Basic Concepts of Self-Consistent-Field Theory

S. M. Blinder

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S. M. BLINDER

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48104

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According to Hartree's self-consistent-field (SCF) model of the atom, the motion of each electron in the effective field of the N-1 others is governed by a one-particle Schrödinger equation. Self-consistency of the electronic charge distribution with its own electrostatic field leads to a set of coupled integrodifferential equations (Hartree equations) for N one-particle wave-functions (atomic orbitals). The Hartree equations were subsequently shown to be precisely the conditions for optimization of an approximate wavefunction consisting of a product of atomic orbitals. An improved formalism, due to Slater and to Fock, represents the atomic wavefunction by a determinant built of atomic spin-orbitals and is thereby consistent with the Pauli principle. Application of the variational principle to a Slater determinant leads to a set of N coupled equations (Hartree–Fock equations), quite similar to Hartree's equations but con-taining, in addition, exchange interactions—an effect having no classical analog. The error inherent in the Hartree–Fock method, known as electron correlation, arises from smoothing-out of interelectronic repulsive interactions into effective Coulomb and exchange potentials. It accounts for roughly a 1% error in the total energy but is magnified in energy differences, which are more directly related to experimental quantities. A significant improvement in computational facility is achieved if the orbital functions are expanded in terms of a finite set of basis functions. The integrodifferential equations are thereby transformed into algebraic equations (Roothaan's equations) for the expansion coefficients. The analytic approach makes it possible to apply the self-consistent-field method to molecular systems. To date, SCF cal-culations have been carried out, in some form, for all the atoms in the periodic table and for a growing list of diatomic and polyatomic molecules.

THE fundamental idea of the self-consistent field (SCF) occurs in a well-known law in the theory of vacuum tubes. The "three-halves-power law" governing space-charge limited cath-ode emission in a diode is derived by calculating the space-charge density and the current density as functions of the potential field between the plates. But the field is itself determined, through Poisson's equation, by the space-charge distribu-tion. Requiring self-consistency of cause and effect of the space charge leads to a formula for maximum current density. The derivation is given in detail in Appendix A.

Applications of the self-consistent-field (SCF) approach to the motions of electrons in atoms were attempted in the early 1920's, on the basis of the old quantum theory.[1] It was found possible to reproduce quite closely the energy levels of a valence electron (e.g., $3s$ in sodium atom) if the

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[1] E. Fues, Z. Physik 11, 364 (1922); 12, 1 (1922); D. R. Hartree, Proc. Cambridge Phil. Soc. 21, 625 (1923); R. B. Lindsay, J. Math. and Phys. 3, 191 (1924). See, also, J. C. Slater, Rev. Mod. Phys. 35, 484 (1963).

Bohr orbits of the inner electrons were smeared out into a continuous, spherically symmetrical charge distribution—a rather unreasonable thing at the time.

In accordance with wave mechanics (1926), however, a bound electron does behave as a charge cloud, with charge density given by $\rho(\mathbf{r})$ $-e|\psi(\mathbf{r})|^2$. Hartree,[2] using quantum mechanics rather than classical mechanics in the cause-effect relationships, worked out a self-consistent-field theory for atoms.

We illustrate the SCF method for the simplest possible example—the two-electron atom (e.g., helium). Electron 1 is presumed to move in the combined field of the nucleus—taken as a point-positive charge Ze—and electron 2—taken as a continuous negative charge distribution of density $\rho_2(\mathbf{r}) = e|\psi_2(\mathbf{r})|^2$, where $\psi_2(\mathbf{r})$ is the wavefunction describing the state of electron 2. From electrostatics, the form of this potential-energy field is given by

$$V(\mathbf{r}) \equiv V(\psi_2) = -\frac{Ze^2}{r} + e^2 \int d\tau' \frac{|\psi_2(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}. \quad (1)$$

The vector $\mathbf{r}$, with origin at the nucleus, refers here to the instantaneous position of electron 1. The notation $V(\psi_2)$ emphasizes the dependence of the potential on the charge distribution of electron 2. The dynamical behavior of electron 1 is governed by the one-particle Schrödinger equation.

$$\left\{ -\frac{\hbar^2}{2m}\nabla^2 + V(\psi_2) \right\} \psi_1(\mathbf{r}) = \epsilon_1 \psi_1(\mathbf{r}). \quad (2)$$

By an analogous argument, interchanging the labels 1 and 2, the wavefunction for electron 2 is the solution of

$$\left\{ -\frac{\hbar^2}{2m}\nabla^2 + V(\psi_1) \right\} \psi_2(\mathbf{r}) = \epsilon_2 \psi_2(\mathbf{r}). \quad (3)$$

The coupled differential equations (2) and (3), known as the Hartree equations, may be abbreviated,

$$\begin{aligned} \mathcal{H}_1^{\text{eff}}\psi_1(\mathbf{r}) &= \epsilon_1\psi_1(\mathbf{r}), \\ \mathcal{H}_2^{\text{eff}}\psi_2(\mathbf{r}) &= \epsilon_2\psi_2(\mathbf{r}). \end{aligned} \quad (4)$$

[2] D. R. Hartree, Proc. Cambridge Phil. Soc. 24, 89, 111, 246 (1928).

They are coupled in that the solution to the first enters into the differential equation for the second—in the effective Hamiltonian operator $\mathcal{H}_2^{\text{eff}}$—and vice versa. Practical solution of these equations is accomplished by a successive-approximation procedure. The initial "guesses" for the functions are used to calculate $V(\psi_1)$ and $V(\psi_2)$. The Hartree equations—at this stage uncoupled—are then solved for the "first-improved" functions ψ_1 and ψ_2. These are, in turn, used to obtain improved potentials $V(\psi_1)$ and $V(\psi_2)$ and the procedure is continued until input and output functions ψ_1 and ψ_2 agree within the desired accuracy. The wavefunctions and potential fields are then said to be self-consistent. The usual quantum-mechanical restrictions on a bound-state wavefunction—that it be everywhere single-valued, finite and continuous, and that it approach zero at infinity—apply at each stage of the calculation. Each of the Hartree equations is accordingly an eigenvalue problem and is soluble only for certain values of ϵ_i (in general, different at each stage).

Extension of Hartree's method to an N-electron atom is straightforward. Each electron now moves in the potential field of the nucleus plus the $N-1$ other electrons—treated as overlapping charge clouds. N coupled integrodifferential equations must now be solved:

$$\mathcal{H}_i^{\text{eff}}\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}), \quad i = 1 \cdots N, \quad (5)$$

where

$$\mathcal{H}_i^{\text{eff}} \equiv -\frac{\hbar^2}{2m}\nabla^2 + V_i(\psi_1, \psi_2 \cdots \psi_N) \quad (6)$$

and

$$V_i(\psi_1 \cdots \psi_N) \equiv -\frac{Ze^2}{r} + \sum_{j \neq i} e^2 \int d\tau' \frac{|\psi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}. \quad (7)$$

Each distinct set of one-electron functions $\psi_1, \cdots, \psi_N$ which satisfy the Hartree equations (5) can be identified with an electronic configuration—e.g., for helium atom, $1s^2$, $1s2s$, etc. The eigenvalues ϵ_i represent the total one-electron energies in the self-consistent field. For an electron bound in an atom, ϵ_i is a negative number. It is very nearly equal in magnitude to the ionization energy for the ith electron.

Hartree's self-consistent-field method derived originally from intuitive considerations. The more-formal quantum-theoretical foundations of

the SCF approach were worked out by Slater[3] and by Gaunt.[4] The first step is to write down the Hamiltonian operator for the N-electron atom. Neglecting magnetic interactions and other higher-order effects, we have

$$\mathfrak{H} = \sum_{i=1}^{N}\left\{-\frac{\hbar^2}{2m}\nabla_i^2 - \frac{Ze^2}{r_i}\right\} + \sum_{j>i}\sum_{i=1}^{N}\frac{e^2}{r_{ij}}. \qquad (8)$$

The one-electron parts of the Hamiltonian are contained in the first summation. These are the kinetic-energy operators and the nuclear-attraction operators. The second summation—over distinct pairs i, j—represents the interelectronic repulsive interactions. To save some writing, Hartree introduced a system of "atomic units" wherein

$$\hbar = |e| = m = 1.$$

The atomic unit of length is equal to the first Bohr radius, $a_0 = \hbar^2/me^2 = 0.529 \times 10^{-8}$ cm, and the unit of energy is $e^2/a_0 = 27.2$ eV. In atomic units the Hamiltonian (8) is written

$$\mathfrak{H} = \sum_{i=1}^{N}\left\{-\tfrac{1}{2}\nabla_i^2 - \frac{Z}{r_i}\right\} + \sum_{j>i}\sum_{i=1}^{N}\frac{1}{r_{ij}}. \qquad (9)$$

The Schrödinger equation for the N-electron problem takes the form

$$\mathfrak{H}\Psi(\mathbf{r}_1\cdots\mathbf{r}_N) = E\Psi(\mathbf{r}_1\cdots\mathbf{r}_N), \qquad (10)$$

where E is the total energy of the atom—the energy which would be required to dissociate completely the $(N+1)$-particle system.

