

## Chapter 3

# Self-Consistent Fields

In this chapter, we consider the problem of determining an approximate wave function for an  $N$ -electron atom. We assume that each electron in the atom moves independently in the nuclear Coulomb field and the average field of the remaining electrons. We approximate the electron-electron interaction by a central potential  $U(r)$ , and we construct an  $N$ -electron wave function for the atomic ground state as an antisymmetric product of one-electron orbitals. Next, we evaluate the energy of the atom in its ground state using this wave function. We invoke the variational principle, requiring that the energy be stationary with respect to small changes in the orbitals with the constraint that the wave function remain normalized, to determine the orbitals. This leads to the Hartree-Fock (HF) equations. Solving the HF equations, we determine the one-electron orbitals, the one-electron energies, and the central potential  $U(r)$  self-consistently.

### 3.1 Two-Electron Systems

Let us start our discussion of many-electron atoms by considering a two-electron (heliumlike) ion with nuclear charge  $Z$ . The two-electron Hamiltonian may be written

$$H(\mathbf{r}_1, \mathbf{r}_2) = h_0(\mathbf{r}_1) + h_0(\mathbf{r}_2) + \frac{1}{r_{12}}, \quad (3.1)$$

with

$$h_0(\mathbf{r}) = -\frac{1}{2}\nabla^2 - \frac{Z}{r}. \quad (3.2)$$

The term  $1/r_{12}$  in Eq.(3.1) is the Coulomb repulsion between the two electrons. The two-electron wave function  $\Psi(\mathbf{r}_1, \mathbf{r}_2)$  satisfies the Schrödinger equation

$$H(\mathbf{r}_1, \mathbf{r}_2)\Psi(\mathbf{r}_1, \mathbf{r}_2) = E\Psi(\mathbf{r}_1, \mathbf{r}_2). \quad (3.3)$$

We seek bound-state solutions to this equation.

The two-electron Hamiltonian is symmetric with respect to the interchange of the coordinates  $\mathbf{r}_1$  and  $\mathbf{r}_2$ . It follows that  $\Psi(\mathbf{r}_2, \mathbf{r}_1)$  is an eigenfunction of  $H$  having the same eigenvalue as  $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ . Moreover, the symmetric and antisymmetric combinations,

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) \pm \Psi(\mathbf{r}_2, \mathbf{r}_1), \quad (3.4)$$

are also eigenfunctions, energy degenerate with  $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ . The symmetric combination in Eq.(3.4) gives the two-particle wave function appropriate to a system of two interacting bosons; for example, an atom consisting of two  $\pi^-$  mesons in a nuclear Coulomb field repelling one another by the Coulomb force. For electrons and other fermions, the antisymmetric combination in Eq.(3.4) is the appropriate choice.

As an approximation to the two-electron Hamiltonian in Eq.(3.1), let us consider the *Independent-Particle* Hamiltonian

$$H_0(\mathbf{r}_1, \mathbf{r}_2) = h(\mathbf{r}_1) + h(\mathbf{r}_2), \quad (3.5)$$

where

$$h(\mathbf{r}) = h_0(\mathbf{r}) + U(r) = -\frac{1}{2}\nabla^2 + V(r). \quad (3.6)$$

The Hamiltonian  $H_0$  describes the independent motion of two particles in a potential  $V(r) = -Z/r + U(r)$ . The potential  $U(r)$  is chosen to approximate the effect of the Coulomb repulsion  $1/r_{12}$ . The full Hamiltonian  $H$  is then given by  $H = H_0 + V(\mathbf{r}_1, \mathbf{r}_2)$ , where

$$V(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{r_{12}} - U(r_1) - U(r_2). \quad (3.7)$$

If we let the orbital  $\psi_a(\mathbf{r})$  represent a solution to the one-electron Schrödinger equation,

$$h(\mathbf{r})\psi_a(\mathbf{r}) = \epsilon_a\psi_a(\mathbf{r}), \quad (3.8)$$

belonging to eigenvalue  $\epsilon_a$ , then the product wave function  $\Psi_{ab}(\mathbf{r}_1, \mathbf{r}_2) = \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)$  is a solution to the two-electron problem,

$$H_0\Psi_{ab}(\mathbf{r}_1, \mathbf{r}_2) = E_{ab}\Psi_{ab}(\mathbf{r}_1, \mathbf{r}_2), \quad (3.9)$$

belonging to energy  $E_{ab}^{(0)} = \epsilon_a + \epsilon_b$ .

The lowest energy two-electron eigenstate of  $H_0$  is a product of the two lowest energy one-electron orbitals. For atomic potentials, these are the  $1s$  orbitals corresponding to the two possible orientations of spin,  $\psi_{1s\mu}(\mathbf{r}) = (P_{1s}(r)/r)Y_{00}(\hat{r})\chi_\mu$ , with  $\mu = \pm 1/2$ . The corresponding antisymmetric product state is

$$\begin{aligned} \Psi_{1s,1s}(\mathbf{r}_1, \mathbf{r}_2) &= \frac{1}{4\pi} \frac{1}{r_1} P_{1s}(r_1) \frac{1}{r_2} P_{1s}(r_2) \\ &\quad \frac{1}{\sqrt{2}}(\chi_{1/2}(1)\chi_{-1/2}(2) - \chi_{-1/2}(1)\chi_{1/2}(2)). \end{aligned} \quad (3.10)$$

The factor  $1/\sqrt{2}$  is introduced here to insure that  $\langle \Psi_{1s1s} | \Psi_{1s1s} \rangle = 1$ . The wave function in Eq.(3.10) is an approximation to the ground-state wave function for a two-electron ion.

The orbital angular momentum vector  $\mathbf{L} = \mathbf{L}_1 + \mathbf{L}_2$  and the spin angular momentum  $\mathbf{S} = \frac{1}{2}\sigma_1 + \frac{1}{2}\sigma_2$  commute with  $H$  as well as  $H_0$ . It follows that the eigenstates of  $H$  and  $H_0$  can also be chosen as eigenstates of  $L^2$ ,  $L_z$ ,  $S^2$  and  $S_z$ . The combination of spin functions in Eq.(3.10),

$$\frac{1}{\sqrt{2}}(\chi_{1/2}(1)\chi_{-1/2}(2) - \chi_{-1/2}(1)\chi_{1/2}(2)), \quad (3.11)$$

is an eigenstate of  $S^2$  and  $S_z$  with eigenvalues 0 and 0, respectively. Similarly, the product of spherical harmonics  $Y_{00}(\hat{r}_1)Y_{00}(\hat{r}_2)$  is an eigenstate of  $L^2$  and  $L_z$  with eigenvalues 0 and 0, respectively.

Let us approximate the electron interaction by simply replacing the charge  $Z$  in the Coulomb potential by an effective charge  $\zeta = Z - \sigma$ . This corresponds to choosing the electron-electron potential  $U(r) = (Z - \zeta)/r$ . The potential  $V(r)$  in the single-particle Hamiltonian is  $V(r) = -\zeta/r$ . The one-electron solutions to Eq.(3.8) are then known analytically; they are

$$P_{1s}(r) = 2\zeta^{3/2} r e^{-\zeta r}. \quad (3.12)$$

The corresponding two-electron energy eigenvalue is  $E_{1s1s}^{(0)} = -\zeta^2$  a.u. We can easily obtain the first-order correction to this energy by applying first-order perturbation theory:

$$E_{1s1s}^{(1)} = \langle \Psi_{1s1s} | \frac{1}{r_{12}} - U(r_1) - U(r_2) | \Psi_{1s1s} \rangle. \quad (3.13)$$

The first term in (3.13) can be written

$$\langle \Psi_{1s1s} | \frac{1}{r_{12}} | \Psi_{1s1s} \rangle = \frac{1}{(4\pi)^2} \int dr_1 d\Omega_1 \int dr_2 d\Omega_2 P_{1s}^2(r_1) P_{1s}^2(r_2) \frac{1}{r_{12}}. \quad (3.14)$$

The Coulomb interaction in this equation can be expanded in terms of Legendre polynomials to give

$$\frac{1}{r_{12}} = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \sum_{l=0}^{\infty} \frac{r_{<}^l}{r_{>}^{l+1}} P_l(\cos \theta), \quad (3.15)$$

where  $r_{<} = \min(r_1, r_2)$  and  $r_{>} = \max(r_1, r_2)$ , and where  $\theta$  is the angle between the vectors  $\mathbf{r}_1$  and  $\mathbf{r}_2$ . With the aid of this expansion, the angular integrals can be carried out to give

$$\langle \Psi_{1s1s} | \frac{1}{r_{12}} | \Psi_{1s1s} \rangle = \int_0^{\infty} dr_1 P_{1s}^2(r_1) \int_0^{\infty} dr_2 P_{1s}^2(r_2) \frac{1}{r_{>}}. \quad (3.16)$$

It should be noted that after the angular integrations, only the monopole contribution from (3.15) survives. The function

$$v_0(1s, r_1) = \int_0^{\infty} dr_2 P_{1s}^2(r_2) \frac{1}{r_{>}} \quad (3.17)$$

is just the potential at  $r_1$  of a spherically symmetric charge distribution having radial density  $P_{1s}^2(r)$ . In terms of this function, we may write

$$\langle \Psi_{1s1s} | \frac{1}{r_{12}} | \Psi_{1s1s} \rangle = \int_0^\infty P_{1s}^2(r) v_0(1s, r) dr. \quad (3.18)$$

The two remaining integrals in Eq.(3.13) are easily evaluated. We find

$$\langle \Psi_{1s1s} | U(r_1) | \Psi_{1s1s} \rangle = \langle \Psi_{1s1s} | U(r_2) | \Psi_{1s1s} \rangle = \int_0^\infty P_{1s}^2(r) U(r) dr. \quad (3.19)$$

Combining (3.18) and (3.19), we obtain the following expression for the first-order energy:

$$E_{1s1s}^{(1)} = \int_0^\infty P_{1s}^2(r) (v_0(1s, r) - 2U(r)) dr. \quad (3.20)$$

Using the specific form of the  $1s$  radial wave function given in Eq.(3.12), we can evaluate  $v_0(1s, r)$  analytically using Eq.(3.17) to obtain

$$v_0(1s, r) = (1 - e^{-2\zeta r})/r - \zeta e^{-2\zeta r}. \quad (3.21)$$

Using this result, we find

$$\int_0^\infty P_{1s}^2(r) v_0(1s, r) dr = \frac{5}{8}\zeta. \quad (3.22)$$

The integral of  $U(r) = (Z - \zeta)/r$  in Eq.(3.20) can be evaluated using the fact that  $\langle 1s | 1/r | 1s \rangle = \zeta$ . Altogether, we find

$$E_{1s1s}^{(1)} = \frac{5}{8}\zeta - 2(Z - \zeta)\zeta. \quad (3.23)$$

Combining this result with the expression for the lowest-order energy, we obtain

$$E_{1s1s} = E_{1s1s}^{(0)} + E_{1s1s}^{(1)} = -\zeta^2 + \frac{5}{8}\zeta - 2(Z - \zeta)\zeta. \quad (3.24)$$

The specific value of  $\zeta$  in this equation is determined with the aid of the variational principle, which requires that the parameters in the approximate wave function be chosen to minimize the energy. The value of  $\zeta$  which minimizes the energy in Eq.(3.24) is found to be  $\zeta = Z - 5/16$ . The corresponding value of the energy is  $E_{1s1s} = -(Z - 5/16)^2$ . For helium,  $Z = 2$ , this leads to a prediction for the ground-state energy of  $E_{1s1s} = -2.848$  a.u., which is within 2% of the experimentally measured energy  $E_{1s1s}^{\text{exp}} = -2.903$  a.u..

