

# Introduction to the Hartree-Fock method

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A fundamental bottleneck in both classical and quantum mechanics is the *three-body problem*. That is, the motion of systems in which three or more masses interact cannot be solved analytically, so that approximation methods must be utilized. This chapter introduces the basic ideas of the self-consistent field (SCF) and Hartree-Fock (HF) methods, which provide the foundation for the vast majority of computational work on the electronic structure of atoms and molecules. More advanced generalizations of HF are discussed in [Chapter 3](#). Conceptual developments beyond HF, including density-functional and Monte-Carlo methods, are introduced in subsequent chapters.

## 1 HARTREE SELF-CONSISTENT FIELD THEORY

A precursor of SCF methods might have been the attempts to study the motions of electrons in many electron atoms in the 1920s, on the basis of the Old Quantum Theory. The energy levels of a valence electron, such as the 3s-electron in sodium, could be reproduced quite closely if the Bohr orbits of the innerelectrons were smeared out into a continuous spherically symmetric charge distribution [1–3]. After the development of wave mechanics in 1926, it was recognized by Hartree [4] that Bohr orbits must be replaced by continuous charge clouds of electrons, such that the charge density of a single electron is given by  $\rho(\mathbf{r}) = -e|\psi(\mathbf{r})|^2$ . Here,  $e$  is the magnitude of the electron charge ( $1.602 \times 10^{-19}$  coulomb) and the charge density  $\rho(\mathbf{r})$  follows the Born interpretation of the atomic orbital  $\psi(\mathbf{r})$ .

The approaches to atomic and molecular structure that are to be described in this chapter are classified as *ab initio* (“from the beginning”) methods, since no experimental or semiempirical parameters are used (other than the fundamental physical constants).

The simplest application of Hartree’s SCF method is the helium atom, with two electrons. Electron 1, which occupies the atomic orbital  $\psi_1(\mathbf{r}_1)$ , moves in the field of the nucleus and electron 2. The potential energy of an electron with charge  $-e$  a distance  $r$  from a nucleus of charge  $+Ze$  follows directly from Coulomb’s law, with

$$V(r) = -\frac{Ze^2}{r}. \quad (1)$$

(We use Gaussian units to avoid the unnecessary factors  $4\pi\epsilon_0$ , and, in any event, we will soon be switching to atomic units.) To review, the Schrödinger equation for a hydrogen-like atom can be written

$$\left\{ -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r} \right\} \psi(\mathbf{r}) = \epsilon\psi(\mathbf{r}), \quad (2)$$

where the energy for principal quantum number  $n$  is given by  $\epsilon_n = -Z^2e^2/2a_0n^2$ , with  $a_0$  equal to the Bohr radius  $\hbar^2/me^2$ . The one-electron functions  $\psi(\mathbf{r})$ , when used in the context of a multielectron system, are called *orbitals* [5], an adjective, used as a noun, to denote the quantum-mechanical analog of classical *orbits*. For an electron at point  $\mathbf{r}$  interacting with the charge distribution of a second electron in an atomic orbital  $\psi(\mathbf{r}')$ , the potential energy is given by

$$V(\mathbf{r}) = e^2 \int d^3\mathbf{r}' \frac{|\psi(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}. \quad (3)$$

Thus, the total potential energy for electron 1 is given by

$$V_1(\mathbf{r}_1) = V_1[\psi_2] = -\frac{Ze^2}{r_1} + e^2 \int d^3\mathbf{r}_2 \frac{|\psi_2(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (4)$$

where the notation  $V_1[\psi_2]$  indicates that  $V_1$  is a *functional* of  $\psi_2$ , emphasizing the dependance on the charge distribution of electron 2. In Hartree's method, electron 1 obeys the effective one-particle Schrödinger equation

$$\left\{ -\frac{\hbar^2}{2m}\nabla^2 + V_1[\psi_2] \right\} \psi_1(\mathbf{r}_1) = \epsilon_1\psi_1(\mathbf{r}_1), \quad (5)$$

where  $\epsilon_1$  is the orbital energy of electron 1, negative for bound states. Analogously, interchanging the labels 1 and 2, the orbital function for electron 2 is the solution of

$$\left\{ -\frac{\hbar^2}{2m}\nabla^2 + V_2[\psi_1] \right\} \psi_2(\mathbf{r}_2) = \epsilon_2\psi_2(\mathbf{r}_2). \quad (6)$$

The coupled integro-differential equations (5), (6), known as the *Hartree equations*, can be represented in symbolic form by

$$\mathcal{H}_i^{\text{eff}}\psi_i(\mathbf{r}_i) = \epsilon_i\psi_i(\mathbf{r}_i), \quad i = 1, 2. \quad (7)$$

These are coupled in the sense that the solution to the first equation enters the second equation (via the effective Hamiltonian operator  $\mathcal{H}_2^{\text{eff}}$  containing  $V_2[\psi_1]$ ), and vice versa. A solution to these equations can be found, in principle, by a successive approximation procedure. An initial “guess” of the functions  $\psi_1$  and  $\psi_2$  is used to

compute the potential energies  $V_1[\psi_2]$  and  $V_2[\psi_1]$ . Each Hartree equations can then be solved to give “first-improved” orbital functions  $\psi_1^{(1)}$  and  $\psi_2^{(1)}$ . These, in turn, are used to recompute  $V_1^{(1)}$  and  $V_2^{(1)}$ , and the new Hartree equations are solved to give second-improved orbital functions. The iterative procedure is continued until the input and output functions agree to within some desired accuracy. The orbital functions 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—apply at each stage of the computation. Each Hartree equation is thus an eigenvalue problem, soluble only for certain discrete values of  $\epsilon_i$  (in general, different in each stage). For the helium atom the orbital functions  $\psi_1$  and  $\psi_2$  turn out to be identical. This does not violate the Pauli principle since the two orbitals can have opposite spins. Note that the Hartree method does not itself take spin into account.

Extension of the Hartree method to an  $N$ -electron atom is straightforward. Each electron now moves in the potential field of the nucleus plus the overlapping charge clouds of  $N - 1$  other electrons. Now  $N$  coupled integro-differential equations are to be solved:

$$\mathcal{H}_i^{\text{eff}} \psi_i(\mathbf{r}_i) = \epsilon_i \psi_i(\mathbf{r}_i), \quad i = 1 \dots N, \quad (8)$$

where

$$\mathcal{H}_i^{\text{eff}} = -\frac{\hbar^2}{2m} \nabla^2 + V_i[\psi_1, \psi_2 \dots \psi_N], \quad (9)$$

and

$$V_i[\psi_1, \psi_2 \dots \psi_N] = -\frac{Ze^2}{r_i} + \sum_{j \neq i} e^2 \int d^3 \mathbf{r}_j \frac{|\psi_j(\mathbf{r}_j)|^2}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (10)$$

Each set of orbital functions  $\psi_1 \dots \psi_N$  can be identified with an electronic configuration, for example,  $1s^2 2s^2 2p^6 3s$  for the Na atom. It is left to the good sense of the user not to allow more than two of the orbitals  $\psi_1 \dots \psi_N$  to be the same.<sup>1</sup> The different orbital pairs should also be constructed to be mutually orthogonal. The eigenvalues  $\epsilon_i$  should be negative for bound orbitals. Their magnitudes are approximations to the ionization energies of the corresponding electrons.

At this point, it is convenient to introduce atomic units, which simplifies all of the previous formulas by removing the repetitive physical constants. We set

$$\hbar = e \left( \text{or } \frac{e}{\sqrt{4\pi\epsilon_0}} \right) = m = 1. \quad (11)$$

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<sup>1</sup>Ignoring this restriction has been dubbed “inconsistent field theory.”

The unit of length is the *Bohr* equal to the Bohr radius  $a_0 = \hbar^2/me^2 = 0.529177 \times 10^{-10}$  m. The unit of energy is the *Hartree*, equal to  $e^2/a_0$ , corresponding to 27.2114 eV. Expressed in atomic units, the Schrödinger equation for a hydrogen-like atom (2) simplifies to

$$\left\{ -\frac{1}{2} \nabla^2 - \frac{Z}{r} \right\} \psi(\mathbf{r}) = \epsilon \psi(\mathbf{r}), \quad (12)$$

with  $\epsilon_n = -Z^2/2n^2$ .

Hartree's SCF method, as described so far, followed entirely from intuitive considerations of atomic structure. We turn next to a more rigorous quantum-theoretical derivation of the method [6,7]. The first step is to write down the Hamiltonian operator for an  $N$ -electron atom. Now using atomic units, neglecting magnetic interactions and other higher-order effects:

$$H = \sum_{i=1}^N \left\{ -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right\} + \sum_{i>j=1}^N \frac{1}{r_{ij}}. \quad (13)$$

The one-electron parts of the Hamiltonian—the kinetic energy and nuclear attraction operators—are contained in the first summation. The second summation, over  $N(N-1)/2$  distinct pairs  $i, j$ , represents the interelectronic repulsive interactions. The interelectronic distances are denoted  $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ . The  $N$ -electron wavefunction is approximated by a *Hartree product*:

$$\Psi(\mathbf{r}_1 \dots \mathbf{r}_N) = \psi(\mathbf{r}_1) \psi(\mathbf{r}_2) \dots \psi(\mathbf{r}_N), \quad (14)$$

where  $\psi(\mathbf{r}_i)$  are the one-electron orbitals. These should consist of mutually orthonormal functions

$$\int d^3\mathbf{r} \psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) = \langle \psi_i | \psi_j \rangle = \delta_{ij}, \quad (15)$$

with none repeated more than twice (maximum of two electrons per atomic orbital). Note that we have now introduced Dirac notation, for compactness. A fully separable wavefunction such as Eq. (14) would be exact only if the Hamiltonian were a sum of one-electron parts. This is not the case since the electron coordinates are inextricably mixed by the  $r_{ij}^{-1}$  terms, representing mutual electron repulsion. We therefore must consider approximate solutions of the  $N$ -particle Schrödinger equation, optimized in accordance with the variational principle. This means minimizing the ratio of integrals

$$\mathcal{E} = \frac{\int \dots \int d^3\mathbf{r}_1 \dots d^3\mathbf{r}_N \Psi^* H \Psi}{\int \dots \int d^3\mathbf{r}_1 \dots d^3\mathbf{r}_N |\Psi|^2} = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \quad (16)$$

This gives an upper limit to the exact ground state energy  $E_0$ :  $\mathcal{E} \geq E_0$ .

