

Improved Quantum Theory of Many-Electron Systems. II. The Basic Method*

WILLIAM A. GODDARD, III†

Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California

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A general method of obtaining accurate and useful many-electron wave functions for atoms and molecules is developed. The method involves the proper optimization of a many-electron function which is an eigenfunction of total spin and which satisfies Pauli's principle. The procedure is somewhat similar to that in which one obtains the Hartree-Fock wave function by properly optimizing a Slater determinant. There are three key features of the new method: (1) The wave function remains accurate as the nuclei configuration is changed from the equilibrium configuration to that of the dissociated molecule; (2) the many-electron wave function can be interpreted in an independent-particle scheme; (3) the independent-particle states are no longer always required to be symmetry functions for the spatial symmetry group as in the Hartree-Fock method. In addition, the energy calculated using the new method is always lower than the Hartree-Fock energy, and the method is applicable to states of any total spin and number of particles. Calculations using this method are reported for the H₂ and LiH molecules.

INTRODUCTION

IN Paper I of this series¹ we considered various expansions of the exact many-electron eigenfunctions of the Hamiltonian^{2,3}

$$H = \sum_{i=1}^N -\frac{1}{2}\nabla_i^2 + \sum_{i=1}^N V(i) + \sum_{i>j=1}^N \frac{1}{r_{ij}}, \quad (1)$$

where $V(i)$ is the electrostatic potential at i due to all of the nuclei. Because the eigenfunctions of this Hamiltonian are eigenfunctions of total spin and total spin projection (\hat{S}^2 and \hat{S}_z) and satisfy Pauli's principle, expansions were considered which explicitly exhibit this type of behavior. The simplest such function for some systems is a (Slater) determinant of one-electron functions (spin orbitals⁴). Such a function could be an exact wave function in the absence of the electron-electron interactions. In fact, if the spin orbitals in the determinant are each factored into a spatial part and a spin part and if the orbitals are all properly optimized with respect to each other, one obtains a rather good approximation to the exact many-electron wave function—this procedure is called the Hartree-Fock method.

The Hartree-Fock Method

Since the Hartree-Fock (HF) method *does* yield a good approximation to the exact wave function and

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¹ W. A. Goddard, III, preceding paper, Phys. Rev. **157**, 73 (1967); hereafter referred to as I.

² Atomic units are used, $e = \hbar = m_e = 1$; thus, the unit of energy is 1 Hartree = 27.211 eV and the unit of length is 1 Bohr = 0.52917 Å (see Ref. 3).

³ E. R. Cohen and J. W. M. DuMond, Rev. Mod. Phys. **37**, 537 (1965).

⁴ We use the expression spin orbital to indicate a function of the spatial and spin coordinates of one electron and orbital to indicate a function of only the spatial coordinates of one electron.

since the development of the new method follows a similar pattern, it is appropriate here to sketch some of the advantages and disadvantages of the Hartree-Fock method for the ground states of molecules (this analysis also applies to nonconducting nonmagnetic solids). We will take $S=0$ since most molecular ground states are singlets and since in this case some ambiguities and inconsistencies which can occur for higher spin do not arise. We let

$$\Psi_{\text{HF}}(1, \dots, N) = N! \Omega_{11}^{[N]} \Phi \chi,$$

where

$$\Phi(1, 2, \dots, N) = \phi_{i_1}(1) \phi_{i_2}(2) \cdots \phi_{i_n}(n) \phi_{i_1}(n+1) \cdots \phi_{i_n}(N),$$

each ϕ_i is an orbital,⁴

$$\chi(1, 2, \dots, N) = \alpha(1) \alpha(2) \cdots \alpha(n) \beta(n+1) \cdots \beta(N),$$

α and β satisfy $\hat{S}_z \alpha = \frac{1}{2} \alpha$ and $\hat{S}_z \beta = -\frac{1}{2} \beta$, $\Omega_{11}^{[N]}$ is the antisymmetrizer (see I), $N=2n$, and the orbitals form an orthonormal set. The criterion for selecting the orbitals to be used in Φ is that $E = \langle \Psi_{\text{HF}} | H | \Psi_{\text{HF}} \rangle / \langle \Psi_{\text{HF}} | \Psi_{\text{HF}} \rangle$ be stationary under changes in any of the orbitals where the variation is constrained by the requirement that the set of orbitals remain orthonormal under the variation. The result is that the orbitals are the simultaneous solutions of

$$H^{\text{HF}} \phi_i = \epsilon_i \phi_i, \quad (2)$$

where i assumes the values $1, 2, \dots, n$, and H^{HF} is a one-electron operator which itself involves the orbitals that are solutions of (2). The specific form of H^{HF} is dictated by the variational condition, and the result is that $H^{\text{HF}}(i) = h(i) + U(i)$, where $h(i) = -\frac{1}{2} \nabla_i^2 + V(i)$ represents the usual one-electron term for an electron and $U(i)$ represents an average over the two-electron terms of (1) [specifically, $U(i) = 2J(i) - K(i)$, where the $J(i)$ and $K(i)$ are the well-known Coulomb and exchange terms, respectively]. Thus, this one-electron Hamiltonian H^{HF} is equivalent to the Hamiltonian of an electron moving in the nuclear field $V(i)$ and in the

average field $U(i)$ due to the other electrons. Since each of the states ϕ_i ($i=1, \dots, n$) is an eigenfunction of H^{HF} , each of these states may be interpreted as the state of an electron moving in the average field due to the other electrons (that is, each of the electrons can be considered independently). This independent-particle property of the Hartree-Fock orbitals is extremely important because it allows us to break the many-electron wave function into physically meaningful units which can be readily interpreted. The usefulness of such an independent-particle interpretation is attested by its ubiquity; it permeates practically all the areas of physics and chemistry dealing with atoms, molecules, or solids and thus is intertwined throughout most of our concepts of such many-electron systems. It is especially important to note that the independent-particle interpretation does *not* result merely because the many-electron wave function can be written as a linear combination of terms, each of which is a product of orbitals, nor does it necessarily result even if the wave function can be written as a Slater determinant. Instead, the independent-particle interpretation results because the orbitals are eigenfunctions [as in (2)] of a one-electron Hamiltonian which includes all one-electron terms and a best possible average over the many-electron terms appropriate for the system of particles. The special virtue of the Hartree-Fock method is that (at least for singlet states) it yields the best possible many-electron wave function which can be given an independent-particle interpretation in which all of the orbitals are orthogonal.

Some of the important advantages to the Hartree-Fock method are:

- (1) the enormous conceptual simplification *due* to the independent-particle interpretation allowed;
- (2) the high accuracy for the total energy, 96% for H_2 ,⁵ 98.5% for He,^{6,7} 99% for LiH,⁸ and even higher for the larger atoms and molecules (e.g., 99.5% for N_2 ⁹);
- (3) the good accuracy for some spin-independent one-electron properties;
- (4) the practicability of *ab initio* solutions for moderately large molecules (e.g., F_2 with 18 electrons by Wahl¹⁰); and
- (5) the suitability as zero-order states for perturbation schemes.¹¹

⁵ W. Kolos and C. C. J. Roothaan, *Rev. Mod. Phys.* **32**, 219 (1960).

⁶ C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, *Rev. Mod. Phys.* **32**, 186 (1960).

⁷ *Atomic Energy Levels*, edited by C. E. Moore, Natl. Bur. Std. (U. S.) Circ. No. 467 (U. S. Government Printing and Publishing Office, Washington 25, D. C., 1949).

⁸ S. L. Kahalas and R. K. Nesbet, *J. Chem. Phys.* **39**, 529 (1963).

⁹ P. E. Cade, K. D. Sales, and A. C. Wahl, *J. Chem. Phys.* **44**, 1973 (1966).

¹⁰ A. C. Wahl, *J. Chem. Phys.* **41**, 2600 (1964).

¹¹ R. M. Stevens, R. M. Pitzer, and W. N. Lipscomb, *J. Chem. Phys.* **38**, 550 (1963); R. M. Stevens and W. N. Lipscomb, *ibid.*

However, there are also some serious deficiencies in the Hartree-Fock method, viz.:

(1) Despite the high accuracy for the total energy, the error in energy is of the order of even the largest energies of interest, e.g., the binding energy which is 1.1% of the total energy for LiH and 0.2% for N_2 .

(2) The spin distribution near the nuclei for non-singlet systems is poorly described.

(3) The dissociation of molecules as the nuclei are moved apart to infinity is usually predicted incorrectly. For example, for H_2 at $R=\infty$ the Hartree-Fock wave function predicts that the probability for both electrons being near one nucleus is the same as the probability for them being near different nuclei; the error in energy at $R=\infty$ is 7.74 eV¹² (the binding energy of H_2 is 4.75 eV¹³). Another example is LiH, for which the Hartree-Fock wave function dissociates to Li^+ and H^- . This improper behavior of the Hartree-Fock wave function for large internuclear distances considerably complicates attempts to study such things as chemical reactions and molecular scattering.

(4) For totally symmetric, nondegenerate, singlet states (the common case for molecular ground states), the Hartree-Fock orbitals must be basis functions for the irreducible representations of the spatial symmetry group¹⁴ (we abbreviate this by calling them symmetry functions). This is also a disadvantage as will soon be brought out.