Generally, in the independent-particle approximation, the energy can be expressed in terms of the radial wave function as

$$E_{1s1s} = \langle \Psi_{1s1s} | h_0(\mathbf{r}_1) + h_0(\mathbf{r}_2) + \frac{1}{r_{12}} | \Psi_{1s1s} \rangle. \quad (3.25)$$

The expectation values of the single-particle operators  $h_0(\mathbf{r}_1)$  and  $h_0(\mathbf{r}_2)$  are identical. The first term in (3.25) can be reduced to

$$\langle \Psi_{1s1s} | h_0(\mathbf{r}_1) | \Psi_{1s1s} \rangle = \int_0^\infty dr \left( -\frac{1}{2} P_{1s}(r) \frac{d^2 P_{1s}}{dr^2} - \frac{Z}{r} P_{1s}^2(r) \right). \quad (3.26)$$

Integrating by parts, and making use of the previously derived expression for the Coulomb interaction in (3.18), we obtain

$$E_{1s1s} = \int_0^\infty dr \left[ \left( \frac{dP_{1s}}{dr} \right)^2 - 2 \frac{Z}{r} P_{1s}^2(r) + v_0(1s, r) P_{1s}^2(r) \right]. \quad (3.27)$$

The requirement that the two-particle wave function be normalized,  $\langle \Psi_{1s1s} | \Psi_{1s1s} \rangle = 1$ , leads to the constraint on the single electron orbital

$$N_{1s} = \int_0^\infty P_{1s}(r)^2 dr = 1. \quad (3.28)$$

We now invoke the variational principle to determine the radial wave functions. We require that the energy be stationary with respect to variations of the radial function subject to the normalization constraint. Introducing the Lagrange multiplier  $\lambda$ , the variational principle may be written

$$\delta(E_{1s1s} - \lambda N_{1s}) = 0. \quad (3.29)$$

We designate the variation in the function  $P_{1s}(r)$  by  $\delta P_{1s}(r)$ , and we require  $\delta P_{1s}(0) = \delta P_{1s}(\infty) = 0$ . Further, we note the identity

$$\delta \frac{dP_{1s}}{dr} = \frac{d}{dr} \delta P_{1s}. \quad (3.30)$$

With the aid of (3.30) we obtain

$$\begin{aligned} \delta(E_{1s1s} - \lambda N_{1s}) = 2 \int_0^\infty \left( -\frac{d^2 P_{1s}}{dr^2} - 2 \frac{Z}{r} P_{1s}(r) \right. \\ \left. + 2v_0(1s, r) P_{1s}(r) - \lambda P_{1s}(r) \right) \delta P_{1s}(r). \end{aligned} \quad (3.31)$$

Requiring that this expression vanish for arbitrary variations  $\delta P_{1s}(r)$  satisfying the boundary conditions leads to the Hartree-Fock equation

$$-\frac{1}{2} \frac{d^2 P_{1s}}{dr^2} - \frac{Z}{r} P_{1s}(r) + v_0(1s, r) P_{1s}(r) = \epsilon_{1s} P_{1s}(r), \quad (3.32)$$

where we have defined  $\epsilon_{1s} = \lambda/2$ . The HF equation is just the radial Schrödinger equation for a particle with orbital angular momentum 0 moving in the potential

$$V(r) = -\frac{Z}{r} + v_0(1s, r). \quad (3.33)$$

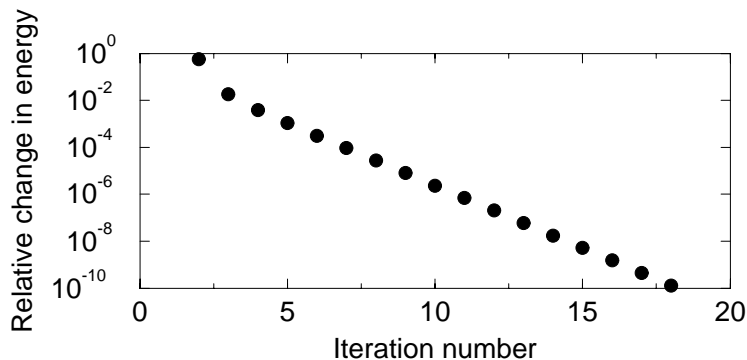


Figure 3.1: Relative change in energy  $(E^{(n)} - E^{(n-1)})/E^{(n)}$  as a function of the iteration step number  $n$  in the iterative solution of the HF equation for helium,  $Z = 2$ .

The HF equation is solved iteratively. We start the iterative solution by approximating the radial HF function  $P_{1s}(r)$  with a screened  $1s$  Coulomb function having effective charge  $\zeta = Z - 5/16$ . We use this wave function to evaluate  $v_0(1s, r)$ . We then solve (3.32) using the approximate potential  $v_0(1s, r)$ . The resulting radial function  $P_{1s}(r)$  is used to construct a second approximation to  $v_0(1s, r)$ , and the iteration is continued until self-consistent values of  $P_{1s}(r)$  and  $v_0(1s, r)$  are obtained. The pattern of convergence for this iteration procedure is illustrated in Fig. 3.1 where we plot the relative change in the single-particle energy as a function of the iteration step. After 18 steps, the energy has converged to 10 figures.

The resulting value of single-particle energy is found to be  $\epsilon_a = -0.9179\dots$  a.u.. The total energy of the two-electron system can be written

$$E_{1s1s} = \langle 1s | 2h_0 + v_0(1s, r) | 1s \rangle = 2\epsilon_{1s} - \langle 1s | v_0(1s, r) | 1s \rangle. \quad (3.34)$$

From this, we find  $E_{1s,1s} = -2.861\dots$  a.u., only a slight improvement over the value obtained previously using a screened Coulomb field to approximate the electron-electron interaction. The HF energy is the most accurate that can be obtained within the framework of the independent-particle model. To achieve greater accuracy, we must go beyond the independent-particle model and treat the correlated motion of the two electrons.

In Fig. 3.2, we plot the functions  $P_{1s}(r)$  and  $v_0(1s, r)$  found by solving the HF equation for neutral helium,  $Z = 2$ . The potential  $v_0(1s, r)$  has the following limiting values:

$$\lim_{r \rightarrow 0} v_0(1s, r) = \langle 1s | \frac{1}{r} | 1s \rangle, \quad (3.35)$$

$$\lim_{r \rightarrow \infty} v_0(1s, r) = \frac{1}{r}. \quad (3.36)$$

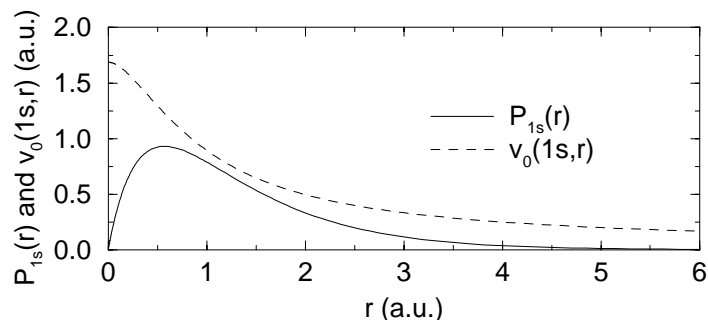


Figure 3.2: Solutions to the HF equation for helium,  $Z = 2$ . The radial HF wave function  $P_{1s}(r)$  is plotted in the solid curve and electron potential  $v_0(1s, r)$  is plotted in the dashed curve.

### 3.2 HF Equations for Closed-Shell Atoms

For a system of  $N$ -electrons, the Hamiltonian is

$$H(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_{i=1}^N h_0(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}}, \quad (3.37)$$

where  $h_0$  is the single-particle operator for the sum of the kinetic energy and the electron-nucleus interaction given in Eq.(3.2), and where  $1/r_{ij}$  is the Coulomb interaction energy between the  $i^{\text{th}}$  and  $j^{\text{th}}$  electrons. We seek approximate solutions to the  $N$ -electron Schrödinger equation

$$H(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N). \quad (3.38)$$

The solutions corresponding to electrons (and other fermions) are completely antisymmetric with respect to the interchange of any two coordinates

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_j, \dots, \mathbf{r}_N) = -\Psi(\mathbf{r}_1, \dots, \mathbf{r}_j, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N). \quad (3.39)$$

It is perhaps worthwhile repeating here an observation by Hartree (1957, p. 16) concerning “exact” solutions to Eq.(3.38) in the many-electron case. If we consider, for example, the 26 electron iron atom, the function  $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$  depends on  $3 \times 26 = 78$  variables. Using a coarse grid of only 10 points for each variable, it would require  $10^{78}$  numbers to tabulate the wave function for iron. Since this number exceeds the estimated number of particles in the solar system, it is difficult to understand how the wave function would be stored even if it could be calculated! Of more practical interest are approximations to “exact” solutions and methods for systematically improving the accuracy of such approximations.

Again, we start with the independent-particle approximation. We write  $H = H_0 + V$ , with

$$H_0(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_{i=1}^N h(\mathbf{r}_i), \quad (3.40)$$

$$V(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} - \sum_{i=1}^N U(r_i), \quad (3.41)$$

where, as in the previous section,  $U(r)$  is an appropriately chosen approximation to the electron interaction potential and where  $h(r) = h_0 + U(r)$ . If we let  $\psi_a(\mathbf{r})$  be an eigenfunction of  $h$  having eigenvalue  $\epsilon_a$ , then

$$\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) \cdots \psi_n(\mathbf{r}_N) \quad (3.42)$$

is an eigenfunction of  $H_0$  with eigenvalue

$$E_{ab\dots n}^{(0)} = \epsilon_a + \epsilon_b + \cdots + \epsilon_n.$$

Moreover, each of the  $N!$  product functions obtained by permuting the indices  $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$  in the wave function (3.42), is degenerate in energy with that wave function. A completely antisymmetric product wave function is given by the Slater determinant

$$\Psi_{ab\dots n}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_a(\mathbf{r}_1) & \psi_b(\mathbf{r}_1) & \cdots & \psi_n(\mathbf{r}_1) \\ \psi_a(\mathbf{r}_2) & \psi_b(\mathbf{r}_2) & \cdots & \psi_n(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_a(\mathbf{r}_N) & \psi_b(\mathbf{r}_N) & \cdots & \psi_n(\mathbf{r}_N) \end{vmatrix}. \quad (3.43)$$

The antisymmetric two-particle wave function  $\Psi_{1s1s}(\mathbf{r}_1, \mathbf{r}_2)$  used in the previous section is a special case of a Slater-determinant wave function with  $n_a = 1, l_a = 0, m_a = 0, \mu_a = 1/2$  and  $n_b = 1, l_b = 0, m_b = 0, \mu_b = -1/2$ . Here, we specify the orbitals by their quantum numbers; for example,  $a = (n_a, l_a, m_a, \mu_a)$ . Since the determinant vanishes if two columns are identical, it follows that the quantum numbers  $a, b, \dots, n$  must be distinct. The fact that the quantum numbers of the orbitals in an antisymmetric product wave function are distinct is called the Pauli exclusion principle.

In the following paragraphs, we will need to evaluate diagonal and off-diagonal matrix elements of many-particle operators between Slater-determinant wave functions. Many-particle operators  $F$  of the form

$$F = \sum_{i=1}^N f(\mathbf{r}_i), \quad (3.44)$$

such as  $H_0$  itself, are called *one-particle operators*. Operators  $G$  of the form

$$G = \frac{1}{2} \sum_{i \neq j} g(r_{ij}), \quad (3.45)$$



such as the Coulomb interaction energy, are called *two-particle operators*. The following rules will help us evaluate matrix elements of one- and two-particle operators:

**Rule 1**

$$\langle \Psi_{a'b'\dots n'} | F | \Psi_{ab\dots n} \rangle = 0,$$

if the indices  $\{a', b', \dots, n'\}$  and  $\{a, b, \dots, n\}$  differ in more than one place.

**Rule 2**

$$\langle \Psi_{ab\dots k'\dots n} | F | \Psi_{ab\dots k\dots n} \rangle = f_{k'k},$$

if only the two indices  $k$  and  $k'$  differ.

**Rule 3**

$$\langle \Psi_{ab\dots n} | F | \Psi_{ab\dots n} \rangle = \sum_{i=a}^n f_{ii},$$

if the indices in the two sets are identical.

**Rule 4**

$$\langle \Psi_{a'b'\dots n'} | G | \Psi_{ab\dots n} \rangle = 0,$$

if the indices  $\{a', b', \dots, n'\}$  and  $\{a, b, \dots, n\}$  differ in more than two places.

**Rule 5**

$$\langle \Psi_{ab\dots k'l'\dots n} | G | \Psi_{ab\dots k\dots l\dots n} \rangle = g_{k'l'kl} - g_{k'l'l'k},$$

if only the pairs  $k, l$  and  $k', l'$  in the two sets differ.

**Rule 6**

$$\langle \Psi_{ab\dots k'\dots n} | G | \Psi_{ab\dots k\dots n} \rangle = \sum_{i=a}^n (g_{k'iki} - g_{k' iik}),$$

if only the indices  $k$  and  $k'$  in the two sets differ.