Slater[3] and Gaunt[4] showed that the Hartree equations (5) are precisely the conditions for optimization of an approximate solution to (10) having the simple separable form

$$\Psi(\mathbf{r}_1\cdots\mathbf{r}_N) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\cdots\psi_N(\mathbf{r}_N). \qquad (11)$$

The rigorous solutions of (10)—which have never been obtained in closed form—are, of course, not separable in this way because electron coordinates are inextricably mixed by the r_{ij}^{-1} terms in the Hamiltonian. Optimization of any approximate ground-state eigenfunction is obtained, in accordance with the variational principle, by minimizing the ratio of integrals

$$E = \frac{\int\cdots\int d\tau_1\cdots d\tau_N \Psi^*\mathfrak{H}\Psi}{\int\cdots\int d\tau_1\cdots d\tau_N |\Psi|^2}, \qquad (12)$$

consistent with the chosen form for Ψ. If each of the factors of (11) is normalized, i.e.,

$$\int d\tau_i |\psi_i(\mathbf{r}_i)|^2 = 1, \quad i = 1\cdots N, \qquad (13)$$

then (12) may be expressed as the sum

$$E = \sum_{i=1}^{N} H_i + \sum_{j>i}\sum_{i=1}^{N} J_{ij}, \qquad (14)$$

having defined

$$H_i \equiv \int d\tau\, \psi_i^*(\mathbf{r})\left\{-\tfrac{1}{2}\nabla^2 - \frac{Z}{r}\right\}\psi_i(\mathbf{r}), \qquad (15)$$

and

$$J_{ij} \equiv \int\int d\tau\, d\tau' \frac{|\psi_i(\mathbf{r})|^2 |\psi_j(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}. \qquad (16)$$

The integrals H_i are expectation values of the one-electron operators of the Hamiltonian (9). The J_{ij}, known as Coulomb integrals, represent potential energies of interaction between interpenetrating charge distributions. If we now apply the variational principle and minimize (14) consistent with the N conditions (13) we obtain the Hartree equations (5) for the set of "best possible" one-electron functions. The details are given in Appendix B.

The one-electron functions $\psi_i(\mathbf{r})$ are known as "orbitals"—a term coined by Mulliken.[5] "Orbital," an adjective used as a noun, is the quantum-mechanical analog of the classical orbit—the maximal description of the causal behavior of a dynamical system. The complete description of an electron's state includes also its spin quantization. The latter may be regarded as an internal degree of freedom having two possible states, denoted by the spin functions α or β. Unless magnetic interactions are included in the Hamiltonian, space and spin variables for each electron are rigorously separable. We define the composite

[3] J. C. Slater, Phys. Rev. 32, 339 (1928).
[4] J. A. Gaunt, Proc. Cambridge Phil. Soc. 24, 328 (1928).
[5] R. S. Mulliken, Phys. Rev. 41, 49 (1932).

spin-orbital functions

$$\phi(x) = \psi(\mathbf{r}) \begin{cases} \alpha \\ \beta \end{cases} \quad \text{or} \qquad (17)$$

denoting by x the four-dimensional manifold of space and spin coordinates. Often, for brevity, we write $\phi(i)$ instead of $\phi(x_i)$. We also abbreviate combined integration over space coordinates and summation over spin coordinates by integration over x, i.e.,

$$\sum_{\text{spin}} \int d\tau \equiv \int dx. \qquad (18)$$

A product of spin-orbitals of the form

$$\Psi(1 \cdots N) = \phi_1(1)\phi_2(2) \cdots \phi_N(N), \qquad (19)$$

is known as a Hartree product and corresponds to an electronic configuration, as mentioned earlier. Thus far, no restrictions have appeared on identity of functional forms of two or more spin orbitals. Nothing—except our good sense—deters us from contemplating a ground-state configuration such as $1s^3$ for lithium atom. A further deficiency of the Hartree formalism is the explicit labeling of electrons in orbitals. Both of the above defects are rectified by constructing an anti-symmetrized N-electron wavefunction, such that

$$\Phi(\cdots i,j \cdots) = -\Phi(\cdots j,i \cdots), \qquad (20)$$

in accord with the fact that electrons are indistinguishable particles obeying Fermi–Dirac statistics. The simplest, totally antisymmetric, N-particle function is the determinantal form

$$\Phi(1 \cdots N) = \frac{1}{(N!)^{\frac{1}{2}}} \begin{vmatrix} \phi_1(1) & \phi_2(1) & \cdots \phi_N(1) \\ \phi_1(2) & \phi_2(2) & \cdots \phi_N(2) \\ \phi_1(N)\phi_2(N) & \cdots \phi_N(N) \end{vmatrix}. \quad (21)$$

This form was suggested originally by Heisenberg[6] and Dirac[7] and applied to the N-electron problem by Slater.[8] In the latter connection, (21) is known as a Slater determinant. The factor $(N!)^{-\frac{1}{2}}$ normalizes $\Phi(1 \cdots N)$ when the spin orbitals form an orthonormal set:

$$\int dx \phi_i^*(x)\phi_j(x) = \delta_{ij}. \qquad (22)$$

[6] W. Heisenberg, Z. Physik **38**, 411 (1926); **39**, 499 (1926); **41**, 239 (1927).
[7] P. A. M. Dirac, Proc. Roy. Soc. (London) **A112**, 661 (1926).
[8] J. C. Slater, Phys. Rev. **34**, 1293 (1929).

The exclusion principle is accounted for since the determinant vanishes identically unless the N spin orbitals form a linearly independent set.

An open-shell configuration of an atom or molecule must, in general, be represented by a sum of Slater determinants in order that $\Phi(1 \cdots N)$ be an eigenfunction of total spin and orbital angular momenta. As an illustration, consider the $1s^2$ and $1s2s$ configurations of helium atom. The $1s^2$ closed-shell ground state may be approximated by a single determinant

$$\Phi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s\alpha}(1) & \phi_{1s\beta}(1) \\ \phi_{1s\alpha}(2) & \phi_{1s\beta}(2) \end{vmatrix},$$

which is an eigenfunction of the total spin with eigenvalues $S=0$, $M_S=0$. The states $S=1$, $M_S = \pm 1$ of the open-shell configuration $1s2s$ can likewise be written as single determinants:

$$\Phi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s\alpha}(1) & \phi_{2s\alpha}(1) \\ \phi_{1s\alpha}(2) & \phi_{2s\alpha}(2) \end{vmatrix},$$

for $S=1$, $M_S=1$ and

$$\Phi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s\beta}(1) & \phi_{2s\beta}(1) \\ \phi_{1s\beta}(2) & \phi_{2s\beta}(2) \end{vmatrix},$$

for $S=1$, $M_S=-1$. The states of the same configuration with $M_S=0$ must, however, be written as a sum of the two determinants. These are

$$\Phi(1,2) = \frac{1}{\sqrt{2}} \left\{ \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s\alpha}(1) & \phi_{2s\beta}(1) \\ \phi_{1s\alpha}(2) & \phi_{2s\beta}(2) \end{vmatrix} \right.$$
$$\left. \pm \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s\beta}(1) & \phi_{2s\alpha}(1) \\ \phi_{1s\beta}(2) & \phi_{2s\beta}(2) \end{vmatrix} \right\}.$$

The $(+)$ sign corresponds to $S=1$, $M_S=0$ and is the third component of the $1s2s\ ^3\Sigma$ term. The $(-)$ sign corresponds to $S=0$, $M_S=0$ and represents the $1s2s\ ^1\Sigma$ state.