We have already mentioned that most of our concepts of atoms, molecules, and solids implicitly or explicitly assume that the electronic wave function can be interpreted in terms of independent-particle states. In addition, except for conduction electrons in metals, conduction states in semiconductors, and π -electron states in conjugated molecules, it is essentially always assumed that these independent-particle states are localized mainly near one or two centers (i.e., into nonbonding, inner-shell, or bonding states). The concepts based on this idea of localized independent-particle states have been consistent with the properties of these systems, and thus we would like our theoretically derived independent-particle scheme to be at least *capable* of allowing localized independent-particle states. The point is that for far too many systems of interest (e.g., all crystalline solids) the requirement that the Hartree-Fock orbitals be symmetry functions prevents them from being localized (e.g., in crystalline solids the translational symmetry implies that the symmetry functions are Bloch-type functions and thus are spread throughout the entire solid, even for the innermost inner-shell electrons). There have been some attempts to alleviate this serious defect in the Hartree-

40, 2238 (1964); **41**, 184 (1964); O. Sinanoğlu, *Proc. Roy. Soc. (London)* **A260**, 379 (1961); *J. Chem. Phys.* **36**, 706, 3198 (1962).

¹² P.-O. Löwdin, *Advan. Chem. Phys.* **2**, 207 (1959).

¹³ G. Herzberg and A. Monfils, *J. Mol. Spectry.* **5**, 482 (1960).

¹⁴ C. C. J. Roothaan, *Rev. Mod. Phys.* **23**, 69 (1951).

Fock method by transforming the orbitals into localized states.¹⁵ Specifically, the Slater determinant for a state containing only doubly occupied orbitals is left invariant under any unitary transformation of the HF orbitals among themselves; thus a unitary transformation might generally be found which would yield somewhat localized new orbitals which when placed in the Slater determinant would yield the same Hartree-Fock many-electron wave function. The problem—and it is a fundamental one—is that the new orbitals no longer satisfy the Hartree-Fock equations (2), and thus *the transformed orbitals cannot be given an independent-particle interpretation*. Since the whole purpose behind performing the transformation in the first place was to obtain states more amenable to chemical interpretation, the loss of the basic property which permits the interpretation would seem to be catastrophic.

With these points in mind we proceed to try to derive a method of obtaining approximate wave functions which eliminates some of the major disadvantages of the Hartree-Fock method while retaining most of the important advantages. Before developing the new method, we will consider an expansion of the exact wave function.

In I some operators G_i^μ were defined each of which upon operating on any function of the spatial-spin coordinates of N electrons yields an eigenfunction of \hat{S}^2 which satisfies Pauli's principle. It was then shown that the exact wave function can always be written as

$$\Psi_{\text{exact}}^{S,M}(1, \dots, N) = G_i^\mu(\Phi\chi_f(M)), \quad (3)$$

where Φ is some (complicated) function of the spatial coordinates of N electrons, $\chi_f(M)$ is a specific product of the spin factors α and β with $\hat{S}_z\chi_f = M\chi_f$, and $\bar{\mu} = [n, m]$, $n + m = N$, $n - m = 2S$. An obvious scheme is to ask for the best approximation to the exact many-electron wave function by $G_i^\mu(\Phi\chi_f(M))$, where Φ is restricted to be a simple product of orbitals. The best such approximation to a ground-state wave function will always have a lower energy than the best Hartree-Fock approximation (see Appendix A) and, in addition, will be an eigenfunction of spin.

In this paper we develop the general equations which lead to the orbitals to use in Φ in order to obtain the best $G_i^\mu\Phi\chi$ approximation to the exact wave function. In particular, we will find that the GI method *does* indeed yield an independent particle approximation but the orbitals *need not* necessarily be symmetry functions for the complete spatial symmetry group. Even more importantly the wave function *does* dissociate properly as the nuclei move apart to infinity. In addition, the spin distribution is much more accurate than for the Hartree-Fock wave function.

The basic equations for the new method are derived in Sec. I. In Sec. II we consider some properties of the GI wave functions, including the restrictions due to spatial symmetry conditions and the changes in the wave function which occur as the molecule dissociates. A generalization of the new method is presented in Sec. III, and in Sec. IV some other methods of calculating electronic wave functions are compared to the new method. Some of the important applications for the new method are mentioned in Sec. V, and a summary is presented in Sec. VI.

I. THE EQUATIONS FOR THE BEST $G_i^\mu\Phi\chi$ WAVE FUNCTION

In this section, we derive the general equations with which one obtains the best approximation to the exact wave function by a function of the form $G_i^\mu\Phi\chi$, where Φ is the product of N one-electron spatial functions or orbitals.⁴ Our criterion for choosing the best $G_i^\mu\Phi\chi$ is that it yield the lowest energy; thus, a necessary condition is that $E = \langle G_i^\mu\Phi\chi | H | G_i^\mu\Phi\chi \rangle / \langle G_i^\mu\Phi\chi | G_i^\mu\Phi\chi \rangle$ be stationary under variations of the orbital components of Φ .

In I, G_i^μ was defined as

$$G_i^\mu = \sum_r \zeta_{\sigma r} O_{r_i}^\mu \omega_{\bar{r}_i}^\mu, \quad (4)$$

where $O_{r_i}^\mu$ is a specific sum of permutations of the spatial coordinates of N electrons, $\omega_{\bar{r}_i}^\mu$ is a specific sum of permutations of the spin coordinates of N electrons, ζ_σ is the parity of the permutation σ , the μ , r , and i refer to the Young tableaux (fixing the total spin fixes μ), the sum over r is from 1 through f^μ , f^μ is an integer, and i can have any integer value from 1 through f^μ . The only properties of the $O_{r_i}^\mu$ and $\omega_{\bar{r}_i}^\mu$ operators needed in this section are

$$O_{ij}^\mu O_{kl}^\beta = \delta^{\mu\beta} \delta_{jk} O_{il}^\mu$$

and

$$\langle \Phi | O_{ij}^\mu \Phi' \rangle = \langle O_{ji}^\mu \Phi | \Phi' \rangle$$

and similarly for $\omega_{\bar{r}_i}^\mu$. Hence, if some operator on the spatial coordinates, \hat{F} , is invariant under all permutations, then

$$\langle G_i^\mu\Phi\chi | \hat{F} | G_i^\mu\Phi'\chi' \rangle = f^\mu \langle \Phi | \hat{F} | O_{ii}^\mu\Phi' \rangle \langle \chi | \omega_{\bar{r}_i}^\mu\chi' \rangle.$$

Letting \hat{F} be the Hamiltonian, we obtain

$$E = \langle \Phi | H | O_{ii}^\mu\Phi \rangle / \langle \Phi | O_{ii}^\mu\Phi \rangle. \quad (5)$$

In varying E , we require that the orbitals remain normalized. Hence if

$$I = E - \sum_{j=1}^N \epsilon_{jj'} \langle \phi_j | \phi_j \rangle,$$

¹⁵ G. H. Wannier, Phys. Rev. **52**, 191 (1937); J. Lennard-Jones, Proc. Roy. Soc. (London) **A198**, 1, 14 (1949); J. A. Pople, Quart. Rev. (London) **11**, 273 (1957); C. Edmiston and K. Ruedenberg, Rev. Mod. Phys. **35**, 457 (1963).

we require that

$$\delta I = \frac{\delta \langle \Phi | H O_{ii} | \Phi \rangle}{\langle \Phi | O_{ii} \Phi \rangle} - \frac{\langle \Phi | H O_{ii} | \Phi \rangle}{\langle \Phi | O_{ii} \Phi \rangle^2} \delta \langle \Phi | O_{ii} \Phi \rangle - \sum_{j=1}^N \epsilon_{jj}' \delta \langle \phi_j | \phi_j \rangle = 0.$$

We note that $\langle \Phi | O_{ii} \Phi \rangle > 0$ if $G_i^\mu \Phi \neq 0$ and we let

$$\epsilon_{jj}' = \epsilon_{jj} / \Theta^\mu \langle \Phi | O_{ii} \Phi \rangle;$$

hence we obtain

$$\delta \langle \Phi | (H - E) \Theta^\mu O_{ii}^\mu | \Phi \rangle - \sum_{j=1}^N \epsilon_{jj} \delta \langle \phi_j | \phi_j \rangle = 0,$$

where the Θ^μ is incorporated for later convenience. Thus, letting

$$\delta_k \Phi = \left(\prod_{j \neq k} \phi_j \right) \delta \phi_k = \Phi_k \delta \phi_k$$

we require

$$\langle \delta_k \Phi | (H - E) \Theta O_{ii} | \Phi \rangle + \langle \Phi | (H - E) \Theta O_{ii} | \delta_k \Phi \rangle - \epsilon_{kk} \langle \delta \phi_k | \phi_k \rangle - \epsilon_{kk} \langle \phi_k | \delta \phi_k \rangle = 0.$$

Although the $\langle \delta \phi_k |$ and $|\delta \phi_k \rangle$ are not linearly independent, we can treat them as such since the above equation is satisfied by any infinitesimal $|\delta \phi_k \rangle$ including $i|\delta \phi_k \rangle$ (see Messiah¹⁶). Thus the above equation and the similar one for $i|\delta \phi_k \rangle$ can be combined (multiply the latter equation by i and take the sum and difference) to obtain

$$\begin{aligned} \langle \delta_k \Phi | (H - E) \Theta O_{ii} | \Phi \rangle &= \epsilon_{kk} \langle \delta \phi_k | \phi_k \rangle; \\ \langle \Phi | (H - E) \Theta O_{ii} | \delta_k \Phi \rangle &= \epsilon_{kk} \langle \phi_k | \delta \phi_k \rangle. \end{aligned} \quad (6)$$