We next give a derivation of the Hartree equations. Using the orthonormalized orbitals  $\psi_i(\mathbf{r})$ , satisfying Eq. (15), the total wavefunction is found to be normalized as well:

$$\langle \Psi | \Psi \rangle = \langle \psi_1 \psi_2 \dots \psi_N | \psi_1 \psi_2 \dots \psi_N \rangle = \langle \psi_1 | \psi_1 \rangle \langle \psi_2 | \psi_2 \rangle \dots \langle \psi_N | \psi_N \rangle = 1. \quad (17)$$

Thus the variational energy can be written, with detailed specification of  $\Psi$  and  $H$ ,

$$\begin{aligned} \mathcal{E} = & \sum_i \left\langle \psi_1 \psi_2 \dots \psi_N \left| \left\{ -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right\} \right| \psi_1 \psi_2 \dots \psi_N \right\rangle \\ & + \sum_{i>j} \left\langle \psi_1 \psi_2 \dots \psi_N | r_{ij}^{-1} | \psi_1 \psi_2 \dots \psi_N \right\rangle, \end{aligned} \quad (18)$$

where we have separately written the contributions from the one-electron and two-electron parts of the Hamiltonian. We now define the one-electron integrals

$$H_i = \int d^3 \mathbf{r} \, \psi_i^*(\mathbf{r}) \left\{ -\frac{1}{2} \nabla^2 - \frac{Z}{r} \right\} \psi_i(\mathbf{r}), \quad (19)$$

and the two electron integrals

$$J_{ij} = \iint d^3 \mathbf{r} d^3 \mathbf{r}' \frac{|\psi_i(\mathbf{r})|^2 |\psi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}. \quad (20)$$

The  $H_i$  are known as *core integrals*, while the  $J_{ij}$  are called *Coulomb integrals* since they represent the electrostatic interactions of interpenetrating electron-charge clouds. After carrying out the integrations implicit in Eq. (18), we obtain

$$\mathcal{E} = \sum_i H_i + \sum_{i>j} J_{ij}, \quad (21)$$

as an approximation to the total energy of the  $N$ -electron atom.

We can now apply the variational principle to determine the “best possible” set of atomic orbitals  $\psi_1 \dots \psi_N$ . Formally, a minimum of  $\mathcal{E}$  is sought by variation of the functional forms of the  $\psi_i$ . The minimization is not unconditional; however, since the  $N$  normalization conditions (15) must be maintained. A conditional minimum problem becomes equivalent to an unconditional problem by application of Lagrange’s method of undetermined multipliers. The  $\psi_i$  and  $\psi_i^*$  are formally treated as independent functional variables. The Lagrange multipliers are denoted  $\epsilon_i$  in anticipation of their later emergence as energies in the Hartree equations. Accordingly, we seek the minimum of the functional

$$\mathcal{L}[\psi_1 \dots \psi_N, \psi_1^* \dots \psi_N^*] = \mathcal{E}[\psi_1 \dots \psi_N, \psi_1^* \dots \psi_N^*] - \sum_{i=1}^N \epsilon_i \langle \psi_i | \psi_i \rangle. \quad (22)$$

Expressing  $\mathcal{L}$  in terms of the original integrals, using Eqs. (15), (19), (20), we obtain

$$\mathcal{L}[\psi, \psi^*] = \sum_i \int d^3 \mathbf{r} \, \psi_i^*(\mathbf{r}) \left\{ -\frac{1}{2} \nabla^2 - \frac{Z}{r} + \sum_{j \neq i} \int d^3 \mathbf{r}' \frac{|\psi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} - \epsilon_i \right\} \psi_i(\mathbf{r}). \quad (23)$$

The variation of  $\mathcal{L}[\psi, \psi^*]$  in terms of variations in all the  $\psi_i$  and  $\psi_i^*$  is given by

$$\delta\mathcal{L} = \sum_i \frac{\partial\mathcal{L}}{\partial\psi_i} \delta\psi_i + \sum_i \frac{\partial\mathcal{L}}{\partial\psi_i^*} \delta\psi_i^* = 0. \quad (24)$$

Since the minimum in  $\mathcal{L}$  is unconditional, this result must hold for arbitrary variations of all the  $\delta\psi_i$  and  $\delta\psi_i^*$ . This is possible only if each of the coefficients of these variations vanish, that is,

$$\frac{\partial\mathcal{L}}{\partial\psi_i} = \frac{\partial\mathcal{L}}{\partial\psi_i^*} = 0, \quad i = 1 \dots N. \quad (25)$$

Let us focus on one particular term in the variation  $\delta\mathcal{L}$ , namely the term linear in  $\delta\psi_k^*$  for some  $i = k$ . From the condition  $\frac{\partial\mathcal{L}}{\partial\psi_k^*} = 0$  applied to Eq. (23), we are led to the Hartree equations<sup>2</sup>

$$\left\{ -\frac{1}{2}\nabla^2 - \frac{Z}{r} + \sum_{j \neq k} \int d^3\mathbf{r}' \frac{|\psi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \right\} \psi_k(\mathbf{r}) = \epsilon_k \psi_k(\mathbf{r}), \quad k = 1 \dots N, \quad (26)$$

in agreement with Eqs. (8)–(10). We have used the facts that the first summation  $\sum_i$  reduces to a single term with  $i = k$  and the vanishing of the integral  $\int d^3\mathbf{r} \dots$  for arbitrary values of  $\delta\psi_k^*$  implies that the remaining integrand is identically equal to 0.

## 2 DETERMINANTAL WAVEFUNCTIONS

The electron in each orbital  $\psi_i(\mathbf{r})$  is a spin  $\frac{1}{2}$  particle and thus has two possible spin orientations w.r.t. an arbitrary spatial direction,  $m_s = +\frac{1}{2}$  or  $m_s = -\frac{1}{2}$ . The spin function is designated  $\sigma$ , which can correspond to one of the two possible spin states  $\sigma = \alpha$  or  $\sigma = \beta$ . We define a composite function, known as a *spin-orbital*

$$\phi(x) = \psi(\mathbf{r})\sigma, \quad \sigma = \begin{cases} \alpha \\ \beta, \end{cases} \quad (27)$$

denoting by  $x$  the four-dimensional manifold of space and spin coordinates. For example, a hydrogen-like spin-orbital is labeled by four quantum numbers, so  $a = \{n, l, m, m_s\}$ . We will abbreviate combined integration over space coordinates and summation over spin coordinates by

$$\sum_{\text{spin}} \int d^3\mathbf{r} = \int dx. \quad (28)$$

<sup>2</sup>The Hartree equations might appear today to have only historical significance, but their generalization leads to the Kohn-Sham equations of modern density-functional theory.

A Hartree product of spin-orbitals now takes the form

$$\Psi(1 \dots N) = \phi_a(1)\phi_b(2) \dots \phi_n(N). \quad (29)$$

For further brevity, we have replaced the variables  $x_i$  simply by their labels  $i$ .

To be physically valid, a simple Hartree product must be generalized to conform to two quantum-mechanical requirements. First is the Pauli exclusion principle, which states that no two spin-orbitals in an atom can be the same. This allows an orbital to occur twice, but only with opposite spins. Second, the metaphysical perspective of the quantum theory implies that individual interacting electrons must be regarded as indistinguishable particles. One cannot uniquely label a specific particle with an ordinal number; the indices given must be interchangeable. Thus each of the  $N$  electrons must be equally associated with each of the  $N$  spin-orbitals. Since we have now undone the unique connection between electron number and spin-orbital label, we will henceforth designate the spin-orbital labels as lower-case letters  $a, b, \dots, n$  while retaining the labels  $1, 2, \dots, N$  for electron numbers. The simplest example is again the  $1s^2$  ground state of helium atom. Let the two occupied spin-orbitals be  $\phi_a(1) = \psi_{1s}(1)\alpha(1)$  and  $\phi_b(2) = \psi_{1s}(2)\beta(2)$ . To fulfill the necessary quantum requirements, we can construct the (approximate) ground state wavefunction in the form

$$\Psi_0(1, 2) = \frac{1}{\sqrt{2}} \left( \phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1) \right). \quad (30)$$

Inclusion of the term with interchanged particle labels,  $\phi_a(2)\phi_b(1)$ , fulfills the indistinguishability requirement. The factor  $\frac{1}{\sqrt{2}}$  preserves normalization for the linear combination (assuming that  $\phi_a$  and  $\phi_b$  are individually orthonormalized). The exclusion principle is also satisfied, since the function would vanish identically if spin-orbitals  $a$  and  $b$  were the same. A general consequence of the Pauli principle is the *antisymmetry principle* for identical fermions, whereby

$$\Psi(2, 1) = -\Psi(1, 2). \quad (31)$$

The function (30) has the form of a  $2 \times 2$  determinant

$$\Psi_0(1, 2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_a(1) & \phi_b(1) \\ \phi_a(2) & \phi_b(2) \end{vmatrix}. \quad (32)$$

The generalization for a function of  $N$  spin-orbitals, which is consistent with the Pauli and indistinguishability principles, is an  $N \times N$  Slater determinant<sup>3</sup>

$$\Psi(1 \dots N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_a(1) & \phi_b(1) & \dots & \phi_n(1) \\ \phi_a(2) & \phi_b(2) & \dots & \phi_n(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_a(N) & \phi_b(N) & \dots & \phi_n(N) \end{vmatrix}. \quad (33)$$

<sup>3</sup>The determinantal form was first proposed by Heisenberg [8,9] and Dirac [10]. Slater first used it in the application to a many-electron system [11].