Using the wavefunction (21) and the Hamiltonian (9) in the expression (10) for the total energy, we obtain a generalization of (14) for a determinantal function:

$$E = \sum_{i=1}^{N} H_i + \sum_{j>i}^{N} \sum_{i=1}^{N} (J_{ij} - K_{ij}). \qquad (23)$$

This formula was first derived by Slater[8] (see Appendix C for details). It is interesting to note that the energy expression (23), which involves summation over occupied spin orbitals, arises from the Hamiltonian (9), which contains sums over particle labels. In (23) the following definitions are employed:

$$H_i \equiv \int dx \phi_i^*(x) \left\{ -\tfrac{1}{2}\nabla^2 - \frac{Z}{r} \right\} \phi_i(x),$$ (24)

$$J_{ij} \equiv \int\int dx\, dx' \phi_i^*(x) \phi_j^*(x')$$
$$\times |\mathbf{r}-\mathbf{r}'|^{-1} \phi_j(x') \phi_i(x),$$ (25)

$$K_{ij} \equiv \int\int dx\, dx' \phi_i^*(x) \phi_j^*(x')$$
$$\times |\mathbf{r}-\mathbf{r}'|^{-1} \phi_i(x') \phi_j(x).$$ (26)

The one-electron integrals (24) and the Coulomb integrals (25) are equivalent to the earlier definitions (15) and (16), respectively, since the spin parts contribute only factors of unity. The "exchange integrals" (26) differ from (25) only by interchange of the last two indices i and j. These terms arise from the permutations inherent in the determinantal form. Note that K_{ij} vanishes, due to the spin orthogonality, unless $\phi_i(x)$ and $\phi_j(x)$ have the same spin component. Exchange integrals account for energy differences between singlet and triplet configurations, an effect missing in the simple Hartree theory.

The conditions for optimization of a determinantal function, in accordance with the variational principle, were derived by Slater[9] and independently by Fock.[10] The N "best-possible" spin-orbital functions $\phi_i(x)$ are the solutions of a set of N coupled integrodifferential equations quite similar to the Hartree equations (5). These are known as the Hartree–Fock equations and may also be put in the form of effective one-particle Schrödinger equations,

$$\mathcal{H}_i^{\text{eff}} \phi_i(x) = \epsilon_i \phi_i(x), \quad i=1\cdots N.$$ (27)

The effective Hartree–Fock Hamiltonian may be written

$$\mathcal{H}_i^{\text{eff}} \equiv -\tfrac{1}{2}\nabla^2 - \frac{Z}{r} + \sum_{j\neq i} \int dx' \phi_j^*(x')$$
$$\times |\mathbf{r}-\mathbf{r}'|^{-1}(1-\mathcal{P}_{ij})\phi_j(x'),$$ (28)

where $\mathcal{P}_{ij}$ is an operator which exchanges the subscripts i and j occurring to the right of it, e.g., $\mathcal{P}_{ij}\phi_j(x')\phi_i(x) = \phi_i(x')\phi_j(x)$. The derivation is given in Appendix D.[11] Each Hartree–Fock equation (27) differs from the corresponding Hartree equation (5) by addition of the terms

$$-\sum_{j\neq i} \left[\int dx' \phi_j^*(x') |\mathbf{r}-\mathbf{r}'|^{-1}\mathcal{P}_{ij}\phi_j(x') \right]\phi_i(x)$$

$$\equiv -\sum_{j\neq i} \left[\int dx' \phi_j^*(x') |\mathbf{r}-\mathbf{r}'|^{-1}\phi_i(x') \right]\phi_j(x).$$ (29)

Equations (27) constitute an eigenvalue problem of a more generalized type than Eqs. (5) because of the terms (29) linear in the $\phi_j(x)$ occurring in the equation for $\phi_i(x)$. But successive-approximation techniques can be applied as well to the solutions of the Hartree–Fock problem.

The summation (29) can be interpreted physically in terms of fictitious "exchange forces" between electrons of parallel spin—over and above ordinary Coulombic repulsions which comprise the closely related terms

$$\sum_{j\neq i} \left[\int dx' \phi_j^*(x') |\mathbf{r}-\mathbf{r}'|^{-1}\phi_j(x') \right]\phi_i(x).$$ (30)

Since the exchange integrals K_{ij} are always positive,[12] the total energy E is lowered by the operation of exchange forces [see Eq. (23)], the contributions $J_{ij}-K_{ij}$ replacing the simple Coulombic potential energies J_{ij} for electron pairs with parallel spins.

Further insight into the exchange phenomenon is gained by considering the behavior of a many-electron wavefunction $\Phi(\cdots x_i, x_j \cdots)$ near a configuration point $x_i = x_j = x'$. By the anti-symmetry property, $\Phi(\cdots x', x' \cdots) = 0$; thus the probability density of finding two electrons of parallel spin at the same point in space is exactly zero. The same is not true for two electrons of

[9] J. C. Slater, Phys. Rev. 35, 210 (1930).
[10] V. Fock, Z. Physik 61, 126 (1930).

[11] An excellent treatment of the Hartree–Fock method is given in J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960), Vols. I and II, particularly Vol. II, Chap. 17. See, also, J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill Book Company, Inc., New York, 1963), Vol. I, Chap. 5 and Appendices 4 and 7.
[12] See, for example, J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960), Vol. I, p. 486.

opposite spin, for $\Phi(\cdots\mathbf{r}'\alpha,\mathbf{r}'\beta\cdots)$ does not necessarily vanish. Exchange forces—also known as exclusion forces—tend to keep electrons of the same spin apart and thereby reduce their repulsive energy, consistent with the results of the preceding paragraph. The region around each electron effectively excluded to electrons of the same spin is known as the Fermi hole, being a property of Fermi–Dirac particles.

A further aspect of exchange appears if the summation in (28) is rewritten $\sum\limits_{j=1}^{N}$, including the term $j=i$, which vanishes identically. The summations (29) and (30) are then both augmented by a term corresponding to $j=i$. It might then be construed that an electron's exchange interaction with itself exactly cancels its Coulombic self-energy—which is finite for classical charge clouds.

The eigenvalues ϵ_i of the Hartree–Fock equations may be related to the integrals (24), (25), and (26), evaluated using the optimized spin-orbital functions $\phi_i(x)$. Multiplying the ith equation in (27) by $\phi_i^*(x)$ and integrating over dx, we obtain

$$\epsilon_i = H_i + \sum_{j=1}^{N}(J_{ij}-K_{ij}), \quad i=1\cdots N. \quad (31)$$

This is a generalization of (B13) (Appendix B) for the Hartree equations. For closed-shell systems $-\epsilon_i$ equals the ionization potential for the ith electron: minus the total energy of the atom, plus the total energy of the ion formed by removing electron i. This result is known as Koopmans' theorem.[13] Summing over the one-electron energies (31) and comparing with the total energy (23), we find

$$\sum_{i=1}^{N}\epsilon_i = \sum_{i=1}^{N}H_i + \sum_{j\neq i}\sum_{i=1}^{N}(J_{ij}-K_{ij})$$

$$= \sum_{i=1}^{N}H_i + 2\sum_{j>i}\sum_{i=1}^{N}(J_{ij}-K_{ij})$$

$$= E + \sum_{j>i}\sum_{i=1}^{N}(J_{ij}-K_{ij}). \quad (32)$$

The sum of the N ionization energies is greater

[13] T. A. Koopmans, Physica 1, 104 (1933).

than the total energy since interelectronic repulsion terms $J_{ij}-K_{ij}$ are counted twice over. From (31) and (32) we may obtain an alternative expression for the total energy

$$E = \tfrac{1}{2}\sum_i(\epsilon_i+H_i). \quad (33)$$

The Hartree–Fock method does not, of course, give an exact solution of the N-electron Schrödinger equation—only the best solution of determinantal form. Physically, the approximation inherent in the self-consistent-field approach is equivalent to replacing particle-like r_{ij}^{-1} Coulomb interactions by continuous electrostatic interactions among charge clouds. The error in the Hartree–Fock approximation is known as "correlation"[14] since it involves more detailed correlation of electron positions than is possible on a charge-cloud description. This subject has received a good deal of theoretical attention in recent years.[15]

