CHAPTER 11

Many-Electron Atoms

11.1 THE HARTREE-FOCK SELF-CONSISTENT-FIELD METHOD

For hydrogen the exact wave function is known. For helium and lithium, very accurate wave functions have been calculated by including interelectronic distances in the variation functions. For atoms of higher atomic number, the best approach to finding a good wave function lies in first calculating an approximate wave function using the Hartree–Fock procedure, which we shall outline in this section. The Hartree–Fock method is the basis for the use of atomic and molecular orbitals in many-electron systems.

The Hamiltonian operator for an $n$-electron atom is

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{n} \nabla_i^2 - \sum_{i=1}^{n} \frac{Ze^2}{r_i} + \sum_{i<j}^{n-1} \frac{e^2}{r_{ij}}$$  \hspace{1cm} (11.1)

where an infinitely heavy point nucleus was assumed (Section 6.6). The first sum in (11.1) contains the kinetic-energy operators for the $n$ electrons. The second sum is the potential energy (6.58) for the attractions between the electrons and the nucleus of charge $Ze^2$; for a neutral atom, $Z = n$. The last sum is the potential energy of the inter-electronic repulsion; the restriction $j > i$ avoids counting the same interelectronic repulsion twice and avoids terms like $e^2/r_{ii}$. The Hamiltonian (11.1) is incomplete, because it omits spin–orbit and other interactions. The omitted terms are usually small and will be considered in Sections 11.6 and 11.7.

The Hartree SCF Method. Because of the interelectronic repulsion terms $e^2/r_{ij}$, the Schrödinger equation for an atom is not separable. Recalling the perturbation treatment of helium (Section 9.3), we can obtain a zeroth-order wave function by neglecting these repulsions. The Schrödinger equation would then separate into $n$ one-electron hydrogenlike equations: The zeroth-order wave function would be a product of $n$ hydrogenlike (one-electron) orbitals:

$$\psi^{(0)} = f_1(r_1, \theta_1, \phi_1)f_2(r_2, \theta_2, \phi_2) \cdots f_n(r_n, \theta_n, \phi_n)$$  \hspace{1cm} (11.2)

where the hydrogenlike orbitals are

$$f = R_n(r)Y_l^m(\theta, \phi)$$  \hspace{1cm} (11.3)

For the ground state of the atom, we would feed two electrons with opposite spin into each of the lowest orbitals, in accord with the Pauli exclusion principle, giving the ground-state configuration. Although the approximate wave function (11.2) is qualitatively useful, it is gravely lacking in quantitative accuracy. For one thing, all the orbitals
use the full nuclear charge $Z$. Recalling our variational treatments of helium and lithium, we know we can get a better approximation by using different effective atomic numbers for the different orbitals to account for screening of electrons. The use of effective atomic numbers gives considerable improvement, but we are still far from having an accurate wave function. The next step is to use a variation function that has the same form as (11.2) but is not restricted to hydrogen-like or any other particular form of orbitals. Thus we take

$$\phi = g_1(r_1, \theta_1, \phi_1)g_2(r_2, \theta_2, \phi_2) \cdots g_n(r_n, \theta_n, \phi_n)$$  (11.4)

and we look for the functions $g_1, g_2, \ldots, g_n$, that minimize the variational integral $\int \phi^* \hat{H} \phi \, dv / \int \phi^* \phi \, dv$. Our task is harder than in previous variational calculations, where we guessed a trial function that included some parameters and then varied the parameters. In (11.4) we must vary the functions $g_i$. [After we found the best possible functions $g_i$, Eq. (11.4) will still be only an approximate wave function. The many-electron Schrödinger equation is not separable, so the true wave function cannot be written as the product of $n$ one-electron functions.]

To simplify matters somewhat, we approximate the best possible atomic orbitals with orbitals that are the product of a radial factor and a spherical harmonic:

$$g_i = h_i(r_i)Y_{\ell_i}^{\ell_0} ( \theta_i, \phi_i)$$  (11.5)

This approximation is generally made in atomic calculations.

The procedure for calculating the $g_i$'s was introduced by Hartree in 1928 and is called the Hartree self-consistent-field (SCF) method. Hartree arrived at the SCF procedure by intuitive physical arguments. The proof that Hartree's procedure gives the best possible variation function of the form (11.4) was given by Slater and by Fock in 1930. [For the proof and a review of the SCF method, see S. M. Blinder, Am. J. Phys., 33, 431 (1965).]

