy (often
called ionization potential) for that atom. It is the energy difference between the highest
occupied energy level and that corresponding to \( n = \infty \), i.e., complete removal. It is
possible to remove more than one electron and the succeeding energies are the second,
third, fourth, etc., ionization energies.28 Ionization energies are always endothermic
and thus are always assigned a positive value in accord with common thermodynamic
convention. The various ionization energies of an atom are related to each other by a
polynomial equation which will be discussed in more detail later in this chapter. (See
Tables 2.5A and 2.5B.)

For the nontransition elements (alkali and alkaline earth metals and the nonmetals)
there are fairly simple trends with respect to ionization energy and position in the
periodic chart. Within a given family, increasing \( n \) tends to cause reduced ionization
energy because of the combined effects of size and shielding. The transition and post-
transition elements show some anomalies in this regard and these will be discussed
later. Within a given series, there is a general tendency for the ionization energy to
increase with increase in atomic number. This is a result of the tendency for \( Z^+ \) to
increase progressing from left to right. There are two other factors which prevent this
increase from being monotonic. One is the change in type of orbital which occurs as
one goes from Group IIA \( (s \) orbital) to Group IIA \( (p \) orbital). The second is the ex-
change energy between electrons of like spin. This stabilizes a system of parallel elec-
tron spins because electrons having the same spin tend to avoid each other as a result
of the Pauli exclusion principle. The electrostatic repulsions between electrons are thus
reduced. We have seen previously that this tends to maximize the number of unpaired
electrons (Hund's principle of maximum multiplicity) and also accounts for the "anom-
alous" behavior of Cu and Cr. It also tends to make it more difficult to remove the
electron from the nitrogen atom than would otherwise be the case. As a result of this
stabilization, the ionization energy of nitrogen is greater than that of oxygen (see
Fig. 2.19).

**Ionization**
The electrons which are lost on ionization are those that lie at the higher energy levels
and therefore require the least energy to remove. One would expect, therefore, that
electrons would be lost on ionization in the reverse order in which they were filled
(see "Aufbau Principle"). There is a tendency for this to be true. However, there are
some very important exceptions, notably in the transition elements, which are responsi-
ble for the characteristic chemistry of these elements. In general, transition elements
react as follows:

\[ 1s^2 2s^2 2p^6 3s^2 3p^6 3d^4 4s^2 \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 3d^n \]

This is true not only for the first transition series, but for the heavier metals also; the
ns\(^2 \) electrons are lost before the \( n - 1d \) or \( n - 2f \) electrons. This gives a common \( n + 2 \)
oxidation state to transition metals, although in many cases there is a more stable
higher or lower oxidation state.

This phenomenon is puzzling because it contradicts simple energetics:
If the 4s level is lower and fills first, then its electrons should be more stable and be
ionized last, shouldn't they? One might ask if there is a possible reversal of energy
levels within the transition series. If the relative energies of the 3d and 4s levels are
examined, it is found that they lie very close together and that the energy of the 3d level
decreases with increasing atomic number. This is often advanced as the explanation
for the electronic configuration for Cu. If the 3d level has dropped below the 4s at
atomic number 29, then the ground state must be 3d\(^{10} \) 4s\(^{1} \). Nevertheless, this can
have no effect on the phenomena we are investigating since we are inquiring as to the
difference in configuration between ground state of the neutral atom and the ionic states
of the same element. Since all of the transition metals in the first series (with exception
of Cr and Cu) have a 3d\(^{4} \) 4s\(^{1} \) ground state for the neutral atom and a stable 3d\(^{4} \) 4s\(^{0} \) state
for the dipositive ion, the source of our problem must be sought in the difference
between atom and ion, not in trends along the series. However, the trend of the 3d
orbitals across the series can give us a clue as to what is happening. It appears that as
the atomic number goes up, and hence as \( Z^+ \) increases, the energy levels approach more
closely that in the hydrogen atom, namely, all levels having the same principle quantum
number being degenerate and lying below those of the next quantum number. Now in
the ion, the effective nuclear charge increases markedly because of the net ionic charge