The foregoing discussion of the Hartree and Hartree–Fock methods has been completely general regarding the functional forms of the orbitals $\psi(\mathbf{r})$ and spin orbitals $\phi(x)$. For atomic systems these are always taken in practice to be separable functions in spherical polar coordinates, i.e.,

$$\phi_{nlmm_s}(x) = R_{nl}(r)\,Y_{lm}(\theta,\phi)\begin{cases}\alpha\\ \text{or,}\\ \beta\end{cases} \quad (34)$$

where the $Y_{lm}(\theta,\phi)$ are spherical harmonics. This specification of the form of orbital functions is known as the central-field approximation since the factorization would be rigorously true for an electron in a central field. The Hartree–Fock method would be prohibitive computationally but for the central-field approximation. It has been conjectured, however, that the true correlation energy might be appreciably reduced if exact Hartree–Fock solutions were obtainable Under the central-field approximation, dependence on the angles may be treated analytically and the N Hartree–Fock equations reduce to integrodifferential equation in r alone. Conventional numerical techniques thereby become ap-

[14] This terminology is due to E. P. Wigner, Phys. Rev. 46, 1002 (1934).
[15] See, for example, P.-O. Löwdin, Advan. Chem. Phys. 2, 207 (1959).

plicable. A detailed exposition of the Hartree–Fock method applied to atomic systems is given in Hartree's book.[16]

A significant improvement in the computational facility of the SCF method was introduced by Roothaan.[17] Almost all current work on atomic and molecular wavefunctions is based on this or related procedures. Instead of approaching the Hartree–Fock method as a numerical problem, the spin orbitals are represented as linear combinations in a given set of basis functions, i.e.,

$$\phi_i(x) = \sum_{\alpha=1}^{N'} c_{i\alpha} X_\alpha(x). \tag{35}$$

By the analytic SCF method, the integro-differential equations for the functions $\phi_i(x)$ are transformed into linear algebraic equations for the coefficients $c_{i\alpha}$. The latter form is especially suitable for digital-computer programming. The choice of the basis set $X_\alpha(x)$ in which the spin orbitals are expanded is critical, but considerable experience has been gained in choosing optimal basis sets. Roothaan's procedure can be conveniently applied also to molecular systems, being, in fact, an extension of the LCAO (linear combination of atomic orbitals) approximation.

When the SCF method is applied to molecules, the only formal modification necessitated is the replacement of each of the nuclear attraction terms Z/r in the Hamiltonian (9) and elsewhere by a sum $\sum_n Z_n/r_n$. In the following discussion of the analytic Hartree–Fock method, we use the form appropriate for molecular systems.

From a basis set containing N' linearly independent functions $X_1(x)\cdots X_{N'}(x)$, the same number of atomic or molecular spin orbitals can be constructed. If N is the number of occupied spin orbitals, it is necessary that $N' \geq N$. For $N' = N$, we have what is known as a minimal basis set.

To derive the algebraic equivalents of the Hartree-Fock equation, we consider first the forms of the energy integrals H_i, J_{ij}, and K_{ij}. Substituting the linear development (35) for the $\phi_i(x)$ in the relations (24), (25), and (26), we

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[16] D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957).
[17] C. C. J. Roothaan, Rev. Mod. Phys. 23, 69 (1951).

obtain

$$H_i = \sum_{\alpha,\beta} c_{i\alpha}{}^* c_{i\beta} [\alpha|\beta], \tag{36}$$

$$J_{ij} = \sum_{\alpha,\beta,\gamma,\delta} c_{i\alpha}{}^* c_{i\beta} c_{j\gamma}{}^* c_{j\delta} [\alpha\beta|\gamma\delta], \tag{37}$$

$$K_{ij} = \sum_{\alpha,\beta,\gamma,\delta} c_{i\alpha}{}^* c_{i\beta} c_{j\gamma}{}^* c_{j\delta} [\alpha\delta|\gamma\beta], \tag{38}$$

having defined the one-electron integrals

$$[\alpha|\beta] \equiv \int dx X_\alpha{}^*(x) \left\{ -\tfrac{1}{2}\nabla^2 - \sum_n \frac{Z_n}{r_n} \right\} X_\beta(x), \tag{39}$$

and the two-electron integrals

$$[\alpha\beta|\gamma\delta] \equiv \int\int dx\,dx' X_\alpha{}^*(x) X_\beta(x)$$
$$\times |\mathbf{r}-\mathbf{r}'|^{-1} X_\gamma{}^*(x') X_\delta(x'). \tag{40}$$

The two-electron integrals are further classified as two-, three-, or four-center integrals according to the number of distinct indices α, β, γ, δ. Roothaan has remarked that the computational difficulties encountered in evaluating three- and four-center integrals have delayed molecular calculations by about ten years.

As they have been defined, the integrals (39) and (40) vanish unless basis functions X_α and X_β have the same spin. In addition, (40) vanishes unless X_γ and X_δ have the same spin. The reader should note that in conventional usage the labels $\alpha\beta\gamma\delta$ refer generally to orbitals rather than spin orbitals.

Substituting (36)–(38) in the energy expression (23) we have

$$E(c_{i\alpha}, c_{i\alpha}{}^*) = \sum_i \sum_{\alpha\beta} c_{i\alpha}{}^* \{ [\alpha|\beta] + \tfrac{1}{2} \sum_j \sum_{\gamma\delta} c_{j\gamma}{}^* c_{j\delta}$$
$$\times ([\alpha\beta|\gamma\delta] - [\alpha\delta|\gamma\beta]) \} c_{i\beta}. \tag{41}$$

We seek a minimum in E with respect to variation of the coefficients $c_{i\alpha}$ subject, however, to the orthonormalization conditions (22) which may be written

$$\sum_{\alpha\beta} c_{i\alpha}{}^* c_{j\beta} S_{\alpha\beta} = \delta_{ij}, \tag{42}$$

with

$$S_{\alpha\beta} \equiv \int dx X_\alpha{}^*(x) X_\beta(x), \tag{43}$$

the basis set not being, in general, orthonormal. Applying Lagrange's method for constrained minimum problems (see Appendices B and D) we may consider unconditional minimization of the quantity

$$F(c_{i\alpha}, c_{i\alpha}{}^*) \equiv E(c_{i\alpha}, c_{i\alpha}{}^*) - \sum_{ij} \lambda_{ij} \sum_{\alpha\beta} c_{i\alpha}{}^* c_{j\beta} S_{\alpha\beta}, \quad (44)$$

where the N^2 quantities λ_{ij} are the undetermined multipliers. If we are dealing with a closed-shell system we may specify that the set of coefficients $c_{i\alpha}$ also diagonalize the Λ-matrix (see Appendix D). The last sum in (44) accordingly becomes

$$- \sum_i \epsilon_i \sum_{\alpha\beta} c_{i\alpha}{}^* c_{i\beta} S_{\alpha\beta}$$

and the minimization function, written in full,

$$F(c_{i\alpha}, c_{i\alpha}{}^*) = \sum_i \sum_{\alpha\beta} c_{i\alpha}{}^* \{ [\alpha|\beta] + \tfrac{1}{2} \sum_j \sum_{\gamma\delta} c_{j\gamma}{}^* c_{j\delta}$$

$$\times ([\alpha\beta|\gamma\delta] - [\alpha\delta|\gamma\beta]) - \epsilon_i S_{\alpha\beta} \} c_{i\beta}. \quad (45)$$

The conditions for unconditional minimization of (45) are

$$\partial F / \partial c_{i\alpha} = 0, \quad \partial F / \partial c_{i\alpha}{}^* = 0, \quad i = 1 \cdots N,$$
$$\alpha = 1 \cdots N', \quad (46)$$

which leads to the N' simultaneous equations

$$\sum_\beta (H_{\alpha\beta} - \epsilon_i S_{\alpha\beta}) c_{i\beta} = 0 \quad \alpha = 1 \cdots N' \quad (47)$$

and their complex conjugates. We have abbreviated

$$H_{\alpha\beta} \equiv [\alpha|\beta]$$
$$+ \sum_j \sum_{\gamma\delta} c_{j\gamma}{}^* c_{j\delta} ([\alpha\beta|\gamma\delta] - [\alpha\delta|\gamma\beta]). \quad (48)$$

The linear equations (47) are known as the Roothaan equations and are seen to be the algebraic equivalents of the Hartree–Fock equations (27).

For nontrivial solutions of (47) we require the vanishing of the $N' \times N'$ secular determinant

$$\det (H_{\alpha\beta} - \epsilon_i S_{\alpha\beta}) = 0, \quad (49)$$

which provides N' eigenvalues ϵ_i and N' sets of spin-orbital coefficients $c_{i\alpha}$. The preceding differs from the conventional diagonalization problem in that the matrix elements $H_{\alpha\beta}$ depend on the coefficients $c_{i\alpha}$. After the set $c_{i\alpha}$ obtained at one stage of the calculation, the $H_{\alpha\beta}$ must be recomputed and the secular equation solved again until self-consistency is attained. Elaborate computer programs have been developed whereby the entire procedure can be carried out automatically.

