

inert component, it is easy to calculate from the equilibrium conditions that

$$(\alpha_T)_{\text{chem}} = \frac{1}{2}[\alpha_d(1 - \alpha_d)](\Delta H/RT).$$

But, we find from Eq. (9), that the chemical part of α_T reduces to this form provided either $2D_{23} = D_{13}$ or $D_{12} = 0$. The first of these conditions mean that the diffusion cross sections are such that there is no "drag." The second condition means there is no flux of reacting species and hence again the absence of drag.

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Improved Quantum Theory of Many-Electron Systems. III. The GF Method*

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A general method of calculating accurate and useful many-electron wavefunctions for atoms and molecules has previously been described. This general method besides achieving lower energies than do the Hartree-Fock and unrestricted Hartree-Fock methods still yields an independent particle interpretation of the many-electron wavefunction, correctly describes dissociation of molecules and solids, and can be used on systems of any total spin. There are several possible approaches for the general method; here we concentrate on one of these, GF method, which is equivalent to optimizing the orbitals in the unrestricted Hartree-Fock method *after* spin projection rather than before. The detailed equations (the GF equations), for the GF method are derived here for all values of total spin and number of particles.

INTRODUCTION

In a previous paper¹ (called II) we derived a general method of obtaining accurate many-electron wavefunctions. This method, which is called the GI method, is more accurate than and removes several defects of the Hartree-Fock method but at the same time still allows an independent-particle interpretation of the many-electron wavefunction. We emphasized in II how important the retention of the independent-particle interpretation is to the understanding of the nature of molecules and solids. In this paper we continue the development for a very important case (applicable for any number of electrons, any total spin, and any nuclear configuration) of the general method by deriving all the equations in detail.

We are interested in obtaining accurate but useful approximate many-electron wavefunctions for atoms and molecules. We approximate the Hamiltonian for such a system by fixing the nuclei and neglecting all relativistic terms and spin interactions, i.e., we consider

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

where $V(i)$ is the potential due to the nuclei, $h(i) = -\frac{1}{2}\nabla_i^2 + V(i)$ is a one-electron operator, and $g(i, j) = r_{ij}^{-1}$ is a two-electron operator. For this Hamiltonian the electronic wavefunction must be an eigenfunction of total spin and must satisfy the Pauli principle. In a previous paper² (called I) we defined an operator G_i^{γ} which upon operating on *any* function of the spatial and spin coordinates of N electrons yields a function which is an eigenfunction of \hat{S}^2 and which satisfies the Pauli principle. In addition we showed that the exact many-electron wavefunction can be written as

$$\psi_{\text{exact}}^{S,M}(1, \dots, N) = G_i^{\gamma S}[\Phi(1, \dots, N)\chi(1, \dots, N)], \quad (2)$$

where

$$\chi = \alpha(1)\alpha(2)\cdots\alpha(\nu)\beta(\nu+1)\cdots\beta(N), \quad (3)$$

α and β are eigenfunctions of \hat{s}_z with eigenvalues $+\frac{1}{2}$ and $-\frac{1}{2}$, respectively, and Φ is some function of the spatial coordinates of the N electrons. In II we considered a function $G_i^{\gamma S}\Phi\chi'$, where Φ is restricted to be a product of N one-electron functions, and derived the equations which these one-electron functions (orbitals) must satisfy in order to obtain the best (lowest energy) approximation to the exact many-electron wavefunction. We found that such a wavefunction leads to an independent particle interpretation of the many-

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† Contribution No. 3514.

¹ W. A. Goddard III, Phys. Rev., **157**, 81 (1967), hereafter called II.

² W. A. Goddard III, Phys. Rev., **157**, 73 (1967), hereafter called I.

electron wavefunction and has a lower energy than does the Hartree-Fock wavefunction. In addition some serious defects in the Hartree-Fock method (e.g., improper dissociation, nonlocalized orbitals) were discussed which need not occur for the new wavefunctions. There are actually several linearly independent functions $G_i^{\gamma^a}\Phi_\chi$ of the same spin which we could have used. However one of these, the case of $i=f^\gamma$ (the last in the standard way of numbering), is equivalent to optimizing a Slater determinant after spin projection (rather than before) and hence is a natural generalization of the Hartree-Fock and unrestricted Hartree-Fock methods, where now nonorthogonal orbitals are allowed but the resulting many-electron wavefunction is an eigenfunction of \hat{S}^2 . In addition for $i=f^\gamma$ the resulting equations are more practicable to solve at the present time, and furthermore, this case seems able to account for a large amount of molecular correlation energy. For this reason we will consider wavefunctions of the form $G_f^{\gamma^s}\Phi_\chi$ and derive the explicit coefficients for the equations which lead to the best such $G_f\Phi_\chi$ wavefunction.