There are  $N!$  possible permutations of  $N$  electron among  $N$  spin-orbitals, which accounts for the normalization constant  $1/\sqrt{N!}$ . A general property of determinants is that they identically equal to 0 if any two columns (or rows) are equal; this conforms to the Pauli exclusion principle. A second property is that, if any two columns are interchanged, the determinant changes sign. This expresses the antisymmetry principle for an  $N$ -electron wavefunction:

$$\Psi(\dots j \dots i \dots) = -\Psi(\dots i \dots j \dots). \quad (34)$$

A closed-shell configuration of an atom or molecule contains  $N/2$  pairs of orbitals, doubly occupied with  $\alpha$  and  $\beta$  spins; this can be represented by a single Slater determinant. However, an open shell configuration must, in general, be represented by a sum of Slater determinants, so that  $\Psi(1 \dots N)$  will be an eigenfunction of total spin and orbital angular momenta. As a simple illustration, consider the  $1s^2$  and  $1s2s$  configurations of helium atom. The  $1s^2$  ground state can be represented by a single determinant

$$\Psi_0(1, 2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s\alpha}(1) & \phi_{1s\beta}(1) \\ \phi_{1s\alpha}(2) & \phi_{1s\beta}(2) \end{vmatrix}, \quad (35)$$

which is an eigenfunction of the spin with eigenvalues  $S = 0, M_S = 0$ . The  $1s2s$  states with  $S = 1, M_S = \pm 1$  can likewise be represented by single determinants:

$$\Psi(1, 2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s\alpha}(1) & \phi_{2s\alpha}(1) \\ \phi_{1s\alpha}(2) & \phi_{2s\alpha}(2) \end{vmatrix}, \quad (36)$$

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

$$\Psi(1, 2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s\beta}(1) & \phi_{2s\beta}(1) \\ \phi_{1s\beta}(2) & \phi_{2s\beta}(2) \end{vmatrix}, \quad (37)$$

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

$$\Psi(1, 2) = \frac{1}{\sqrt{2}} \left[ \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s\alpha}(1) & \phi_{2s\beta}(1) \\ \phi_{1s\alpha}(2) & \phi_{2s\beta}(2) \end{vmatrix} \pm \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s\beta}(1) & \phi_{2s\alpha}(1) \\ \phi_{1s\beta}(2) & \phi_{2s\alpha}(2) \end{vmatrix} \right]. \quad (38)$$

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

### 3 HARTREE-FOCK EQUATIONS

The HF method is most usefully applied to molecules. We must, therefore, generalize the Hamiltonian to include the interaction of the electrons with multiple nuclei, located at the points  $\mathbf{R}_1, \mathbf{R}_2, \dots$ , with nuclear charges  $Z_1, Z_2, \dots$ :



$$H = \sum_i \left\{ -\frac{1}{2} \nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}} \right\} + \sum_{i>j} \frac{1}{r_{ij}}. \quad (39)$$

We use the abbreviation  $r_{iA} = |\mathbf{r}_i - \mathbf{R}_A|$ . In accordance with the Born-Oppenheimer approximation, we assume that the positions of the nuclei  $\mathbf{R}_1, \mathbf{R}_2, \dots$  are fixed. Thus there are no nuclear kinetic energy terms such as  $-\frac{1}{2M_A} \nabla_A^2$ . The internuclear potential energy  $V_{\text{nucl}}(R) = \sum_{A,B} \frac{Z_A Z_B}{R_{AB}}$  is constant for a given nuclear conformation, which is added to the result after the electronic energy is computed. Note that the total energy  $\mathcal{E}(R)$  as well as the one-electron energies  $\epsilon_i(R)$  are dependent on the nuclear conformation, abbreviated simply as  $R$ . It is of major current theoretical interest to plot *energy surfaces*, which are the molecular energies as functions of the conformation parameters  $R$ .

We are now ready to calculate the approximate variational energy corresponding to HF wavefunctions [12,13]

$$\mathcal{E} = \langle \Psi_{\text{HF}} | H | \Psi_{\text{HF}} \rangle. \quad (40)$$

We will now refer to the one-electron functions making up a Slater determinant as *molecular orbitals*. To derive the energy formulas, it is useful to reexpress the determinantal functions in a more directly applicable form. Recall that an  $N \times N$  determinant is a linear combination of  $N!$  terms, obtained by permutation of the  $N$  electron labels  $1, 2, \dots, N$  among the  $N$  molecular orbitals. Whenever necessary, we will label the spin-orbitals by  $r, s \dots n$  to distinguish them from the particle labels  $i, j \dots N$ . We can then write

$$\Psi_{\text{HF}} = \frac{1}{\sqrt{N!}} \sum_{p=1}^{N!} (-1)^p \mathcal{P}_p [\phi_r(1) \phi_s(2) \dots \phi_n(N)], \quad (41)$$

where  $\mathcal{P}_p$  is one of  $N!$  permutations labeled by  $p = 1 \dots N!$ . Permutations are classified as either *even* or *odd*, according to whether they can be composed of an even or an odd number of binary exchanges. The products resulting from an even permutation are *added*, in the linear combination, while those from an odd permutation are *subtracted*. Even permutations are labeled by even  $p$ , odd permutations by odd  $p$ . Thus each product in the sum is multiplied by  $(-1)^p$ . Let us first consider the normalization bra-ket of  $\Psi_{\text{HF}}$

$$\langle \Psi_{\text{HF}} | \Psi_{\text{HF}} \rangle = \frac{1}{N!} \left\langle \sum_{p=1}^{N!} (-1)^p \mathcal{P}_p [\phi_r(x_1) \phi_s(x_2) \dots] \left| \sum_{p'=1}^{N!} (-1)^{p'} \mathcal{P}_{p'} [\phi_r(x'_1) \phi_s(x'_2) \dots] \right. \right\rangle. \quad (42)$$

Because of the orthonormality of the molecular orbitals  $\phi_r, \phi_s, \dots$ , the only nonzero terms of this double summation will be those with  $x'_1 = x_1, x'_2 = x_2, \dots, x'_N = x_N$ . There will be  $N!$  such terms, thus the bra-ket reduces to

$$\langle \Psi_{\text{HF}} | \Psi_{\text{HF}} \rangle = \langle \phi_r(x_1) \phi_s(x_2) \dots | \phi_r(x_1) \phi_s(x_2) \dots \rangle = \langle \phi_r | \phi_r \rangle \langle \phi_s | \phi_s \rangle \dots \langle \phi_n | \phi_n \rangle = 1. \quad (43)$$

The core contributions to the energy involves terms in the one-electron sum in Eq. (39). Defining the core operator

$$\mathcal{H}(x) = \left\{ -\frac{1}{2} \nabla^2 - \sum_A \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} \right\}, \quad (44)$$

the expression for the core integral  $H_r$  reduces to

$$H_r = \langle \phi_r(x) | \mathcal{H}(x) | \phi_r(x) \rangle, \quad r = 1, 2, \dots, n. \quad (45)$$

In analogy with Eq. (43) for case of the normalization bra-ket, all the other factors  $\langle \phi_b | \phi_s \rangle$ ,  $s \neq r$  are equal to 1. This is analogous to Eq. (19), the definition of the core integral in the Hartree method, except that now spin-orbitals, rather than simple orbitals are now used. Actually, the scalar products of the spin functions  $\sigma_r$  give factors of 1, so that only the space-dependent orbital functions are involved in the computation, just as in the Hartree case.

We consider next the interelectronic repulsions  $r_{ij}^{-1}$ . Following an analogous calculation, all contributions except those containing particle numbers  $i$  or  $j$  give factors of 1. What remains is

$$\langle r_{ij}^{-1} \rangle = \langle \phi_r(x_i) \phi_s(x_j) | r_{ij}^{-1} | \phi_r(x_i) \phi_s(x_j) \rangle - \langle \phi_r(x_i) \phi_s(x_j) | r_{ij}^{-1} | \phi_r(x_j) \phi_s(x_i) \rangle. \quad (46)$$

The minus sign reflects the fact that interchanging two particle labels  $i, j$  multiplies the wavefunction by  $-1$ . The first term earlier corresponds to a Coulomb integral (20); again these are labeled by spin-orbitals, but the computation involves only space-dependent orbital functions:

$$J_{rs} = \langle \phi_r(x_i) \phi_s(x_j) | r_{ij}^{-1} | \phi_r(x_i) \phi_s(x_j) \rangle. \quad (47)$$

The second term in Eq. (46) gives rise to an *exchange integral*:

$$K_{rs} = \langle \phi_r(x_i) \phi_s(x_j) | r_{ij}^{-1} | \phi_r(x_j) \phi_s(x_i) \rangle. \quad (48)$$

This represents a purely quantum-mechanical effect, having no classical analog, and arising from the antisymmetry principle. In terms of the orbitals  $\psi(\mathbf{r})$ , after carrying out the formal integrations over the spin, we can write

$$J_{ij} = \iint d^3\mathbf{r} d^3\mathbf{r}' \frac{|\psi_i(\mathbf{r})|^2 |\psi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \quad (49)$$

and

$$K_{ij} = \iint d^3\mathbf{r} d^3\mathbf{r}' \psi_i(\mathbf{r}) \psi_j(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_i(\mathbf{r}') \psi_j(\mathbf{r}) \langle \sigma_i | \sigma_j \rangle. \quad (50)$$

Unlike  $J_{ij}$ ,  $K_{ij}$  involves the electron spin. Because of the scalar product of the spins associated with  $\phi_i$  and  $\phi_j$ , the exchange integral vanishes if  $\sigma_i \neq \sigma_j$ , in other words, if spin-orbitals  $i$  and  $j$  have opposite spins,  $\alpha, \beta$  or  $\beta, \alpha$ .

The expression for the approximate total energy can now be given by the summation

$$\mathcal{E} = \sum_i H_i + \sum_{i>j} (J_{ij} - K_{ij}). \quad (51)$$

Note that  $K_{ii} = J_{ii}$ , which would cancel any presumed electrostatic self-energy of a spin-orbital. The effective one-electron equations for the HF spin-orbitals can be derived by a procedure analogous to that of Eqs. (22)–(26). A new feature is that the Lagrange multipliers must now take account of  $N^2$  orthonormalization conditions  $\langle \phi_i | \phi_j \rangle = \delta_{ij}$ , leading to  $N^2$  multipliers  $\lambda_{ij}$ . Accordingly

$$\mathcal{L}[\phi, \phi^*] = \mathcal{E}[\phi, \phi^*] - \sum_{i>j} \lambda_{ij} \langle \phi_i | \phi_j \rangle. \quad (52)$$

The Lagrange multipliers  $\lambda_{ij}$  can be represented by a Hermitian matrix. It should therefore be possible to perform a unitary transformation to diagonalize the  $\lambda$ -matrix. Fortunately, we do not have to do this transformation explicitly; we can just assume that the set of spin-orbitals  $\phi_i$  are the results after this unitary transformation has been carried out. The new diagonal matrix elements can be designated  $\epsilon_i = \lambda_{ii}$ . Again, we see that the  $\epsilon_i$  will correspond to the one-electron energies in the solutions of the HF equations. As a generalization of Eq. (26), the contribution to the variation  $\delta\mathcal{L}$  linear in  $\delta\phi_i^*$  is given by

$$\left\{ -\frac{1}{2}\nabla^2 - \sum_A \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} + \sum_{j \neq i} \int d\mathbf{r}' \frac{|\phi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \right\} \phi_i(x) - \sum_{j \neq i} \left\{ \int d\mathbf{r}' \frac{\phi_j^*(\mathbf{r}') \phi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right\} \phi_j(x) = \epsilon_i \phi_i(x). \quad (53)$$

The effective HF Hamiltonian  $\mathcal{H}_{\text{HF}}$  is known as the *Fock operator*, designated  $\mathcal{F}$ . Finally, the HF equations can be written

$$\mathcal{F}\phi_i(x) = \epsilon_i \phi_i(x) \quad i = 1, 2, \dots, n. \quad (54)$$

In contrast to the Hartree equations (26),  $\mathcal{F}\phi_i(x)$  also produces terms linear in the other spin-orbitals  $\phi_j$ ,  $j \neq i$ . Just as in the Hartree case, the coupled set of HF integro-differential equations can, in principle, be solved numerically, using the analogous self-consistency approach, with iteratively improved sets of spin-orbitals.