The lowest N self-consistent eigenvalues of the secular equation (49) pertain to the occupied spin orbitals in the ground state. The solutions $i = N+1$ to N' (for $N' > N$) are known as virtual solutions. They correspond to unoccupied spin orbitals and may be used to construct excited configurations. Generally ϵ_i is positive for the virtual spin orbitals.

In most calculations to date, the basis function $\chi_\alpha(x)$, in both atomic and molecular calculations, are of a form originally suggested by Slater[18]:

$$\chi_{nlmm_s}(x) = r^{n-1} e^{-\zeta_{nl} r} Y_{lm}(\theta, \phi) \begin{Bmatrix} \alpha \\ \beta \end{Bmatrix} \text{ or. } \quad (50)$$

The space part of (50) is known as a Slater-type orbital (STO). This has the general appearance of an atomic orbital but without radial nodes. The SCF results depend rather critically on the values of the exponential parameters ζ_{nl}. Variationally determined values appropriate for atomic calculations were tabulated by Slater.[18] Recently, the possibility of using Gaussian orbitals [$\exp(-\alpha r^2)$ radial dependence] as basis functions in molecular calculations has been suggested.[19] These have the advantage that multicenter integrals can be evaluated in closed form.

We conclude this review with some general remarks on the accuracy of SCF calculations. Perhaps the most spectacular illustration is the comparison of the radial charge density for argon from the Hartree–Fock calculation with that determined by electron diffraction.[20] The two functions are very nearly superposable and the electronic shell structure is clearly shown. The error in the total electronic energy E is generally of the order of 1% in Hartree–Fock calculations. The total energy is not, unfortunately, the quantity of principal chemical interest. More

[18] J. C. Slater, Phys. Rev. **36**, 57 (1930).
[19] F. E. Harris, Rev. Mod. Phys. **35**, 558 (1963), and references cited therein.
[20] L. S. Bartell and L. O. Brockway, Phys. Rev. **90**, 833 (1953). The illustration is reproduced in W. J. Moore, *Physical Chemistry*, (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1962), 3rd ed., p. 509.

significant are excitation energies and molecular binding energies. The latter quantities cannot be calculated directly by SCF methods but rather from differences between total energies. Since the differences are usually quite small fractions of variationally calculated quantities, errors are greatly magnified. Still, excitation energies are generally determined in the correct order and with qualitative accuracy—which is often helpful in correlating spectra. For binding energies, on the other hand, the SCF method alone is inadequate. Citing perhaps the worst case, F_2 appears less stable than two F atoms.[21] Calculating binding energies in this manner has been compared to weighing the captain of an ocean liner by taking the difference in the ship's displacement with and without the captain on board.[22] Some progress has recently been made, however, in incorporating empirical correlation corrections into binding-energy calculations.[23] A general view of the current scope of self-consistent-field theory may be gained from several articles in the April 1960 and July 1963 issues of *Reviews of Modern Physics*.

APPENDIX A. DERIVATION OF THE THREE-HALVES-POWER LAW

Consider a diode having parallel-plate geometry—the cathode in the plane $x=0$, the anode in the plane $x=d$. Take the potential as zero at the cathode, V volts at the anode: $V(0)=0$, $V(d)=V$. Assume that the current density J is independent of x and is related to the space-charge density $\rho(x)$ by

$$J=v(x)\rho(x), \tag{A1}$$

where $v(x)$ is the local electron velocity. If it is further assumed that electrons are emitted at the cathode with zero kinetic energy, then

$$\tfrac{1}{2}m[v(x)]^2=eV(x). \tag{A2}$$

Eliminating the velocity between (A1) and (A2) we obtain

$$V(x)=\frac{m}{2e}\frac{J^2}{[\rho(x)]^2}. \tag{A3}$$

We now introduce Poisson's equation

$$\nabla^2 V(x)=\frac{d^2 V}{dx^2}=-4\pi\rho(x).$$

Eliminating the space-charge density between (A3) and (A4)— this is the step involving self-consistency of potential and space charge—gives a differential equation for $V(x)$:

$$\frac{d^2 V}{dx^2}=\left(\frac{m}{2e}\right)^{\frac{1}{2}}\frac{4\pi J}{V^{\frac{1}{2}}}. \tag{A5}$$

Multiplying by $2(dV/dx)$ and integrating from $x=0$ to $x=x$, we obtain

$$\left(\frac{dV}{dx}\right)^2=E_0^2+16\pi J\left(\frac{m}{2e}\right)^{\frac{1}{2}}V^{\frac{1}{2}}, \tag{A6}$$

where $E_0=(dV/dx)_{x=0}$, the field at the cathode. The maximum current density $J_{\max}$ obtains when $E_0=0$, when the potential increases monotonically between cathode and anode. This leads to the first-order differential equation

$$\frac{dV}{dx}=4\pi^{\frac{1}{2}}J_{\max}^{\frac{1}{2}}\left(\frac{m}{2e}\right)^{\frac{1}{4}}V^{\frac{1}{4}}. \tag{A7}$$

Noting that

$$V^{-1/4}\frac{dV}{dx}=\frac{4}{3}\frac{d}{dx}V^{3/4}$$

and integrating from $x=0$ to $x=d$ we obtain finally

$$J_{\max}=\frac{(2m/e)^{\frac{1}{2}}}{9\pi d^2}V^{\frac{3}{2}}. \tag{A8}$$

This form of the three-halves-power law is known as the Child–Langmuir equation.[24] Other arrangements of cathode and anode—e.g., coaxial cylinders—also lead to a proportionality $J_{\max}\sim V^{\frac{3}{2}}$, with different geometrical factors.

APPENDIX B. VARIATIONAL DERIVATION OF THE HARTREE EQUATIONS

We will first derive the energy expression (14). If each factor of the separable function (11) is normalized, as specified by (13), then $\Psi(\mathbf{r}_1\cdots\mathbf{r}_N)$ is itself normalized, for

$$\int\cdots\int d\tau_1\cdots d\tau_N\Psi^*(\mathbf{r}_1\cdots\mathbf{r}_N)\Psi(\mathbf{r}_1\cdots\mathbf{r}_N)=\left[\int d\tau_1\psi_1^*(\mathbf{r}_1)\psi_1(\mathbf{r}_1)\right]\cdots\left[\int d\tau_N\psi_N^*(\mathbf{r}_N)\psi_N(\mathbf{r}_N)\right]=1. \tag{B1}$$

The energy integral (12) may now be written

$$E=\int\cdots\int d\tau_1\cdots d\tau_N\psi_1^*(\mathbf{r}_1)\cdots\psi_N(\mathbf{r}_N)\left\{\sum_{i=1}^{N}\left(-\tfrac{1}{2}\nabla_i^2-\frac{Z}{r_i}\right)+\sum_{i>j}^{N}\sum_{i=1}^{N}\frac{1}{r_{ij}}\right\}\psi_1(\mathbf{r}_1)\cdots\psi_N(\mathbf{r}_N). \tag{B2}$$

[21] B. J. Ransil, Rev. Mod. Phys. **32**, 239, 245 (1960).
[22] C. A. Coulson, *Valence* (Oxford University Press, London, 1952), p. 88.
[23] L. C. Allen, E. Clementi and H. M. Gladney, Rev. Mod. Phys. **35**, 465 (1963).
[24] C. D. Child, Phys. Rev. **32**, 492 (1911); I. Langmuir, Phys. Rev. **2**, 450 (1913); Phys. Zeit. **15**, 348 (1914). The above derivation follows that given by I. Langmuir and K. T. Compton, Rev. Mod. Phys. **3**, 191 (1931), especially pp. 237 ff.