**Rule 7**

$$\langle \Psi_{ab\dots n} | G | \Psi_{ab\dots n} \rangle = \frac{1}{2} \sum_{i,j} (g_{ijij} - g_{ijji}),$$

if the two sets are identical, where both sums extend over all of the indices  $\{a, b, \dots, n\}$

In the above rules, we have introduced the notation:

$$f_{ab} = \langle a | f | b \rangle = \int d^3r \psi_a^\dagger(\mathbf{r}) f(\mathbf{r}) \psi_b(\mathbf{r}), \quad (3.46)$$

$$g_{abcd} = \langle ab | g | cd \rangle = \int d^3r_1 \int d^3r_2 \psi_a^\dagger(\mathbf{r}_1) \psi_b^\dagger(\mathbf{r}_2) g(r_{12}) \psi_c(\mathbf{r}_1) \psi_d(\mathbf{r}_2). \quad (3.47)$$

With the aid of these rules, we easily work out the expectation value of the  $H_0$  and  $H$ , using a Slater determinant wave function:

$$E_{ab\cdots n}^{(0)} = \sum_a (h_0)_{aa} + \sum_a U_{aa}, \quad (3.48)$$

$$E_{ab\cdots n}^{(1)} = \frac{1}{2} \sum_{ab} (g_{abab} - g_{abba}) - \sum_a U_{aa}, \quad (3.49)$$

$$E_{ab\cdots n} = \sum_a (h_0)_{aa} + \frac{1}{2} \sum_{ab} (g_{abab} - g_{abba}), \quad (3.50)$$

where the sums extend over all one-electron orbital quantum numbers in the set  $\{a, b, \dots, n\}$ . The terms  $g_{abab}$  and  $g_{abba}$  are matrix elements of the Coulomb interaction  $g(r_{12}) = 1/r_{12}$ . The term  $g_{abab}$  is called the *direct* matrix element of the operator  $g(r_{12})$  and  $g_{abba}$  is called the *exchange* matrix element.

The lowest-energy eigenstate of  $H_0$  for an  $N$ -electron atom is a product of the  $N$  lowest-energy one-electron orbitals. For two-electron atoms, these are the two  $1s$  orbitals with different spin projections. In atomic model potentials, such as those discussed in the previous chapter, the lowest few orbital eigenvalues are ordered in the sequence  $\epsilon_{1s} < \epsilon_{2s} < \epsilon_{2p} < \epsilon_{3s} < \epsilon_{3p}$ . (The ordering beyond this point depends on the potential to some extent and will be considered later.)

For three- or four-electron atoms (lithium and beryllium), the ground state-wave function is taken to be a Slater determinant made up of two  $1s$  orbitals, and one or two  $2s$  orbitals. The radial probability density functions for these atoms have two distinct maxima, one corresponding to the  $1s$  electrons near  $1/Z$  a.u., and a second corresponding to the  $2s$  electron near 1 a.u.. This variation of the density is referred to as the atomic shell structure. Electronic orbitals having the same principal quantum number  $n$  belong to the same shell; their contribution to the radial density is localized. Orbitals having the same principal quantum number, but different angular quantum numbers, belong to different subshells. They contribute fine structure to the radial density function of the atom. The  $2s$  subshell is complete after including the two  $2s$  orbitals with different spin projections. We continue through the first row of the periodic table, adding successive  $2p$  electrons with different values of  $m$  and  $\mu$  until the  $n = 2$  shell is complete at neon,  $Z = 10$ . This building up scheme can be continued throughout the periodic system.

Slater-determinant wave functions for atoms with closed subshells can be shown to be eigenstates of  $L^2, L_z, S^2$  and  $S_z$ . The eigenvalues of all four of these operators are 0. Similarly, Slater-determinant wave function for atoms with one electron beyond closed subshells, or for atoms with a single hole in an otherwise filled subshell, are also angular momentum eigenstates. To construct angular momentum eigenstates for other open-shell atoms, linear combinations of Slater determinants, coupled together with Clebsch-Gordan coefficients, are used. We defer further discussion of open-shell atoms until the next chapter and concentrate here on the case of atoms with closed subshells.

We define the configuration of an atomic state to be the number and type of one-electron orbitals present in the Slater-determinant wave function represent-

ing that state. A configuration having  $k$  orbitals with principal quantum number  $n$  and angular quantum number  $l$  is designated by  $(nl)^k$ . The configurations of the ground states of the closed-shell atoms being considered are: helium  $(1s)^2$ ; beryllium  $(1s)^2(2s)^2$ ; neon  $(1s)^2(2s)^2(2p)^6$ ; magnesium  $(1s)^2(2s)^2(2p)^6(3s)^2$ ; argon  $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6$ , calcium  $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2$ ; and so forth.

The orbitals  $\psi_a(\mathbf{r})$  are decomposed into radial, angular, and spin components as  $\psi_a(\mathbf{r}_i) = (P_{n_a l_a}(r_i)/r_i)Y_{l_a m_a}(\hat{r}_i)\chi_{\mu_a}(i)$ , and the terms in the expression for the energy (3.50) are worked out. First, we evaluate  $(h_0)_{aa}$  to obtain:

$$(h_0)_{aa} = \int_0^\infty dr P_{n_a l_a} \left( -\frac{1}{2} \frac{d^2 P_{n_a l_a}}{dr^2} + \frac{l_a(l_a+1)}{2r^2} P_{n_a l_a} - \frac{Z}{r} P_{n_a l_a} \right). \quad (3.51)$$

We note that this term has the same value for each of the  $2(2l_a+1)$  orbitals in the  $n_a l_a$  subshell. The integral on the right-hand side of this equation is often denoted by  $I(n_a l_a)$ . On integrating by parts, we can rewrite Eq. (3.51) as

$$I(n_a l_a) = \int_0^\infty dr \left[ \frac{1}{2} \left( \frac{dP_{n_a l_a}}{dr} \right)^2 + \frac{l_a(l_a+1)}{2r^2} P_{n_a l_a}^2 - \frac{Z}{r} P_{n_a l_a}^2 \right]. \quad (3.52)$$

We will need this term later in this section.

Next, we examine the direct Coulomb matrix element  $g_{abab}$ . To evaluate this quantity, we make use of the decomposition of  $1/r_{12}$  given in Eq.(3.15). Further, we use the well-known identity

$$P_l(\cos \theta) = \sum_{m=-l}^l (-1)^m C_{-m}^l(\hat{r}_1) C_m^l(\hat{r}_2), \quad (3.53)$$

to express the Legendre polynomial of  $\cos \theta$ , where  $\theta$  is the angle between the two vectors  $\mathbf{r}_1$  and  $\mathbf{r}_2$ , in terms of the angular coordinates of the two vectors in an arbitrary coordinate system. Here, as in Chapter 1, the quantities  $C_m^l(\hat{r})$  are tensor operators, defined in terms of spherical harmonics by:

$$C_m^l(\hat{r}) = \sqrt{\frac{4\pi}{2l+1}} Y_{lm}(\hat{r}).$$

With the aid of the above decomposition, we find:

$$\begin{aligned} g_{abab} = & \sum_{l=0}^{\infty} \sum_{m=-l}^l (-1)^m \int_0^\infty dr_1 P_{n_a l_a}^2(r_1) \int d\Omega_1 Y_{l_a m_a}^*(\hat{r}_1) C_{-m}^l(\hat{r}_1) Y_{l_a m_a}(\hat{r}_1) \\ & \int_0^\infty dr_2 P_{n_b l_b}^2(r_2) \left( \frac{r_{<}^l}{r_{>}^{l+1}} \right) \int d\Omega_2 Y_{l_b m_b}^*(\hat{r}_2) C_m^l(\hat{r}_2) Y_{l_b m_b}(\hat{r}_2). \end{aligned} \quad (3.54)$$

The angular integrals can be expressed in terms of reduced matrix elements of

the tensor operator  $C_m^l$  using the Wigner-Eckart theorem. We find

$$g_{abab} = \sum_{l=0}^{\infty} \begin{array}{c} \left| \begin{array}{c} l_a m_a \\ \hline l_a m_a \end{array} \right|_{l_0} \begin{array}{c} \left| \begin{array}{c} l_b m_b \\ \hline l_b m_b \end{array} \right|_{l_0} \langle l_a || C^l || l_a \rangle \langle l_b || C^l || l_b \rangle R_l(n_a l_a, n_b l_b, n_a l_a, n_b l_b), \end{array} \quad (3.55)$$

where

$$R_l(a, b, c, d) = \int_0^{\infty} dr_1 P_a(r_1) P_c(r_1) \int_0^{\infty} dr_2 P_b(r_2) P_d(r_2) \left( \frac{r_{<}^l}{r_{>}^{l+1}} \right). \quad (3.56)$$

These integrals of products of four radial orbitals are called Slater integrals. The Slater integrals can be written in terms of multipole potentials. We define the potentials  $v_l(a, b, r)$  by

$$v_l(a, b, r) = \int_0^{\infty} dr_2 P_a(r_2) P_b(r_2) \left( \frac{r_{<}^l}{r_{>}^{l+1}} \right). \quad (3.57)$$

We may then write

$$R_l(a, b, c, d) = \int_0^{\infty} dr P_a(r) P_c(r) v_l(b, d, r) \quad (3.58)$$

$$= \int_0^{\infty} dr P_b(r) P_d(r) v_l(a, c, r). \quad (3.59)$$

The potentials  $v_l(a, b, r)$  are often expressed in the form  $v_l(a, b, r) = Y_l(a, b, r)/r$ . The functions  $Y_l(a, b, r)$  are called Hartree screening functions. Later, we will designate the functions  $v_l(a, a, r)$  using the slightly simpler notation  $v_l(a, r)$ . The function  $v_0(a, r)$  is the potential at  $r$  due to a spherically symmetric charge distribution with radial density  $P_a(r)^2$ . The functions  $v_l(b, r)$  have the following limiting forms which will be used later:

$$\lim_{r \rightarrow 0} v_l(a, r) = r^l \langle a | \frac{1}{r^{l+1}} | a \rangle, \quad (3.60)$$

$$\lim_{r \rightarrow \infty} v_l(a, r) = \frac{1}{r^{l+1}} \langle a | r^l | a \rangle. \quad (3.61)$$

Following the outline of the calculation for the direct integral  $g_{abab}$ , we may write the exchange integral  $g_{abba}$  as

$$g_{abba} = \sum_{l=0}^{\infty} \sum_{m=-l}^l \delta_{\mu_a \mu_b} \begin{array}{c} \left| \begin{array}{c} l_b m_b \\ \hline l_b m_b \end{array} \right|_{l_0} \begin{array}{c} \left| \begin{array}{c} l_b m_b \\ \hline l_b m_b \end{array} \right|_{l_0} \langle l_b || C^l || l_b \rangle^2 R_l(n_a l_a, n_b l_b, n_b l_b, n_a l_a). \end{array} \quad (3.62)$$

Let us carry out the sum over the magnetic quantum numbers  $m_b$  and  $\mu_b$  in Eq.(3.55). We make use of the identity

$$\begin{array}{c} \left| \begin{array}{c} l_b \\ \hline l_0 \end{array} \right|_{l_0} = \delta_{l_0} \sqrt{2l_b + 1} \end{array} \quad (3.63)$$

to obtain

$$\begin{aligned} \sum_{m_b \mu_b} g_{abab} &= 2\sqrt{\frac{2l_b+1}{2l_a+1}} \langle l_a || C^0 || l_a \rangle \langle l_b || C^0 || l_b \rangle R_0(n_a l_a, n_b l_b, n_a l_a, n_b l_b) \\ &= 2(2l_b+1) R_0(n_a l_a, n_b l_b, n_a l_a, n_b l_b). \end{aligned} \quad (3.64)$$

To carry out the sum over the magnetic quantum numbers  $m_b$  and  $\mu_b$  and  $m$  in Eq.(3.62), we use the identity

$$\frac{l_a m_a}{-} \circlearrowleft \begin{matrix} l_b \\ + \end{matrix} \frac{l_a m_a}{+} = \frac{1}{2l_a+1} \quad (3.65)$$

and find

$$\sum_{m_b \mu_b} g_{abba} = \sum_l \frac{\langle l_b || C^l || l_a \rangle^2}{2l_a+1} R_l(n_a l_a, n_b l_b, n_b l_b, n_a l_a). \quad (3.66)$$

The sum over  $l$  extends over all values permitted by the angular momentum and parity selection rules contained in  $\langle l_b || C^l || l_a \rangle$ , namely,  $|l_a - l_b| \leq l \leq l_a + l_b$ , with the constraint that the sum  $l_a + l_b + l$  is an even integer.