The significance of the one-electron eigenvalues  $\epsilon_i$  can be found by premultiplying the HF equation (53) by  $\phi_i^*(x)$  and integrating over  $x$ . Using the definitions of  $H_i$ ,  $J_{ij}$ , and  $K_{ij}$ , we find

$$\epsilon_i = H_i + \sum_j (J_{ij} - K_{ij}). \quad (55)$$

Consider now the difference in energies of the  $N$ -electron system and the  $(N - 1)$ -electron system with the spin-orbital  $\phi_k$  removed

$$\begin{aligned} \mathcal{E}(N) - \mathcal{E}(N - 1) &= \sum_{i=1}^N H_i + \sum_{i>j=1}^N (J_{ij} - K_{ij}) \\ &\quad - \left[ \sum_{i=1}^{N-1} H_i + \sum_{i>j=1}^{N-1} (J_{ij} - K_{ij}) \right]_{i,j \neq k} = H_k + \sum_{j=1}^{N-1} (J_{kj} - K_{kj}) = \epsilon_k. \end{aligned} \quad (56)$$

Therefore, the magnitudes of the eigenvalues  $\epsilon_k$  are approximations for the ionization energies of the corresponding spin-orbitals  $\phi_k$ . Since the  $\epsilon_k$  are negative,  $\text{IP}_k = |\epsilon_k|$ . This result is known as *Koopmans' theorem*. It is not exact since it assumes “frozen” spin-orbitals, when the  $N$ -electron system becomes an  $(N - 1)$ -electron positive ion. In actual fact, the separately optimized orbitals for an atom or molecule and its positive ion will be different.

It can be shown that the magnitudes of the Coulomb and exchange integrals satisfy the inequalities

$$\frac{1}{2}(J_{ii} + J_{jj}) \geq J_{ij} \geq K_{ij} \geq 0. \quad (57)$$

In general,  $K_{ij}$  is an order of magnitude smaller than the corresponding Coulomb integral  $J_{ij}$ . HF expressions for the total energy can readily explain why the triplet state of, for example, the  $1s2s \ ^3S$  configuration of helium atom is lower in energy than the singlet of the same configuration  $1s2s \ ^1S$ . Denoting the two-determinant functions in Eq. (38) as  $\Psi(^1,^3S)$  for the (+) and (−) signs, respectively, we compute the expectation value of the two-electron Hamiltonian for helium (with  $Z = 2$ ). After some algebra, the following result is found:

$$\mathcal{E}(^1,^3S) = \left\langle \Psi(^1,^3S) \left| \sum_{i=1}^2 \left\{ -\frac{1}{2} \nabla_i^2 - \frac{2}{r_i} \right\} + \frac{1}{r_{12}} \right| \Psi(^1,^3S) \right\rangle = H_{1s} + H_{2s} + J_{1s,2s} \pm K_{1s,2s}. \quad (58)$$

Therefore, since  $K > 0$ , the triplet, with the (−) sign, has the lower energy. One caution, however, is again the fact that the singlet and triplet states have different optimized orbitals, so that the values of  $K_{1s,2s}$  (as well as  $J_{1s,2s}$ ,  $H_{1s}$ , and  $H_{2s}$ ) are not equal. But even with separately optimized orbitals, the conclusion remains valid.

One can also give a simple explanation of Hund's first rule based on exchange integrals. For a given electron configuration, the term with maximum multiplicity has the lowest energy. The multiplicity  $2S + 1$  is maximized when the number of parallel spins is as large as possible, while conforming to the Pauli principle. But more parallel spins give more contributions of the form  $-K_{ij}$ , thus lower energy.

## 4 HARTREE-FOCK EQUATIONS USING SECOND QUANTIZATION

In much of the recent literature on theoretical developments beyond the HF method (“post-HF”), it has become common to express operators and state vectors using *second quantization*, which is based on *creation* and *annihilation operators*. This formalism was originally introduced to represent physical processes that involved actual creation or destruction of elementary particles, photons, or excitations (such as phonons). In a majority of applications of second quantization to quantum chemistry, no electrons are actually created or annihilated. The operators just serve as a convenient and operationally useful device in terms of which quantum-mechanical states, operators, commutators, and expectation values can be represented. To make the notation more familiar to the reader, we will, in this section, reexpress the HF equations in the language of second quantization.

A common way to introduce creation and annihilation operators is via an alternative algebraic approach to the one-dimensional harmonic oscillator. The Schrödinger equation, in atomic units, can be written

$$\frac{1}{2} \left\{ -\frac{d^2}{dq^2} + \omega^2 q^2 \right\} \psi_n(q) = \epsilon_n \psi_n(q), \quad \epsilon_n = \left( n + \frac{1}{2} \right) \omega, \quad n = 1, 2, \dots \quad (59)$$

Now define the operators

$$a = \frac{1}{\sqrt{2}}(q + ip) = \frac{1}{\sqrt{2}} \left( q + \frac{d}{dq} \right), \quad a^\dagger = \frac{1}{\sqrt{2}}(q - ip) = \frac{1}{\sqrt{2}} \left( q - \frac{d}{dq} \right), \quad (60)$$

where  $p = -i d/dq$  is the dimensionless momentum operator. The canonical commutation relation  $[q, p] = i$  implies

$$[a, a^\dagger] = 1, \quad (61)$$

and the Hamiltonian operator then simplifies to

$$H = \left( a^\dagger a + \frac{1}{2} \right) \omega. \quad (62)$$

With the wavefunction  $\psi_n(x)$  written in Dirac notation as  $|n\rangle$ , the Schrödinger equation in Eq. (59) becomes

$$H|n\rangle = \left( a^\dagger a + \frac{1}{2} \right) \omega |n\rangle = \left( n + \frac{1}{2} \right) \omega |n\rangle. \quad (63)$$

This implies the relation

$$a^\dagger a |n\rangle = n |n\rangle. \quad (64)$$

The harmonic oscillator equations can be reinterpreted as representing an assembly of photons, or other Bose-Einstein particles, in which  $|n\rangle$  is the state with  $n$  particles

and  $a^\dagger$  is the *number operator*, which counts the number of particles in the state, called the *occupation number*.

Consider now the commutation relation

$$[a^\dagger a, a^\dagger] = a^\dagger [a, a^\dagger] + [a^\dagger, a^\dagger] a = a^\dagger. \quad (65)$$

Applying this to the state  $|n\rangle$ , we have

$$[a^\dagger a, a^\dagger]|n\rangle = a^\dagger a a^\dagger |n\rangle - a^\dagger a^\dagger a |n\rangle = a^\dagger |n\rangle, \quad (66)$$

which can be rearranged to

$$a^\dagger a (a^\dagger |n\rangle) = (n+1) (a^\dagger |n\rangle). \quad (67)$$

The interpretation of the last equation is that  $a^\dagger |n\rangle$  is an eigenfunction of the number operator  $a^\dagger a$  with the eigenvalue  $n+1$ . Thus  $a^\dagger$  is a *creation operator*, which increases the number of bosons in the state  $|n\rangle$  by 1. The norm of  $a^\dagger |n\rangle$  is given by

$$\langle a^\dagger n | a^\dagger n \rangle = \langle n | a a^\dagger | n \rangle = (n+1) \langle n | n \rangle. \quad (68)$$

Thus, if both  $|n\rangle$  and  $|n+1\rangle$  are normalized, we have the precise relation for the creation operator

$$a^\dagger |n\rangle = \sqrt{n+1} |n+1\rangle. \quad (69)$$

By an analogous sequence of steps beginning with  $[a^\dagger a, a] = -a$ , we find

$$a |n\rangle = \sqrt{n} |n-1\rangle, \quad (70)$$

showing that  $a$  acts as the corresponding *annihilation operator* for the bosons.

The  $n = 0$  ground state of the harmonic oscillator corresponds to a state containing no bosons,  $|0\rangle$ , called the *vacuum state*. A state  $|n\rangle$  can be built from the vacuum state by applying  $a^\dagger$   $n$  times:

$$|n\rangle = \frac{1}{\sqrt{n!}} (a^\dagger)^n |0\rangle. \quad (71)$$

By contrast, the annihilation operator applied to the vacuum state gives zero. The vacuum state is said to be *quenched* by the action of the annihilation operator.<sup>4</sup>

$$a|0\rangle = 0. \quad (72)$$

In the event that the state contains several different variety of bosons, with occupation numbers  $n_1, n_2, \dots$ , the corresponding states will be designated

$$|\Psi\rangle = |n_1, n_2 \dots n_N\rangle. \quad (73)$$

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<sup>4</sup>An interesting philosophical conundrum to ponder is the difference between the vacuum state and zero. One way to look at it: the vacuum state is like an empty box; zero means that the box is also gone.

This is called the *occupation-number representation*, the *n-representation*, or *Fock space*. In the language of second quantization, one does not ask “which particle is in which state,” but rather, “how many particles are there in each state.” The *vacuum state*, in which all  $n_i = 0$ , will be abbreviated by

$$|O\rangle = |0_1, 0_2 \dots 0_N\rangle. \quad (74)$$

(Another common notation is  $|\text{vac}\rangle$ .)