I. THE GF EQUATIONS

The GF method consists of finding the best approximation to the exact wavefunction (2) by a function of the form

$$G_f^{\gamma^s}\Phi_\chi,$$

where χ is a product of one-electron spin functions as in (3), Φ is restricted to be a simple product of one-electron spatial functions (i.e., orbitals), the total spin projection is S , and γ corresponds to the total spin.³

The tableau S_f^γ is shown in Fig. 1, where the total spin S is given by $S=n-\frac{1}{2}N$. The many-electron wavefunction changes sign under interchange of any two of the first n orbitals and also under interchange of any two of the last $m=N-n$ orbitals. We call each of these sets an antisymmetric set. In Appendix A we show that the energy is left invariant under the transformation which orthogonalizes each of these two sets of orbitals; hence, we may take

$$\begin{aligned} \Phi(1\cdots N) &= \phi_{1a}(1)\phi_{2a}(2)\cdots\phi_{na}(n) \\ &\times \phi_{1b}(n+1)\phi_{2b}(n+2)\cdots\phi_{mb}(N), \end{aligned} \quad (4)$$

where the set $\{\phi_{1a}\}$ is orthonormal as is the set $\{\phi_{1b}\}$.

Since we want the best possible $G_f(\Phi_{\text{prod}}\chi)$ type function we require that the total energy

$$\begin{aligned} E &= \langle G_f^{\gamma}\Phi_\chi | H | G_f^{\gamma}\Phi_\chi \rangle / \langle G_f^{\gamma}\Phi_\chi | G_f^{\gamma}\Phi_\chi \rangle \\ &= \langle \Phi | HO_{ff}^\gamma | \Phi \rangle / \langle \Phi | O_{ff}^\gamma \Phi \rangle \end{aligned} \quad (5)$$

be stationary with respect to variation of any of the

³ We often omit the superscript γ in the following.

$$S_f^\gamma = \begin{array}{|c|c|} \hline 1 & n+1 \\ \hline 2 & n+2 \\ \hline 3 & \vdots \\ \hline \vdots & N \\ \hline n & \\ \hline \end{array}$$

FIG. 1. The S_f^γ tableau.

orbitals of Φ . That is we require^{4,5}

$$\begin{aligned} \delta \langle \Phi | (H-E)\Theta O_{ff} | \Phi \rangle - \sum_{i,j=1}^n \epsilon_{ij}^a \delta \langle \phi_{ia} | \phi_{ja} \rangle \\ - \sum_{i,j=1}^m \epsilon_{ij}^b \delta \langle \phi_{ib} | \phi_{jb} \rangle = 0 \end{aligned} \quad (6a)$$

for all $\delta\phi_i$. The first term is real; hence we can form the difference between the above equation and its complex conjugate to obtain the result that ϵ^a and ϵ^b are Hermitian.

Now consider the unitary transformation U^a of the a set of orbitals among themselves, $\phi_{ia} = \sum_j \phi'_{ja} U_{ij}^a$. From Appendix A the first term of (6a) becomes $\delta \langle \Phi' | (H-E)\Theta O_{ff} | \Phi' \rangle$. The second term becomes

$$\sum_{ijkl} U_{ki}^{a^*} \epsilon_{ij}^a U_{jl}^a \delta \langle \phi'_{ka} | \phi'_{la} \rangle,$$

and since ϵ^a is Hermitian, a U^a can always be found to diagonalize ϵ^a . By similarly considering a transformation U^b we obtain

$$\begin{aligned} \delta \langle \Phi | (H-E)\Theta O_{ff} | \Phi \rangle - \sum_k \epsilon_{kk}^a \delta \langle \phi_{ka} | \phi_{ka} \rangle \\ - \sum_k \epsilon_{kk}^b \delta \langle \phi_{kb} | \phi_{kb} \rangle = 0 \end{aligned} \quad (6b)$$