We are now in a position to evaluate the expression for the energy given in Eq.(3.50). We find

$$\begin{aligned} E_{ab\dots n} &= \sum_{n_a l_a} 2(2l_a+1) \left\{ I(n_a l_a) + \sum_{n_b l_b} (2l_b+1) \left( R_0(n_a l_a, n_b l_b, n_a l_a, n_b l_b) \right. \right. \\ &\quad \left. \left. - \sum_l \Lambda_{l_a l_b} R_l(n_a l_a, n_b l_b, n_b l_b, n_a l_a) \right) \right\}, \end{aligned} \quad (3.67)$$

with

$$\Lambda_{l_a l_b} = \frac{\langle l_a || C^l || l_b \rangle^2}{2(2l_a+1)(2l_b+1)} = \frac{1}{2} \begin{pmatrix} l_a & l & l_b \\ 0 & 0 & 0 \end{pmatrix}^2. \quad (3.68)$$

The coefficients  $\Lambda_{l_a l_b}$  are symmetric with respect to an arbitrary interchange of indices. Values of  $\Lambda_{l_a l_b}$  for  $0 \leq l_a \leq l_b \leq 4$  are given in Table 3.1.

To maintain normalization of the many-electron wave function, we must require that the radial functions corresponding to a fixed value of  $l$  be orthonormal. Therefore,

$$N_{n_a l_a, n_b l_a} = \int_0^\infty dr P_{n_a l_a}(r) P_{n_b l_a}(r) = \delta_{n_a n_b}. \quad (3.69)$$

Introducing Lagrange multipliers to accommodate the constraints in Eq.(3.69), we can express the variational principle as:

$$\delta(E_{ab\dots n} - \sum_{n_a n_b l_a} \lambda_{n_a l_a, n_b l_a} N_{n_a l_a, n_b l_a}) = 0, \quad (3.70)$$

and we demand  $\lambda_{n_a l_a, n_b l_a} = \lambda_{n_b l_a, n_a l_a}$ .

Table 3.1: Coefficients of the exchange Slater integrals in the nonrelativistic Hartree-Fock equations:  $\Lambda_{l_a l_b}$ . These coefficients are symmetric with respect to any permutation of the three indices.

$l_a$	$l$	$l_b$	$\Lambda_{l_a l_b}$	$l_a$	$l$	$l_b$	$\Lambda_{l_a l_b}$	$l_a$	$l$	$l_b$	$\Lambda_{l_a l_b}$
0	0	0	1/2	2	0	2	1/10	3	1	4	2/63
0	1	1	1/6	2	2	2	1/35	3	3	4	1/77
0	2	2	1/10	2	4	2	1/35	3	5	4	10/1001
0	3	3	1/14	2	1	3	3/70	3	7	4	35/2574
0	4	4	1/18	2	3	3	2/105				
				2	5	3	5/231	4	0	4	1/18
1	0	1	1/6	2	2	4	1/35	4	2	4	10/693
1	2	1	1/15	2	4	4	10/693	4	4	4	9/1001
1	1	2	1/15	2	6	4	5/286	4	6	4	10/1287
1	3	2	3/70					4	8	4	245/21879
1	2	3	3/70	3	0	3	1/14				
1	4	3	2/63	3	2	3	2/105				
1	3	4	2/63	3	4	3	1/77				
1	5	4	5/198	3	6	3	50/300				

The equation obtained by requiring that this expression be stationary with respect to variations  $\delta P_{n_a l_a}(r)$  is found to be

$$\begin{aligned}
& -\frac{1}{2} \frac{d^2 P_{n_a l_a}}{dr^2} + \frac{l_a(l_a+1)}{2r^2} P_{n_a l_a}(r) - \frac{Z}{r} P_{n_a l_a}(r) + \\
& \sum_{n_b l_b} (4l_b+2) \left( v_0(n_b l_b, r) P_{n_a l_a}(r) - \sum_l \Lambda_{l_a l_b} v_l(n_b l_b, n_a l_a, r) P_{n_b l_b}(r) \right) \\
& = \epsilon_{n_a l_a} P_{n_a l_a}(r) + \sum_{n_b \neq n_a} \epsilon_{n_a l_a, n_b l_a} P_{n_b l_a}(r), \quad (3.71)
\end{aligned}$$

where  $\epsilon_{n_a l_a, n_b l_a} = \lambda_{n_a l_a, n_b l_a} / (4l_a + 2)$  and  $\epsilon_{n_a l_a} = \lambda_{n_a l_a, n_a l_a} / (4l_a + 2)$ .

For orientation, let us examine several special cases. Let us first consider the case of helium for which there is a single  $1s$  orbital and a single HF equation. The only nonvanishing angular coefficient in the second line of Eq.(3.71) is  $\Lambda_{000} = 1/2$ . The entire second row of the equation reduces to

$$2 \left( v_0(1s, r) P_{1s}(r) - \frac{1}{2} v_0(1s, r) P_{1s}(r) \right) = v_0(1s, r) P_{1s}(r).$$

The HF equation, Eq.(3.71), reduces to Eq.(3.32) derived in the previous section.

For the case of beryllium, there are two distinct radial orbitals for the  $1s$

and  $2s$  shells, respectively. The second line of Eq.(3.71) takes the form

$$\begin{aligned} & \left( v_0(1s, r) + 2v_0(2s, r) \right) P_{1s} - v_0(2s, 1s, r) P_{2s}(r), \quad \text{for } n_a l_a = 1s, \\ & \left( 2v_0(1s, r) + v_0(2s, r) \right) P_{2s} - v_0(1s, 2s, r) P_{1s}(r), \quad \text{for } n_a l_a = 2s. \end{aligned}$$

The two HF equations for beryllium become

$$\begin{aligned} -\frac{1}{2} \frac{d^2 P_{1s}}{dr^2} + \left( -\frac{Z}{r} + v_0(1s, r) + 2v_0(2s, r) \right) P_{1s} - v_0(2s, 1s, r) P_{2s}(r) \\ = \epsilon_{1s} P_{1s}(r) + \epsilon_{1s, 2s} P_{2s}(r), \quad (3.72) \end{aligned}$$

$$\begin{aligned} -\frac{1}{2} \frac{d^2 P_{2s}}{dr^2} + \left( -\frac{Z}{r} + 2v_0(1s, r) + v_0(2s, r) \right) P_{2s} - v_0(1s, 2s, r) P_{1s}(r) \\ = \epsilon_{1s, 2s} P_{1s}(r) + \epsilon_{2s} P_{2s}(r). \quad (3.73) \end{aligned}$$

The off-diagonal Lagrange multiplier  $\epsilon_{1s, 2s}$  is chosen so as to insure the orthogonality of the  $1s$  and  $2s$  radial orbitals. Multiplying Eq.(3.72) by  $P_{2s}(r)$  and Eq.(3.73) by  $P_{1s}(r)$ , subtracting the resulting equations, and integrating from 0 to  $\infty$ , we obtain the identity

$$(\epsilon_{1s} - \epsilon_{2s}) \int_0^\infty dr P_{1s}(r) P_{2s}(r) = -\frac{1}{2} \left( P_{2s} \frac{dP_{1s}}{dr} - P_{1s} \frac{dP_{2s}}{dr} \right)_0^\infty. \quad (3.74)$$

For solutions regular at 0 and  $\infty$ , the right-hand side of this equation vanishes. Since  $\epsilon_{2s} \neq \epsilon_{1s}$ , the solutions to Eqs.(3.72) and (3.73) are orthogonal for arbitrary values of the off-diagonal Lagrange multiplier. We make the simplest choice here, namely,  $\epsilon_{1s, 2s} = 0$ . The HF equations then reduce to a pair of radial Schrödinger equations coupled together by the potential function  $v_0(1s, 2s, r) = v_0(2s, 1s, r)$ .

As in the example of beryllium, it is easily shown for a general closed-shell atom that the orbitals associated with a specific value of  $l$  and different values of  $n$  are orthogonal no matter what value is chosen for the off-diagonal Lagrange multipliers. We take advantage of this fact to simplify the HF equations by choosing  $\epsilon_{n_a l_a, n_b l_a} = 0$  for all values of  $n_a, n_b$  and  $l_a$ .

Generally, we define the Hartree-Fock potential  $V_{\text{HF}}$  by specifying its action on an arbitrary radial orbital  $P_*(r)$ . Writing  $V_{\text{HF}} P_*(r) = V_{\text{dir}} P_*(r) + V_{\text{exc}} P_*(r)$  we find,

$$V_{\text{dir}} P_*(r) = \sum_b (4l_b + 2) v_0(b, r) P_*(r), \quad (3.75)$$

$$V_{\text{exc}} P_*(r) = \sum_b (4l_b + 2) \sum_l \Lambda_{l_b l_*} v_l(b, *, r) P_b(r). \quad (3.76)$$

In the above equations, the sum over  $b$  is understood to mean a sum over  $n_b$  and  $l_b$ . The direct potential  $V_{\text{dir}}$  is a multiplicative operator. It is just the potential

due to the spherically averaged charge distribution of all atomic electrons. The exchange potential  $V_{\text{exc}}$  is, by contrast, a nonlocal operator defined by means of an integral. The direct part of the HF potential has the following limits

$$\lim_{r \rightarrow 0} V_{\text{dir}}(r) = \sum_b (4l_b + 2) \langle b | \frac{1}{r} | b \rangle, \quad (3.77)$$

$$\lim_{r \rightarrow \infty} V_{\text{dir}}(r) = \frac{N}{r}, \quad (3.78)$$

where  $N = \sum_b (4l_b + 2)$  = number of electrons in the atom. For neutral atoms, the direct part of the HF potential precisely cancels the nuclear potential at large  $r$ . The asymptotic potential for a neutral atom is, therefore, dominated by the monopole parts of the exchange potential at large  $r$ . Using the fact that  $\Lambda_{l_b 0 l_a} = \delta_{l_b l_a} / (4l_a + 2)$ , and the fact that the limiting value of  $v_0(n_b l_a, n_a l_a, r)$  is

$$\lim_{r \rightarrow \infty} v_0(n_b l_a, n_a l_a, r) = \frac{1}{r} \int_0^\infty dr P_{n_b l_a}(r) P_{n_a l_a}(r) = \frac{\delta_{n_b n_a}}{r}, \quad (3.79)$$

we find that

$$\lim_{r \rightarrow \infty} V_{\text{exc}} P_a(r) = -\frac{1}{r} P_a(r). \quad (3.80)$$

The sum of the nuclear potential and the HF potential, therefore, approaches the ionic potential  $(N - 1)/r$  for large  $r$ . With the above definitions, we may write the HF equation for an atom with closed subshells as

$$-\frac{1}{2} \frac{d^2 P_a}{dr^2} + \left( V_{\text{HF}} - \frac{Z}{r} + \frac{l_a(l_a + 1)}{2r^2} \right) P_a(r) = \epsilon_a P_a(r), \quad (3.81)$$

where the index  $a$  ranges over the occupied subshells ( $n_a l_a$ ). The HF equations are a set of radial Schrödinger equations for electrons moving in a common central potential  $V(r) = -Z/r + U(r)$ . By comparison with Eq.(2.12), the “best” value for the average central potential  $U(r)$  is seen to be the nonlocal HF potential  $V_{\text{HF}}$ .

Once the HF equations have been solved, the energy can be determined from Eq.(3.50), which may be written in terms of radial orbitals as

$$E_{ab\dots n} = \sum_a \epsilon_a - \sum_a (V_{\text{HF}})_{aa} + \frac{1}{2} \sum_{ab} (g_{abab} - g_{abba}) \quad (3.82)$$

$$= \sum_a \epsilon_a - \frac{1}{2} \sum_{ab} (g_{abab} - g_{abba}). \quad (3.83)$$

Here, we have made use of the fact that  $(V_{\text{HF}})_{aa} = \sum_b (g_{abab} - g_{abba})$ . Expressing the energy in terms of Slater integrals, we find

$$E_{ab\dots n} = \sum_a 2[l_a] \left[ \epsilon_a - \sum_b [l_b] \left( R_0(a, b, a, b) - \sum_l \Lambda_{l_a l_b} R_l(a, b, b, a) \right) \right], \quad (3.84)$$

with  $[l_a] \stackrel{\text{def}}{=} 2l_a + 1$ .