Taking the complex conjugate of the second equation and subtracting from the first, we see that ϵ_{kk} must be real and the two equations are equivalent.¹⁶ Thus, since (6) must be true for all $\delta \phi_k$, the coefficient of $\delta \phi_k^*$ is

$$\begin{aligned} \left\{ \sum_j \langle \delta \phi_k | h | \phi_j \rangle D_j^k + \sum_{\substack{s,t \\ j \neq k}} \langle \delta \phi_k \phi_j | g | \phi_s \phi_t \rangle D_{st}^{kj} - E \sum_{u \neq k} \langle \delta \phi_k | \phi_u \rangle D_u^k + \sum_{\substack{l \\ u, s \neq k}} \langle \phi_s | h | \phi_l \rangle \langle \delta \phi_k | \phi_u \rangle D_{tu}^{sk} \right. \\ \left. + \frac{1}{2} \sum'_{\substack{i,j \\ s,t,u \neq k}} \langle \phi_s \phi_t | g | \phi_i \phi_j \rangle \langle \delta \phi_k | \phi_u \rangle D_{iju}^{stk} - \epsilon_{kk} \langle \delta \phi_k | \phi_k \rangle \right\} = 0. \end{aligned} \quad (9)$$

In order that $\delta I = 0$ for all $\delta \phi_k^*$, we may require that the coefficient of $\delta \phi_k^*$ be zero. Since every term in (9) contains ϕ_k , we may write the coefficient of $\delta \phi_k^*$ as $H(k)\phi_k - \epsilon_{kk}\phi_k$; hence we obtain

$$H(k)\phi_k = \epsilon_{kk}\phi_k, \quad (10)$$

where $k \in [1, 2, \dots, N]$ and

$$\begin{aligned} H(k)\phi_k = \left\{ D_k^k \hat{h} \phi_k + \sum_{j, v \neq k} \langle v | k \rangle D_{jk}^{kv} \hat{h} \phi_j + \sum_{s, u \neq k} \langle s | h | k \rangle D_{ku}^{sk} \phi_u + \sum_{u, v, s, t \neq k} \langle s | h | t \rangle \langle v | k \rangle D_{tuk}^{skv} \phi_u \right. \\ \left. + \sum_{j, t \neq k} \left[\left(\int \phi_j g \phi_t \right) D_{kt}^{kj} \phi_k + \left(\int \phi_j g \phi_k \right) D_{tk}^{kj} \phi_t \right] + \sum_{j, s, t, v \neq k} \left(\int \phi_j g \phi_t \right) \langle v | k \rangle D_{stk}^{kju} \phi_s + \sum_{j, s, t, u \neq k} \langle st | g | kj \rangle D_{kju}^{stk} \phi_u \right. \\ \left. + \frac{1}{2} \sum'_{i, j, s, t, u, v \neq k} \langle st | g | ij \rangle \langle v | k \rangle D_{iju}^{stk} \phi_u - E \sum_{u, v \neq k} \langle v | k \rangle D_{uk}^{kv} \phi_u \right\}. \end{aligned} \quad (11)$$

¹⁶ A. Messiah, *Quantum Mechanics* (John Wiley & Sons, Inc., New York, 1962), Vol. II, p. 764.

¹⁷ $(dx_j) \equiv dx_1 dx_2 \cdots dx_{j-1} dx_{j+1} \cdots dx_N$, $(dx_j k') = \prod_{i \neq j, k} dx_i$, etc.

zero,¹⁷

$$\int \Phi_k^* (H - E) \Theta O_{ii} \Phi (dx_k') = \epsilon_{kk} \phi_k. \quad (7)$$

Hence, the condition for the best $G_i^\mu \Phi$ is that the N equations in (7) must be satisfied. These equations are actually coupled since the Φ_k and Φ contain the solutions of the other equations. However, if we let

$$H_k^{\mu i} \phi_k \equiv \int \Phi_k^* (H - E) \Theta^\mu O_{ii}^\mu \Phi (dx_k'),$$

then Eqs. (7) have the appearance of eigenvalue problems,

$$H_k^{\mu i} \phi_k = \epsilon_{kk} \phi_k. \quad (8)$$

This operator $H_k^{\mu i}$ contains the one-electron operator for an electron plus another term which is due to the interactions of the electrons. Hence, we can interpret $H_k^{\mu i}$ as the Hamiltonian for one electron moving in the average field due to the $N-1$ other electrons, and thus, we can interpret the ϕ_k as the state of an electron moving in the average field of the other electrons. That is, the best $G_i^\mu \Phi$ wave function is susceptible to an independent-particle interpretation.

We will now obtain the specific form of (7). Let D_k^j be the coefficient of $\phi_j^*(j)\phi_k(j)$ in $\int \Phi^*(1, \dots, N) \Theta O_{ii} \times \Phi(1, \dots, N) (dx_j')$, let D_{pq}^{jk} be the coefficient of $\phi_j^*(j) \times \phi_k^*(k) \phi_p(j) \phi_q(k)$ in $\int \Phi^*(1, \dots, N) \Theta O_{ii} \Phi(1, \dots, N) \times (dx_j k')$, and similarly for D_{qmn}^{jkp} , etc. Then

$$E = \left(\sum_{i,j} \langle \phi_i | h | \phi_j \rangle D_j^i + \sum_{ijkl} \langle \phi_i \phi_j | g | \phi_k \phi_l \rangle D_{kl}^{ij} \right) / \langle \Phi | \Theta O_{ii} \Phi \rangle$$

and

$$I = \Theta \langle \Phi | \left(\sum_j h(j) + \sum_{j < l} g(j, l) - E \right) O_{ii} | \Phi \rangle - \sum_j \epsilon_{jj} \langle \phi_j | \phi_j \rangle$$

and the terms containing $\delta \phi_k^*$ in δI are

Equations (10), which yield the orbitals to use in constructing the best $G_i^\mu\Phi X$ wave function, are called the GI equations in general; if a specific i ($i=1, 2, \dots, f$), say 1, 3, or f , is to be referred to, then the Eqs. (10) are called the G1 equations, the G3 equations, or the GF equations, respectively.

The GI equations are a coupled set of nonlinear integropartial differential equations and thus are difficult to solve in general. A conceivable method of solving these equations would be to select some complete set of functions $\{X_\mu\}$ and expand each orbital in terms of these,

$$\phi_i = \sum_{\mu} C_{\mu i} X_{\mu}. \quad (12)$$

Since the X_μ are known, all of the integrals can be taken at once, with the result being an infinite set of algebraic equations for the $C_{\mu i}$. Although we cannot solve these in general, an obvious method of obtaining approximate solutions to (10) is to use a finite, and thus incomplete, set of basis functions $\{X_\mu: \mu=1, 2, \dots, M\}$. The resulting finite set of nonlinear algebraic equations for the $C_{\mu i}$ can be readily solved iteratively, and the resulting solutions can probably be made to approach the exact solutions of (10) by choosing larger and larger basis sets. This general approach has been shown by Roothaan, co-workers, and others^{8,6,9,10,14,18,19} to be a powerful method of solving for approximate solutions of the Hartree-Fock equations [which have the same symbolic form as (10)]; we will use such a Roothaan expansion to solve the GI equations. We thus substitute the expansion (12) in (6) and take δ_k to be a variation of the $C_{\mu k}$ coefficients; the result is the same as (9), where $\delta\phi_k = \sum_{\mu} (\delta C_{\mu k}) X_{\mu}$. Setting the coefficient of $\delta C_{\mu k}^*$ equal to zero, we obtain

$$H_{\mu\nu}(k)C_{\nu k} = S_{\mu\nu}C_{\nu k}\epsilon_{kk}, \quad (13)$$

where $k \in \{1, 2, \dots, N\}$, $S_{\mu\nu} = \langle X_\mu | X_\nu \rangle$, and

$$\begin{aligned} H_{\mu\nu}(k) = & \{D_k^k \langle \mu | h | \nu \rangle + \sum_{v, j \neq k} \langle \mu | h | j \rangle \langle v | \nu \rangle D_{jk}^{kv} \\ & + \sum_{u, t \neq k} \langle \mu | u \rangle \langle t | h | \nu \rangle D_{uk}^{kt} + \sum_{s, t, u, v \neq k} \langle \mu | u \rangle \langle v | \nu \rangle \langle s | h | t \rangle D_{ukt}^{kvs} + \sum_{j, t \neq k} [\langle \mu | j | g | \nu t \rangle D_{kt}^{kj} + \langle \mu | j | g | t \nu \rangle D_{tk}^{kj}] \\ & + \sum_{j, s, t, v \neq k} \langle \mu | j | g | st \rangle \langle v | \nu \rangle D_{skt}^{kvsj} + \sum_{j, s, t, u \neq k} \langle \mu | u \rangle \langle st | g | \nu j \rangle D_{ukj}^{kst} + \frac{1}{2} \sum_{i, j, s, t, u, v \neq k} \langle \mu | u \rangle \langle v | \nu \rangle \langle st | g | ij \rangle D_{ukij}^{kvsst} \\ & - E \sum_{u, v} \langle \mu | u \rangle \langle v | \nu \rangle D_{uk}^{kv} \}. \quad (14) \end{aligned}$$

Equations (13) will be referred to as the GIR equations (for Roothaan expansion) or else just as the GI equations. The solutions to (13), the vectors \mathbf{C}_k , will be referred to as the GI orbitals just as are the solutions to (10). In general, Eqs. (13) can be rewritten such that there are fewer than N different operators $H(k)$, e.g., there are just two such operators for the GF equations.²⁰ This will be discussed in Sec. III.