(where the primes have been dropped) which is the same as the equation we dealt with in II and hence leads to

$$\langle \delta_k \Phi | (H-E)\Theta O_{ff} | \Phi \rangle = \epsilon_{kk} \langle \delta\phi_k | \phi_k \rangle \quad (6c)$$

as in II, where $\delta_k \Phi$ is the same as Φ but with ϕ_k replaced by $\delta\phi_k$. Since (6c) is satisfied for all $\delta\phi_k$, the coefficient of $\delta\phi_k$ must be zero. Thus we obtain

$$\begin{aligned} H^{ka} \phi_{ka} &= \epsilon_{kk}^a \phi_{ka} & k=1, 2, \dots, n, \\ H^{bb} \phi_{kb} &= \epsilon_{kk}^b \phi_{kb} & k=1, 2, \dots, m, \end{aligned} \quad (7)$$

where H^{ka} is given by Eqs. (11) of II⁶ (in this case the sums over v and u in II are for vb and ub since va and ua

⁴ We use $\langle \psi_1 | H | \psi_2 \rangle$ merely to indicate the integral $\int \psi_1^* H \psi_2 dx$. Whether the integral is N dimensional or of some other dimension is determined by the dimension of ψ .

⁵ For later convenience we have multiplied (6a) by a constant $\Theta^\gamma = N!/f^\gamma$, where f^γ is the degree of the γ irreducible representation of the symmetric group S_N .

⁶ Equation (11) of II is just the operator equivalent to the matrix $H_{\mu\nu}^{ka}$ given in Eq. (10) below.

are orthogonal to ka) and similarly for H^{kb} . Taking a in terms of a finite basis set, we obtain⁷ Roothaan expansion

$$\begin{aligned} \phi_{ia} &= \sum_{\mu} \chi_{\mu} C_{\mu i}^a, & H_{\mu\nu}^{ka} C_{\nu k}^a &= S_{\mu\nu} C_{\nu k}^a \epsilon_{kk}^a, \\ \phi_{ib} &= \sum_{\mu} \chi_{\mu} C_{\mu i}^b, & H_{\mu\nu}^{kb} C_{\nu k}^b &= S_{\mu\nu} C_{\nu k}^b \epsilon_{kk}^b, \end{aligned} \quad (8)$$

where $S_{\mu\nu} = \langle \chi_{\mu} | \chi_{\nu} \rangle$ and⁸

$$\begin{aligned} H_{\mu\nu}^{ka} &= \{ \langle \mu | h | \nu \rangle D_{ka}^{ka} + \sum_{s \neq ka; \nu} \langle \mu | h | s \rangle \langle vb | \nu \rangle D_{s,ka}^{ka, vb} + \sum_{i, u} \langle \mu | ub \rangle \langle i | h | \nu \rangle D_{ub,ka}^{ka, i} \\ &+ \sum_{i, u, v; s \neq ka} \langle \mu | ub \rangle \langle i | h | s \rangle \langle vb | \nu \rangle D_{ub, s, ka}^{ka, i, vb} + \sum_{i, s} [\langle \mu, i | g | \nu, s \rangle D_{ka, s}^{ka, i} + \langle \mu, i | g | s, \nu \rangle D_{s, ka}^{ka, i}] \\ &+ \sum_{i, v; s, t \neq ka} \langle \mu, i | g | s, t \rangle \langle vb | \nu \rangle D_{s, t, ka}^{ka, i, vb} + \sum_{i, j, t; u} \langle \mu | ub \rangle \langle i, j | g | \nu, t \rangle D_{ub, ka, t}^{ka, i, j} \\ &+ \frac{1}{2} \sum_{i, j; u, v; s, t \neq ka} \langle \mu | ub \rangle \langle vb | \nu \rangle \langle i, j | g | s, t \rangle D_{ub, ka, s, t}^{ka, vb, i, j} - E \sum_{u, v} \langle \mu | ub \rangle \langle vb | \nu \rangle D_{ub, ka}^{ka, vb} \}. \end{aligned} \quad (10)$$

The first- and second-order reduced spatial density matrices,⁹ D_j^i and D_{ki}^{ij} , are derived in Appendix B. Now it would appear that $H_{\mu\nu}^{ka}$ is a function of k ; however, we show in Appendix C that terms may be added to each $H_{\mu\nu}^{ka}$ to obtain a new function $H_{\mu\nu}^a$ which is not a function of k but which is such that the solutions of (10) are also eigenfunctions of H^a and similarly for H^b . This is analogous to the procedure of changing the Hartree-Fock equations to a form which is independent of k by adding the self-repulsion term to both the Coulomb and exchange terms.