Hartree's procedure is as follows. We first guess a product wave function

$$\phi_0 = s_1(r_1, \theta_1, \phi_1)s_2(r_2, \theta_2, \phi_2) \cdots s_n(r_n, \theta_n, \phi_n)$$  (11.6)

where each $s_i$ is a normalized function of $r_i$ multiplied by a spherical harmonic. A reasonable guess for $s_0$ would be a product of hydrogen-like orbitals with effective atomic numbers. For the function (11.6), the probability density of electron $i$ is $|s_i|^2$. We now focus attention on electron 1 and regard electrons 2, 3, \ldots, $n$ as being smeared out to form a static distribution of electric charge through which electron 1 moves. We are thus averaging out the instantaneous interactions between electron 1 and the other electrons. The potential energy of interaction between point charges $Q_1$ and $Q_2$ is $V_{12} = Q_1 Q_2 / r_{12} = Q_1 Q_2 / 4\pi \epsilon_0 r_{12}$ [Eqs. (6.58) and (1.38)]. We now take $Q_1$ and smear it out into a continuous charge distribution such that $\rho_2$ is the charge density, the charge per unit volume. The infinitesimal charge in the infinitesimal volume $dV_2$ is $\rho_2 \, dv_2$, and summing up the interactions between $Q_1$ and the infinitesimal elements of charge, we have

$$V_{12} = \frac{Q_1}{4\pi \varepsilon_0} \int \frac{\rho_2}{r_{12}} \, dv_2$$

where $\varepsilon_0 = \varepsilon^2 / 4\pi \varepsilon_0$. Adding in the interactions with the other electrons, we have

$$V_{12} + V_{13} + \cdots + V_{1n} = \sum_{i=2}^n \frac{Q_1}{r_{ij}} \, dv_i$$

The potential energy of interaction between electron 1 and the other electrons and the nucleus is then

$$V_{1}(r_1, \theta_1, \phi_1) = \sum_{i=2}^n \frac{|s_i|^2}{r_{ij}} \, dv_i - \frac{Ze^2}{r_1}$$  (11.7)

Now we make a further approximation beyond assuming the wave function to be a product of one-electron orbitals. We assume that the effective potential acting on an electron in an atom can be adequately approximated by a function of $r$ only. This central-field approximation can be shown to be generally accurate. We therefore average $V_{1}(r_1, \theta_1, \phi_1)$ over the angles to arrive at a potential that depends only on $r_1$:

$$V_{1}(r_1) = \frac{\int_0^\infty \int_0^\pi V_{1}(r_1, \theta_1, \phi_1) \sin \theta \, d\theta \, d\phi}{\int_0^\infty \int_0^\pi \sin \theta \, d\theta \, d\phi}$$  (11.8)

We now use $V_{1}(r_1)$ as the potential energy in a one-electron Schrödinger equation,

$$\left[ -\frac{\hbar^2}{2m_e} \nabla_1^2 + V_{1}(r_1) \right] \chi_1(1) = 1 \chi_1(1)$$  (11.9)

and solve for $\chi_1(1)$, which will be an improved orbital for electron 1. In (11.9), $e_1$ is the energy of the orbital of electron 1 at this stage of the approximation. Since the potential energy in (11.9) is spherically symmetric, the angular factor in $e_1(1)$ is a spherical harmonic involving quantum numbers $l_1$ and $m_1$. We then go on to find the quantum numbers $n_1$ as $n_1 = l_1 + 1 + k$, where $k = 0, 1, 2, \ldots$. We thus have $1s, 2s, 2p, \ldots$ on the orbitals of orbital energy $e_1$ increasing with $n$ just as in hydrogen-like atoms, and the number of interior radial nodes ($n_1 - l_1 - 1$) is the same as in hydrogen-like atoms (Section 6.9). However, since $V_{1}(r_1)$ is not a simple Coulomb potential, the radial factor $R_{1}(r_1)$ is not a hydrogen-like function. Of the set of solutions $R_{1}(r_1)$, we take the one that corresponds to the orbital we are improving. For example, if electron 1 is a 1s electron in the beryllium $1s^22s^2$ configuration, then $V_{1}(r_1)$ is calculated from the guessed orbitals of one 1s electron and two 2s electrons, and we use the radial solution of (11.9) with $k = 0$ to find an improved $1s$ orbital.
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We now go to electron 2 and regard it as moving in a charge cloud of density

$$-e^2 \left[ |x_e(1)|^2 + |x_e(3)|^2 + |x_e(4)|^2 + \cdots + |x_e(n)|^2 \right]$$

due to the other electrons. We calculate an effective potential energy $V_e(x_2)$ and solve a one-electron Schrödinger equation for electron 2 to get an improved orbital $\mathcal{S}_e(2)$. We continue this process until we have a set of improved orbitals for all $n$ electrons. Then we go back to electron 1 and repeat the process. We continue to calculate improved orbitals until there is no further change from one iteration to the next. The final set of orbitals gives the Hartree self-consistent-field wave function.