There will exist creation and annihilation operators  $a_1^\dagger, a_2^\dagger \dots, a_1, a_2 \dots$ . Assuming that the bosons do not interact,  $a$  and  $a^\dagger$  operators for different varieties will commute. The following generalized commutation relations are satisfied:

$$[a_i, a_j^\dagger] = \delta_{ij}, \quad [a_i, a_j] = [a_i^\dagger, a_j^\dagger] = 0. \quad (75)$$

For bosons, the occupation numbers  $n_i$  are not restricted and the wavefunction of a composite state is symmetric w.r.t. any permutation of indices. Things are, of course, quite different for the case of electrons, or other fermions. The exclusion principle limits the occupation numbers for fermions,  $n_i$  to either 0 or 1. Also, as we have seen, the wavefunction of the system is antisymmetric for any odd permutation of particle indices.

The behavior of fermions can be elegantly accounted for by replacing the boson commutation relations (75) by corresponding *anticommutation relations*. The anticommutator of two operators is defined by

$$\{A, B\} \equiv AB + BA, \quad (76)$$

and the basic anticommutation relations for fermion creation and annihilation operators are given by

$$\{a_i, a_j^\dagger\} = \delta_{ij}, \quad \{a_i, a_j\} = \{a_i^\dagger, a_j^\dagger\} = 0. \quad (77)$$

These relations are intuitively reasonable, since the relation  $a_i^\dagger a_j^\dagger = -a_j^\dagger a_i^\dagger$  is an alternative expression of the antisymmetry principle (34), while  $a_i^\dagger a_i^\dagger = 0$  accords with the exclusion principle.

The state (73) can be constructed by successive operations of creation operators on the  $N$ -particle vacuum state

$$|\Psi\rangle = a_1^\dagger a_2^\dagger \dots a_N^\dagger |0_1, 0_2 \dots 0_N\rangle = \prod_k a_k^\dagger |O\rangle. \quad (78)$$

Let us next consider the representation of matrix elements in second-quantized notation. We wish to replace the expectation value of an operator  $\mathcal{A}$  for the state  $|\Psi\rangle$  with one evaluated for the vacuum state  $|O\rangle$ :

$$\langle\Psi|\mathcal{A}|\Psi\rangle \Rightarrow \langle O|\mathcal{A}_{\text{SQ}}|O\rangle. \quad (79)$$

We introduce the convention that an annihilation operator, say  $a_k$ , acting on the  $N$ -electron vacuum state, which we temporarily designate  $|\text{O}_N\rangle$ , produces the  $(N-1)$ -electron vacuum state  $|\text{O}_{N-1}\rangle$ , in which  $0_k$  is deleted. For a one-electron operator, say  $\mathcal{H}(x)$ , such as the core term (45) in the HF equations, we can write

$$\sum_k \langle \Psi | \mathcal{H}(x_k) | \Psi \rangle = \sum_r H_{rr}, \quad H_{rr} = \langle \phi_r(x) | \mathcal{H}(x) | \phi_r(x) \rangle, \quad (80)$$

noting that the  $k$  summation is over particles, while the  $r$  summation is over spin-orbital labels. We can now show that the rule for transcribing a single-particle operator into second-quantized form is given by

$$\sum_k \mathcal{H}(x_k) \Rightarrow \sum_r H_{rr} a_r^\dagger a_r, \quad (81)$$

noting that

$$\left\langle \text{O} \left| \sum_r H_{rr} a_r^\dagger a_r \right| \text{O} \right\rangle = \sum_r H_{rr} \langle \text{O}_N | a_r^\dagger a_r | \text{O}_N \rangle = \sum_r H_{rr} \langle \text{O}_{N-1} | \text{O}_{N-1} \rangle = \sum_r H_{rr}, \quad (82)$$

since the  $|\text{O}_{N-1}\rangle$  are normalized. This agrees with Eq. (80) and verifies the rule (81). For a two-particle operator, such as the electron repulsion  $r_{ij}^{-1}$ , we have

$$\sum_{i>j} r_{ij}^{-1} = \frac{1}{2} \sum_{i \neq j} r_{ij}^{-1} \Rightarrow \frac{1}{2} \sum_{r,s,r',s'} \langle \phi_r(i) \phi_s(j) | r_{ij}^{-1} | \phi_{r'}(i) \phi_{s'}(j) \rangle a_r^\dagger a_s^\dagger a_{r'} a_{s'}, \quad (83)$$

where  $a_{r'} a_{s'} = a_r a_s$  or  $-a_s a_r$ . With use of the truncated vacuum state  $|\text{O}_{N-2}\rangle$ , in analogy with the above, we find

$$\begin{aligned} \sum_{i>j} \langle \Psi | r_{ij}^{-1} | \Psi \rangle &= \frac{1}{2} \sum_{r,s,r',s'} \langle \text{O} | \langle \phi_r(i) \phi_s(j) | r_{ij}^{-1} | \phi_{r'}(i) \phi_{s'}(j) \rangle a_r^\dagger a_s^\dagger a_{r'} a_{s'} | \text{O} \rangle \\ &= \sum_{r>s} \langle \phi_r(i) \phi_s(j) | r_{ij}^{-1} (|\phi_r(i) \phi_s(j)\rangle - |\phi_s(i) \phi_r(j)\rangle) \rangle \langle \text{O}_{N-2} | \text{O}_{N-2} \rangle \\ &= \sum_{r>s} (J_{rs} - K_{rs}), \end{aligned} \quad (84)$$

where we have introduced the notation for Coulomb and exchange integrals (47), (48).

## 5 ROOTHAAN EQUATIONS

A significant improvement in the practical solution of the HF equations was introduced by Roothaan [14]. Almost all current work on atomic or molecular electronic structure is based on this and related procedures. Essentially, the integro-differential equations for the  $\phi_i(x)$  are transformed into linear algebraic equations for a set of



coefficients  $c_{i\alpha}$ . The resulting matrix equations are particularly suitable computers based on von Neumann architecture. Accordingly, the spin-orbitals are represented as linear combinations of a set of  $n$  basis functions  $\{\chi_1(x), \chi_2(x), \dots, \chi_n(x)\}$ :

$$\phi_i(x) = \sum_{\alpha=1}^n c_{i\alpha} \chi_{\alpha}(x), \quad i = 1 \dots N. \quad (85)$$

For  $n = N$ , we have what is called a *minimal basis set*. For more accurate computations, larger basis sets are used, with  $n > N$ , even  $n \gg N$ . Most often, the  $\chi_{\alpha}(x)$  are atomic-like functions, centered about single nuclei in a molecule. Conceptually, this is a generalization of the simple LCAO MO method, in which molecular orbitals of small molecules are approximated by a linear combination of atomic orbitals.

We begin with the HF equations (54)

$$\mathcal{F} \phi_i(x) - \epsilon_i \phi_i(x) = 0, \quad i = 1 \dots N, \quad (86)$$

and substitute the expansion (85), to give

$$\sum_{\alpha} \left\{ \mathcal{F} \chi_{\alpha}(x) - \epsilon_i \chi_{\alpha}(x) \right\} c_{i\alpha} = 0. \quad (87)$$

Next we multiply both sides by  $\chi_{\beta}^*(x)$  and do the four-dimensional integration over  $x$ . The result can be written

$$\sum_{\alpha} \left\{ \langle \chi_{\beta}(x) | \mathcal{F} | \chi_{\alpha}(x) \rangle - \epsilon_i \langle \chi_{\beta}(x) | \chi_{\alpha}(x) \rangle \right\} c_{i\alpha} = 0. \quad (88)$$

Introducing the abbreviations

$$F_{\beta\alpha} = \langle \chi_{\beta}(x) | \mathcal{F} | \chi_{\alpha}(x) \rangle, \quad S_{\beta\alpha} = \langle \chi_{\beta}(x) | \chi_{\alpha}(x) \rangle, \quad (89)$$

we can write

$$\sum_{\alpha} \left\{ F_{\beta\alpha} - \epsilon_i S_{\beta\alpha} \right\} c_{i\alpha} = 0, \quad (90)$$

which can be further abbreviated as the matrix equation

$$\{\mathbf{F} - \epsilon \mathbf{S}\} \mathbf{c} = 0. \quad (91)$$

We need to show, in more detail, the structure of the Fock operator  $\mathcal{F}$  and the corresponding matrix  $F_{\beta\alpha}$ . First, we derive the core, Coulomb, and exchange integrals in terms of the basis functions  $\chi_{\alpha}$ . For the core contribution, substitute Eq. (85) into Eq. (45) to give

$$H_i = \sum_{\alpha, \beta} c_{i\beta}^* c_{i\alpha} [\beta | \alpha], \quad (92)$$

having defined the *one-electron integrals* over the basis functions

$$[\beta|\alpha] = \langle \chi_\beta(x) | \mathcal{H} | \chi_\alpha(x) \rangle. \quad (93)$$

The *core operator* is defined by

$$\mathcal{H} = -\frac{1}{2}\nabla^2 - \sum_A \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|}. \quad (94)$$

The Coulomb and exchange integrals are given by

$$J_{ij} = \sum_{\alpha,\beta} \sum_{\alpha',\beta'} c_{i\beta}^* c_{j\alpha}^* c_{i\beta'} c_{j\alpha'} [\beta\beta'|\alpha,\alpha'], \quad (95)$$

and

$$K_{ij} = \sum_{\alpha,\beta} \sum_{\alpha',\beta'} c_{i\beta}^* c_{j\alpha}^* c_{i\alpha'} c_{j\beta'} [\beta\alpha'|\alpha,\beta'], \quad (96)$$

in terms of the *two-electron integrals*

$$[\alpha\beta|\gamma\delta] = \iint dx dx' \chi_\alpha^*(x) \chi_\beta(x) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \chi_\gamma^*(x') \chi_\delta(x'). \quad (97)$$

In an alternative notation, more consistent with Dirac notation and favored by physicists,

$$\langle \alpha\beta | \gamma\delta \rangle = \left\langle \chi_\alpha(x) \chi_\beta(x') \left| \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right| \chi_\gamma(x) \chi_\delta(x') \right\rangle = [\alpha\gamma|\beta\delta]. \quad (98)$$

We can define the *Coulomb operator*, a term in the Fock operator, by

$$\mathcal{J} = \sum_\beta \int dx' \frac{|\chi_\beta(x')|^2}{|\mathbf{r} - \mathbf{r}'|}, \quad (99)$$

and the *exchange operator*  $\mathcal{K}$ , such that

$$\mathcal{K} \chi_\alpha(x) = \sum_\beta \int dx' \frac{\chi_\beta^*(x') \chi_\alpha(x')}{|\mathbf{r} - \mathbf{r}'|} \chi_\beta(x). \quad (100)$$

Formally,  $\mathcal{K}$  acting on  $\chi_\alpha(x)$  gives a term linear in  $\chi_\beta(x)$ .