The one-electron part is given by

$$\sum_{i=1}^{N} \int \cdots \int d\tau_1 \cdots d\tau_i \cdots d\tau_N \psi_1^*(\mathbf{r}_1) \cdots \psi_i^*(\mathbf{r}_i) \cdots \psi_N^*(\mathbf{r}_N) \left\{ -\tfrac{1}{2}\nabla_i^2 - \frac{Z}{r_i} \right\} \psi_1(\mathbf{r}_1) \cdots \psi_i(\mathbf{r}_i) \cdots \psi_N(\mathbf{r}_N). \tag{B3}$$

In the ith term integration may be immediately carried out over all variables except $\mathbf{r}_i$, giving $N-1$ factors unity. There remains

$$\sum_{i=1}^{N} \int d\tau_i \psi_i^*(\mathbf{r}_i) \left\{ -\tfrac{1}{2}\nabla_i^2 - \frac{Z}{r_i} \right\} \psi_i(\mathbf{r}_i) \equiv \sum_{i=1}^{N} H_i. \tag{B4}$$

The H_i are identical to the integrals (15), except for the change in dummy variable. The two-electron part of (B2) may be written

$$\sum_{j>i} \sum_{i=1}^{N} \int \cdots \int d\tau_1 \cdots d\tau_i d\tau_j \cdots d\tau_N \psi_1^*(\mathbf{r}_1) \cdots \psi_i^*(\mathbf{r}_i) \psi_j^*(\mathbf{r}_j) \cdots \psi_N^*(\mathbf{r}_N) |\mathbf{r}_i - \mathbf{r}_j|^{-1} \psi_1(\mathbf{r}_1) \cdots \psi_i(\mathbf{r}_i) \psi_j(\mathbf{r}_j) \cdots \psi_N(\mathbf{r}_N). \tag{B5}$$

In each term $N-2$ factors unity result from integration over all variables except $\mathbf{r}_i$ and $\mathbf{r}_j$ and (B5) reduces to

$$\sum_{j>i} \sum_{i=1}^{N} \int\int d\tau_i d\tau_j \psi_i^*(\mathbf{r}_i) \psi_j^*(\mathbf{r}_j) |\mathbf{r}_i - \mathbf{r}_j|^{-1} \psi_i(\mathbf{r}_i) \psi_j(\mathbf{r}_j) \equiv \sum_{j>i} \sum_{i=1}^{N} J_{ij}. \tag{B6}$$

Again a change in dummy variables identifies the integrals (B6) with those defined in (16). Adding (B4) and (B6) we finally obtain (14) for the energy expectation value. An alternative way of writing this sum is

$$E = \sum_{i=1}^{N} H_i + \tfrac{1}{2} \sum_{j\neq i} \sum_{i=1}^{N} J_{ij}. \tag{B7}$$

The factor $\tfrac{1}{2}$ accounts for the fact that J_{ji} occurs now, as well as the equivalent J_{ij}, in the double sum.

In accordance with the variational principle, a minimum of E is sought by variation of the functional forms of $\psi_i(\mathbf{r})$, $i = 1 \cdots N$. This minimization is not an unconditional one, however, since the N normalization conditions (13) must be maintained. A conditional minimum problem may be made equivalent to an unconditional one by application of Lagrange's method of undetermined multipliers. Accordingly, we may seek the absolute minimum of the functional

$$F(\psi_i, \psi_i^*) \equiv E(\psi_i, \psi_i^*) - \sum_{i=1}^{N} \epsilon_i \int d\tau_i \psi_i^*(\mathbf{r}_i) \psi_i(\mathbf{r}_i). \tag{B8}$$

The Lagrange multipliers are denoted by ϵ_i, in anticipation of their later emergence as eigenvalues in the Hartree equations. Both the ψ_i and the ψ_i^* are treated as independent functional variables. Alternatively, the real and imaginary parts of ψ_i could have been used. Substituting (B7) for E into (B8) and writing out explicitly all the integrals we obtain

$$F(\psi_i, \psi_i^*) = \sum_{i=1}^{N} \int d\tau \psi_i^*(\mathbf{r}) \left\{ -\tfrac{1}{2}\nabla^2 - \frac{Z}{r} - \epsilon_i \right\} \psi_i(\mathbf{r}) + \tfrac{1}{2} \sum_{j\neq i} \sum_{i=1}^{N} \int\int d\tau d\tau' \psi_i^*(\mathbf{r}) \psi_j^*(\mathbf{r}') |\mathbf{r} - \mathbf{r}'|^{-1} \psi_j(\mathbf{r}') \psi_i(\mathbf{r}). \tag{B9}$$

The variation of $F(\psi_i, \psi_i^*)$ with respect to functional dependence on the ψ_i and ψ_i^* is given by

$$\delta F(\psi_i, \psi_i^*) = \sum_{i=1}^{N} \int d\tau \delta\psi_i^*(\mathbf{r}) \left\{ -\tfrac{1}{2}\nabla^2 - \frac{Z}{r} - \epsilon_i \right\} \psi_i(\mathbf{r}) + \tfrac{1}{2} \sum_{j\neq i} \sum_{i=1}^{N} \int\int d\tau d\tau' [\delta\psi_i^*(\mathbf{r})\psi_j^*(\mathbf{r}') + \psi_i^*(\mathbf{r})\delta\psi_j^*(\mathbf{r}')] |\mathbf{r} - \mathbf{r}'|^{-1} \psi_j(\mathbf{r}')\psi_i(\mathbf{r})$$

$$+ \sum_{i=1}^{N} \int d\tau \psi_i^*(\mathbf{r}) \left\{ -\tfrac{1}{2}\nabla^2 - \frac{Z}{r} - \epsilon_i \right\} \delta\psi_i(\mathbf{r}) + \tfrac{1}{2} \sum_{j\neq i} \sum_{i=1}^{N} \int\int d\tau d\tau' \psi_i^*(\mathbf{r})\psi_j^*(\mathbf{r}') |\mathbf{r} - \mathbf{r}'|^{-1} [\delta\psi_j(\mathbf{r}')\psi_i(\mathbf{r}) + \psi_j(\mathbf{r}')\delta\psi_i(\mathbf{r})]. \tag{B10}$$

The functions $\psi_i^*(\mathbf{r})$ and $\delta\psi_i(\mathbf{r})$ in the third summation may be interchanged because of the Hermitian property of the bracketed operator—or alternatively after integrating by parts twice. The two parts of the second summation are equal because of the symmetry in (B9) between the indices i and j and between the variables $\mathbf{r}$ and $\mathbf{r}'$. The same is true of the last summation. Incorporating these simplifications we obtain

$$\delta F(\psi_i, \psi_i^*) = \int d\tau \sum_{i=1}^{N} \left\{ \delta\psi_i^*(\mathbf{r}) \left[\left\{ -\tfrac{1}{2}\nabla^2 - \frac{Z}{r} - \epsilon_i + \sum_{j\neq i} \int d\tau' \frac{\psi_j^*(\mathbf{r}')\psi_j}{|\mathbf{r} - \mathbf{r}'|}(\mathbf{r}') \right\} \psi_i(\mathbf{r}) \right] \right.$$

$$\left. + \delta\psi_i(\mathbf{r}) \left[\left\{ -\tfrac{1}{2}\nabla^2 - \frac{Z}{r} - \epsilon_i + \sum_{j\neq i} \int d\tau' \frac{\psi_j(\mathbf{r}')\psi_j^*(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right\} \psi_i^*(\mathbf{r}) \right] \right\}. \tag{B11}$$

If (ψ_i, ψ_i^*) is to be a minimum, then $\delta F = 0$. Since the minimum in F is unconditional, each of the variations $\delta\psi_i$, $\delta\psi_i^*$ may be chosen arbitrarily. The last two statements can be consistent only if each of the $2N$ quantities in square brackets vanish identically, i.e.,

$$\left\{ -\tfrac{1}{2}\nabla^2 - \frac{Z}{r} + \sum_{j \neq i} \int d\tau' \frac{|\psi_j(\mathbf{r})|^2}{|\mathbf{r}-\mathbf{r}'|} \right\}\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}),$$
$$i = 1 \cdots N, \quad (B12)$$

and N additional relations which are the complex conjugates of (B12). The set of equations (B12) is identical to (5) thus completing the derivation of the Hartree equations.

Multiplying one of the equations (B12) by $\psi_i(\mathbf{r})$ and integrating over $d\tau$ gives

$$\epsilon_i = H_i + \sum_{j \neq i} J_{ij}, \quad i = 1 \cdots N, \quad (B13)$$

which relates the Hartree equation eigenvalues to the energy integrals (15) and (16). Summing over the eigenvalues we find

$$\sum_{i=1}^{N} \epsilon_i = \sum_{i=1}^{N} H_i + \sum_{j \neq i}\sum_{i=1}^{N} J_{ij} = \sum_{i=1}^{N} H_i + 2\sum_{j > i}\sum_{i=1}^{N} J_{ij}. \quad (B14)$$

Applying (14) or (B7) for the total energy E gives the relation

$$E = \sum_{i} \epsilon_i - \sum_{i=1}^{N} J_{ij}. \quad (B15)$$

The sum of the ionization energies ϵ_i is seen to be greater than the total energy E since each Coulomb term J_{ij} contributes to the ionization energy of two different electrons.