How do we get the energy of the atom in the SCF approximation? It seems natural to take the sum of the orbital energies of the electrons, $e_1 + e_2 + \cdots + e_n$, but this is wrong. In calculating the orbital energy $e_i$, we iteratively solved the one-electron Schrödinger equation (11.9). The potential energy in (11.9) includes, in an average way, the energy of the repulsions between electrons 1 and 2, 1 and 3, ..., 1 and $n$, and between electrons 2 and 1, 2 and 3, ..., 2 and $n$. When we solve for $e_2$, we have an equation whose potential energy includes repulsions between electrons 3 and 1, 3 and 2, ..., 3 and $n$. If we take $\sum_i e_i$, we will count each interelectronic repulsion twice. To correctly obtain the total energy $E$ of the atom, we must take

$$E = \sum_{i=1}^{n} e_i - \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \int \frac{e^{-2|\mathbf{r}_i - \mathbf{r}_j|}}{\mathbf{r}_{ij}} \mathbf{v}_i \mathbf{v}_j d\mathbf{v}_i d\mathbf{v}_j$$

$$E = \sum_{i=1}^{n} e_i - \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} J_{ij}$$

(11.10)

where the average repulsions of the electrons in the Hartree orbitals of (11.4) were subtracted from the sum of the orbital energies, and where the notation $J_{ij}$ was used for Coulomb integrals [Eq. (9.100)].

The set of orbitals belonging to a given principal quantum number $n$ constitutes a shell. The $n = 1, 2, 3, \ldots$ shells are the $K, L, M, \ldots$ shells, respectively. The orbitals belonging to a given $n$ and a given $l$ constitute a subshell. Consider the sum of the Hartree probability densities for the electrons in a filled subshell. Using (11.5), we have

$$2 \sum_{m=-l}^{l} |h_n(r)|^2 |Y_l^m(\theta, \phi)|^2 = 2|h_n(r)|^2 \sum_{m=-l}^{l} |Y_l^m(\theta, \phi)|^2$$

(11.11)

where the factor 2 comes from the pair of electrons in each orbital. The spherical-harmonics addition theorem (Merzbacher, Section 9.7) shows that the sum on the right side of (11.11) equals $(2l + 1)/4\pi$. Hence the sum of the probability densities is $[(2l + 1)/2\pi]|h_n(r)|^2$, which is independent of the angles. A closed subshell gives a spherically symmetric probability density, a result called Unzöld’s theorem. For a half-filled subshell, the factor 2 is omitted from (11.11), and here also we get a spherically symmetric probability density.

The Hartree–Fock SCF Method. The alert reader may have realized that there is something fundamentally wrong with the Hartree product wave function (11.4). Although we have paid some attention to spin and the Pauli principle by putting no more than two electrons in each spatial orbital, any approximation to the true wave function should include spin explicitly and should be antisymmetric to interchange of electrons (Chapter 10). Hence, instead of the spatial orbitals, we must use spin-orbitals and must take an antisymmetric linear combination of products of spin-orbitals. This was pointed out by Fock (and by Slater) in 1930, and an SCF calculation that uses antisymmetrized spin-orbitals is called a Hartree–Fock calculation. We have seen that a Slater determinant of spin-orbitals provides the proper antisymmetry. For example, to carry out a Hartree–Fock calculation for the lithium ground state, we start with the function (10.56), where $f$ and $g$ are guesses for the 1s and 2s orbitals. We then carry out the SCF iterative process until we get no further improvement in $f$ and $g$. This gives the lithium ground-state Hartree–Fock wave function.

The differential equations for finding the Hartree–Fock orbitals have the same general form as (11.9):

$$\mathbf{H}_i = e_i \mathbf{u}_i, \quad i = 1, 2, \ldots, n$$

(11.12)

where $u_i$ is the ith spin-orbital, the operator $\mathbf{H}$, called the Fock (or Hartree–Fock) operator, is the effective Hartree–Fock Hamiltonian, and the eigenvalue $e_i$ is the orbital energy of spin-orbital $i$. However, the Hartree–Fock operator $\mathbf{H}$ has extra terms as compared with the effective Hartree Hamiltonian given by the bracketed terms in (11.9). The Hartree–Fock expression for the total energy of the atom involves exchange integrals $K_{ij}$ in addition to the Coulomb integrals that occur in the Hartree expression (11.10). See Section 13.16. [Actually, Eq. (11.12) applies only when the Hartree–Fock wave function can be written as a single Slater determinant, as it can for closed-subshell atoms and atoms with only one electron outside closed subshells. When the Hartree–Fock wave function contains more than one Slater determinant, the Hartree–Fock equations are more complicated than (11.12).]

The orbital energy $e_i$ in the Hartree–Fock equations (11.12) can be shown to be a good approximation to the negative of the energy needed to ionize a closed-subshell atom by removing an electron from spin-orbital $i$ (Koopmans’ theorem; Section 15.6).

Originally, Hartree–Fock atomic calculations were done by using numerical methods to solve the Hartree–Fock differential equations (11.12), and the resulting orbitals were given as tables of the radial functions for various values of $r$. [The Numerov method (Sections 4.4 and 6.9) can be used to solve the radial Hartree–Fock equations for the radial factors in the Hartree–Fock orbitals; the angular factors are spherical harmonics. See D. R. Hartree, The Calculation of Atomic Structures, Wiley, 1957; C. Froese Fischer, The Hartree–Fock Method for Atoms, Wiley, 1977.]