The Fock operator, acting on a function  $\chi_\alpha(x)$ , can now be written explicitly as

$$\mathcal{F} = \mathcal{H} + \mathcal{J} - \mathcal{K}, \quad (101)$$

and the matrix elements as

$$F_{\beta\alpha} = H_{\beta\alpha} + J_{\beta\alpha} - K_{\beta\alpha} = [\beta|\alpha] + [\beta\beta|\alpha\alpha] - [\beta\alpha|\alpha\beta]. \quad (102)$$

We also need an expression for the orthonormalization bra-kets:

$$\langle \phi_i(x) | \phi_j(x) \rangle = \sum_{\alpha, \beta} c_{i\beta}^* c_{j\alpha} S_{\beta\alpha}, \quad (103)$$

where

$$S_{\beta\alpha} = \langle \chi_\beta(x) | \chi_\alpha(x) \rangle, \quad (104)$$

known as *overlap integrals*. The basis functions need not belong to an orthonormal set. Once all the needed one- and two-electron and overlap integrals for a given basis set are calculated, no further integrations are necessary. Thus the problem reduces to linear algebra involving the coefficients  $c_{i\alpha}$ .

Writing the matrix equation (91) in explicit form, we have

$$\{\mathbf{F} - \epsilon \mathbf{S}\} \mathbf{c} = 0 \quad \Rightarrow \quad \begin{bmatrix} F_{11} - \epsilon S_{11} & F_{12} - \epsilon S_{12} & \dots & F_{1n} - \epsilon S_{1n} \\ F_{21} - \epsilon S_{21} & F_{22} - \epsilon S_{22} & \dots & F_{2n} - \epsilon S_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ F_{n1} - \epsilon S_{n1} & F_{n2} - \epsilon S_{n2} & \dots & F_{nn} - \epsilon S_{nn} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{bmatrix} = 0. \quad (105)$$

This system of  $n$  simultaneous linear equations, usually called the *Roothaan equations*, has  $n$  nontrivial solutions for  $\epsilon_i, c_{i1}, c_{i2} \dots c_{in}$  ( $i = 1 \dots n$ ). The condition for a nontrivial solution is the vanishing of the determinant of the coefficients, that is,

$$\begin{vmatrix} F_{11} - \epsilon S_{11} & F_{12} - \epsilon S_{12} & \dots & F_{1n} - \epsilon S_{1n} \\ F_{21} - \epsilon S_{21} & F_{22} - \epsilon S_{22} & \dots & F_{2n} - \epsilon S_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ F_{n1} - \epsilon S_{n1} & F_{n2} - \epsilon S_{n2} & \dots & F_{nn} - \epsilon S_{nn} \end{vmatrix} = 0. \quad (106)$$

This is an  $n$ th degree polynomial equation in  $\epsilon$ . The  $n$  roots correspond to the eigenvalues  $\epsilon_i$  of the HF equations. The corresponding eigenvectors  $\mathbf{c}_i$ , whose elements are the coefficients  $c_{i1} \dots c_{in}$ , are then found by solution of the set of homogeneous linear equations:

$$\begin{aligned} (F_{11} - \epsilon_i S_{11})c_{i1} + (F_{12} - \epsilon_i S_{12})c_{i2} + \dots + (F_{1n} - \epsilon_i S_{1n})c_{in} &= 0 \\ (F_{21} - \epsilon_i S_{21})c_{i1} + (F_{22} - \epsilon_i S_{22})c_{i2} + \dots + (F_{2n} - \epsilon_i S_{2n})c_{in} &= 0 \\ \vdots & \\ (F_{n1} - \epsilon_i S_{n1})c_{i1} + (F_{n2} - \epsilon_i S_{n2})c_{i2} + \dots + (F_{nn} - \epsilon_i S_{nn})c_{in} &= 0. \end{aligned} \quad (107)$$

This is type of generalized matrix eigenvalue problem, which is readily solved by efficient computer programs particularly suited for von Neumann-type computer architecture.

Note that the elements of the Fock matrix  $F_{\alpha\beta}$  themselves depend on the coefficients  $c_{i\alpha}$ , in the Coulomb and exchange terms. But these coefficients are not obtained until the Roothaan equations are solved. So, paradoxically, it seems like we need to solve the equations before we can even write them down! Clearly, however, a recursive approach can be applied. A first “guess” of the coefficients, say  $c_{i\alpha}^{(0)}$ ,

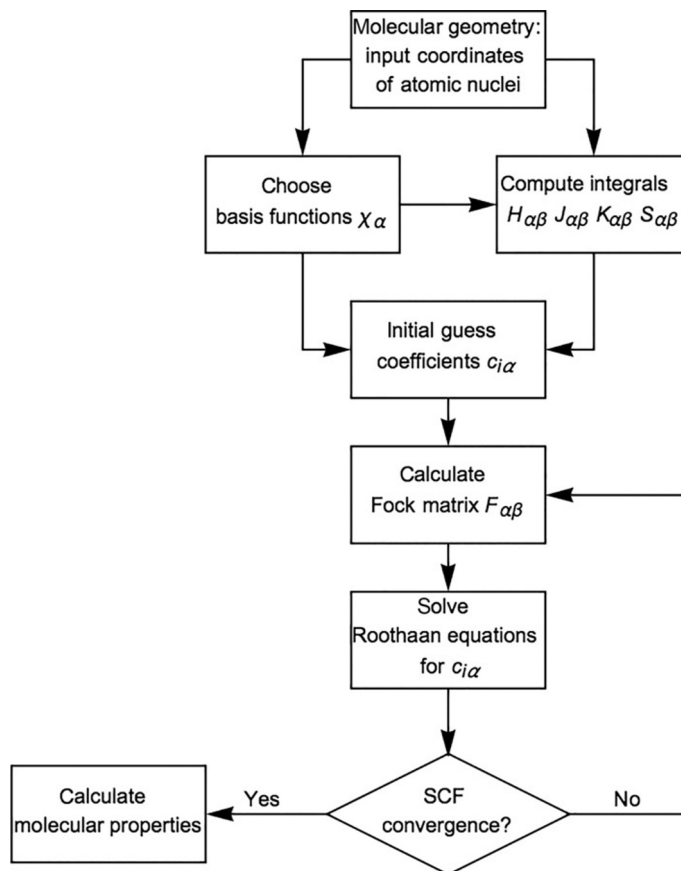


FIG. 1

Flowchart for molecular SCF computation.

is used to construct a Fock matrix. The solution then gives an “improved” set of coefficients, say  $c_{i\alpha}^{(1)}$ . These are then used, in turn, to construct an improved Fock matrix, which can be applied to obtain a second improved set of coefficients  $c_{i\alpha}^{(2)}$ . And this procedure is repeated until *self-consistency* is attained, to some desired level of accuracy. A algorithmic flowchart for a Hartree-Fock-Roothaan SCF computation is shown in Fig. 1.

The integrals involving the basis functions  $\chi_\alpha$ , namely  $[\alpha|\beta]$ ,  $[\alpha\beta|\gamma\delta]$  and  $S_{\alpha\beta}$  remain constant during the computations involving the Roothaan equations. But more accurate computations require ever-larger basis sets and increasingly difficult computations of the Coulomb and exchange integrals. In computations on molecules, the integrals  $[\alpha\beta|\gamma\delta]$  can involve basis functions centered on as many as four different atoms. For many years, the computation of three- and four-center

integrals was the most significant impediment to progress in molecular-structure computations. This barrier has since been largely surmounted by the introduction of Gaussian basis functions (to be discussed in [Chapter 2](#)), as well as the continuing improvement in computational speed and capacity.

The HF method, as described in this chapter, has been applied mainly using single Slater-determinant wavefunctions. This is an instance of a *mean-field approximation*, in which each electron is described as interacting with the averaged nonlocal potential produced by the other electrons. The neglected effects of instantaneous particle-like interactions are known as *electron correlation*. For example, London dispersion forces are due mainly to electron correlation and are thus not correctly accounted for by HF methods. The *total energy* computed by the HF method generally gives over 99% of the experimental value. This might appear impressive, but lots of important chemistry happens in the remaining 1%. The error due to correlation is generally of the order of 0.04 Hartree per electron pair. This is equivalent to about 1 eV or 100 kJ/mol, the same order of magnitude as electron excitations and molecular binding energies. These represent the *differences* between energies with comparable errors, thus HF computations are of only limited value in accounting for spectroscopic or chemical parameters.<sup>5</sup> For example, in the N<sub>2</sub> molecule, the correlation energy represents 0.5% of the total energy but about 50% of the binding energy. To be useful for chemistry, molecular energies must be computed to a precision of at least six decimal places, equivalent to approximately 0.1 kJ/mol.

In addition, HF computations generally neglect magnetic interactions (e.g., spin-orbit coupling) and relativistic effects. These become increasingly important for systems containing heavy atoms, beginning around  $Z > 20$ . Also, usually neglected are the effects of finite nuclear masses, leading to what is known as *mass polarization*.

HF computations are, on the other hand, quite good for representing the shapes of atomic and molecular orbitals and for describing electronic charge distributions, as, for example, radial distribution functions for atoms. Also, in biomolecules, reaction sites and docking geometries can often be successfully predicted.