Thus we obtain

$$\begin{aligned} H_{\mu\nu}^a C_{\nu k}^a &= S_{\mu\nu} C_{\nu k}^a \epsilon_{kk}^a, \\ H_{\mu\nu}^b C_{\nu k}^b &= S_{\mu\nu} C_{\nu k}^b \epsilon_{kk}^b, \end{aligned} \quad (11)$$

where $H_{\mu\nu}^a$ is defined as

$$\begin{aligned} H_{\mu\nu}^a &\equiv \{ \langle \mu | h | \nu \rangle \mathfrak{D}_a^a + \sum_{i, v} [\langle \mu | h | i \rangle \langle vb | \nu \rangle \mathfrak{D}_{i, a^a, vb} + \langle \mu | vb \rangle \langle i | h | \nu \rangle \mathfrak{D}_{vb, a^a, i}] \\ &+ \sum_{u, w} \langle \mu | ub \rangle \langle vb | \nu \rangle \sum_{i, j} \langle i | h | j \rangle \mathfrak{D}_{ub, a, j^a, vb, i} + \sum_{i, j} [\langle \mu, i | g | \nu, j \rangle \mathfrak{D}_{a, j^a, i} + \langle \mu, i | g | j, \nu \rangle \mathfrak{D}_{j, a^a, i}] \\ &+ \sum_{i, j, t; v} [\langle \mu, i | g | j, t \rangle \langle vb | \nu \rangle \mathfrak{D}_{j, a, i^a, vb, i} + \langle \mu | vb \rangle \langle j, t | g | \nu, i \rangle \mathfrak{D}_{vb, a, i^a, j, t}] \\ &+ \sum_{u, v} \langle \mu | ub \rangle \langle vb | \nu \rangle \sum_{i < j; s, t} \langle i, j | g | s, t \rangle \mathfrak{D}_{ub, a, s, t^a, vb, i, j} - E \sum_{u, v} \langle \mu | ub \rangle \langle vb | \nu \rangle \mathfrak{D}_{ub, a^a, vb} \}, \end{aligned} \quad (12)$$

and similarly for $H_{\mu\nu}^b$. The \mathfrak{D} matrices in (12) are derived in Appendix C in terms of the D matrices. This transformation of the $H_{\mu\nu}^{ka}$ to a form independent of k is possible because of the antisymmetric character of the density matrices with respect to the a indices and with respect to the b indices. In the same way, the $H_{\mu\nu}(k)$ of II for $G_r^i \Phi \chi$ can be transformed so that there is one H operator for each antisymmetric set of states in S_i^r . Similarly, the integrodifferential Eqs. (7) can be transformed such that H^a and H^b are used rather than H^{ka} and H^{kb} .

Equations (11) are solved iteratively by guessing the coefficients $\{C_{\nu k}^a\}$ and $\{C_{\nu k}^b\}$, calculating the $H_{\mu\nu}^a$ and $H_{\mu\nu}^b$, and then solving the eigenvalue problem (11) for the new $\{C_{\nu k}^a\}$ and $\{C_{\nu k}^b\}$. This is continued until the process converges.

As discussed in II the Eqs. (7) defining the orbitals which when substituted in Φ yield the lowest-energy $G_r^i \Phi \chi$ type wavefunction are called the GF equations and the best orbitals are called the GF orbitals. Equations (11) which are approximations to the GF equations will be called the GFR equations (to denote the approximation obtained by taking a Roothaan expansion of the orbitals) when it is necessary to distinguish

⁷ We use the Einstein summation convention for Greek subscripts.

⁸ No terms like $\langle va | \nu \rangle$ and $\langle \mu | va \rangle$ appear since $\langle va | ka \rangle = \delta_{vk}$ and hence these terms vanish from (5).

⁹ The spatial density matrices are $D^{-1} D_j^i$ and $D^{-1} D_{ki}^{ij}$, where D is defined in Appendix B. Thus the D_j^i and D_{ki}^{ij} are denoted as reduced spatial density matrices. If from the context it is clear that D_j^i and D_{ki}^{ij} are being discussed, they may be referred to as density matrices.

them from the exact GF equations; otherwise (11) will also be called the GF equations. The solutions to (11) will generally be referred to as the GF orbitals. Note that the electronic energy is expressed in terms of D matrices in Appendix B. Next we will consider a transformation which simplifies the evaluation of the H^a and H^b matrices.