APPENDIX C. DETERMINANTAL WAVEFUNCTIONS

A determinantal function may be constructed from a Hartree product (19) by summing over all possible permutations of the particle labels (or of the subscripts) with coefficients ± 1 for even or odd permutations, respectively. An even (odd) permutation is one which can be obtained by an even (odd) number of simple exchanges starting with 1, 2, $\cdots$, N. There are $N!$ possible permutations of N labels—half even, half odd. The construction of a Slater determinant (21) from a Hartree product (19) may be expressed symbolically

$$\Phi(1 \cdots N) = \mathcal{Q}\Psi(1 \cdots N), \quad (C1)$$

where $\mathcal{Q}$ is the antisymmetrization operator

$$\mathcal{Q} \equiv (N!)^{-\frac{1}{2}} \sum_{r=1}^{N!} (-1)^r \mathcal{P}_r. \quad (C2)$$

The $N!$ permutation operators $\mathcal{P}_r$ are so labeled that even (odd) r corresponds to an even (odd) permutation.

We require three properties of the antisymmetrization operator:

$$\mathcal{Q}^2 = (N!)^{\frac{1}{2}}\mathcal{Q}, \quad (C3)$$

$$\mathcal{Q} = \mathcal{Q}^{\dagger}, \quad (C4)$$

and

$$\mathcal{Q}\mathcal{O} = \mathcal{O}\mathcal{Q}, \quad (C5)$$

where $\mathcal{O}$ is any operator totally symmetrical in the coordinates $x_1 \cdots x_N$. To prove the first result, we write

$$\mathcal{Q}^2 = (N!)^{-1}\sum_{r=1}^{N!}\sum_{s=1}^{N!}(-1)^{r+s}\mathcal{P}_r\mathcal{P}_s = (N!)^{-1}\sum_{r=1}^{N!}\left(\sum_{t=1}^{N!}(-1)^t\mathcal{P}_t = \sum_{t=1}^{N!}(-1)^t\mathcal{P}_t = (N!)^{\frac{1}{2}}\mathcal{Q}.\right. \quad (C6)$$

The second equality in (C6) comes from the fact that the product of two permutation operators is another permutation operator of the same set. The Hermitian property of $\mathcal{Q}$, Eq. (C4), implies the integral relation

$$\int \cdots \int dx_1 \cdots dx_N \xi^*(1 \cdots N)\,\mathcal{Q}\eta(1 \cdots N) = \int \cdots \int dx_1 \cdots dx_N [\mathcal{Q}\xi(1 \cdots N)]^*\eta(1 \cdots N) \quad (C7)$$

for two arbitrary functions $\xi(1 \cdots N)$ and $\eta(1 \cdots N)$. The two integrals in (C7) differ only in the labeling of dummy variables and are thus equivalent. The commutativity relation (C5) follows simply from the definition of a totally symmetrical quantity—i.e., $\mathcal{P}_r\mathcal{O} = \mathcal{O}\mathcal{P}_r$ for all permutations r.

Applying Eqs. (C3), (C4), and (C5) we have

$$\int \cdots \int dx_1 \cdots dx_N \Phi^*(1 \cdots N)\mathcal{O}\Phi(1 \cdots N) = \int \cdots \int dx_1 \cdots dx_N [\mathcal{Q}\Psi(1 \cdots N)]^*\mathcal{O}\mathcal{Q}\Psi(1 \cdots N)$$

$$= \int \cdots \int dx_1 \cdots dx_N \Psi^*(1 \cdots N)\,\mathcal{Q}^2\mathcal{O}\Psi(1 \cdots N) = \int \cdots \int dx_1 \cdots dx_N \Psi^*(1 \cdots N)\sum_{t=1}^{N!}(-1)^t\mathcal{P}_t\mathcal{O}\Psi(1 \cdots N). \quad (C8)$$

By virtue of this important result, integrals over Slater determinants can be related to integrals over Hartree products. We can now prove that $\Phi(1 \cdots N)$ as given by (21) or (C1) is normalized. Setting $\mathcal{O} = 1$ in (C8):

$$\int \cdots \int dx_1 \cdots dx_N |\Phi(1 \cdots N)|^2 = \int \cdots \int dx_1 dx_N \phi_1^*(1) \cdots \phi_N^*(N)\sum_{t=1}^{N!}(-1)^t\mathcal{P}_t\phi_1(1) \cdots \phi_N(N)$$

$$= \int \cdots \int dx_1 \cdots dx_N \phi_1^*(1) \cdots \phi_N^*(N)\phi_1(1) \cdots \phi_N(N) = \left[\int dx_1 |\phi_1(1)|^2\right]\left[\int dx_2 |\phi_2(2)|^2\right] \cdots \left[\int dx_N |\phi_N(N)|^2\right] = 1. \quad (C9)$$

Because of the orthonormality of the set $\phi_i(x)$ [Eqs. (22)], only the identity permutation of the right-hand Hartree product avoids a factor zero.

Next, we turn to the energy expression (23). Setting $\Theta = \sum\limits_{i=1}^{N}\left\{-\tfrac{1}{2}\nabla_i^2 - \dfrac{Z}{r_i}\right\}$ in (C8),

$$\int\cdots\int dx_1\cdots dx_N \Phi^*(1\cdots N)\sum_{i=1}^{N}\left\{-\tfrac{1}{2}\nabla_i^2-\frac{Z}{r_i}\right\}\Phi(1\cdots N)$$

$$=\sum_{i=1}^{N}\int\cdots\int dx_1\cdots dx_N \phi_1^*(1)\cdots\phi_N^*(N)\left\{-\tfrac{1}{2}\nabla_i^2-\frac{Z}{r_i}\right\}\sum_{t=1}^{N!}(-1)^t \mathcal{P}_t\phi_1(1)\cdots\phi_N(N)$$

$$=\sum_{i=1}^{N}\left[\int dx_1\phi_1^*(1)\phi_1(1)\right]\cdots\left[dx_i\phi_i^*(i)\left\{-\tfrac{1}{2}\nabla_i-\frac{Z}{r_i}\right\}\phi_i(i)\right]\cdots\left[\int dx_N\phi_N^*(N)\phi_N(N)\right]=\sum_{i=1}^{N}H_i. \quad (C10)$$

Again only the identity permutation avoids a factor zero. After the integrations are carried out, each term in (C10) consists of $N-1$ factors unity times H_i defined by (24). Finally, setting $\Theta = \tfrac{1}{2}\sum_{j\neq i}\sum_{i=1}r_{ij}^{-1}$, we have

$$\int\cdots\int dx_1\cdots dx_N \Phi^*(1\cdots N)\sum_{j>i}\sum_{i=1}^{N}r_{ij}^{-1}\Phi(1\cdots N)$$

$$=\tfrac{1}{2}\sum_{j\neq i}\sum_{i=1}^{N}\int\cdots\int dx_1\cdots dx_N\phi_1^*(1)\cdots\phi_N^*(N)r_{ij}^{-1}\sum_{t=1}^{N!}(-1)^t\mathcal{P}_t\phi_1(1)\cdots\phi_N(N)$$

$$=\tfrac{1}{2}\sum_{j\neq i}\sum_{i=1}^{N}\int\cdots\int dx_1\cdots dx_N\phi_1^*(1)\cdots\phi_i^*(i)\phi_j^*(j)\cdots\phi_N^*(N)r_{ij}^{-1}\phi_1(1)\cdots[\phi_i(i)\phi_j(j)-\phi_i(j)\phi_j(i)]\cdots\phi_N(N)$$

$$=\tfrac{1}{2}\sum_{j\neq i}\sum_{i=1}^{N}\left[\int dx_1\phi_1^*(1)\phi_1(1)\right]\cdots\left[\int\int dx_i dx_j\phi_i^*(i)\phi_j^*(j)r_{ij}^{-1}\phi_i(i)\phi_j(j)-\int\int dx_i dx_j\phi_i^*(i)\phi_j^*(j)r_{ij}^{-1}\phi_i(j)\phi_j(i)\right]\cdots$$

$$\times\left[\int dx_N\phi_N^*(N)\phi_N(N)\right]=\tfrac{1}{2}\sum_{j\neq i}\sum_{i=1}^{N}(J_{ij}-K_{ij}). \quad (C11)$$