In 1951, Rothena proposed representing the Hartree–Fock orbitals as linear combinations of a complete set of known functions, called basis functions. Thus for lithium we would write the Hartree–Fock 1s and 2s spatial orbitals as

$$f = \sum_i b_i \chi_i, \quad g = \sum_i c_i \chi_i$$

(11.13)

where the $\chi_i’s$ are some complete set of functions, and where the $b_i’s$ and $c_i’s$ are expansion coefficients that are found by the SCF iterative procedure. Since the $\chi_i$ (chi) functions form a complete set, these expansions are valid. The Rothena expansion procedure allows one to find the Hartree–Fock wave function using matrix algebra.
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(see Section 13.16 for details). The Roothaan procedure is readily implemented on a computer and is often used to find atomic Hartree–Fock wave functions and nearly always used to find molecular Hartree–Fock wave functions.

A commonly used set of basis functions for atomic Hartree–Fock calculations is the set of Slater-type orbitals (STOs) whose normalized form is

\[
\frac{(2\xi/a_0)^{n+1/2}}{[2n]^{1/2}} \cdot r^{-n-1} e^{-r/a_0} Y^m(\theta, \phi)
\]

The set of all such functions with \( n, l, \) and \( m \) being integers but with \( \xi \) having all possible positive values forms a complete set. The parameter \( \xi \) is called the orbital exponent. To get a truly accurate representation of the Hartree–Fock orbitals, we would have to include an infinite number of Slater orbitals in the expansions. In practice, one can get very accurate results by using only a few judiciously chosen Slater orbitals. (Another possibility is to use Gaussian-type basis functions; see Section 15.4.)

Clementi and Roetti did Hartree–Fock calculations for the ground state and some excited states of the first 54 elements of the periodic table [E. Clementi and C. Roetti, At. Data Nucl. Data Tables, 14, 177 (1974); Bunge and co-workers have recalculated these wave functions; C. F. Bunge et al., At. Data Nucl. Data Tables, 53, 113 (1993); Phys. Rev. A, 46, 3691 (1992); these wave functions can be found at ftp://ccl.nssc.gov/pub/chemistry/data/atomic-RHF-wavefunctions/tables]. For example, consider the Hartree–Fock ground-state wave function of helium, which has the form [see Eq. (10.41)]

\[
f(1)f(2) \cdot 2^{-1/2}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]
\]

Clementi and Roetti expressed the 1s orbital function \( f \) as the following combination of five 1s Slater-type orbitals:

\[
f = \pi^{-1/2} \sum_{l=1}^{5} c_l \left( \frac{\xi_l}{a_0} \right)^{3/2} e^{-r/a_0}
\]

where the expansion coefficients \( c_l \) are \( c_1 = 0.76838, c_2 = 0.22346, c_3 = 0.04082, c_4 = -0.00994, c_5 = 0.00230 \) and where the orbital exponents \( \xi_l \) are \( \xi_1 = 1.41714, \xi_2 = 2.37862, \xi_3 = 4.39628, \xi_4 = 6.52699, \xi_5 = 7.94252. \) [Note that the largest term in the expansion has an orbital exponent that is similar to the orbital exponent (9.65) for the simple trial function (9.58).] The Hartree–Fock energy is \(-77.9 \) eV, as compared with the true nonrelativistic energy, \(-79.0 \) eV. The 1s orbital energy corresponding to \( f \) was found to be \(-25.0 \) eV, as compared with the experimental helium ionization energy of 24.6 eV.

For the lithium ground state, Clementi and Roetti used a basis set consisting of two 1s STOs (with different orbital exponents) and four 2s STOs (with different orbital exponents). The lithium 1s and 2s Hartree–Fock orbitals were each expressed as a linear combination of all six of these basis functions. The Hartree–Fock energy is \(-202.3 \) eV, as compared with the true energy \(-203.5 \) eV.

Electron densities calculated from Hartree–Fock wave functions are quite accurate. Figure 11.1 compares the radial distribution function of argon (found by integrating the electron density over the angles \( \theta \) and \( \phi \) and multiplying the result by \( r^2 \)) calculated by the Hartree–Fock method with the experimental radial distribution function found by electron diffraction. (Recall from Section 6.6 that the radial distribution function is proportional to the probability of finding an electron in a thin spherical shell at a distance \( r \) from the nucleus.) Note the electronic shell structure in Fig. 11.1. The high nuclear charge in \( ^{36}\text{Ar} \) makes the average distance of the 1s electrons from the nucleus far less than in H or He. Thus there is only a moderate increase in atomic size as we go down a given group in the periodic table. Calculations show that the radius of a sphere containing 98% of the Hartree–Fock electron probability density gives an atomic radius in good agreement with the empirically determined van der Waals radius. [See C. W. Kammer and D. R. Whitten, J. Chem. Phys., 56, 4419 (1972).]