We have now derived the equations—the GI equations—which must be solved in order to determine the product of orbitals to use in $G_i^\mu\Phi X$ to obtain the best such approximation to the exact wave function. These equations are similar to, although more complex than, the Hartree-Fock equations and can be solved in a similar way. In order to solve the GI equations, we must (i) diagonalize two or more Hamiltonians, whereas there is just one to diagonalize in the Hartree-Fock method; (ii) calculate averages over the other occupied

orbitals which are more complicated than in the Hartree-Fock method; and (iii) calculate matrices of the type D_j^i, D_{ki}^{kj} , etc., whereas in the Hartree-Fock method the orthogonality of the orbitals make the corresponding matrices trivial. In both methods we must evaluate all the integrals for the basis functions; because the calculation of these integrals consumes the bulk of the computer time in the Hartree-Fock calculations on molecules (especially for polyatomic molecules), the difficulties in (i), (ii), and (iii), which are mainly just algebraic, do not lead to corresponding increases in computation time for the GI methods. For the actual calculations it is desirable to have explicit general expressions for the D_j^i, D_{ki}^{kj} , etc. matrices; such explicit expressions will be developed for the most important cases in the succeeding articles. We will now proceed to discuss some of the general aspects of the GI wave functions.

II. PROPERTIES OF THE GI WAVE FUNCTIONS

Considerations of Spatial Symmetry

In addition to the invariance of the Hamiltonian (1) under spin transformations and permutations of the

¹⁸ (a) J. A. Pople and R. K. Nesbet, *J. Chem. Phys.* **22**, 571 (1954); (b) A. T. Amos and G. G. Hall, *Proc. Roy. Soc. London* **A263**, 483 (1961); (c) R. K. Nesbet, *Rev. Mod. Phys.* **33**, 28 (1961); (d) R. E. Watson and A. J. Freeman, *Phys. Rev.* **120**, 1125 (1960); (e) D. A. Goodings, *ibid.* **123**, 1706 (1961).

¹⁹ E. Clementi, C. C. J. Roothaan, and M. Yoshimine, *Phys. Rev.* **127**, 1618 (1962); W. M. Huo, *J. Chem. Phys.* **43**, 624 (1965).

²⁰ W. A. Goddard, III, Ph.D. thesis, California Institute of Technology, 1964 (unpublished).

electrons, there are in general other groups of transformations which leave the Hamiltonian invariant. For atoms, molecules, and solids, the most important remaining group is the spatial symmetry group, that is, the group of rotations, inversions, and translations on the (fixed) nuclei which leave $V(i)$ in (1) invariant. The exact wave function must be a basis function for an irreducible representation of the spatial symmetry group, say \mathcal{G} . Since we want our approximate wave function to behave as nearly as possible like the exact wave function, we should require that the approximate wave function also be a symmetry function of \mathcal{G} . In this section, we will consider the restrictions on the many-electron wave function $G_i^\mu\Phi\chi$ resulting from these spatial symmetry conditions.

If the Φ in $G_i^\mu\Phi\chi$ is still restricted to be a product of orbitals (see Sec. III for considerations of the more general case), then in general the orbitals must have some symmetry in order that $G_i^\mu\Phi\chi$ be a symmetry function for \mathcal{G} (for the case of two electrons see Ref. 20). Recall that in the Hartree-Fock method for a totally symmetric, nondegenerate, singlet state with all Hartree-Fock orbitals doubly occupied, the condition on the orbitals is that they too must be symmetry functions of the total \mathcal{G} .¹⁴ In general, the spatial symmetry conditions on the GI orbitals are less restrictive and the GI orbitals are symmetry functions of some subgroup of \mathcal{G} .

In order that the Hartree-Fock or GI wave function be transformed into itself under all symmetry transformations, it is necessary that the space spanned by the orbitals remain invariant under each of the symmetry transformations (see Ref. 14 for the Hartree-Fock case and Appendix C for the GI case). Since the Hartree-Fock orbitals are all eigenfunctions of the same operator, H^{HF} , and since these orbitals all transform among themselves under the transformations of \mathcal{G} , then these transformations commute with H^{HF} and the Hartree-Fock orbitals are symmetry functions for \mathcal{G} . The GI orbitals are never all eigenfunctions of the same operator (there are always at least two different H_i^{GI} for systems containing two or more electrons), and hence, the GI orbitals need not always be symmetry functions of \mathcal{G} .

In general, the spatial symmetry results in some conditions on the GI orbitals, and usually there are several different sets of conditions on the orbitals which can lead to the proper spatial symmetry. Of course, the variational principle automatically selects the appropriate conditions.

Molecular Dissociation

Now we wish to show that the GI method is capable of an accurate description of the electronic wave function for practically any configuration of nuclei.

Probably the most severe test of all configurations of interest is that in which one or more nuclei are arbitrarily far from the remainder of the system. This case

of dissociation must be properly described in order to have any hope of considering such phenomena as chemical reactions and also in order to be able to develop a conceptual description of binding [by separating out the phenomena responsible for molecular formation through comparison with the separated (atomic) system]. That the Hartree-Fock method does not generally describe dissociation properly is a major defect in the method.

Basically the reason for improper dissociation of the Hartree-Fock wave function is that the orbitals are all doubly occupied (for a typical molecule) and hence molecules containing odd-atomic-number atoms (e.g., H, Li, B, N, and F) must dissociate to isolated atoms in ionized states, and nuclei of even atomic number (such as C and O) often dissociate to excited electronic states (by Hund's rule the lowest state for many even-atomic-number atoms has singly occupied orbitals). The basic reason for the proper dissociation of the GI wave functions is that each orbital can be different and for homonuclear diatomic molecules²¹ each orbital is allowed to be localized (i.e., is not forced by symmetry to be delocalized).

In order to demonstrate some of the aspects of the spatial symmetry and molecular dissociation of GI wave functions, we will discuss some actual calculations on H_2 and LiH .

The H_2 Molecule

The GI wave function for H_2 contains two orbitals, ϕ_a and ϕ_b , and can be expanded as²²

$$G_1^{(12)}\phi_a\phi_b\alpha\beta = \frac{1}{2}[\alpha\phi_a\phi_b\alpha\beta + \alpha\phi_b\phi_a\alpha\beta].$$

Table I contains the optimum orbitals²³ for a nuclear configuration near equilibrium ($R=1.4a_0$) and for the nearly dissociated configuration ($R=6.0a_0$). These orbitals are plotted in Fig. 1 where only the ϕ_a orbital is shown since ϕ_b is symmetrically related to ϕ_a . In this figure the GF orbital for $R=6a_0$ is indistinguishable from the hydrogen atom orbital ($R=\infty$). Actually the former is larger for $-0.2 < z < 9$ and the difference is largest at $Z=6a_0$. The ϕ_a and ϕ_b are invariant under

²¹ Only the case of homonuclear molecules is important since only in this case is the symmetry necessarily present for the dissociated molecule.

²² In each case, the many-electron wave function has the form $G_i^\mu\Phi\chi$ as discussed in Sec. I and defined in I; however, for the convenience of those unfamiliar with these operators, we have expanded the $G_i^\mu\Phi\chi$ in terms of Slater determinants (using non-orthogonal orbitals) for each of the wave functions below. Bear in mind, however, that we never use these expansions in terms of Slater determinants. Rather we consider the G_i^μ operator directly in terms of the $O_{r_i^\mu}$ and $\omega_{r_i^\mu}$ operators since in this case we immediately obtain the simple and useful expressions for the optimum orbitals as shown in Sec. I. The matrix elements U_{117} and $U_{j\bar{j}\tau}$ are given in Appendix E of I.

²³ These calculations use Slater orbitals as basis functions; and in all cases the orbital exponents have been optimized. However, the orbital exponents are not in all cases optimized to the number of significant figures given.

TABLE I. The G1 orbitals of H₂. The different nuclei are denoted by A and B. Each 2pσ function is positive toward the other nucleus. The orbital exponents are in parentheses.

	ϕ_a	ϕ_b
	$R=1.4a_0$	
A1s (1.3129)	0.775023	0.121577
A2s (1.1566)	0.111130	0.042025
A2pσ (1.9549)	0.003120	0.037667
B1s (1.3129)	0.121577	0.775023
B2s (1.1566)	0.042025	0.111130
B2pσ (1.9549)	0.037667	0.003120
	$R=6.0a_0$	
A1s (1.0045)	0.993720	0.002525
A2s (0.850)	0.007571	0.002730
A2pσ (0.820)	0.001209	-0.000870
B1s (1.0045)	0.002525	0.993720
B2s (0.850)	0.002730	0.007571
B2pσ (0.820)	-0.000870	0.001209

rotations about the axis (i.e., they are σ functions) and $m_h\phi_a = \phi_b$, $m_h\phi_b = \phi_a$, where m_h is the reflection interchanging the protons. Thus the total wave function has $^1\Sigma^+$ symmetry. For the equilibrium internuclear distance, R_e , the amplitude of ϕ_a is large near nucleus A and smaller but quite significant near nucleus B; as R increases, the amplitude of ϕ_a near A gradually approaches that in the H atom and the amplitude of ϕ_a near B gradually goes to zero. As R increases, ϕ_a becomes more and more like a 1s orbital of H centered at A and ϕ_b becomes more and more like a 1s orbital of H centered at B. Because of this proper dissociation of H₂ we are in the position of being able to follow in detail the changes which occur as two H atoms come together to form H₂, and thus we may expect to gain some insight into the way that the several competing factors balance each other and change in importance as the molecule is being formed. The energies for the G1 wave function and a comparable Hartree-Fock wave function (HF) are in Table II.