In (C11) each term allows of two nonzero permutations—differing by interchange of i and j—and gives, after integration, $N-2$ factors unity times $J_{ij}-K_{ij}$, as defined by (25) and (26). Combining the results (C9), (C10), and (C11) we obtain

$$E=\frac{\int d\tau\,\Phi^*\mathcal{H}\Phi}{\int d\tau\,|\Phi|^2}=\sum_{i=1}^{N}H_i+\tfrac{1}{2}\sum_{j\neq i}\sum_{i=1}^{N}(J_{ij}-K_{ij})=\sum_{i=1}^{N}H_i+\sum_{j=1}^{N}\sum_{i=1}^{N}(J_{ij}-K_{ij}), \quad (C12)$$

in agreement with (23). The last form follows from the identity of J_{ii} and K_{ii}. An alternative derivation of the energy formula is given by Hartree.[25]

APPENDIX D. DERIVATION OF THE HARTREE–FOCK EQUATIONS

The treatment given here applies to a closed-shell system. Generalization of the method for open shells is discussed by Roothaan.[26] The problem is to determine the set of spin-orbital functions $\phi_i(x)$, $i=1\cdots N$, which minimizes the energy expression (23) subject to the N^2 conditions (22). Even though the orthogonality conditions $\int dx\phi_i^*(x)\phi_j(x)=0$ and $\int dx\phi_j^*(x)\phi_i(x)=0$ for $i\neq j$ are equivalent, more symmetrical equations are obtained if they are regarded as independent. In accordance with the method of undetermined multipliers, we seek the unconditional minimum of the functional

$$F(\phi_i,\phi_i^*)=\sum_{i=1}^{N}\int dx\phi_i^*(x)\left\{-\tfrac{1}{2}\nabla^2-\frac{Z}{r}\right\}\phi_i(x)+\tfrac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\int\int dxdx'\phi_i^*(x)\phi_j^*(x')|\mathbf{r}-\mathbf{r}'|^{-1}[\phi_j(x')\phi_i(x)-\phi_i(x')\phi_j(x)]$$

$$-\sum_{i=1}^{N}\sum_{j=1}^{N}\lambda_{ji}\int dx\phi_i^*(x)\phi_j(x). \quad (D1)$$

The N^2 quantities λ_{ji}, j, $i=1\cdots N$, are the Lagrange multipliers. Note that for consistency we must have

$$\lambda_{ij}=\lambda_{ji}^*. \quad (D2)$$

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[25] D. R. Hartree, Ref. 14, p. 39 ff.
[26] C. C. J. Roothaan, Rev. Mod. Phys. **32**, 179 (1960).

Proceeding along the same lines as in Appendix B, we find:

$$\delta F(\phi_i,\phi_i{}^*) = \int dx \sum_{i=1}^{N} \left\{ \delta\phi_i{}^*(x) \left[\left\{ -\tfrac{1}{2}\nabla^2 - \frac{Z}{r} + \sum_{j=1}^{N} \int dx'\phi_j{}^*(x')\, |\mathbf{r}-\mathbf{r}'|^{-1}(1-\mathcal{P}_{ij})\phi_j(x') \right\} \phi_i(x) - \sum_{j=1}^{N} \phi_j(x)\lambda_{ji} \right] \right.$$

$$\left. + \delta\phi_i(x) \left[\left\{ -\tfrac{1}{2}\nabla^2 - \frac{Z}{r} + \sum_{j=1}^{N} \int dx'\phi_j(x')\, |\mathbf{r}-\mathbf{r}|^{-1}(1-\mathcal{P}_{ij})\phi_j{}^*(x') \right\} \phi_i{}^*(x) - \sum_{j=1}^{N} \phi_j{}^*(x)\lambda_{ji}{}^* \right] \right\} \quad (D3)$$

Again, each of the $2N$ quantities in square brackets must vanish, the second N being the complex conjugates of the first N. Introducing the definition (28) for the effective Hartree–Fock Hamiltonian the N conditions for optimization of the spin orbitals may be written

$$\mathcal{H}_i{}^{\text{eff}}\phi_i(x) = \sum_{j=1}^{N} \phi_j(x)\lambda_{ji}, \quad i=1\cdots N. \quad (D4)$$

These equations differ from the Hartree–Fock equations (27) by the presence of off-diagonal multipliers λ_{ij}, $i \neq j$. It is possible, however, to transform (D4) into (27) as described in the next paragraph.

A determinantal wavefunction $\Phi(1\cdots N)$ is invariant under a unitary transformation among its component spin orbitals, i.e.,

$$\Phi(1\cdots N) = \frac{1}{(N!)^{\frac{1}{2}}} \begin{vmatrix} \phi_1(1) & \cdots & \phi_1(N) \\ \phi_N(1) & \cdots & \phi_N(N) \end{vmatrix}$$

$$\frac{1}{(N!)^{\frac{1}{2}}} \begin{vmatrix} \tilde{\phi}_1(1) & \cdots & \tilde{\phi}_1(N) \\ \tilde{\phi}_N(1) & \cdots & \tilde{\phi}_N(N) \end{vmatrix}, \quad (D5)$$

where

$$\phi_i(x) = \sum_{l=1}^{N} \tilde{\phi}_l{}'(x)C_{li}, \quad (D6)$$

and C is any unitary matrix:

$$\sum_{i=1}^{N} C_{ki}{}^*C_{li} = \delta_{kl}, \quad (D7)$$

or symbolically, $C^\dagger C = CC^\dagger = 1$. The form of the functional (D1) is likewise invariant under the transformation (D6). To prove this is straightforward. Make the following substitutions in (D1):

$$\phi_i(x) = \sum_{l=1}^{N} \tilde{\phi}_l(x)C_{li}, \quad \phi_i{}^*(x) = \sum_{k=1}^{N} \tilde{\phi}_k{}^*(x)C_{ki}{}^*,$$

$$\phi_j(x) = \sum_{n=1}^{N} \tilde{\phi}_n(x)C_{nj}, \quad \phi_j{}^*(x) = \sum_{m=1}^{N} \tilde{\phi}_m{}'{}^*(x)C_{mj}{}^*. \quad (D8)$$

The summations over i and j result in

$$\sum_{i=1}^{N} C_{ki}{}^*C_{li} = \delta_{kl}, \quad \sum_{j=1}^{N} C_{mj}{}^*C_{nj} = \delta_{mn}, \quad (D9)$$

and subsequently, the sums over l and m leave only the diagonal terms $l=k$ and $m=n$, respectively. It is seen finally that

$$F(\phi_i,\phi_i{}^*) = \tilde{F}(\tilde{\phi}_k,\tilde{\phi}_k{}^*), \quad (D10)$$

where $\tilde{F}(\tilde{\phi}_k,\tilde{\phi}_k{}^*)$ is obtained from $F(\phi_i,\phi_i{}^*)$ by making the following substitutions: k for i, n for j, $\tilde{\phi}$ for ϕ, $\tilde{\lambda}_{nk}$ for λ_{ji}, provided that

$$\tilde{\lambda}_{nk} = \sum_{i=1}^{N} \sum_{j=1}^{N} C_{nj}\lambda_{ji}C_{ki}{}^*, \quad (D11)$$

or, in matrix notation, $\tilde{\Lambda} = C\Lambda C^\dagger$. The steps leading to Eqs. (D4) can now be carried out in terms of the tilded spin-orbital functions. The result analogous to (D4) is

$$\mathcal{H}_k{}^{\text{eff}}\tilde{\phi}_k(x) = \sum_{n=1}^{N} \tilde{\phi}_n(x)\tilde{\lambda}_{nk}, \quad (D12)$$

where the effective Hamiltonian is written with a tilde to indicate that the potential-energy operators are also expressed in terms of the $\tilde{\phi}_k(x)$. The point of the preceding covariance proof becomes apparent if we specify that the unitary transformation diagonalize the Λ-matrix,

$$\tilde{\lambda}_{nk} = \epsilon_k\delta_{nk}. \quad (D13)$$

This is always possible since Λ is Hermitian [Eq. (D2)]. Thus the set (D4) or (D12) can be in principle, transformed into the Hartree–Fock equations (27). In practice, one assumes a diagonal multiplier matrix initially. The solutions of the Hartree–Fock equations are then automatically the basis which diagonalizes Λ.

For systems containing open shells, it is not, in general, possible to eliminate the off-diagonal Lagrange multipliers.