Although the radial distribution function of an atom shows the shell structure, the electron probability density integrated over the angles and plotted versus \( r \) does not oscillate. Rather, for ground-state atoms this probability density is a maximum at the nucleus (because of the 1s electrons) and continually decreases as \( r \) increases. Similarly, in molecules the maxima in electron probability density usually occur at the nuclei; see, for example, Fig. 13.7. [For further discussion, see H. Weinstein, P. Politzer, and S. Srebnak, Theor. Chim. Acta, 38, 159 (1975).]

Accurate representation of a many-electron atomic orbital (AO) requires a linear combination of several Slater-type orbitals. For rough calculations, it is convenient to have simple approximations for AO's. We might use hydrogenlike orbitals with effective nuclear charges, but Slater suggested an even simpler method: to approximate an AO by a single function of the form (11.14) with the orbital exponent \( \xi \) taken as

\[
\xi = (Z - s)/n
\]

where \( Z \) is the atomic number, \( n \) is the orbital's principal quantum number, and \( s \) is a screening constant calculated by a set of rules (see Problem 15.79). A Slater orbital replaces the polynomial in \( r \) in a hydrogenlike orbital with a single power of \( r \). Hence a single Slater orbital does not have the proper number of radial nodes and does not represent well the inner part of an orbital.

A great deal of computation is required to perform a Hartree–Fock SCF calculation for a many-electron atom. Hartree did several SCF calculations in the 1930s, when
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electronic computers were not in existence. Fortunately, Hartree’s father, a retired
engineer, enjoyed numerical computation as a hobby and helped his son. Nowadays
computers have replaced Hartree’s father.

ORBITALS AND THE PERIODIC TABLE

The orbital concept and the Pauli exclusion principle allow us to understand the peri-
odic table of the elements. An orbital is a one-electron spatial wave function. We have
used orbitals to obtain approximate wave functions for many-electron atoms, writing the
wave function as a Slater determinant of one-electron spin-orbitals. In the crudest
approximation, we neglect all interelectronic repulsions and obtain hydrogenlike
orbitals. The best possible orbitals are the Hartree–Fock SCF functions. We build up
the periodic table by feeding electrons into these orbitals, each of which can hold a pair
of electrons with opposite spin.

gies for the atoms of the periodic table by replacing the complicated expression for the
Hartree–Fock potential energy in the Hartree–Fock radial equations by a much sim-
pler function obtained from the Thomas–Fermi–Dirac method, which uses ideas of sta-
tistical mechanics to get approximations to the effective potential-energy function for
an electron and the electron-density function in an atom (Bethe and Jackiw, Chapter
5). Figure 11.2 shows Latter’s resulting orbital energies for neutral ground-state atoms.
These AO energies are in pretty good agreement with both Hartree–Fock and experi-
mentally found orbital energies (see J. C. Slater, Quantum Theory of Matter, 2nd ed.,

Orbital energies change with changing atomic number Z. As Z increases, the
orbital energies decrease because of the increased attraction between the nucleus and
the electrons. This decrease is most rapid for the inner orbitals, which are less well-
shielded from the nucleus.

For Z > 1, orbitals with the same value of n but different l have different ener-
gies. For example, for the n = 3 orbital energies, we have $e_{3s} < e_{3p} < e_{3d}$ for Z > 1.
The splitting of these levels, which are degenerate in the hydrogen atom, arises from
the interelectronic repulsions. (Recall the perturbation treatment of helium in Section
9.7.) In the limit Z → ∞, orbitals with the same value of n are again degenerate,
because the interelectronic repulsions become insignificant in comparison with the
electron–nucleus attractions.

The relative positions of certain orbitals change with changing Z. Thus in hydro-
gen the 3d orbital lies below the 4s orbital, but for Z in the range from 7 through 20 the
4s is below the 3d. For large values of Z, the 3d is again lower. At Z = 19, the 4s is lower;
therefore $\Psi_{K}$ has the ground-state configuration 1s$^{2}$2s$^{2}$2p$^{6}$3s$^{2}$3p$^{6}$4s. Recall that s orbitals
are more penetrating than p or d orbitals; this allows the 4s orbital to lie below the 3d
orbital for some values of Z. Note the sudden drop in the 3d energy, which starts at Z =
21, when filling of the 3d orbital begins. The electrons of the 3d orbital do not shield
each other very well; hence the sudden drop in 3d energy. Similar drops occur for other
orbitals.