TABLE II. Energy for H₂ at various internuclear distances. Six basis functions were used in the Hartree-Fock and G1 calculations.

R (a.u.)	HF	G1	Exact
1.4	-1.13349 ^a	-1.151526	-1.174475 ^b
6.0	-0.82199 ^a	-1.000552	...
∞	-0.7154 ^c	-1.000000	-1.000000

^a S. Fraga and B. J. Ransil, J. Chem. Phys. **35**, 1967 (1961).

^b W. Kolos and L. Wolniewicz, J. Chem. Phys. **41**, 3663 (1964).

^c Löwdin, p. 244 of Ref. 12.

For totally symmetric homonuclear molecules larger than H₂, the G1 orbitals can localize about the different centers just as in H₂ since the G1 orbitals need only have $C_{\infty v}$ symmetry. Hence we expect such molecules to dissociate properly.

The LiH Molecule

For LiH there are four GF orbitals, ϕ_{1a} , ϕ_{2a} , ϕ_{1b} , and ϕ_{2b} , where ϕ_{2a} is orthogonal to ϕ_{1a} and ϕ_{2b} is orthogonal

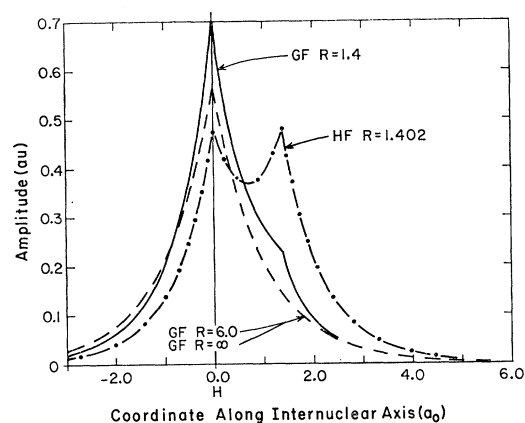


FIG. 1. The orbitals for H₂. The origin is taken at the left proton. R is the internuclear distance.

to ϕ_{1b} . In this case the GF wave function can be expanded as²²

$$G_f^{[2]} \phi_{1a} \phi_{2a} \phi_{1b} \phi_{2b} \alpha \alpha \beta \beta = \frac{1}{3} [2 \alpha \phi_{1a} \phi_{2a} \phi_{1b} \phi_{2b} \alpha \alpha \beta \beta + \alpha \phi_{1a} \phi_{1b} \phi_{2a} \phi_{2b} \alpha \alpha \beta \beta + \alpha \phi_{1a} \phi_{2b} \phi_{1b} \phi_{2a} \alpha \alpha \beta \beta + \alpha \phi_{1b} \phi_{2a} \phi_{1a} \phi_{2b} \alpha \alpha \beta \beta + \alpha \phi_{2b} \phi_{2a} \phi_{1b} \phi_{1a} \alpha \alpha \beta \beta + 2 \alpha \phi_{1b} \phi_{2b} \phi_{1a} \phi_{2a} \alpha \alpha \beta \beta].$$

Table III contains the GF orbitals²³ for the equilibrium nuclear configuration ($R=3.015a_0$) and for the nearly dissociated configuration ($R=10.0a_0$). The bonding orbitals are plotted in Figs. 2 and 3, and the energies are listed in Table IV along with those from some comparable wave functions.

At infinite internuclear distance, the GF orbitals and the GF energy are just the same as those for the separated Li and H atoms; for a minimum basis set, this energy is $-7.918482h$. Thus the calculated binding energies for the Hartree-Fock and GF calculations are 0.0515 h and 0.0664 h , respectively, or 56.0% and 72.3% of the experimental value, respectively. At $10.0a_0$, the ϕ_{1a} and ϕ_{1b} are almost exactly like Li 1s states, and ϕ_{2a} and ϕ_{2b} are almost exactly like a Li 2s and a H 1s state, respectively. At $3.015a_0$, the ϕ_{1a} and ϕ_{1b} are very much like Li 1s states, the ϕ_{2a} is still somewhat like a Li 2s

TABLE III. The coefficients for the GF orbitals of LiH. The orbital exponents are in parentheses.

Orb	Li 1s	Li 2s	Li 2pσ	H 1s
	$R=3.015a_0$			
	(2.6903)	(0.7034)	(0.7815)	(1.0595)
1a	0.996382	0.016064	-0.003885	0.004344
2a	-0.176614	0.772042	0.449490	0.166374
1b	0.995490	0.019080	-0.008055	0.006848
2b	-0.093589	-0.035499	-0.008316	1.023841
	$R=10.0a_0$			
	(2.6906)	(0.6396)	(0.6396)	(1.0000)
1a	0.997703	0.013573	0.000008	-0.000362
2a	-0.178165	1.013008	0.005049	0.009812
1b	0.997164	0.016611	-0.000022	-0.000678
2b	-0.000011	0.000171	-0.000416	1.000017

TABLE IV. Energy of LiH at various internucleus distances. Configuration interaction is denoted by CI.

R	$3.015a_0$	$10.0a_0$	∞
HF ^a (4BF)	-7.96992
CI ^b (4BF)	-7.98361
GF (4BF)	-7.984993	-7.918725	-7.918482
HF ^c (11BF)	-7.985970
HF ^d (16BF)	-7.987313
GF (6BF)	-7.999744	...	-7.932342
GF (16BF)	-8.003687
CI ^e (26BF)	-8.0561
Exact	-8.070	...	-7.978

^a B. J. Ransil, Rev. Mod. Phys. 32, 245 (1960).
^b S. Fraga and B. J. Ransil, J. Chem. Phys. 36, 1127 (1962).
^c S. L. Kahalas and R. K. Nesbet, J. Chem. Phys. 39, 529 (1963). This energy is for $3.02a_0$.
^d P. E. Cade and W. Huo (to be published).
^e J. C. Browne and F. A. Matsen, Phys. Rev. 135, A1227 (1964). This energy is for $3.046a_0$.

state but with hybridization and a much higher amplitude in the region near the proton, and the ϕ_{2b} is still rather much like an H 1s state but with a higher amplitude near the H and a subsidiary 2s-like component near the Li. Thus as the nuclei are pulled apart, the individual GF orbitals gradually deform from bonding and inner shell orbitals into atomic orbitals and the GF energy gradually changes from the molecular energy to the atomic energy. In contrast, the Hartree-Fock wave function dissociates into Li^+ and H^- . Thus the Hartree-Fock method cannot be used to describe the changes in the molecular wave function as the separated Li and H atoms are brought together to form the LiH molecule. The same proper behavior of the GI wave functions can be expected for other totally symmetric heteronuclear molecules.

In general, one is able to describe the separated atoms by a $G_i^\mu\Phi_X$ corresponding to the spatial and spin symmetry of the molecules, and thus most molecules will dissociate properly.

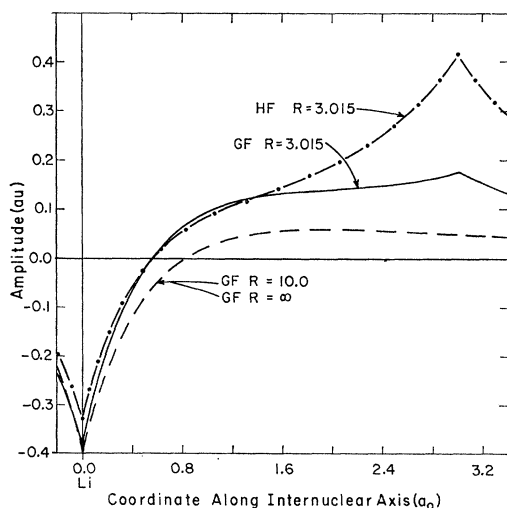


FIG. 2. The ϕ_{2a} bonding orbital for LiH. The origin is taken at the Li nucleus with the proton to the right. R is the internuclear distance.

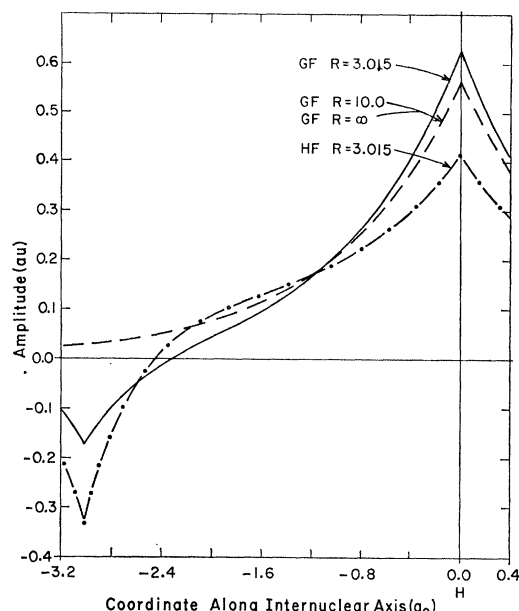


FIG. 3. The ϕ_{2b} bonding orbital for LiH. The origin is taken at the proton with the Li nucleus to the left. R is the internuclear distance.