The HF energy eigenvalue  $\epsilon_c$  is related to the energy required to remove an electron from the subshell  $c$ . If we calculate the energy of an ion with closed subshells except for a vacancy in subshell  $c$ , using a Slater determinant wave function, then we obtain

$$E_{\text{ion}} = \sum_a \langle a|h_0|a \rangle - \langle c|h_0|c \rangle + \frac{1}{2} \sum_{ab} (g_{abab} - g_{abba}) - \sum_a (g_{acac} - g_{caac}). \quad (3.85)$$

Let us use the orbitals from the closed-shell HF approximation for the atom to evaluate this expression. We then obtain

$$E_{\text{ion}} - E_{\text{atom}} = -\langle c|h_0|c \rangle - \sum_a (g_{acac} - g_{caac}) = -\langle c|h_0 + V_{\text{HF}}|c \rangle = -\epsilon_c. \quad (3.86)$$

Thus we find that the removal energy, calculated using HF wave functions for the atom, is the negative of the corresponding HF eigenvalue. This result is called Koopmans' theorem.

In Section 3.1, we have discussed the numerical solution to the HF equation for the  $1s$  orbital in helium. In Section 3.3, we discuss the numerical solution to the coupled system of HF equations that arise for other closed-subshell atoms and ions.

### 3.3 Numerical Solution to the HF Equations

As in the case of helium, the Hartree-Fock equations (3.81) for a general closed-shell atom are solved iteratively. We approximate the HF orbitals by unscreened Coulomb field orbitals initially. This is a fair approximation for the innermost  $1s$  orbitals, but a very poor approximation for the outer orbitals. To create a more realistic starting potential, we do a preliminary self-consistent calculation of the direct part of the HF potential scaled to give the correct ionic charge. The Coulomb orbitals are gradually modified until self-consistency at the level is achieved at a level of 1 part in  $10^3$ . The resulting potential is a good local approximation to HF potential and the resulting orbitals are good approximations to the final HF orbitals for outer as well as inner shells. Moreover, orbitals with the same value of  $l$  but different values of  $n$  are orthogonal. These screened orbitals are used to start the iterative solution of the HF equations. The iteration of the HF equations, including both direct and exchange terms, is then performed until self-consistency is achieved at a level of 1 part in  $10^9$ .

#### 3.3.1 Starting Approximation (HART)

As outlined above, we carry out a self-consistent calculation of single-particle orbitals in a model potential  $U(r)$  as a preliminary step in the solution to the HF equations. The model potential is obtained by scaling the direct part of the HF potential to give a potential with the proper asymptotic behavior.

We choose  $U(r) = 0$ , initially, and use the routine MASTER to solve the radial Schrödinger equation in the unscreened nuclear Coulomb field  $V(r) = -Z/r$  for

Table 3.2: Energy eigenvalues for neon. The initial Coulomb energy eigenvalues are reduced to give model potential values shown under  $U(r)$ . These values are used as initial approximations to the HF eigenvalues shown under  $V_{\text{HF}}$ .

State	Coulomb	$U(r)$	$V_{\text{HF}}$
1s	-50.00000	-29.27338	-32.77244
2s	-12.50000	-1.42929	-1.93039
2p	-12.50000	-0.65093	-0.85041

each occupied orbital  $P_a(r)$ . We accumulate the radial charge density  $\rho(r) = \sum_a (4l_a + 2)P_a(r)^2$ . The direct part of the HF potential is given in terms of  $\rho(r)$  by

$$V_{\text{dir}}(r) = \int_0^\infty dr' \frac{\rho(r')}{r_>}. \quad (3.87)$$

Asymptotically,  $\lim_{r \rightarrow \infty} V_{\text{dir}}(r) = N/r$ , where  $N$  is the number of atomic electrons. To create a model potential with the correct asymptotic behavior, we multiply  $V_{\text{dir}}$  by the factor  $(N-1)/N$ . We use the potential  $U(r) = (1-1/N)V_{\text{dir}}(r)$ , calculated self-consistently, as our starting approximation. We add  $U(r)$  to the nuclear potential and solve the radial equations once again to obtain a second approximation. This second approximation is used to obtain new values of  $\rho(r)$  and  $U(r)$ . These values are used to obtain a third approximation. This iteration procedure is continued until the potential is stable to some desired level of accuracy.

Since this potential is only used as an initial approximation in solving the HF equations, it is not necessary to carry out the self-consistent iteration accurately. We terminate the iterative solution to the equations when the relative change in the eigenvalue for each orbital, from loop to loop in the iteration, is less than 1 part in  $10^3$ .

The iteration procedure described above does not converge in general, but oscillates from loop to loop with increasing amplitude. To eliminate such oscillations, we change the initial Coulomb interaction gradually. If we designate the value of  $U(r)$  from the  $n^{\text{th}}$  iteration loop as  $U^{(n)}(r)$ , then at the  $(n+1)^{\text{st}}$  loop we use the combination

$$U(r) = \eta U^{(n+1)}(r) + (1-\eta)U^{(n)}(r)$$

rather than  $U^{(n+1)}(r)$  to continue the iteration. Choosing  $\eta$  in the range 0.375–0.5 leads to convergence in all cases.

The subroutine HART is designed to carry out the iteration. For the case of neon, it required 13 iterations to obtain the model potential  $U(r)$  self-consistent to 1 part in  $10^3$  using  $\eta = 0.5$ . The resulting eigenvalues are compared with the initial Coulomb eigenvalues and the final HF eigenvalues in Table 3.2.

A comment should be made in connection with the use of the subroutine MASTER. As discussed previously, the routine MASTER itself uses an iterative procedure to determine the radial wave functions. MASTER requires only a few iterations if an accurate estimate of the eigenvalue is provided initially. To produce such an estimate, we use perturbation theory to determine the change in the eigenvalues induced by changing the potential. A small loop is introduced after  $U(r)$  is changed at the end of an iteration step to calculate the first-order change in each of the energy eigenvalues. Perturbation theory gives

$$\delta\epsilon_a = \int_0^\infty dr [U^{(n+1)}(r) - U^{(n)}(r)] P_a^2(r). \quad (3.88)$$

This correction to the energy at the end of the  $n^{\text{th}}$  iteration is added to the output energy  $\epsilon_a$  from MASTER and used as the input energy for the  $(n+1)^{\text{st}}$  loop.

After the iteration in the routine HART is completed, we have a model potential  $U(r)$  and a set of orbitals  $P_a(r)$  and energies  $\epsilon_a$  that provide a suitable starting point for the iterative solution to the HF equations.

### 3.3.2 Refining the Solution (NRHF)

The HF equation for orbital  $P_a$  is written as a pair of inhomogeneous differential equations

$$\frac{dP_a}{dr} - Q_a = 0, \quad (3.89)$$

$$\frac{dQ_a}{dr} + f_a P_a = 2(V_{\text{HF}} - U)P_a, \quad (3.90)$$

where

$$f_a(r) = 2 \left( \epsilon_a - \frac{l_a(l_a + 1)}{2r^2} + \frac{Z}{r} - U(r) \right). \quad (3.91)$$

These equations are to be solved iteratively. We start with functions  $P_a^{(0)}(r)$  and  $Q_a^{(0)}$  obtained from the routine HART described in the previous section. To solve the HF equations, we set up an iteration scheme in which  $P_a(r)$  is replaced by  $P_a^{(n-1)}(r)$  on the right-hand side of Eq.(3.90) in the  $n^{\text{th}}$  approximation. Thus we write,

$$\frac{dP_a^{(n)}}{dr} - Q_a^{(n)} = 0, \quad (3.92)$$

$$\frac{dQ_a^{(n)}}{dr} + f_a^{(n)} P_a^{(n)} = 2(V_{\text{HF}}^{(n-1)} - U)P_a^{(n-1)}, \quad (3.93)$$

where  $f_a^{(n)}$  is given by Eq.(3.91) with  $\epsilon_a$  replaced by  $\epsilon_a^{(n)}$ . The functions  $P_a^{(0)}(r)$  and  $Q_a^{(0)}(r)$  satisfy the homogeneous equations obtained from Eqs.(3.89-3.90)

by dropping the right-hand side and replacing  $f_a$  by  $f^{(0)}$ . From Eqs.(3.92-3.93), we readily obtain the relation

$$\epsilon_a^{(n)} = \epsilon_a^{(0)} + \frac{\int_0^\infty dr P_a^{(0)}(r) \left( V_{\text{HF}}^{(n-1)} - U(r) \right) P_a^{(n-1)}(r)}{\int_0^\infty dr P_a^{(0)}(r) P_a^{(n)}(r)}. \quad (3.94)$$

We use this equation, with  $P_a^{(n)}(r)$  replaced by  $P_a^{(n-1)}(r)$  in the denominator, to obtain an approximate value of  $\epsilon_a^{(n)}$  to use in the function  $f_a^{(n)}(r)$ . This approximate value of  $\epsilon_a^{(n)}$  will be readjusted later in the iteration step to give a properly normalized orbital. The equations (3.92-3.93) are solved by using the method of variation of parameters.

**Solving the inhomogeneous equations:** Consider the pair of inhomogeneous differential equations

$$\frac{dP(r)}{dr} - Q(r) = 0, \quad (3.95)$$

$$\frac{dQ(r)}{dr} + f(r)P(r) = R(r). \quad (3.96)$$

We can obtain solutions to the homogeneous equations (obtained by setting  $R(r) = 0$ ) that are regular at the origin using the routine OUTSCH described in Chapter 2. We designate these solutions by  $P_0$  and  $Q_0$ . Similarly, we can obtain solutions to the homogeneous equations that are regular at infinity by inward integration using the routine INSCH. We designate these solutions by  $P_\infty$  and  $Q_\infty$ . We seek a solution to the inhomogeneous equations (3.95-3.96) in the form

$$P(r) = A(r)P_0(r) + B(r)P_\infty(r), \quad (3.97)$$

$$Q(r) = A(r)Q_0(r) + B(r)Q_\infty(r), \quad (3.98)$$

where  $A(r)$  and  $B(r)$  are functions that are to be determined. Substituting into Eqs.(3.95-3.96), we find that the functions  $A(r)$  and  $B(r)$  satisfy the differential equations

$$\frac{dA}{dr} = -\frac{1}{W}P_\infty(r)R(r), \quad (3.99)$$

$$\frac{dB}{dr} = \frac{1}{W}P_0(r)R(r), \quad (3.100)$$

where  $W = P_0(r)Q_\infty(r) - Q_0(r)P_\infty(r)$  is a constant (independent of  $r$ ) known as the Wronskian of the two solutions. Integrating Eqs.(3.99-3.100), we obtain

a solution to Eqs.(3.95-3.96) regular at the origin and infinity:

$$P(r) = \frac{1}{W} \left( P_\infty(r) \int_0^r dr' P_0(r') R(r') + P_0(r) \int_r^\infty dr' P_\infty(r') R(r') \right), \quad (3.101)$$

$$Q(r) = \frac{1}{W} \left( Q_\infty(r) \int_0^r dr' P_0(r') R(r') + Q_0(r) \int_r^\infty dr' P_\infty(r') R(r') \right). \quad (3.102)$$

This method of solving a linear inhomogeneous set of equations is known as the method of variation of parameters. We use the resulting formulas to obtain numerical solutions to Eqs.(3.92-3.93) at each stage of iteration.