II. A USEFUL TRANSFORMATION ON THE GF ORBITALS

Consider the matrix $S^{AB}(i, j) \equiv \langle \phi_{ia} | \phi_{jb} \rangle$. By considering the Hermitian matrices $\sum_j S^{AB*}(j, i) S^{AB}(j, k)$ and $\sum_j S^{AB*}(i, j) S^{AB}(k, j)$, one can show that a unitary transformation, U^a , of the a set of orbitals among themselves and another unitary transformation, U^b , of the b set of orbitals among themselves can always be found such that S^{AB} is diagonalized.^{10,11} This transformed set of orbitals is quite convenient because in the case of diagonal S^{AB} the expressions for D and \mathfrak{D} become very much simpler since most terms are zero and the remaining ones involve products rather than determinants. We will now show that H^a and H^b are left invariant under the transformation diagonalizing S^{AB} . Every place where H^a depends on some orbital, say ϕ_{ja} , it involves a factor $\phi_{ja}^* \phi_{ja}$ and in every case there is a sum over all j . But

$$\sum_j \phi_{ja}^* \phi_{ja} = \sum_{klj} \phi'_{ka} \phi'_{la} U_{kj} U_{lj}^a = \sum_j \phi'_{ja} \phi'_{ja}$$

is left invariant under unitary transformations. In addition those terms which involve two or more such factors, say $\phi_{ja}^* \phi_{ka} \phi_{ja} \phi_{ka}$ always have determinants which yield zero for the case $j=k$; hence the sums may be taken independently. A similar result occurs for the b orbitals. Thus the H^a and H^b are functions only of the quantities¹²

$$\rho_a(x, x') = \sum_{j=1}^n \phi_{ja}(x') \phi_{ja}^*(x)$$

and

$$\rho_b(x, x') = \sum_{j=1}^m \phi_{jb}(x') \phi_{jb}^*(x)$$

and are invariant under the unitary transformations U^a and U^b . Therefore, the H^a and H^b can be evaluated for the set of transformed orbitals for which S^{AB} is diagonal. However, the eigenfunctions of H^a and H^b need not yield a diagonal S^{AB} since no such constraint is imposed on the variation of the orbitals. If such a

¹⁰ A. T. Amos and G. G. Hall, Proc. Roy. Soc. (London) **A263**, 483 (1961). The proof is on pp. 493-494. This theorem is also stated by P.-O. Löwdin, J. Appl. Phys. Supp. **33**, 251 (1962).

¹¹ I thank Dr. R. M. Pitzer for first suggesting that this transformation might be useful.

¹² P.-O. Löwdin, Advan. Chem. Phys. **2**, 207 (1959), has pointed out that for the case of a spin-projected Slater determinant the fundamental invariants are ρ_a and ρ_b .

constraint were imposed, then we should require new Lagrange multipliers; thus (7) and (11) would not be pseudoeigenvalue equations, and we would lose the justification of our independent particle interpretation as presented in II. All of the \mathfrak{D} required for (12) are explicitly evaluated in Appendix E for the case of diagonal S^{AB} .

III. RELATION TO OTHER METHODS

In II we showed that the spin-polarized extended Hartree-Fock method of Löwdin can be put into a form which is equivalent to the GF method. As was pointed out in II a prime advantage of the GF method is that the spin integrations are trivially simple to perform so that the important spatial relationships become clear. The result is that one quickly obtains explicit equations for actually applying the GF method, whereas although the spin-polarized extended Hartree-Fock method was suggested in 1955, explicit equations had been obtained only for the case of two electrons.

Apparently there are no other methods which improve upon the Hartree-Fock wavefunction while retaining the proper symmetry properties and also yield an independent-particle interpretation; however, some other methods do yield lower energies than the Hartree-Fock method. The unrestricted Hartree-Fock (UHF) method¹³ uses a single Slater determinant but allows the orbitals of α spin to be different than the orbitals of β spin. However, the wavefunction is not an eigenfunction of total spin and yields a higher energy for the ground state than does the GF method. Since the UHF wavefunction is not an eigenfunction of total spin, it does not behave similarly to the exact wavefunction, and we cannot be sure that results from the UHF method are reliable unless we compare with wavefunctions having the proper spin symmetry. It has been suggested that the best orbitals be obtained using the UHF method and the proper spin component then projected out in order to obtain an approximate wavefunction with the correct symmetry. Since in this case the orbitals are optimized for the wrong wavefunction, we do not obtain the best orbitals or even orbitals which can be given an independent particle interpretation; however, we might be able to have more confidence in the predictions obtained with the projected wavefunction. As was shown in II the projected UHF wavefunction is of the GF form so that the GF method is equivalent to optimizing the orbitals *after projection rather than before*.