To help explain the observed electron configurations of the transition elements
and their ions, Vanquickenborne and co-workers calculated Hartree–Fock 3d and 4s
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orbital energies for atoms and ions for \( Z \leq 1 \) to \( Z = 29 \) [L. G. Vanquickenborne, K. Pietrloot, and D. Devoghel, Inorg. Chem., 28, 1805 (1989); J. Chem. Educ., 71, 469 (1994); see also M. P. McRae and E. R. Scerri, J. Chem. Educ., 73, 498 (1996)]. One complication is that a given electron configuration may give rise to many states. [For example, recall the several states of the He 1s, 2s and 1s, 2p configurations (Sections 9.7 and 10.4).] To avoid this complication, Vanquickenborne and co-workers calculated Hartree–Fock orbitals and orbital energies by minimizing the average energy \( E_{av} \) of the states of a given electron configuration, instead of by minimizing the energy of each individual state of the configuration. The average orbitals obtained differ only slightly from the true Hartree–Fock orbitals for a given state of the configuration.

For each of the atoms H to K, Vanquickenborne and co-workers calculated the 3d average orbital energy \( E_{3d} \) for the electron configuration in which one electron is removed from the highest-occupied orbital of the ground-state electron configuration and put in the 3d orbital; they calculated \( E_{3d} \) for these atoms in a similar manner. In agreement with Fig. 11.2, they found \( E_{3d} < E_{4p} \) for atomic numbers \( Z < 6 \) and \( E_{3d} < E_{4s} \) for \( Z = 7 \) to 19 for neutral atoms.

For discussion of the transition elements with \( Z \) from 21 to 29, Fig. 11.2 is inadequate because it gives only a single value for \( E_{3d} \) for each element, whereas \( E_{3d} \) and \( E_{4p} \) for a given atom depend on which orbitals are occupied. This is because the electric field experienced by an electron depends on which orbitals are occupied. Vanquickenborne and co-workers calculated \( E_{3d} \) and \( E_{4p} \) for each of the configurations \( \ldots 3d^44s^2 \ldots \), \( \ldots 3d^14s^3 \ldots \), and \( \ldots 3d^24s^2 \ldots \) and found \( E_{3d} < E_{4p} \) in each of these configurations of the neutral atoms and the \( +1 \) and \( +2 \) ions of the transition elements \( \text{Zn} \) through \( \text{Cu} \) (which is shown in Fig. 11.2).

Since 3d lies below 4s for \( Z \) above 20, one might wonder why the ground-state configuration of, say, \( \text{Sc} \) is \( \ldots 3d^44s^2 \ldots \) rather than \( \ldots 3d^5 \ldots \). Although \( E_{3d} < E_{4p} \) for each of these configurations, this does not mean that the \( \ldots 3d^5 \ldots \) configuration has the lower sum of orbital energies. When an electron is moved from 4s into 3d, \( E_{3d} \) and \( E_{4p} \) are increased. An orbital energy is found by solving a one-electron Hartree–Fock equation that contains potential-energy terms for the average repulsions between the electron in orbital \( i \) and the other electrons in the atom, so \( e_i \) depends on the values of these repulsions and hence on which orbitals are occupied. For the first series of transition elements, the 4s orbital is much larger than the 3d orbital. For example, Vanquickenborne and co-workers found the following \((r) \) values in Sc: \( r_{3d} = 0.89 \) A and \( r_{4s} = 2.09 \) A for \( \ldots 3d^44s^2 \ldots \); \( r_{3d} = 1.11 \) A and \( r_{4s} = 2.29 \) A for \( \ldots 3d^44s^1 \ldots \). Because of this size difference, repulsions involving 4s electrons are substantially less than repulsions involving 3d electrons, and we have \( (4s,4s) < (4s,3d) < (3d,4d) \), where \( (4s,3d) \) denotes the average repulsion between an electron distributed over the 3d orbitals and an electron in a 4s orbital. (These repulsions are expressed in terms of Coulomb and exchange integrals.) When an electron is moved from 4s into 3d, the increase in inter-electronic repulsion that is a consequence of the preceding inequalities raises the orbital energies \( E_{3d} \) and \( E_{4p} \). For example, for \( \text{Zn} \), the \( \ldots 3d^44s^2 \ldots \) configuration has \( E_{3d} = -9.35 \) eV and \( E_{4p} = -5.72 \) eV, whereas the \( \ldots 3d^44s^1 \ldots \) configuration has \( E_{3d} = -5.23 \) eV and \( E_{4p} = -5.06 \) eV. For the \( \ldots 3d^24s^2 \ldots \) configuration, the sum of valence-electron orbital energies is \( 9.35 \) eV + \( Z(-5.72) \) eV = \( -20.79 \) eV, whereas for the \( \ldots 3d^34s^1 \ldots \) configuration, this sum is \( 2(-5.23) \) eV = \( -10.46 \) eV. Thus, despite the fact that \( E_{3d} < E_{4p} \) for each configuration, transfer of an electron from 4s to 3d raises the sum of valence-electron orbital energies in Sc. [As we saw in Eq. (11.10) for the Hartree–Fock method, and will see in Section 13.16 for the Hartree–Fock–Fock method, the Hartree and Hartree–Fock expressions for the energy of an atom contain terms in addition to the sum of orbital energies, so we must look at more than the sum of orbital energies to see which configuration is most stable.]