## 6 ATOMIC HF RESULTS

The most frequently used basis functions in atomic HF computations are *Slater-type orbitals* (STOs), first introduced in 1930 [15]. These are exponential functions suggested by hydrogenic solutions of the Schrödinger equation, but lacking radial nodes, and thus are not mutually orthogonal. STOs have the general form (not normalized):

$$\chi_{n,l,m}(r, \theta, \phi) = r^{n-1} e^{-\zeta r} Y_{l,m}(\theta, \phi), \quad (108)$$

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<sup>5</sup>An analogy due to C.A. Coulson: First, we weigh the ship with the captain aboard and then we weigh the ship with the captain ashore; the difference gives the captain's weight.

where  $Y_{l,m}(\theta, \phi)$  is a spherical harmonic,  $n$  is an integer (usually) that plays the role of the principal quantum number, and  $\zeta$  is an *effective nuclear charge*, chosen to account for the partial shielding by other electrons. STOs exhibit exponential decay at long range and appropriate behavior as  $r \rightarrow 0$  (Kato's cusp condition<sup>6</sup>). Slater originally suggested a set of rules for the effective nuclear charge

$$\zeta = \frac{Z - \sigma}{n}, \quad (109)$$

where  $\sigma$  is a *screening constant*. Clementi and Raimondi [16] gave improved orbital exponents based on optimized SCF computations. For example, for argon,  $Z = 18$ :

$$\zeta_{1s} = 17.5075, \quad \zeta_{2s} = 6.1152, \quad \zeta_{2p} = 7.0041, \quad \zeta_{3s} = 2.5856, \quad \zeta_{3p} = 2.2547.$$

A *minimal basis set* is one in which the number of basis functions  $n$  is the same as the number of occupied orbitals  $N$ . The small number of variable exponential parameters  $\zeta$  limits the flexibility of the wavefunction. A first step in improving upon a minimal basis set is a sum of two terms in each basis function, so that the radial part of the STO is generalized to

$$c_1 r^{n-1} e^{-\zeta_1 r} + c_2 r^{n-1} e^{-\zeta_2 r}. \quad (110)$$

This is known as a *double-zeta basis set*. The optimal orbital exponents  $\zeta_1$  and  $\zeta_2$  are generally larger and smaller than the original  $\zeta$ , which allows for better representation of the “expanded” and “contracted” regions of the atomic orbital. There are obvious generalizations to multiple-zeta basis sets, with three or more terms.

STOs are most appropriate for computations on atomic systems. For molecular quantum-chemical computations, however, efficient evaluation of multicenter Coulomb and exchange integrals, involving basis functions centered on more than one atom, are extremely difficult using STOs (although recent theoretical developments and increasing computer power are improving the situation). For this reason, alternative *Gaussian-type orbitals* (GTOs) were first proposed by Boys [17]. These have the general form

$$\chi(x, y, z) = x^m y^n z^p e^{-\alpha r^2}, \quad (111)$$

with angular dependence usually represented by the Cartesian factors. The main advantage of Gaussian basis functions is the *Gaussian product theorem*, according to which product of two GTOs centered on two different atoms can be transformed into a finite sum of Gaussians centered on a point along the axis connecting them. For example, a two-center integral involving  $1s$  functions centered about nuclei  $A$  and  $B$  can be reduced using

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<sup>6</sup>In a many-electron system,  $\frac{1}{\psi} \frac{\partial \psi}{\partial r_{iA}} \Big|_{r_{iA} \rightarrow 0} = -Z_A$  and  $\frac{1}{\psi} \frac{\partial \psi}{\partial r_{ij}} \Big|_{r_{ij} \rightarrow 0} = \pm \frac{1}{2}$ .

$$e^{-\alpha(\mathbf{r}-\mathbf{R}_A)^2} \times e^{-\beta(\mathbf{r}-\mathbf{R}_B)^2} = Ke^{-(\alpha+\beta)(\mathbf{r}-\mathbf{R}_0)^2}, \quad \mathbf{R}_0 = \frac{\alpha\mathbf{R}_A + \beta\mathbf{R}_B}{\alpha + \beta}. \quad (112)$$

As a consequence, four-center integrals can be reduced to finite sums of two-center integrals, with a speedup of several orders of magnitude compared with STOs.

Gaussian functions, with their  $e^{-\alpha r^2}$  exponential dependence, compared to the more realistic  $e^{-\zeta r}$  dependence, are obviously not very good physical representations of atomic orbitals. They are inaccurate in describing the cusp behavior, as  $r \rightarrow 0$ , and the exponential decay, as  $r \rightarrow \infty$ . In order to minimize these deficiencies but still take advantage of the computational properties of Gaussian functions, Pople [18] suggested the use of *contracted Gaussian type orbitals* (CGTOs). These are linear combination of Gaussian “primitives,” with coefficients and exponents fixed, to simulate the behavior of STOs. Fig. 2 shows the optimal approximations of a 1s STO by up to three Gaussian primitives. The approximations of STOs by a sum of three Gaussians are called the STO-3G basis set, and are the simplest CGTO set, which can produce HF results of useful accuracy. Basis sets will be discussed in much greater detail in the following chapters.

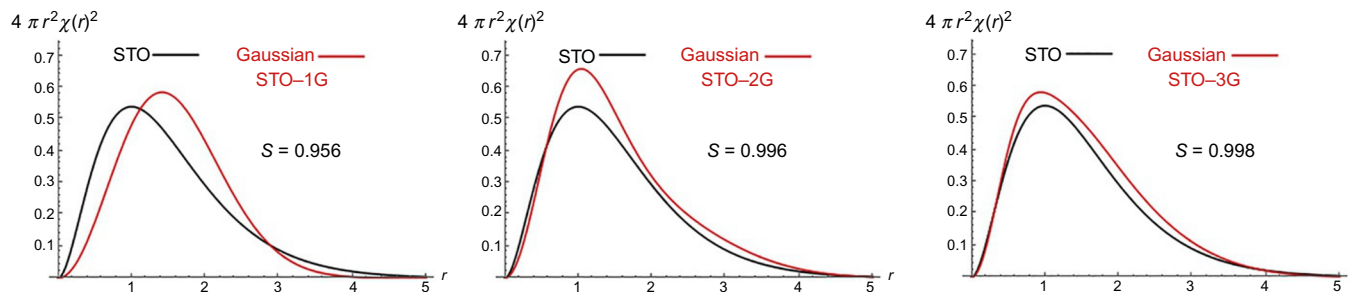
HF computations have by now been carried out on all the atoms of the periodic table and most atomic ions. Table 1 shows the results for atomic numbers  $Z = 2-20$ , including the experimental values obtained from a sum of the  $Z$  ionization energies of each atom [19]. The energy values are expressed in Hartrees. As discussed earlier, even the best HF computations cannot reproduce the experimental energies, largely due to the exclusion of correlation energy.

The eigenvalues of the Roothaan matrix represent the energies of the individual spin-orbitals, which, by Koopmans’ theorem, are approximations to ionization energies of the atom. The first ionization energy, which is the difference in ground-state energies of the atom and its positive ion, is of particular significance. The periodic properties of these ionization energies are well known and these trends are very well accounted for by high-quality HF computations. Fig. 3 shows a recent compendium [20] of the experimental and calculated ionization energies for elements H through Xe ( $Z = 1-54$ ).

As mentioned earlier, HF computations are fairly reliable in determining the shapes of electronic distributions in atoms and molecules. In particular, the shell structure of many-electron atoms can be exhibited in HF results. An early success was the detection of the radial distribution function for the argon atom, as shown in Fig. 4. The SCF computation of Hartree [21] is compared with the electron-diffraction experimental result of Bartell and Brockway [22]. This is a very impressive result, both for theory and for experiment.

## 7 POST-HF METHODS

Several extensions of the HF method have been developed to enable more accurate computations on atoms and molecules, in particular, to account for the effects of

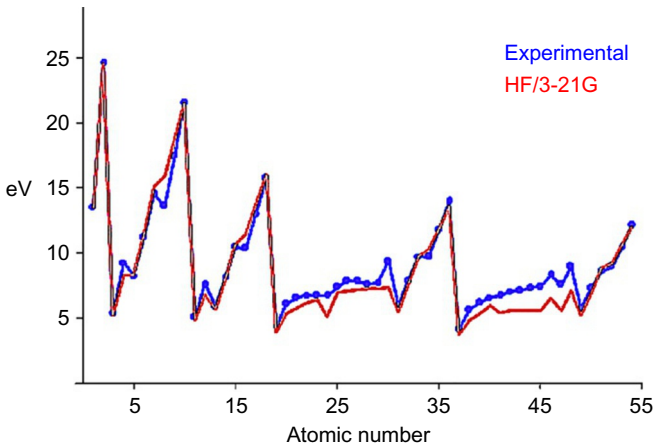
**FIG. 2**

Radial distribution functions for contracted Gaussians representing the 1s STO. The overlap integral  $S$  is shown for each of the STO-nG functions.



Table 1 HF Computations for Atoms

Z	Atom	Configuration	Exact	H-F
2	He	1s <sup>2</sup> 1S	−2.903385	−2.8616799
3	Li	1s <sup>2</sup> 2s 2S	−7.477976	−7.432726
4	Be	1s <sup>2</sup> 2s <sup>2</sup> 1S	−14.668449	−14.573023
5	B	1s <sup>2</sup> 2s <sup>2</sup> 2p 2P	−24.658211	−24.529060
6	C	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>2</sup> 3P	−37.855668	−37.688618
7	N	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>3</sup> 4S	−54.611893	−54.400934
8	O	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>4</sup> 3P	−75.109991	−74.809398
9	F	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>5</sup> 2P	−99.803888	−99.409349
10	Ne	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 1S	−128.830462	−128.547098
11	Na	[Ne]3s 2S	−162.428221	−161.858911
12	Mg	[Ne]3s <sup>2</sup> 1S	−200.309935	−199.614636
13	Al	[Ne]3s <sup>2</sup> 3p 2P	−242.712031	−241.876707
14	Si	[Ne]3s <sup>2</sup> 3p <sup>2</sup> 3P	−289.868255	−288.854362
15	P	[Ne]3s <sup>2</sup> 3p <sup>3</sup> 4S	−341.946219	−340.718780
16	S	[Ne]3s <sup>2</sup> 3p <sup>4</sup> 3P	−399.034923	−397.504895
17	Cl	[Ne]3s <sup>2</sup> 3p <sup>5</sup> 2P	−461.381223	−459.482072
18	Ar	[Ne]3s <sup>2</sup> 3p <sup>6</sup> 1S	−529.112009	−526.817512
19	K	[Ar]4s 2S	−601.967492	−599.164786
20	Ca	[Ar]4s <sup>2</sup> 1S	−680.101971	−676.758185



**FIG. 3**  
Experimental and calculated IE value of atoms H-Xe.  
(Krishnamohan GP, Mathew T, Saju S, Joseph JT. World J Chem Educ 2017;5:112–9; licensed under a Creative Commons Attribution 4.0 International License.)