So far we have had in mind methods suitable for *ab initio* calculations; an approximate method which is important in considering π -electron systems in alternate hydrocarbons is the alternate molecular orbital (AMO)

¹³ J. A. Pople and R. K. Nesbet, J. Chem. Phys. **22**, 571 (1954); A. T. Amos and G. G. Hall, Proc. Roy. Soc. London **A263**, 483 (1961); R. K. Nesbet, Rev. Mod. Phys. **33**, 28 (1961).

method which was originally suggested by Löwdin.¹⁴ We presume that the π electrons can be described independently of the σ electrons, we expand the Hartree-Fock orbitals in a Roothaan basis set consisting of one p_z orbital on each of the N carbon atoms, and we assume that the spatial symmetry group is C_{Nv} . In this case the set of Roothaan basis functions transforms into a set of symmetry functions with each irreducible representation occurring once so that the combinations are essentially determined by symmetry. Hence if N is even, $N=2n$, just n of these π -electron molecular orbitals are occupied in the Hartree-Fock wavefunction. Each of the n unoccupied orbitals corresponds to one of the n occupied orbitals in such a way that mixing in of the unoccupied orbitals splits the Hartree-Fock orbitals into pairs so that the members of a pair tend to have maximum amplitudes near different atoms. Löwdin proposed that the Hartree-Fock orbitals be allowed to split in this way but that his projection operator be used to obtain an eigenfunction of total spin. Apparently the AMO method is able to account for a large portion of the improvement obtained by a general limited¹⁵ configuration interaction. In spite of some success the AMO method as described is based on rather crude approximations. In particular; the basis set used is the smallest possible such set; it has been found from *ab initio* calculations on smaller molecules that for such sets even a full limited configuration-interaction calculation using the unoccupied Hartree-Fock orbitals might yield a poorer energy than the exact Hartree-Fock calculation. The molecular spatial symmetry group is not C_{Nv} for most molecules of interest; the real symmetry group is usually much smaller which means that the Hartree-Fock orbitals and the unoccupied orbitals may interact in a more complicated way.

The AMO wavefunction is just a special case of the GF wavefunction and although the removal of any of the above restrictions could cause problems in the AMO method, the GF method should handle the unrestricted problem quite well. In addition the orbitals obtained using the GF method can be given an independent-particle interpretation.

We recall from II that there are several alternative GI methods. It may seem somewhat arbitrary to select one of these over the others for calculation of wavefunctions. But bear in mind that *all* of the GI methods yield better energies than the Hartree-Fock wavefunctions and that the *exact* wavefunction can always be written as $G_i\Phi\chi$ for *one* specific i (where Φ is a complicated function of the spatial coordinates). Hence,

¹⁴ (a) R. Pauncz, J. deHeer, and P.-O. Löwdin, *J. Chem. Phys.* **36**, 2247, 2257 (1962); (b) J. deHeer, *ibid.* **37**, 2080 (1962); (c) R. Pauncz, *ibid.* **37**, 2739 (1962); (d) J. deHeer and R. Pauncz, *ibid.* **39**, 2314 (1963).

¹⁵ Limited CI in this context implies that the only unoccupied MO which can be used are those described by the minimum basis set (a p_z orbital on each center).

each of the GI methods forms a rather well-defined approximation to the exact wavefunction and each could be made to approximate the exact wavefunction arbitrarily well by allowing Φ to be a sum of terms rather than a single product.