For the +2 ions of the transition metals, the reduction in screening makes the valence 3d and 4s electrons feel a larger effective nuclear charge \( Z_{eff} \) than in the neutral atoms. By analogy to the H–atom equation \( E = -(Z^2/n^2)(e^2/2a) \) (Eq. (6.94)), the orbital energies \( E_{3d} \) and \( E_{4p} \) are each roughly proportional to \( Z_{eff}^2 \) and the energy difference \( E_{4p} - E_{3d} \) is roughly proportional to \( Z_{eff} \). The difference \( E_{4p} - E_{3d} \) is thus much larger in the transition-metal ions than in the neutral atoms, the increase in valence-electron repulsion is no longer enough to make the 4s to 3d transfer energetically unfavorable, and the +2 ions have ground-state configurations with no 4s electrons.

Figure 11.2 shows that the separation between ns and np orbitals is much less than that between np and nd orbitals, giving the familiar ns²np⁶ stable octet.

The orbital concept is the basis for most qualitative discussions of the chemistry of atoms and molecules. The use of orbitals, however, is an approximation. To reach the true wave function, we must go beyond a Slater determinant of spin-orbitals. Two review articles on atomic orbitals are R. S. Berry, J. Chem. Educ., 43, 283 (1966) and I. Cohen and T. Bustard, J. Chem. Educ., 43, 187 (1966).

### 11.3 ELECTRON CORRELATION

Energies calculated by the Hartree–Fock method are typically in error by about \( \frac{1}{2} \)% for light atoms. On an absolute basis this is not much, but for the chemist it is too large. For example, the total energy of the carbon atom is about \(-1000\) eV, and \( \frac{1}{2} \)% of this is \( 5 \) eV. Chemical single-bond energies run about \( 5 \) eV. Calculating a bond energy by taking the difference between Hartree–Fock molecular and atomic energies, which are in error by several electronvolts for light atoms, is an unreliable procedure. We must seek a way to improve Hartree–Fock wave functions and energies. (Our discussion will apply to molecules as well as atoms.)

A Hartree–Fock SCF wave function takes into account the interactions between electrons only in an average way. Actually, we must consider the instantaneous interactions between electrons. Since electrons repel each other, they tend to keep out of each other’s way. For example, in helium, if one electron is close to the nucleus at a given instant, it is energetically more favorable for the other electron to be far from the nucleus at that instant. One sometimes speaks of a Coulomb hole surrounding each electron in an atom. This is a region in which the probability of finding another electron is small. The motions of electrons are correlated with each other, and we speak of **electron correlation**. We must find a way to introduce the instantaneous electron correlation into the wave function.

Actually, a Hartree–Fock wave function does have some instantaneous electron correlation. A Hartree–Fock function satisfies the antisymmetry requirement of the Pauli principle. Therefore [Eq. (10.20)], it vanishes when two electrons with the same
spin have the same spatial coordinates. For a Hartree–Fock function, there is little probability of finding electrons of the same spin in the same region of space, so a Hartree–Fock function has some correlation of the motions of electrons with the same spin. This makes the Hartree–Fock energy lower than the Hartree energy. One sometimes refers to a Fermi hole around each electron in a Hartree–Fock wave function, thereby indicating a region in which the probability of finding another electron with the same spin is small.

The correlation energy \( E_{\text{corr}} \) is the difference between the exact nonrelativistic energy \( E_{\text{Bohr}} \) and the (nonrelativistic) Hartree–Fock energy \( E_{\text{HF}} \):

\[
E_{\text{corr}} = E_{\text{Bohr}} - E_{\text{HF}}
\]  
(11.16)

where \( E_{\text{Bohr}} \) and \( E_{\text{HF}} \) should both either include corrections for nuclear motion or omit these corrections. For the He atom, the (nonrelativistic) Hartree–Fock energy uncorrected for nuclear motion is \(-2.86168(\hbar^2/a_0)\) [E. Clementi and C. Roetti, At. Data Nucl. Data Tables, 14, 177 (1974)] and variational calculations (Section 9.4) give the exact nonrelativistic energy uncorrected for nuclear motion as \(-2.90372(\hbar^2/a_0)\). Therefore, \( E_{\text{corr}} = -2.90372(\hbar^2/a_0) + 2.86168(\hbar^2/a_0) = -0.04204(\hbar^2/a_0) = -1.14 \text{ eV} \). For atoms and molecules where \( E_{\text{Bohr}} \) cannot be accurately calculated, one combines the experimental energy with estimates for relativistic and nuclear-motion corrections to get \( E_{\text{Bohr}} \). For neutral atoms, \( E_{\text{corr}} \) increases roughly linearly with the number of electrons: \( E_{\text{corr}} = -0.01701(\hbar^2/a_0) \) [E. Clementi and G. Corongiu, Int. J. Quantum Chem., 62, 571 (1997)]. The percentage \( (E_{\text{corr}}/E_{\text{Bohr}}) \times 100\% \) decreases with increasing atomic number. Some values are 6.5% for Li, 0.4% for Na, 0.2% for K.