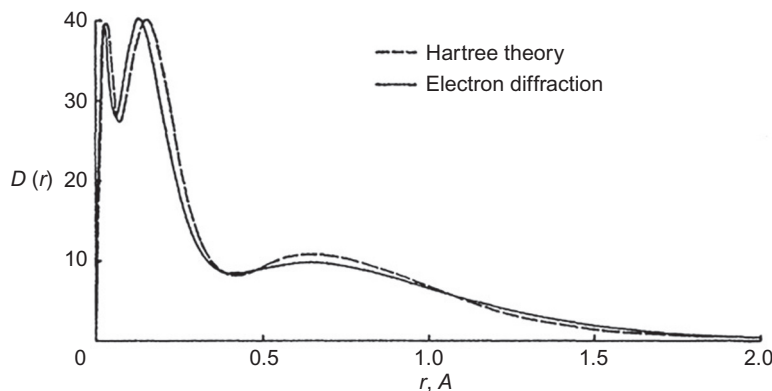


FIG. 4

Radial distribution function for argon atom [22].

electron correlation. Such improved accuracy is necessary to treat chemically significant properties of molecules, including bond energies and geometric parameters—bond lengths and angles. In addition, there are spectroscopic frequencies, dipole moments, magnetic properties, and NMR coupling constants. Post-HF methods will be discussed in detail in the following chapters, but we will give a short introduction here to the main ideas of configuration interaction (CI), Møller-Plesset perturbation theory and the coupled-cluster method.

A single Slater-determinant  $|\Phi_0\rangle$ , with occupied spin-orbitals  $\phi_1, \phi_2 \dots \phi_N$  can serve as a *reference configuration* for an  $N$ -electron system. Basis sets of dimension  $n > N$  will also produce higher-energy spin-orbitals  $\phi_r, \phi_s \dots$ , with  $\epsilon_r, \epsilon_s > \epsilon_N$ , known as *virtual spin-orbitals*, which are unoccupied in the ground state. These might have energies  $\epsilon_r, \epsilon_s > 0$ . Now an excited configuration can be constructed by promoting one of the electrons from an occupied spin-orbital, say  $\phi_i$ , to one of the virtual orbitals, say  $\phi_r$ . We write the corresponding Slater determinant as  $|\Phi_i^r\rangle$ . We can also construct *doubly excited* configurations by promoting *two* electrons from occupied spin-orbitals  $\phi_i, \phi_j$  to virtual spin-orbitals  $\phi_r, \phi_s$ . Such determinants are denoted  $|\Phi_{ij}^{rs}\rangle$ . In the jargon of quantum chemistry, the singly and doubly excited configurations are called *singles* and *doubles*, respectively. This can be extended to give *triples*, *quadruples*, etc. The improved ground state, enhanced by CI, can now be represented by a linear combinations of Slater determinants:

$$|\Psi\rangle = c_0|\Phi_0\rangle + \sum_{i,r} c_i^r |\Phi_i^r\rangle + \sum_{i,j,r,s} c_{ij}^{rs} |\Phi_{ij}^{rs}\rangle + \dots \quad (i, j \dots \leq N; r, s \dots > N). \quad (113)$$

The coefficients  $c_0, c_i^r \dots$  are optimized using a linear variational method. This CI function can *in principle* approach the exact solution of the  $N$ -electron Schrödinger equation, as completeness of the one-electron basis set  $\{\phi_i(x)\}$  is enhanced and the

number of CI contributions  $|\Phi\rangle$  is increased. But practical consideration and computational limitations require significant truncation of the CI space. A widely used approximation, called “CISD,” truncates the CI expansion to just single and double excitations relative to the reference configuration. Since the Hamiltonian contains only one- and two-electron terms, only singly and doubly excited configurations can interact directly with  $|\Phi_0\rangle$ .<sup>7</sup> CISD computations can typically account for over 90% of the correlation energy in small molecules. Appropriate strategies for a variety of CI computations will be discussed in detail in succeeding chapters.

A second post-HF method we will describe is *Møller-Plesset perturbation theory* [23]. Recalling the molecular Hamiltonian (Eq. 39), we treat the core terms as an unperturbed Hamiltonian

$$\mathcal{H}_0 = \sum_i \left\{ -\frac{1}{2} \nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}} \right\}, \quad (114)$$

and the electron repulsion terms as a perturbation

$$\mathcal{V} = \sum_{i>j} \frac{1}{r_{ij}} = \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}}. \quad (115)$$

The solution of the HF equations for the ground-state configuration wavefunction  $|\Phi_0\rangle$  implies the relation

$$\langle \Phi_0 | \mathcal{H}_0 | \Phi_0 \rangle + \langle \Phi_0 | \mathcal{V} | \Phi_0 \rangle = E_0^{\text{HF}}. \quad (116)$$

Thus the HF energy formally represents the sum of the unperturbed and first-order perturbation energies

$$E_0^{\text{HF}} = E_0^{(0)} + E_0^{(1)}. \quad (117)$$

In Rayleigh-Schrödinger perturbation theory, the second-order energy is given by

$$E_0^{(2)} = - \sum_{n \neq 0} \frac{\langle \Phi_0 | \mathcal{V} | \Phi_n \rangle \langle \Phi_n | \mathcal{V} | \Phi_0 \rangle}{E_n^{(0)} - E_0^{(0)}}, \quad (118)$$

where the  $|\Phi_n\rangle$  are excited configurations, such as those encountered in CI. We limit the  $|\Phi_n\rangle$  to double excitations, noting that, by Brillouin’s theorem, single excitations do not contribute.

To evaluate the matrix elements of  $\mathcal{V}$ , we recall the result for a single Slater determinant

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<sup>7</sup>If the same basis functions (not individually optimized) are used in building all configurations, then Brillouin’s theorem states that all  $\langle \Phi_0 | \Phi_i^r \rangle = 0$ , so that single excitations do not contribute to the ground state.

$$\langle \Phi_0 | \mathcal{V} | \Phi_0 \rangle = \frac{1}{2} \sum_{i,j} \left( \langle ij | ij \rangle - \langle ij | ji \rangle \right), \quad (119)$$

using the notation of Eq. (98). It can be shown analogously that

$$\langle \Phi_0 | \mathcal{V} | \Phi_{ij}^{rs} \rangle = \frac{1}{2} \sum_{i,j,r,s} \left( \langle ij | rs \rangle - \langle ij | sr \rangle \right). \quad (120)$$

Therefore, the second-order Møller-Plesset energy, often denoted  $E_{\text{MP2}}$ , is given by

$$E_0^{(2)} = -\frac{1}{4} \sum_{i,j}^{\text{occ}} \sum_{r,s}^{\text{virt}} \frac{|\langle ij | rs \rangle - \langle ij | sr \rangle|^2}{\epsilon_r + \epsilon_s - \epsilon_i - \epsilon_j}, \quad (121)$$

representing an approximate correlation energy correction to the HF energy  $E_0^{\text{HF}}$ .

Finally, we mention *coupled cluster* (CC) techniques. These were adapted from nuclear physics and applied to atoms and molecules, largely the work of Čížek [24] and Paldus. Formally, CC applies an exponential cluster operator to the HF wavefunction to obtain the exact solution:

$$|\Psi\rangle = e^T |\Phi_0\rangle. \quad (122)$$

The cluster operator is written in the form

$$T = T_1 + T_2 + T_3 + \dots, \quad (123)$$

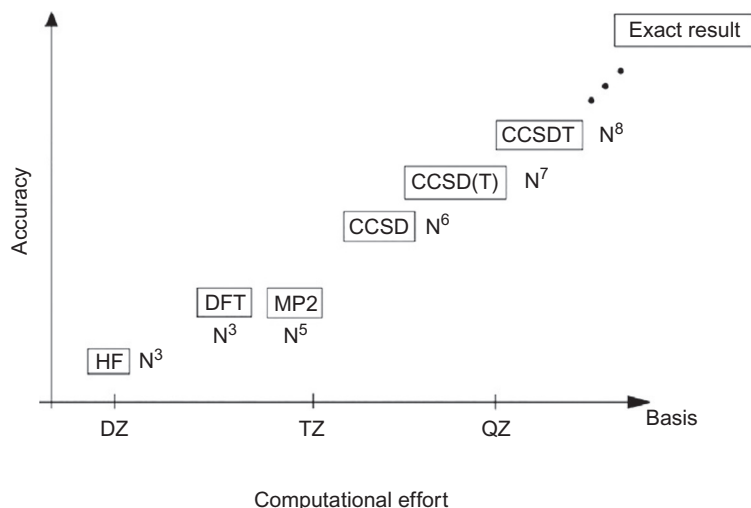
where  $T_1$  is the operator for single excitations,  $T_2$  for double excitations, and so forth. The excitation operators act as follows:

$$T_1 |\Phi_0\rangle = \sum_{i,r} t_i^r |\Phi_i^r\rangle, \quad T_2 |\Phi_0\rangle = \frac{1}{4} \sum_{i,j,r,s} t_{ij}^{rs} |\Phi_{ij}^{rs}\rangle, \dots \quad (124)$$

The exponential operator  $e^T$  is actually defined by its Taylor series expansion. Considering only the cluster operators  $T_1$  and  $T_2$ , we can write:

$$e^T = 1 + T + \frac{1}{2!} T^2 + \dots = 1 + T_1 + T_2 + \frac{1}{2} T_1^2 + T_1 T_2 + \frac{1}{2} T_2^2 + \dots \quad (125)$$

These formal relations must, of course, be converted to explicit formulas for actual computations on atoms and molecules. For example, the number of excitations must necessarily be truncated. Coupled-cluster theory, in its several variations, is the de facto standard of modern ab initio computational chemistry, able to accurately account for the chemical properties of a large variety of moderate-sized molecules.

**FIG. 5**

Pople diagram for ab initio computations.

(Adapted, with permission, from lecture by Alexander A. Auer at MMER Summerschool; 2014, Available from: [https://cec.mpg.de/fileadmin/media/Presse/Medien/Auer\\_Electron\\_Correlation.pdf](https://cec.mpg.de/fileadmin/media/Presse/Medien/Auer_Electron_Correlation.pdf).)

A *Pople diagram*<sup>8</sup> provides a general description of the computational effort needed to achieve a given level of accuracy in ab initio molecular computations, as shown in Fig. 5. Key to the diagram: Power of N shows the scaling of the number of computer operations for each method; double-, triple-, quadruple-zeta (DZ, TZ, QZ), Hartree-Fock (HF), density-functional theory (DFT), second-order Møller-Plesset (MP2), coupled-cluster singles and doubles, single, doubles and triples (CCSD, CCSDT), usually experimental result (exact result).

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