Other Properties

The GI wave functions have many other convenient properties. The Hellmann-Feynman and Brillouin theorems apply, calculations on many excited states (even of the same symmetry as lower states) lead to upper bounds on the energy, the first-order perturbation energy for one-electron operators is given by the expectation value of the perturbation Hamiltonian, and for atoms the exact GI orbitals satisfy the cusp condition. Before comparing the GI method to some other methods, we will consider an extension of the GI method.

III. AN EXTENSION OF THE GI METHOD

The GI method consists of finding the best approximation to the exact wave function by a function of the form $G_i^\mu\Phi_X$, where Φ is restricted to be a simple product of one-electron functions. However, there are situations where one may wish to relax this restriction (e.g., to account for more correlation energy or to describe, say, excited states of atoms which do not have the largest L consistent with the given S for the particular configuration being considered).

We wish to point out that we could have considered the best approximation to the exact wave function by a function of the form $\mathcal{P}G_i^\mu\Phi_X$, where Φ is still a simple product of orbitals and \mathcal{P} is a projection operator which projects out the components of $G_i^\mu\Phi_X$ not having the proper spatial symmetry. In this case the energy expression becomes

$$E = \langle \Phi | H \mathcal{P} | O_{ii}^\mu \Phi \rangle / \langle \Phi | \mathcal{P} | O_{ii}^\mu \Phi \rangle,$$

since the \mathcal{O} is symmetric in the electron coordinates. Thus, the new equations for the best orbitals will be formally the same as the previous ones if O_{ii}^μ is replaced by $\mathcal{O}O_{ii}^\mu$. However, the formalism hides a great deal of complexity. For example, the $O_{ii}^\mu\Phi$ contains exactly the same orbitals (in different arrangements) as in Φ so that the GI equations can all be expressed in terms of simple density matrices and the one- and two-electron integrals for H , but the $\mathcal{O}O_{ii}^\mu\Phi$ not only contains the original orbitals in new arrangements, but also can contain orbitals which were not present in Φ (e.g., if Φ contains a product say $p_x p_x$ and the total wave function has S symmetry we can expect $\mathcal{O}\Phi$ to contain the sum $p_x p_x + p_y p_y + p_z p_z$). One can, at least formally, interpret each of the new one-electron Hamiltonians (which each contain the projection operator \mathcal{O}) as equivalent to the Hamiltonian for an electron moving in the average field of the other electrons; thus one can, at least formally, interpret each of the solutions to these equations (the best orbitals) as the state of an electron moving in the average field of the other electrons. We might call the method described above the extended GI method, in analogy to Löwdin's use of the term extended to describe a similar extension of the Hartree-Fock method.

IV. RELATION TO OTHER METHODS

We will now discuss some relationships between the GI method and several other methods.

As is shown in Appendix A, the Hartree-Fock wave function for every case in which the single Slater determinant is an eigenfunction of spin is just a special case of all of the $G_i^\mu\Phi$ wave functions (i.e., a set of orbitals can be placed in Φ so that $G_i\Phi$ is a single determinant). Hence, every GI wave function can be expected to yield an energy lower than the Hartree-Fock energy and all of the GI methods can be considered as generalizations of the Hartree-Fock method in which some restrictions are removed.

Besides the GI method, apparently only one other method has been suggested which would improve upon the Hartree-Fock energy with a wave function of the proper spin symmetry and yet retain an independent-particle interpretation—this is the extended Hartree-Fock method of Löwdin.^{12,24,25,26}

Löwdin develops a method of projecting out an eigenfunction of total spin from a general N -electron wave function.^{12,24} To do this, he defines an operator,

$$\mathcal{O}_i = \prod_{k \neq l} \frac{\hat{S}^2 - k(k+1)}{l(l+1) - k(k+1)},$$

where k goes through $\frac{1}{2}N$, $(N/2-1)$, \dots , 0 or $\frac{1}{2}$ except $k=l$. He then suggests that the Hartree-Fock wave

function be improved by allowing the spin orbitals with α spin to have different spatial functions from the spin orbitals with β spin, but instead of using the resulting determinant, which is not an eigenfunction of \hat{S}^2 , he suggests that the wave function be approximated by $\mathcal{O}_i D$, where D is the determinant of N spin orbitals. This method of finding the best such $\mathcal{O}_i D$ approximation by varying the N -spin orbitals in D until $\langle \mathcal{O}_i D | H | \mathcal{O}_i D \rangle / \langle \mathcal{O}_i D | \mathcal{O}_i D \rangle$ is minimized is called the extended Hartree-Fock method.^{12,24} Löwdin suggests factoring each spin orbital into a spatial part and a spin part which is either α or β (i.e., an eigenfunction of S_z) and varying the N orbitals to minimize the energy. However, Löwdin did not restrict himself to using only a spin-projection operator. Since some important new complications occur when using spatial or spatial-spin projection operators, we will refer to the above method of applying a spin-projection operator to a Slater determinant and then optimizing the orbitals as the spin-polarized extended Hartree-Fock method [in analogy with the term spin-polarized as used in reference to the unrestricted Hartree-Fock (UHF) method^{18d}].

Löwdin also suggests that the variational conditions can be put into the form of an eigenvalue problem, and although he does not explicitly obtain the form of the operator, he does point out¹² that $\mathcal{O}_i D$ is characterized by two spatial densities $\rho_+(\mathbf{r}_1, \mathbf{r}_2)$ and $\rho_-(\mathbf{r}_1, \mathbf{r}_2)$ which may be varied to minimize the energy. Apparently because of this lack of a specific form for the equations to be solved, there have been no calculations using the spin-polarized extended Hartree-Fock method²⁷ except for the simple case of $N=2$ (see Davidson and Jones²⁷ for some nontrivial calculations on H_2).

In Appendix B we show that by using the ω_{ii}^μ operators we can put the spin-polarized extended Hartree-Fock wave function into a form which is equivalent with the GF wave function. The two methods differ basically in that the GF method allows the spin integrations to be taken in a trivially simple way so that the important spatial relationships stand out. Of course, the GF method (and hence the spin-polarized extended Hartree-Fock method) is just one case of the general GI method of obtaining accurate many-electron wave functions which allow an independent-particle interpretation.

There have been some other calculations made using the different-orbitals-for-different-spins idea of Slater and Löwdin. In the UHF method¹⁸ the wave function is approximated by a single Slater determinant, but we allow the orbitals for α spin to differ from those for β spin. The orbitals are optimized, and the resulting function leads to an independent-particle interpretation. However, the UHF wave function does *not* have the proper spin symmetry. One could project out all components of spin except one in order to obtain a wave function of the proper spin symmetry, but the UHF

²⁴ P.-O. Löwdin, Phys. Rev. **97**, 1509 (1955).

²⁵ The same term extended Hartree-Fock is also used to denote a somewhat different method. See Ref. 26.

²⁶ P.-O. Löwdin, Phys. Rev. **97**, 1474 (1955).

²⁷ E. R. Davidson and L. L. Jones, J. Chem. Phys. **37**, 1918 (1962); S. M. Blinder, Advan. Quant. Chem. **2**, 47 (1965).

orbitals would not be optimized for the projected UHF wave function and hence could not be given an independent-particle interpretation. If we optimize the function after projection, then we have the GF method.

The Weinbaum²⁸ calculation on H₂ can be shown to be equivalent to a G1 calculation using just two basis functions; hence, his wave function can be transformed into a form like $G_1\phi_a\phi_b\chi$ (Coulson and Fischer²⁹ recognized the transformation) and the ϕ_a and ϕ_b can be given an independent-particle interpretation (this does not seem to have been recognized). However, no generalization of the Weinbaum approach to include systems with more electrons which also admits an independent-particle interpretation has been previously reported. The GI method forms such a generalization.

Matsen and co-workers³⁰ have utilized the different-orbitals-for-different-spins idea in calculations on two-, three-, and four-electron atoms and molecules. Matsen has used proper eigenfunctions of \hat{S}^2 for his wave functions but has concentrated more on configuration interaction in order to obtain very accurate energies; consequently most of the calculations use many orbitals and are not candidates for independent-particle interpretations.

The alternate orbital method (suggested by Löwdin) which appears of much value for π -electron systems may be considered as a special case of the GF method which uses a minimum set of basis functions. This will be discussed in more detail in Paper III of this series.

The Heitler-London and Wang wave functions for H₂, which are the prototypes for the valence bond method, are just special cases of the G1 wave functions where not only is the number of basis functions limited to two but the coefficients are fixed. Since the coefficients are fixed, the Heitler-London and Wang wave functions *cannot* be given an independent-particle interpretation in the sense described above (although these wave functions are sometimes discussed as if the orbitals actually could be interpreted as each containing an electron). Because of the fair accuracy and appealing form of the Heitler-London and Wang wave functions, attempts have been made to generalize to the case of more electrons. The general method which is called the valence-bond (VB) method has actually been rather useful conceptually but ineffectual quantitatively.