**Normalizing the orbitals:** The orbitals obtained using Eqs.(3.101-3.102) are regular at the origin and infinity, however, they are not properly normalized. To obtain normalized orbitals at the  $n^{\text{th}}$  step of iteration, it is necessary to adjust the eigenvalue  $\epsilon_a^{(n)}$  from the approximate value given in (3.94). Let us suppose that the norm of the solution to the inhomogeneous equations is

$$\int_0^\infty dr P^2(r) = N \neq 1. \quad (3.103)$$

We modify the energy eigenvalue by a small amount  $\delta\epsilon$ . This induces small changes  $\delta P$  and  $\delta Q$  in the radial functions  $P(r)$  and  $Q(r)$ . These small changes in the solution satisfy the pair of inhomogeneous equations

$$\frac{d\delta P}{dr} - \delta Q(r) = 0, \quad (3.104)$$

$$\frac{d\delta Q}{dr} + f(r) \delta P(r) = -2\delta\epsilon P(r). \quad (3.105)$$

The solution to this equation, found by variation of parameters, is

$$\delta P(r) = -2\delta\epsilon \hat{P}(r), \quad (3.106)$$

$$\delta Q(r) = -2\delta\epsilon \hat{Q}(r), \quad (3.107)$$

with

$$\hat{P}(r) = \frac{1}{W} \left( P_\infty(r) \int_0^r dr' P_0(r') P(r') + P_0(r) \int_r^\infty dr' P_\infty(r') P(r') \right), \quad (3.108)$$

$$\hat{Q}(r) = \frac{1}{W} \left( Q_\infty(r) \int_0^r dr' P_0(r') P(r') + Q_0(r) \int_r^\infty dr' P_\infty(r') P(r') \right). \quad (3.109)$$

We must choose  $\delta\epsilon$  to insure that the orbital  $P + \delta P$  is properly normalized. Thus, we require (neglecting terms of order  $\delta P^2$ ) that

$$\int_0^\infty dr P(r)^2 + 2 \int_0^\infty dr P(r) \delta P(r) = 1. \quad (3.110)$$

This equation can be rewritten as

$$\delta\epsilon = \frac{N - 1}{4 \int_0^\infty dr P(r) \hat{P}(r)}. \quad (3.111)$$

Equation (3.111) is itself used iteratively to obtain a properly normalized orbital. Usually a single iteration is sufficient to obtain functions normalized to parts in  $10^{12}$ , although occasionally two iterations are required to obtain this accuracy.

Once starting orbitals have been obtained from the routine HART, first-order and second-order corrections are made to each orbital. A selection scheme is then set up in which the orbitals with the largest values of the relative change in energy are treated in order. For example, if we are considering the Be atom which has 2 orbitals, we iterate the 1s orbital twice then we iterate the 2s orbital twice. At this point, we chose the orbital with the largest value of  $|\epsilon_a^{(2)} - \epsilon_a^{(1)}|/|\epsilon_a^{(2)}|$  and iterate this orbital until the relative change in energy is no longer the larger of the two. We then iterate the other orbital until the relative change in energy is no longer the larger. The selection procedure continues until the changes in relative energies of both orbitals are less than one part in  $10^9$ .

Once the iteration has converged to this level of accuracy, we calculate the total energy, check the orthogonality and normalization of the orbitals, and write the radial functions to an output data file for use in other applications.

In Table 3.3, we list the HF eigenvalues and total energies for the noble gases helium, neon, argon, krypton and xenon. In this table, we also give the average values of  $r$  and  $1/r$  for each individual subshell. It should be noticed that  $\langle nl|r|nl\rangle$  and  $\langle nl|1/r|nl\rangle$  depend strongly on the principal quantum number  $n$  but only weakly on the angular momentum quantum number  $l$  within a shell. For comparison, we also give the negative of the removal energy ( $-B_{nl}$ ) for an electron in the shell  $nl$  which, according to Koopmans' theorem, is approximately the HF eigenvalue  $\epsilon_{nl}$ . The experimental binding energies presented in this table are averages over the fine-structure components.

In Fig. 3.3, we show the radial wave functions for the occupied orbitals in neon and argon. The 1s orbitals peak at about  $1/Z$  a.u. whereas the outer orbitals peak at about 1 a.u. and become insignificant beyond 4 a.u. for both elements. In Fig. 3.4, we plot the radial densities for the elements beryllium, neon, argon and krypton. The shell structure of these elements is evident in the figure.

### 3.4 Atoms with One Valence Electron

Let us consider the alkali-metal atoms lithium, sodium, potassium, rubidium and cesium, all of which have one valence electron outside of closed shells. We

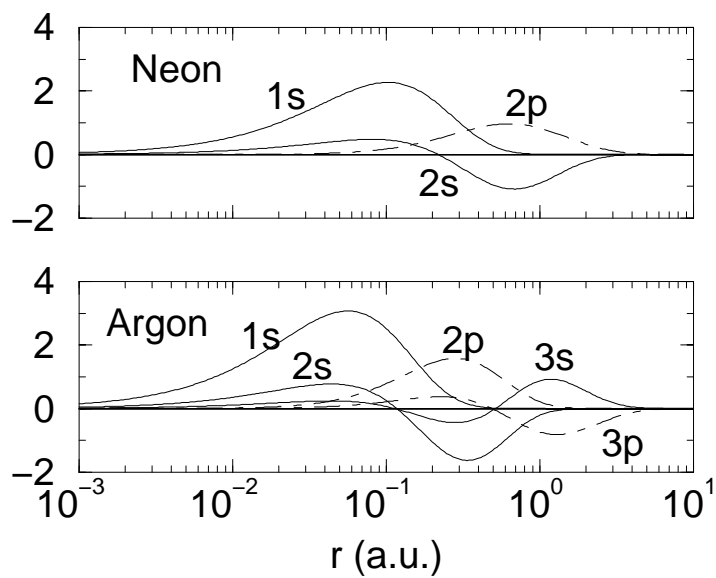


Figure 3.3: Radial HF wave functions for neon and argon.

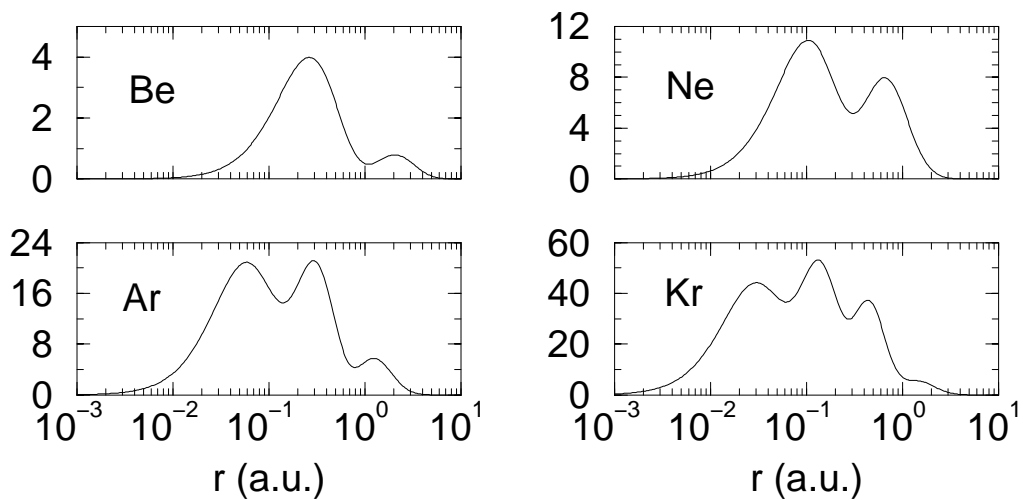


Figure 3.4: Radial HF densities for beryllium, neon, argon and krypton.

Table 3.3: HF eigenvalues  $\epsilon_{nl}$ , average values of  $r$  and  $1/r$  for noble gas atoms. The negative of the experimental removal energies  $-B_{\text{exp}}$  from Bearden and Burr (1967, for inner shells) and Moore (1957, for outer shell) is also listed for comparison.

Atom	$nl$	$\epsilon_{nl}$	$\langle r \rangle$	$\langle 1/r \rangle$	$-B_{\text{exp}}$
Helium	$1s$	-0.917956	.92727	1.68728	-0.903
	$E_{\text{tot}}$	-2.861680			
Neon	$1s$	-32.772443	.15763	9.61805	-31.86
	$2s$	-1.930391	.89211	1.63255	-1.68
	$2p$	-.850410	.96527	1.43535	-0.792
	$E_{\text{tot}}$	-128.547098			
Argon	$1s$	-118.610350	.08610	17.55323	-117.70
	$2s$	-12.322153	.41228	3.55532	-12.00
	$2p$	-9.571466	.37533	3.44999	-9.10
	$3s$	-1.277353	1.42217	.96199	-0.93
	$3p$	-.591017	1.66296	.81407	-0.579
	$E_{\text{tot}}$	-526.817512			
Krypton	$1s$	-520.165468	.04244	35.49815	-526.47
	$2s$	-69.903082	.18726	7.91883	-70.60
	$2p$	-63.009785	.16188	7.86843	-62.50
	$3s$	-10.849467	.53780	2.63756	...
	$3p$	-8.331501	.54263	2.52277	-8.00
	$3d$	-3.825234	.55088	2.27694	-3.26
	$4s$	-1.152935	1.62939	.80419	-0.88
	$4p$	-.524187	1.95161	.66922	-0.514
	$E_{\text{tot}}$	-2752.054983			
Xenon	$1s$	-1224.397777	.02814	53.46928	-1270.14
	$2s$	-189.340123	.12087	12.30992	-200.39
	$2p$	-177.782449	.10308	12.29169	-181.65
	$3s$	-40.175663	.31870	4.44451	-36.72
	$3p$	-35.221662	.30943	4.52729	-34.44
	$3d$	-26.118869	.28033	4.30438	-24.71
	$4s$	-7.856302	.74527	1.84254	...
	$4p$	-6.008338	.77702	1.74149	...
	$4d$	-2.777881	.87045	1.50874	...
	$5s$	-.944414	1.98096	.64789	...
	$5p$	-.457290	2.33798	.54715	-0.446
$E_{\text{tot}}$	-7232.138370				



take the wave function of an alkali-metal atom to be a Slater determinant composed of orbitals from the closed shells and a single valence orbital  $\psi_v$ . The energy is given by the expression

$$E_{ab\dots nv} = \sum_a \langle a|h_0|a \rangle + \langle v|h_0|v \rangle + \frac{1}{2} \sum_{ab} (g_{baba} - g_{abba}) + \sum_a (g_{avav} - g_{vaav}), \quad (3.112)$$

where the sums over  $a$  and  $b$  extend over all closed subshells. We can use the results from the previous section to carry out the sums over the magnetic substates of the closed shells to obtain

$$E_{ab\dots nv} = E_{ab\dots n} + I(n_v l_v) + \sum_{n_a l_a} 2[l_a] \left( R_0(avav) - \sum_k \Lambda_{l_a k l_v} R_k(vaav) \right), \quad (3.113)$$

where  $E_{ab\dots n}$  is the energy of the closed core given in Eq.(3.67). Let us assume that the orbitals for the closed shells have been determined from a HF calculation for the closed ionic core. The core energy in Eq.(3.113) is then fixed. The valence orbital in Eq.(3.113) is determined variationally. The requirement that the energy be stationary under variations of the valence electron radial function  $P_v(r)$ , subject to the constraint that the valence orbital remain normalized, leads to the differential equation

$$-\frac{1}{2} \frac{d^2 P_v}{dr^2} + \left( V_{\text{HF}} - \frac{Z}{r} + \frac{l_v(l_v + 1)}{2r^2} \right) P_v = \epsilon_v P_v, \quad (3.114)$$

where  $V_{\text{HF}}$  is the core HF potential written down in Eqs.(3.75-3.76). This homogeneous equation can be solved using the variation of parameters scheme described in the previous section, once the core orbitals are known. Since the equation is homogeneous, the solution can be trivially normalized. The potential in Eq.(3.113) is the HF potential of the  $N - 1$  electron ion; it is referred to as the  $V_{\text{HF}}^{N-1}$  potential.

Since the valence electron and those core electrons that have the same orbital angular momentum as the valence electron move in precisely the same potential, it follows that the corresponding radial functions are orthogonal. Thus,

$$\int_0^\infty dr P_v(r) P_a(r) = 0 \quad \text{for } l_a = l_v. \quad (3.115)$$

The total energy of the atom can be expressed in terms of the HF eigenvalue  $\epsilon_v$  as

$$E_{ab\dots nv} = E_{ab\dots n} + \epsilon_v, \quad (3.116)$$

where, again,  $E_{ab\dots n}$  is the energy of the ionic core. It follows that the binding energy of the valence electron is just the negative of the corresponding eigenvalue  $B_v = E_{\text{ion}} - E_{\text{atom}} = -\epsilon_v$ .

Eigenvalues of the low-lying states of the alkali-metal atoms are presented in Table 3.4. These values agree with measured binding energies at the level of a few percent for lithium. This difference between HF eigenvalues and experiment grows to approximately 10% for cesium.

Table 3.4: Energies of low-lying states of alkali-metal atoms as determined in a  $V_{\text{HF}}^{N-1}$  Hartree-Fock calculation.