We have already indicated two of the ways in which we may provide instantaneous electron correlation. One method is to introduce the interelectronic distances \( r_{ij} \) into the wave function (Section 9.4). This method is only practicable for systems with a few electrons.

Another method is configuration interaction. We found (Sections 9.3 and 10.4) the zero-order wave function for the helium \( 1s^2 \) ground state to be \( 1s(1s)(2\alpha 1\beta)(2\alpha - 2\beta)(1\alpha 2\beta)/\sqrt{2} \). We remarked that first- and higher-order corrections to the wave function will mix in contributions from excited configurations, producing configuration interaction (CI), also called configuration mixing (CM).

The most common way to do a configuration-interaction calculation on an atom or molecule uses the variation method. One starts by choosing a basis set of one-electron functions \( \chi \). In principle, this basis set should be complete. In practice, one is limited to a basis set of finite size. One hopes that a good choice of basis functions will give a good approximation to a complete set. For atomic calculations, STOs [Eq. (11.14)] are often chosen as the basis functions. The SCF atomic (or molecular) orbitals \( \phi \) are written as linear combinations of the basis-set members [see (11.13)], and the Hartree–Fock equations (11.12) are solved to give the coefficients in these linear combinations. The number of atomic (or molecular) orbitals obtained equals the number of basis functions used. The lowest-energy orbitals are the occupied orbitals for the ground state. The remaining unoccupied orbitals are called virtual orbitals.

Using the set of occupied and virtual spin-orbitals, one can form antisymmetric many-electron functions that have different orbital occupancies. For example, for helium, one can form functions that correspond to the electron configurations \( 1s^2, 1s^2, 1s2p, 2s^2, 2s2p, 2p^2, 2p^4, 1s3s, \) and so on. Moreover, more than one function can correspond to a given electron configuration. Recall the functions (10.27) to (10.30) corresponding to the helium \( 1s2s \) configuration. Each such many-electron function \( \Phi \) is a Slater determinant or a linear combination of a few Slater determinants. Use of more than one Slater determinant is required for certain open-shell functions such as (10.44) and (10.45). Each \( \Phi \) is called a configuration state function or a configuration function or simply a "configuration." (This last name is unfortunate, since it leads to confusion between an electron configuration such as \( 1s^2 \) and a configuration function such as \( |1s1s\rangle \).

As we saw in perturbation theory, the true atomic (or molecular) wave function \( \psi \) contains contributions from configurations other than the one that makes the main contribution to \( \psi \), so we express \( \psi \) as a linear combination of the configuration functions \( \Phi \):

\[
\psi = \sum_i c_i \Phi_i
\]  
(11.17)

We then regard (11.17) as a linear variation function (Section 8.5). Variation of the coefficients \( c_i \) to minimize the variational integral leads to the equation

\[
det(H - \varepsilon_S) = 0
\]  
(11.18)

where \( H_{ij} = \langle \Phi_i | H | \Phi_j \rangle \) and \( S_{ij} = \langle \Phi_i | \Phi_j \rangle \). Commonly, the \( \Phi \) functions are orthonormal, but if they are not orthogonal, they can be made so by the Schmidt method. Only configuration functions whose angular-momentum eigenvalues are the same as those of the state \( \psi \) will contribute to the expansion (11.17); see Section 11.5.

Because the many-electron configuration functions \( \Phi \) are ultimately based on a one-electron basis set that is a complete set, the set of all possible configuration functions is a complete set for the many-electron problem: any antisymmetric many-electron function (including the exact wave function) can be expressed as a linear combination of the \( \Phi \) functions. [For a proof of this, see Szabo and Ostlund, Section 2.2.7.] Therefore, if one starts with a complete one-electron basis set and includes all possible configuration functions, a CI calculation will give the exact atomic (or molecular) wave function \( \psi \) for the state under consideration. In practice, one is limited to a finite, incomplete basis set, rather than an infinite, complete basis set. Moreover, even with a modest-size basis set, the number of possible configuration functions is extremely large, and one usually does not include all possible configuration functions. Part of the "art" of the CI method is choosing those configurations that will contribute the most.

Because it generally takes very many configuration functions to give a truly accurate wave function, configuration-interaction calculations for systems with more than a few electrons are time-consuming, even on supercomputers. Other methods for allowing for electron correlation are discussed in Sections 15.17 to 15.20.

In summary, to do a CI calculation, we choose a one-electron basis set \( \chi \), iteratively solve the Hartree–Fock equations (11.12) to determine one-electron atomic (or molecular) orbitals \( \phi \) as linear combinations of the basis set, form many-electron con-