With the VB method the description by one "configuration" is of poor accuracy, and the introduction of more configurations is quite complex, improves the accuracy too slowly, and destroys the appealing interpretation attributed to the valence-bond wave function.

Probably a main motivation behind developments of the valence-bond method is the belief that the one-electron states of chemical interest should be localized into (perhaps hybridized) one-center bonding and non-bonding states. Although the valence-bond wave function gives the illusion of being so interpreted in terms of such one-electron states, the basis for such an interpretation is not clear since the orbitals are *not* eigenfunctions of a one-electron Hamiltonian describing the motion of an electron moving in an average field of the other electrons. It is interesting to note that just as the Heitler-London wave function is a special, restricted case of a G1 wave function, the general valence-bond wave functions (including the extended valence-bond wave function³¹) are also special, restricted cases (containing fixed coefficients, orthogonality assumptions, minimum number of basis functions, etc.) of certain GI wave functions. Of course, the GI wave function yields a rigorous independent-particle interpretation, can be described by any number of basis functions, needs no orthogonality assumptions, can yield accurate energies for a single configuration, and is adapted to automatic calculation. In addition to all of this, specific chemical assumptions need not be introduced into the GI method; hence, we have the opportunity to derive from first principles the valid chemical concepts and in so doing to refine, develop, and enrich these concepts.

V. DISCUSSION ON APPLICATIONS

From the discussion on dissociation it is clear that there are a myriad of exciting new types of calculations which can now be made.

We can study formation and dissociation of a molecule, atom by atom or group by group.

Similarly, we can study chemical reactions in detail and actually determine the reaction path and the activated complex. In addition, since our orbitals can be given an independent-particle interpretation which may correspond to bonding states, inner-shell states, etc., we may be able to study the detailed changes which occur in the bonding states as the activated complex is formed.

We can consider the various possible equilibrium configurations and investigate the changes in the bonding orbitals as the molecule is formed and as deformations are made such as rotating the CH₃ groups of ethane with respect to each other.

In addition, we expect to answer such questions as: Is the carbon-carbon bond of ethylene described better as a pair of bent bonds or as a σ and a π bond?

Since the GI calculations are valid for states with nonzero spin, we can treat systems in which radicals

²⁸ S. Weinbaum, *J. Chem. Phys.* **1**, 593 (1933).

²⁹ C. A. Coulson and I. Fischer, *Phil. Mag.* **40**, 386 (1949).

³⁰ G. F. Brigman and F. A. Matsen, *J. Chem. Phys.* **27**, 829 (1957); R. P. Hurst, J. D. Gray, G. H. Brigman, and F. A. Matsen, *Mol. Phys.* **1**, 189 (1958); G. H. Brigman, R. P. Hurst, J. D. Gray, and F. A. Matsen, *J. Chem. Phys.* **29**, 251 (1958).

³¹ J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill Book Company, Inc., New York, 1963), Vol. 1.

are involved, and we can expect good values not only for the one-electron spatial properties but also for such properties as the spin distribution.³²

Thus we should be able to calculate good electronic wave functions and properties for practically any configuration of chemical interest, and in addition we can interpret this wave function directly in an independent, particle scheme which allows states with chemical significance.

So far, all discussions have been with *ab initio* calculations on atoms and molecules implicitly in mind. The reason is that we feel it is appropriate, if possible, to perform *ab initio* calculations on small representative systems and then to examine the results to see which, if any, approximations can be made which would allow calculations on much larger systems. It is not necessarily true, of course, that we can analyze the *ab initio* calculation using some method and extract useful approximations, but the GI method has some characteristics (e.g., the independent-particle interpretation, proper dissociation, and occurrence of localized states) which lead us to believe that, indeed, we might be able to extract such useful approximations. For example, with the GI method we expect the characteristics of the bonding states to be clearly related to the atoms involved.

VI. SUMMARY AND CONCLUSION

The GI method yields accurate many-electron wave functions for atoms, molecules, and solids; these many-electron wave functions can correctly describe dissociation of molecules and can be given an independent-particle interpretation which may correspond quite directly with chemical concepts. This method can be considered as a direct generalization and synthesis of the Hartree-Fock and valence-bond methods which retains many of the best and eliminates many of the worst features of both. Although the GI method is conceptually simple, the actual calculation is more complicated than Hartree-Fock calculations. Even so, the results of the calculations are quite simple and lucid.

It is to be emphasized that the GI method is not a method which requires *ad hoc* insertions of such restrictions as bonding states, hybridization, localized states, constancy of states for different systems, etc. Rather, it is a general method appropriate for *ab initio* calculations which, because of its properties (i.e., independent-particle interpretation, proper dissociation of molecules, minimum of symmetry conditions on the orbitals), might *predict* such chemical concepts as are really valid. It should also be emphasized that although accuracy of a many-electron wave function is probably

a necessary condition for extracting reliable and chemically important concepts concerning the changes in an electronic system responsible for the binding, it is certainly not a sufficient condition. Even if we had a method of obtaining wave functions which was capable of yielding wave functions which could predict many properties arbitrarily well, we would not necessarily gain any understanding of the systems; that is, we might not have any idea of the differences which occur when we add or subtract an electron, or replace one atom by another, or consider a series of molecules such as CH₄, C₂H₆, and C₃H₈ or C₂H₂, C₂H₄, and C₂H₆. Our real long-range objective is to build up enough understanding of electronic systems so that we can pinpoint the salient features of binding and predict the wave function for a system on which we have not made detailed calculations and for which no experimental information is available. In view of this objective we should concentrate on methods which have the necessary essential features for the ideal method; we believe that these necessary features are just the ones discussed in the Introduction and that the GI method embodies these in a satisfactory way.

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APPENDIX A: RELATION BETWEEN THE HARTREE-FOCK WAVE FUNCTION AND THE GI WAVE FUNCTIONS

Consider some system for which the Hartree-Fock single-determinant wave function is an eigenfunction of S^2 . If $N=n+m$ and $2S=n-m$, then this state will have m doubly occupied orbitals and $n-m$ singly occupied orbitals. Now consider $G_i^\mu \Phi \chi$, where $\bar{\mu}=[n,m]$, and place the Hartree-Fock orbitals in Φ in such an order that upon replacing the numerals 1 through N of the tableaux S_i^μ by the respective orbital labels of Φ , each two-element row contains the same label twice and the one-element rows contain the nonrepeated labels. Then the $G_i^\mu \Phi \chi$ for all i are equal to each other³³ (within a phase factor). We see that³⁴ $\Omega_{11}^{[1^N]}(\tau\Phi)\chi$ is nonzero only if the n orbitals corresponding to α spin are different, but there are a total of only n different orbitals; in addition, $\Omega_{11}^{[1^N]}(\tau\Phi)\chi$ is nonzero only if the m orbitals corresponding to β spin are different, and once n dif-

³³ See Appendix D of I, also pp. 18-21 of Ref. 20.

³⁴ Recall that $N\Omega_{11}^{[1^N]} = \sum_{\sigma} \xi_{\sigma} \sigma$, where σ acts on the total coordinates of the electrons, i.e., $\Omega_{11}^{[1^N]}$ antisymmetrizes any function of N coordinates upon which it acts.

³² W. A. Goddard, III, following paper, Phys. Rev. 157, 93 (1967).

ferent orbitals have been assigned to α positions there are just m orbitals left to assign to β spin. Hence, every nonzero $\Omega_{11}^{[1^N]}(\tau\Phi)\chi$ can be written as $\Omega_{11}^{[1^N]}(\tau_a\tau_b\Phi)\chi$, where τ_a permutes only electrons with α spin and τ_b permutes only electrons with β spin. But $\tau_a\tau_b\chi=\chi$ and $\Omega_{11}^{[1^N]}(\tau_a\tau_b\Phi)(\tau_a\tau_b\chi)=\zeta_{\tau_a\tau_b}\Omega_{11}^{[1^N]}\Phi\chi$; hence [using Eq. (C2) of Appendix C of I],

$$G_i^\mu\Phi\chi=(N!/(\Theta^\mu)\Omega_{11}^{[1^N]}[(O_{ii}^\mu\Phi)\chi]=[N!/(\Theta^\mu)^2] \\ \times \sum_{\tau} U_{ii\tau} \zeta_{\tau} \Omega_{11}^{[1^N]}\Phi\chi = \text{const} \Omega_{11}^{[1^N]}\Phi\chi.$$

However, $\Omega_{11}^{[1^N]}\Phi\chi$ is just the Slater determinant; therefore, for those cases where the Hartree-Fock wave function is an eigenfunction of \hat{S}^2 , the Hartree-Fock wave function is a special case of $G_i^\mu\Phi\chi$ for every i . This means that every GI wave function will, in general, have a lower energy than the Hartree-Fock energy.