Some of the features of the GF method are: (i) the process of optimizing a general spin-projected Slater determinant corresponds to the GF method; (ii) the exact wavefunction can be written in a rather well defined configuration interaction form; (iii) it is far simpler computationally than the other GI methods and appears practicable for most molecular systems which have been treated by the Hartree-Fock method; (iv) it appears to do especially well at removing molecular correlation energy (as compared to improving the atomic distribution) so that the description of bonding processes may be as accurate as that yielded by other GI methods; (v) because of the lack of required orthogonality conditions for general GI wavefunctions, the GI methods other than the GF method do not retain the sharp shell structure obtained with the Hartree-Fock method and retained in the GF method; (vi) even the GF method removes such disadvantages of the Hartree-Fock method as the improper description of spin distribution in nonsinglet systems; and (vii) the GF wavefunction has more antisymmetry conditions among the orbitals than for any other GI wavefunction; hence it is the most appropriate for describing systems such as metals in which electron-electron repulsion is most significant.

IV. SUMMARY AND DISCUSSION

We have derived the detailed equations for obtaining the best approximation to the exact eigenfunctions of (1) by $G_i\Phi\chi$, where Φ is a single product of one-electron functions. The GF method leads to better energies than the Hartree-Fock and UHF methods and yet the calculations are still practicable. Not only does the GF method improve significantly upon the Hartree-Fock method for the equilibrium configuration of molecules, but the GF method correctly describes dissociation so that for large separations the improvement over the Hartree-Fock case is enormous. The result is that the percentage difference between the GF energy and the exact energy is only a slight function of the internuclear coordinates so that the GF method can be expected to yield an accurate shape for the potential surface (of the interaction of atoms). This should make the GF method valuable in studying chemical reactions and molecular scattering. In addition this smoothly varying error makes the GF wavefunction an appropriate zero-order function for a perturbation analysis. Although such an analysis is much more complicated than one using the Hartree-Fock wavefunction, the Hartree-Fock wavefunction may not be at all useful at large internuclear distances in a perturbation scheme.

In addition to improvements in accuracy the GF wavefunction yields an independent-particle interpretation of the many-electron wavefunction which is more closely related to chemical concepts than would be allowed by the Hartree-Fock method. This interpretation is especially cogent for diatomic molecules. By studying the changes in the GF orbitals as a function of internuclear distances for the diatomic molecules, we may hope to learn a great deal concerning the processes involved in binding. Such a study could not be made with the Hartree-Fock method because of the improper dissociation.

The above considerations were mainly concerned with the molecular ground state; the GF method should also be of greater value for dealing with excited states than the Hartree-Fock method. The reason is that the Hartree-Fock method is biased—it treats some states rather uniformly as a function of internuclear distance (even dissociating properly) and for other states the error may increase astronomically as, say, the internuclear distances increase. The result is that a diagram of Hartree-Fock energy for the various excited electronic states as a function of internuclear distance may have all sorts of artificial crossings and mixed-up asymptotic behavior. Since the GF wavefunctions will generally change properly with distance, we can hope for a big improvement in dealing with such problems.

In addition, nonsinglet states of atoms and molecules are allowed to have polarized cores (since the doubly occupied orbitals restriction is removed); hence, we expect good values for the spin density at the nucleus (this has already been demonstrated¹⁶ by calculations on Li).

APPENDIX A

Here we show that the total energy is left invariant under the transformation orthogonalizing the orbitals corresponding to an antisymmetric set of indices.

Consider a set, A , of indices, $\{j_1, j_2, \dots, j_n\}$ for which $O_{ri}(j_p, j_q) = -O_{ri}$ for all $p, q \leq n$ for which $p \neq q$ (such a set as A is referred to as an antisymmetric set). If some transformation S is made upon those orbitals in Φ corresponding to these indices,

$$\phi_i = \sum_k S_{ik} \phi'_k, \quad (\text{A1})$$

then

$$O_{ri}\Phi = (\det S) O_{ri}\Phi', \quad (\text{A2})$$

where Φ' contains the primed orbitals in place of the unprimed ones.

The proof is as follows:

$$O_{ri}\Phi = \sum_{k_1, k_2, \dots, k_n} S_{1k_1} S_{2k_2} \dots S_{nk_n} \times O_{ri} \phi'_{k_1} \phi'_{k_2} \dots \phi'_{k_n} \phi_{n+1} \dots \phi_N,$$

¹⁶ W. A. Goddard III, Phys. Rev. 157, 93 (1967).