Lithium		Sodium		Potassium		Rubidium		Cesium	
$nl$	$\epsilon_{nl}$	$nl$	$\epsilon_{nl}$	$nl$	$\epsilon_{nl}$	$nl$	$\epsilon_{nl}$	$nl$	$\epsilon_{nl}$
2s	-1.196304	3s	-1.181801	4s	-1.146954	5s	-1.137201	6s	-1.123013
3s	-0.073797	4s	-0.070106	5s	-0.060945	6s	-0.058139	7s	-0.053966
4s	-0.038474	5s	-0.037039	6s	-0.033377	7s	-0.032208	8s	-0.030439
5s	-0.023570	6s	-0.022871	7s	-0.021055	8s	-0.020461	9s	-0.019551
2p	-1.128637	3p	-1.109438	4p	-1.095553	5p	-1.090135	6p	-1.084056
3p	-0.056771	4p	-0.050321	5p	-0.045563	6p	-0.043652	7p	-0.041463
4p	-0.031781	5p	-0.028932	6p	-0.026773	7p	-0.025887	8p	-0.024858
5p	-0.020276	6p	-0.018783	7p	-0.017628	8p	-0.017147	9p	-0.016584
3d	-0.055562	3d	-0.055667	3d	-0.058117	4d	-0.060066	5d	-0.066771
4d	-0.031254	4d	-0.031315	4d	-0.032863	5d	-0.033972	6d	-0.037148
5d	-0.020002	5d	-0.020038	5d	-0.020960	6d	-0.021570	7d	-0.023129

### 3.5 Dirac-Fock Equations

The Hartree-Fock theory is easily extended to include relativistic effects. We start with a many-body Hamiltonian patterned after its nonrelativistic counterpart:

$$H(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_{i=1}^N h_0(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}}. \quad (3.117)$$

In the relativistic case, the one-electron Hamiltonian  $h_0(\mathbf{r})$  is taken to be the Dirac Hamiltonian

$$h_0(\mathbf{r}) = c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta c^2 - Z/r. \quad (3.118)$$

The resulting many-body Hamiltonian is called the Dirac-Coulomb Hamiltonian. It provides a useful starting point for discussions of relativistic effects in atoms. The Dirac-Coulomb Hamiltonian must be supplemented by the Breit interaction to understand fine-structure corrections precisely. We will ignore the Breit interaction initially, and return to it after we have derived the Dirac-Fock equations.

The reader must be cautioned that there are difficulties associated with applications of the Dirac-Coulomb Hamiltonian (with or without the Breit Interaction) in higher-order perturbation theory calculations. These difficulties can only be resolved by recourse to Quantum Electrodynamics. We will discuss these difficulties and their solution when we take up relativistic many-body perturbation theory. For doing calculations at the Hartree-Fock level of approximation,

the Dirac-Coulomb Hamiltonian is the appropriate point of departure.

As in the nonrelativistic case, we introduce an average central potential  $U(r)$  and the corresponding one-electron Hamiltonian  $h(\mathbf{r})$ :

$$h(\mathbf{r}) = c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta c^2 + V(r), \quad (3.119)$$

with  $V(r) = -Z/r + U(r)$ . The Dirac-Coulomb Hamiltonian can then be written as  $H = H_0 + V$  with

$$H_0 = \sum_i h(\mathbf{r}_i) \quad (3.120)$$

$$V = \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} - \sum_{i=1}^N U(r_i). \quad (3.121)$$

If  $\varphi_a(\mathbf{r})$  is an eigenfunction of the one-electron Dirac Hamiltonian  $h(\mathbf{r})$  with eigenvalue  $\epsilon_a$ , then the product wave function

$$\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) \cdots \varphi_n(\mathbf{r}_N) \quad (3.122)$$

is an eigenfunction of  $H_0$  with eigenvalue

$$E_{ab\dots n}^{(0)} = \epsilon_a + \epsilon_b + \cdots + \epsilon_n.$$

A properly antisymmetrized product wave function is given by the Slater determinant:

$$\Psi_{ab\dots n}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_a(\mathbf{r}_1) & \varphi_b(\mathbf{r}_1) & \cdots & \varphi_n(\mathbf{r}_1) \\ \varphi_a(\mathbf{r}_2) & \varphi_b(\mathbf{r}_2) & \cdots & \varphi_n(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_a(\mathbf{r}_N) & \varphi_b(\mathbf{r}_N) & \cdots & \varphi_n(\mathbf{r}_N) \end{vmatrix}. \quad (3.123)$$

We take the wave function for the ground-state of a closed-shell atom to be a Slater determinant formed from the  $N$  lowest-energy single-particle orbitals and evaluate the expectation value of the energy. We find that

$$E_{ab\dots n} = \sum_a \langle a|h_0|a \rangle + \frac{1}{2} \sum_{ab} (g_{abab} - g_{abba}). \quad (3.124)$$

This is just the expression obtained previously in the nonrelativistic case. Here, however, the Coulomb matrix elements  $g_{abcd}$  are to be evaluated using Dirac orbitals rather than nonrelativistic orbitals. As in Chapter 2, we write the one-electron Dirac orbital  $\varphi_a(\mathbf{r})$  in terms of spherical spinors as

$$\varphi_a(\mathbf{r}) = \frac{1}{r} \begin{pmatrix} iP_a(r)\Omega_{\kappa_a m_a}(\hat{r}) \\ Q_a(r)\Omega_{-\kappa_a m_a}(\hat{r}) \end{pmatrix}. \quad (3.125)$$

Before we can carry out the sums over magnetic quantum numbers, it is necessary to do an angular momentum decomposition of the Coulomb integrals

$g_{abcd}$ . In making this decomposition, we use the fact that

$$\begin{aligned} \varphi_a^\dagger(\mathbf{r}) \varphi_c(\mathbf{r}) &= \\ & \frac{1}{r^2} [P_a(r)P_c(r) \Omega_{\kappa_a m_a}^\dagger(\hat{r}) \Omega_{\kappa_c m_c}(\hat{r}) + Q_a(r)Q_c(r) \Omega_{-\kappa_a m_a}^\dagger(\hat{r}) \Omega_{-\kappa_c m_c}(\hat{r})] \\ &= \frac{1}{r^2} [P_a(r)P_c(r) + Q_a(r)Q_c(r)] \Omega_{\kappa_a m_a}^\dagger(\hat{r}) \Omega_{\kappa_c m_c}(\hat{r}). \end{aligned} \quad (3.126)$$

Introducing the expansion

$$\frac{1}{r_{12}} = \sum_{kq} \frac{r_{<}^k}{r_{>}^{k+1}} (-1)^q C_{-q}^k(\hat{r}_1) C_q^k(\hat{r}_2), \quad (3.127)$$

the Coulomb integral  $g_{abcd}$  can be written

$$g_{abcd} = \sum_{kq} (-1)^q \langle \kappa_a m_a | C_{-q}^k | \kappa_c m_c \rangle \langle \kappa_b m_b | C_q^k | \kappa_d m_d \rangle R_k(abcd), \quad (3.128)$$

where  $R_k(abcd)$  is the (relativistic) Slater integral defined by

$$\begin{aligned} R_k(abcd) &= \int_0^\infty dr_1 [P_a(r_1)P_c(r_1) + Q_a(r_1)Q_c(r_1)] \times \\ & \int_0^\infty dr_2 \frac{r_{<}^k}{r_{>}^{k+1}} [P_b(r_2)P_d(r_2) + Q_b(r_2)Q_d(r_2)]. \end{aligned} \quad (3.129)$$

The angular matrix elements in Eq.(3.128) are given by

$$\langle \kappa_a m_a | C_q^k | \kappa_b m_b \rangle = \int d\Omega \Omega_{\kappa_a m_a}^\dagger(\hat{r}) C_q^k(\hat{r}) \Omega_{\kappa_b m_b}(\hat{r}). \quad (3.130)$$

Since the spherical spinors are angular momentum eigenstates and since the functions  $C_q^k(\hat{r})$  are spherical tensor operators, the Wigner-Eckart theorem may be used to infer the dependence on the magnetic quantum numbers. We obtain,

$$\langle \kappa_a m_a | C_q^k | \kappa_b m_b \rangle = - \begin{array}{c} |j_a m_a \\ \hline kq \\ \hline |j_b m_b \end{array} \langle \kappa_a || C^k || \kappa_b \rangle. \quad (3.131)$$

The reduced matrix element  $\langle \kappa_a || C^k || \kappa_b \rangle$  is found to be

$$\langle \kappa_a || C^k || \kappa_b \rangle = (-1)^{j_a+1/2} \sqrt{[j_a][j_b]} \begin{pmatrix} j_a & j_b & k \\ -1/2 & 1/2 & 0 \end{pmatrix} \Pi(l_a + k + l_b), \quad (3.132)$$

where

$$\Pi(l) = \begin{cases} 1, & \text{if } l \text{ is even} \\ 0, & \text{if } l \text{ is odd} \end{cases}. \quad (3.133)$$

With these definitions, we may write

$$g_{abcd} = \sum_k - \begin{array}{c} |j_a m_a \\ \hline k \\ \hline |j_c m_c \end{array} + \begin{array}{c} |j_b m_b \\ \hline k \\ \hline |j_d m_d \end{array} X_k(abcd), \quad (3.134)$$

where

$$X_k(abcd) = (-1)^k \langle \kappa_a || C^k || \kappa_c \rangle \langle \kappa_b || C^k || \kappa_d \rangle R_k(abcd). \quad (3.135)$$

Let us carry out the sum over  $m_b$  of the direct and exchange Coulomb matrix elements in Eq.(3.124). To this end, we make use of the easily verified identities

$$- \begin{array}{c} \begin{array}{c} \leftarrow j_a m_a \\ \leftarrow k \\ \leftarrow j_a m_a \end{array} \quad \begin{array}{c} \begin{array}{c} \rightarrow j_b \\ \rightarrow \\ \rightarrow \end{array} \end{array} = \sqrt{\frac{[j_b]}{[j_a]}} \delta_{k0}, \quad (3.136)$$

and

$$\begin{array}{c} \begin{array}{c} \leftarrow j_a m_a \\ \leftarrow k \\ \leftarrow j_a m_a \end{array} \quad \begin{array}{c} \begin{array}{c} \rightarrow j_a m_a \\ \rightarrow \\ \rightarrow \end{array} \end{array} = (-1)^{j_a - j_b + k} \frac{1}{[j_a]}. \quad (3.137)$$

With the aid of the first of these identities, we find

$$\begin{aligned} \sum_{m_b} g_{abab} &= \sqrt{\frac{[j_b]}{[j_a]}} X_0(abab) \\ &= [j_b] R_0(abab), \end{aligned} \quad (3.138)$$

where we have used the fact that

$$\langle \kappa_a || C^0 || \kappa_a \rangle = \sqrt{[j_a]}. \quad (3.139)$$

Using the second graphical identity above, we find that

$$\sum_{m_b} g_{abba} = \sum_k (-1)^{j_a - j_b + k} \frac{1}{[j_a]} X_k(abba) \quad (3.140)$$

$$= [j_b] \sum_k \Lambda_{\kappa_a k \kappa_b} R_k(abba), \quad (3.141)$$

with

$$\Lambda_{\kappa_a k \kappa_b} = \frac{\langle \kappa_a || C^k || \kappa_b \rangle^2}{[j_a][j_b]} = \begin{pmatrix} j_a & j_b & k \\ -1/2 & 1/2 & 0 \end{pmatrix}^2 \Pi(l_a + k + l_b). \quad (3.142)$$

It is now a simple matter to carry out the double sum over magnetic quantum numbers in the expression for the Coulomb energy in Eq.(3.124). We obtain

$$\frac{1}{2} \sum_{m_a m_b} (g_{abab} - g_{abba}) = \frac{1}{2} [j_a][j_b] \left( R_0(abab) - \sum_k \Lambda_{\kappa_a k \kappa_b} R_k(abba) \right). \quad (3.143)$$

The terms  $\langle a | h_0 | a \rangle$  in Eq.(3.124) are independent of  $m_a$ . They are given by the radial integral

$$\begin{aligned} I_a = \langle a | h_0 | a \rangle &= \int_0^\infty dr \left\{ P_a \left( -\frac{Z}{r} + c^2 \right) P_a + c P_a \left( \frac{d}{dr} - \frac{\kappa}{r} \right) Q_a \right. \\ &\quad \left. - c Q_a \left( \frac{d}{dr} + \frac{\kappa}{r} \right) P_a + Q_a \left( -\frac{Z}{r} - c^2 \right) Q_a \right\}. \end{aligned} \quad (3.144)$$

The energy can therefore be expressed as

$$E_{ab\dots n} = \sum_a [j_a] \left\{ I_a + \frac{1}{2} \sum_b [j_b] \left[ R_0(abab) - \sum_k \Lambda_{\kappa_a k \kappa_b} R_k(abba) \right] \right\}, \quad (3.145)$$

where the indices  $a$  and  $b$  refer to  $(n_a \kappa_a)$  and  $(n_b \kappa_b)$ , respectively.