APPENDIX B: SPIN-POLARIZED HARTREE-FOCK AND GF WAVE FUNCTIONS

We show that the spin-polarized extended Hartree-Fock wave function $\Theta_l\alpha\Psi$ is equivalent to the GF wave functions $G_j^\mu\Phi\chi$. The Ψ is a product of N spin orbitals, and Θ_l is the projection operator for $S=l$. From I we know that $\sum_i \omega_{ii}^\mu$ projects out just the $S=l$ component (if μ corresponds to l) so we take $\Theta_l = \sum_i \omega_{ii}^\mu$. We write

$$\alpha = \sum_i \zeta_{it} = \sum_{i=1}^{N!} \zeta_{\tau_i} \tau_i \sigma_i,$$

where σ_i operates on spin coordinates and τ_i operates on spatial coordinates. We also factor each spin orbital into a spatial part and a spin part and take the spin part to be either α or β (i.e., an eigenfunction of \hat{S}_z) and write $\Psi = \Phi\chi$, where Φ is a product of N orbitals and χ is a product of N spin functions (α or β). Now $\alpha t = \zeta_t \alpha$ for any permutation of the spatial-spin coordinates t ; hence, we can choose t_1 to be a permutation which orders χ so that all the α 's appear first and all the β 's last; this form is denoted by χ_1 .

Using $\omega_{ii} = (1/\Theta)\sum_t U_{iit} t$ from I, we obtain

$$\Theta_l \alpha \Phi \chi_1 = \sum_i \omega_{ii} \alpha \Phi \chi_1 \\ = \sum_j \sum_i \omega_{ii} \zeta_{\tau_j} (\tau_j \Phi) (\sigma_j \chi_1) \\ = (1/\Theta) \sum_{i,j,t} \zeta_{\tau_j} U_{iit} (\tau_j \Phi) (t \sigma_j \chi_1).$$

Let $t\sigma_j = \sigma_j t'$ and note that $\sum_i U_{iit}$ is the trace [hence, $\text{tr}(U_i) = \text{tr}(U_\sigma U_\nu U_{\sigma^{-1}}) = \text{tr}(U_\nu U_{\sigma^{-1}} U_\sigma) = \text{tr}(U_\nu)$, i.e., t and t' are elements of the same class and consequently have the same character]. Therefore,

$$\Theta_l \alpha \Phi_1 = \alpha \sum_i \Phi(\omega_{ii} \chi_1).$$

But if χ_1 has $M_s = S$, then from I $\omega_{ii} \chi_1 = \delta_{i\bar{j}} \omega_{\bar{j}\bar{j}} \chi_1$; thus $\Theta \alpha \Phi \chi = \alpha (\Phi \omega_{\bar{j}\bar{j}} \chi_1)$. But from Appendix C of I, $\alpha (\Phi \omega_{\bar{j}\bar{j}} \chi_1) = (\Theta/N!) G_f(\Phi \chi_1)$, where $\Theta/N! = 1/f$ is just a constant; hence, $\Theta \alpha \Phi \chi_1 = (\Theta/N!) G_f \Phi \chi$. That is, the spin-polarized extended Hartree-Fock wave function is equivalent to the GF wave function.

APPENDIX C: SPATIAL SYMMETRY FOR N ELECTRONS

For N particles and a nondegenerate $G_r \Phi \chi$, let $\Phi = \phi_1 \phi_2 \cdots \phi_N$ and consider the ϕ_i to be linearly independent. If $R G_r \Phi \chi = C_R G_r \Phi \chi$, then $R O_{ii} \Phi = C_R O_{ii} \Phi$ since the $\omega_{\bar{r}\bar{i}} \chi$ for different r are linearly independent. Let $R \phi_j = \theta_j + C_j \phi_j'$, where θ_j is a linear combination of the ϕ_j and each ϕ_j' is orthogonal to all of the ϕ_j . We will show that all $C_j = 0$, that is, that the space spanned by the ϕ_j is left invariant under R .

(i) First consider the ϕ_j' to be linearly independent. Every permutation of S_N occurs in O_{ii} with nonzero coefficient, so consider the following term in $R O_{ii} \Phi$, $\phi_1' \phi_2' \cdots \phi_N'$. This term appears just once in $R O_{ii} \Phi$ and is orthogonal to all terms in $O_{ii} \Phi$, so one of the coefficients, say C_N , can be required to be zero. Then consider the term $\phi_1' \phi_2' \phi_3' \cdots \phi_{N-1}' \theta_N$; since $\theta_N \neq 0$, one coefficient, e.g., C_{N-1}' , must be zero. Continuing, we find that all the $C_i = 0$, and thus the space spanned by the ϕ_i is invariant under R .

(ii) Now consider the case where there are $N-1$ linearly independent ϕ_i' and where the set ϕ_2', \cdots, ϕ_N' is linearly independent. Expand ϕ_1' as

$$\phi_1' = \sum_{j=2}^N d_j \phi_j'$$

and consider the terms of $R O_{ii} \Phi$ yielding $\phi_2' \phi_2' \phi_3' \phi_4' \cdots \phi_N'$. The coefficient is $C_1 C_2 d_2 [1 + U_{ii(1,2)}] C_3 C_4 \cdots C_N$. If we assume $C_1 C_2 d_2 [1 + U_{ii(1,2)}] \neq 0$, then $C_3 C_4 \cdots C_N = 0$; continuing as in (i), we can show that $C_3 = C_4 = \cdots = C_N = 0$ and hence that $C_1 C_2 d_2 [1 + U_{ii(1,2)}] = 0$. Thus if $U_{11(1,2)} \neq -1$, then $C_1 C_2 d_2 = 0$. But if $C_1 = 0$, the nonzero ϕ_i' are linearly independent and we can use (i) to prove that all $C_j = 0$; therefore, take $C_1 \neq 0$. Since $C_1 \neq 0$, at least one d_j and the corresponding C_j must be nonzero; we take $d_2 \neq 0$ and $C_2 \neq 0$. Hence, C_j and C_k are nonzero only if $U_{ii(j,k)} = -1$. Assume C_1, C_2, \cdots, C_k are nonzero and consider the terms in $O_{11} \Phi$, like $\theta_1 \phi_2' \phi_3' \cdots \phi_N'$. If $\theta_1, \theta_2, \cdots, \theta_k$ are linearly independent, this has as coefficient $C_2 C_3 \cdots C_N$ and we can proceed as in (i) to show that all $C_j = 0$. If $\theta_1, \theta_2, \cdots, \theta_k$ are linearly dependent, then since $U_{ii(j,k)} = -1$, the terms in $R O_{jj} \Phi$ containing $\theta_1, \theta_2, \cdots$, and θ_k are zero and hence $R O_{jj} \Phi$ has no term proportional to $O_{jj} \Phi$. Hence the C_1, C_2, \cdots, C_k are all zero.

(iii) If there are only $N-r$ linearly independent ϕ_j' ,

then we proceed as in (ii) except that we know that $O_{ii}\Phi'=0$ for any Φ' with the same orbital more than twice.

This is all quite easy to visualize in Hilbert space; since R must leave all scalar products invariant, the vectors must all move together under R , but since $G_i\Phi X$ is transformed essentially into itself, we can at most

allow rotations within the space spanned by these vectors. Thus, the set of GI orbitals in Φ form a basis for a reducible representation of \mathcal{G} . The reason that we cannot completely reduce this representation is that the GI orbitals are not all eigenfunctions of the same one-electron Hamiltonian (as in the Hartree-Fock method).

Magnetic Hyperfine Structure of Lithium

WILLIAM A. GODDARD, III

Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California

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For the first time a spin-polarized extended Hartree-Fock calculation on a three-electron system, Li, is reported. The calculations are discussed with primary emphasis on the hyperfine splitting spectrum which is determined by the spin density at the nucleus, $Q(0) = \langle \psi | \sum_i s_z(i) \delta(r_i) | \psi \rangle / S$. We calculate $Q(0)$ for the ground state to be 0.2403, as compared with the experimental value of 0.2313.

INTRODUCTION

THERE has been a great deal of interest in constructing electronic wave functions for atoms accurate enough to predict the effective magnetic field at the nucleus due to the electrons.¹⁻⁴ The difficulty has been in obtaining accurate values for the part of the field due to the Fermi contact term¹⁻⁴

$$\mathbf{H}_c = (8\pi/3)g\mu_0 Q(0)\mathbf{S},$$

where

$$Q(0) = \langle \psi | \sum_i s_z(i) \delta(r_i) | \psi \rangle / S \quad (1)$$

is called the spin-density at the nucleus. For example, for the ground states of N and Mn^{++} the Hartree-Fock wave function leads to $\mathbf{H}_c = 0$ in flagrant disagreement with experiment.^{3,5} Similarly, the large negative magnetic fields at the nuclei of some transition-metal atoms, as observed by Mössbauer experiments on metals, are inconsistent with the predictions using Hartree-Fock wave functions.^{1,2}

Probably the most widely used method to improve upon the Hartree-Fock method for this property has been the unrestricted Hartree-Fock (UHF) method.^{4,6-9}

This method has had some success⁸ but does not seem to account for the \mathbf{H}_c in B^{10} , N^{11} , O^{10} , F^{12} , P^{13} , or in the transition element atoms in metals.² In the UHF method the wave function is approximated by a single Slater determinant, as in the Hartree-Fock method, but we now allow different orbitals for the different spins. Since the inner-shell or core states are not exactly spin paired, they can contribute to the spin density at the nucleus, $Q(0)$. A glaring flaw in this approach^{3,7,10-15} is that the UHF wave function is not an eigenfunction of S^2 . One could, of course, project out from the UHF wave function the components of incorrect multiplicity, but although the UHF orbitals are optimum for the Slater determinant, they will not be optimum for the projected wave function.¹⁵

It has long been known that the proper solution is to optimize the orbitals *after* the projection rather than *before*.^{1,3,11,15,16} Unfortunately, this procedure, the spin-

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