Again, as in the nonrelativistic case, we require that  $E_{ab\dots n}$  be stationary with the constraint that the radial functions having the same angular quantum number  $\kappa$  but different principal quantum numbers  $n$  be orthogonal. This requirement is combined with the normalization condition in the equation

$$N_{n_a \kappa_a, n_b \kappa_a} = \int_0^\infty dr [P_{n_a \kappa_a}(r) P_{n_b \kappa_a}(r) + Q_{n_a \kappa_a}(r) Q_{n_b \kappa_a}(r)] = \delta_{n_a n_b}. \quad (3.146)$$

Introducing Lagrange multipliers  $\lambda_{n_a \kappa_a, n_b \kappa_a}$  (assumed to be symmetric with respect to  $n_a$  and  $n_b$ ), the variational condition is

$$\delta(E_{ab\dots n} - \sum_{ab} \delta_{\kappa_a \kappa_b} \lambda_{n_a \kappa_a, n_b \kappa_a} N_{n_a \kappa_a, n_b \kappa_b}) = 0, \quad (3.147)$$

with respect to variations in the radial functions  $P_a$  and  $Q_a$ . The variations  $\delta P_a(r)$  and  $\delta Q_a(r)$  are required to vanish at the origin and infinity. After an integration by parts, the variational condition immediately leads to the ‘‘Dirac-Fock’’ differential equations

$$\left( V_{\text{HF}} - \frac{Z}{r} + c^2 \right) P_a + c \left( \frac{d}{dr} - \frac{\kappa}{r} \right) Q_a = \epsilon_a P_a + \sum_{n_b \neq n_a} \epsilon_{n_a \kappa_a, n_b \kappa_a} P_{n_b \kappa_a} \quad (3.148)$$

$$-c \left( \frac{d}{dr} + \frac{\kappa}{r} \right) P_a + \left( V_{\text{HF}} - \frac{Z}{r} - c^2 \right) Q_a = \epsilon_a Q_a + \sum_{n_b \neq n_a} \epsilon_{n_a \kappa_a, n_b \kappa_a} Q_{n_b \kappa_a}. \quad (3.149)$$

Here, the HF potential  $V_{\text{HF}}$  is defined by its action on a radial orbital. Thus, if  $R_a(r)$  represents either the large component radial function  $P_a(r)$  or the small component function  $Q_a(r)$ , then

$$V_{\text{HF}} R_a(r) = \sum_b [j_b] \left( v_0(b, b, r) R_a(r) - \sum_k \Lambda_{\kappa_a k \kappa_b} v_k(b, a, r) R_b(r) \right). \quad (3.150)$$

The (relativistic) screening potentials in this equation are given by

$$v_k(a, b, r) = \int_0^\infty dr' \frac{r_{<}^k}{r_{>}^{k+1}} [P_a(r') P_b(r') + Q_a(r') Q_b(r')]. \quad (3.151)$$

In Eqs.(3.148, 3.149), we have introduced the notation  $\epsilon_a = \lambda_{n_a \kappa_a, n_a \kappa_a} / [j_a]$  and  $\epsilon_{n_a \kappa_a, n_b \kappa_a} = \lambda_{n_a \kappa_a, n_b \kappa_a} / [j_a]$ .

Just as in the nonrelativistic case, the radial orbitals belonging to a particular value of the angular quantum number  $\kappa$  but different values of the principal quantum number  $n$  are orthogonal for arbitrary values of the off-diagonal Lagrange multiplier  $\epsilon_{n_a \kappa_a, n_b \kappa_a}$ . We make the simplest choice here, namely,  $\epsilon_{n_a \kappa_a, n_b \kappa_a} = 0$ . With this choice, the Dirac-Fock equations become a set of coupled, non-linear eigenvalue equations. These equations are to be solved self-consistently to obtain the occupied orbitals and the associated energy eigenvalues.

The total energy of the atom may be easily calculated, once the Dirac-Fock equations have been solved using Eq.(3.145). Alternatively, it can be written in terms of the Dirac-Fock eigenvalues as

$$E_{ab\dots n} = \sum_a [j_a] \epsilon_a - \frac{1}{2} \sum_{ab} [j_a][j_b] \left( R_0(abab) - \sum_k \Lambda_{\kappa_a k \kappa_b} R_k(abba) \right). \quad (3.152)$$

As in the nonrelativistic case, Koopmans' theorem leads to the interpretation of the energy eigenvalue  $\epsilon_a$  as the negative of the removal energy of an electron from subshell  $a$  ( $-B_a$ ).

**Numerical Considerations:** The numerical techniques used to solve the Dirac-Fock equations are similar to those used in the nonrelativistic case. Starting from Coulomb wave functions, a model potential  $U(r)$ , taken to be the direct part of the HF potential scaled to give the correct asymptotic behavior, is obtained iteratively using the Dirac routine MASTER. The Dirac-Fock equations are rewritten as inhomogeneous equations, in a form suitable for iteration starting from the model-potential orbitals:

$$\begin{aligned} \left( U - \frac{Z}{r} + c^2 - \epsilon_a^{(n)} \right) P_a^{(n)} + c \left( \frac{d}{dr} - \frac{\kappa}{r} \right) Q_a^{(n)} = \\ - \left( V_{\text{HF}}^{(n-1)} - U \right) P_a^{(n-1)} \end{aligned} \quad (3.153)$$

$$\begin{aligned} -c \left( \frac{d}{dr} + \frac{\kappa}{r} \right) P_a^{(n)} + \left( U - \frac{Z}{r} - c^2 - \epsilon_a^{(n)} \right) Q_a^{(n)} = \\ - \left( V_{\text{HF}}^{(n-1)} - U \right) Q_a^{(n-1)}. \end{aligned} \quad (3.154)$$

These equations are solved at each stage of iteration and the energy adjusted using a variation of parameters scheme similar to that used in the nonrelativistic case. We leave it to the reader to write out the detailed formulas for solving the inhomogeneous equations. The iteration procedure is continued until the relative change in energy for each orbital is less than one part in  $10^9$ . At this point the total energy is calculated, the orthogonality of the orbitals is checked and the wave functions are written to an external file for use in other applications.

As an example, we present the eigenvalues obtained from a Dirac-Fock calculation of the closed-shell mercury atom ( $Z=80$ ) in Table 3.5. These eigenvalues

Table 3.5: Dirac-Fock eigenvalues (a.u.) for mercury,  $Z = 80$ .  $E_{\text{tot}} = -19648.8585$  a.u.. For the inner shells, we also list the experimental binding energies from Bearden and Burr (1967) for comparison.

$nl_j$	$\epsilon_{nl_j}$	$-B_{nl_j}$	$nl_j$	$\epsilon_{nl_j}$	$-B_{nl_j}$
$1s_{1/2}$	-3074.2259	-3054.03			
$2s_{1/2}$	-550.2508	-545.35			
$3s_{1/2}$	-133.1130	-125.86			
$4s_{1/2}$	-30.6482	-27.88			
$5s_{1/2}$	-5.1030	-3.96			
$6s_{1/2}$	-0.3280	-0.384			
$2p_{1/2}$	-526.8546	-522.17	$2p_{3/2}$	-455.1566	-451.44
$3p_{1/2}$	-122.6388	-120.48	$3p_{3/2}$	-106.5451	-104.63
$4p_{1/2}$	-26.1240	-24.88	$4p_{3/2}$	-22.1886	-20.98
$5p_{1/2}$	-3.5379	-2.64	$5p_{3/2}$	-2.8420	-2.12
$3d_{3/2}$	-89.4368		$3d_{5/2}$	-86.0201	
$4d_{3/2}$	-14.7967		$4d_{5/2}$	-14.0526	
$5d_{3/2}$	-0.6501		$5d_{5/2}$	-0.5746	
$4f_{5/2}$	-4.4729		$4f_{7/2}$	-4.3117	

are also compared with experimental removal energies in the table. The ground-state configuration consists of 22 subshells:  $(1s_{1/s})^2 \cdots (5d_{3/2})^4 (5d_{5/2})^6 (6s_{1/s})^2$ . The fine-structure splitting between levels having the same  $n$  and  $l$  but different  $j$  is evident in both the theoretical and experimental energies. The differences between the experimental and theoretical energies is partly due to the approximation involved in interpreting energy eigenvalues as binding energies (Koopmans' theorem) and partly to the neglect of the Breit interaction and QED corrections. When these effects are considered, the agreement between theory and experiment improves to one part in  $10^5$  the inner electrons.

**Nuclear Finite Size:** In this example, we have included the effects of nuclear finite size by replacing the nuclear Coulomb potential  $-Z/r$  with the potential of a finite charge distribution. We assume that the nucleus is described by a uniform ball of charge of radius  $R$ . Under this assumption, the nuclear potential can be written

$$V_{\text{nuc}}(r) = \begin{cases} -Z/R (3/2 - r^2/2R^2) & r < R \\ -Z/r & r \geq R \end{cases} \quad (3.155)$$

The root-mean-square radius of a uniform charge distribution  $R_{\text{rms}}$  is related to its radius  $R$  through

$$R = \sqrt{5/3} R_{\text{rms}}. \quad (3.156)$$



Table 3.6: Dirac-Fock eigenvalues  $\epsilon$  of valence electrons in Cs ( $Z = 55$ ) and theoretical fine-structure intervals  $\Delta$  are compared with measured energies (Moore).  $\Delta_{nl} = \epsilon_{nlj=l+1/2} - \epsilon_{nlj=l-1/2}$

$nl_j$	$\epsilon$	$\Delta_{nl}$	$-B_{\text{exp}}$	$\Delta_{\text{exp}}$
$6s_{1/2}$	-.1273680		-0.143100	
$6p_{1/2}$	-.0856159		-0.092168	
$6p_{3/2}$	-.0837855	0.001830	-0.089643	0.002525
$5d_{3/2}$	-.0644195		-0.077035	
$5d_{5/2}$	-.0645296	-0.000110	-0.076590	0.000445
$7s_{1/2}$	-.0551873		-0.058646	
$7p_{1/2}$	-.0420214		-0.043928	
$7p_{3/2}$	-.0413681	0.000653	-0.043103	0.000825
$6d_{3/2}$	-.0360870		-0.040177	
$6d_{5/2}$	-.0360899	-0.000029	-0.039981	0.000196
$8s_{1/2}$	-.0309524		-0.032302	
$4f_{5/2}$	-.0312727		-0.031596	
$4f_{7/2}$	-.0312737	0.000000	-0.031595	-0.000001

High-energy electron-nucleus scattering experiments and measurements of energies of muonic xrays allow one to determine  $R_{\text{rms}}$  for many nuclei reliably. A tabulation of  $R$  and  $R_{\text{rms}}$  throughout the periodic table by analysis of such experiments is given by Johnson and Soff. The radii of nuclei for which no direct measurements are available can be estimated using the empirical formula

$$R_{\text{rms}} = 0.836A^{1/3} + 0.570 \text{ fm} \quad A > 9, \quad (3.157)$$

which fits the available data to  $\pm 0.05$  fm.

**Atoms with One-Valence Electron:** Again, in parallel with the nonrelativistic theory, we can obtain wave functions for atoms with one-electron beyond closed shells by solving the valence orbital Dirac-Fock equations in the fixed  $V_{\text{HF}}^{N-1}$  potential of the closed shell ion. As an example, we show the Dirac-Fock eigenvalues for the 13 lowest states in Cs ( $Z = 55$ ) in Table 3.6. For this atom, theoretical eigenvalues and experimental removal energies agree to about 10%. The theoretical fine-structure splitting for  $np$  levels ( $\Delta_{np} = \epsilon_{np_{3/2}} - \epsilon_{np_{1/2}}$ ) agrees with experiment only in order of magnitude, whereas, the fine-structure interval for  $nd$  levels disagrees with experiment even in sign. To understand these differences, we must consider correlation effects as well as the Breit interaction. In the following chapter, we introduce perturbation theoretic methods for treating correlation corrections.



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