where for convenience the antisymmetric set of indices taken as 1 to n and the other indices as $n+1, \dots, N$. If

$$\Phi'_k \equiv \phi'_{k_1} \dots \phi'_{k_n} \phi_{n+1} \dots \phi_N$$

contains one of the antisymmetric indices twice, say $k_p = k_q$, then

$$O_{ri}\Phi'_k = \frac{1}{2} O_{ri} [\epsilon + (p, q)] \Phi'_k = 0;$$

hence, we can presume that each of the antisymmetric indices occurs once and only once in \mathbf{k} so that $\Phi'_k = \tau \Phi'$ where $\Phi' = \phi'_1 \phi'_2 \dots \phi'_n \phi_{n+1} \dots \phi_N$ and τ operates on the first n indices. But $O_{ri}\tau = \zeta_\tau O_{ri}$ so that

$$O_{ri}\Phi = \sum_{\tau \in \mathfrak{S}_n} \zeta_\tau S_{1r(1)} S_{2r(2)} \dots S_{nr(n)} O_{ri}\Phi' = (\det S) O_{ri}\Phi'.$$

The transformation in (A1) does not change expectation values since $G_i \tau \Phi \chi = (\det S) G_i \tau \Phi \chi$ and hence the $(\det S)^2$ is cancelled by the normalization denominator. In particular we may let S be the transformation orthogonalizing the antisymmetric set of orbitals to show that the energy is unchanged by this orthogonalization.

APPENDIX B

In this section we evaluate the quantities needed to obtain the expectation values for one- and two-electron spatial operators with $G_i \tau \Phi \chi$ type wavefunctions. If F is such an operator, then from I and II

$$\langle F \rangle = \langle \Phi | F \Theta O_{ff} \tau | \Phi \rangle / \langle \Phi | \Theta O_{ff} \tau | \Phi \rangle,$$

where from I

$$\hat{O}_{ff} \tau = (1/\Theta^\gamma) \sum_{\tau \in \mathfrak{S}_N} U_{ff\tau} \tau^\dagger$$

and the tableau $S_f \tau$ is given in Fig. 1. We need to know the general form for $U_{ff\tau}$. From Appendix E of I we can always write $\tau = \tau_a \tau_b \tau_r$ where τ_a permutes letters $\leq n$, τ_b permutes letters $> n$, and τ_r is a product of r disjoint transpositions each involving a letter $\leq n$ and a letter $> n$ [e.g., $\tau_2 = (1, n+3)(5, n+1)$ for a case where $n \geq 5$]. In this case, from Eq. (E2) of I,

$$U_{ff\tau} = \zeta_{\tau_a} \zeta_{\tau_b} \binom{n}{r}^{-1},$$

where ζ_τ is the parity of τ and $\binom{n}{r}$ is a binomial coefficient. In the following we take Φ as a product of orbitals as in (4) and presume the a set and the b set to each be orthogonal.

A. The Denominator D

We define

$$D \equiv \Theta^\gamma \langle \Phi | O_{ff} \tau | \Phi \rangle = \sum_{\tau} U_{ff\tau} \langle \Phi | \tau \Phi \rangle. \quad (\text{B1})$$

$$\begin{aligned}
 D &= \sum_{r=0}^m \frac{(r!)^2}{\binom{n}{r}} \sum_{P_r, Q_r} |O_{11}^{[1^r]} s(p_1 a; p_1 b) \dots s(p_r a; q_r b)|^2 \\
 D_{ka, tb}^{ia, ja} &= - \sum_{r=1}^{\binom{n-2}{m-1}} \frac{r!(r+1)!}{\binom{n}{r+1}} \sum_{P_r, Q_r} \{ (ka, ia) O_{11}^{[1^r]} s(p_1 a; q_1 b) \dots \} \times \\
 &\quad \sum_{\substack{l, k \notin P_r \\ l \in P_r \\ t \notin Q_r}} [O_{11}^{[1^{r+1}]} s(tb; ja) s(q_1 b; p_1 a) \dots] \\
 D_{ia, ia}^{ia, ia} &= \sum_{r=0}^{\binom{M-1}{m}} \frac{(r!)^2}{\binom{n}{r}} \sum_{P_r, Q_r} |O_{11}^{[1^r]} s(p_1 a; q_1 b) \dots s(p_r a; q_r b)|^2 \\
 D_{kb, tb}^{ia, ja} &= \sum_{r=0}^{\binom{n-2}{m-2}} \frac{r!(r+2)!}{\binom{n}{r+2}} \sum_{P_r, Q_r} [O_{11}^{[1^{r+2}]} s(kb; ia) s(tb; ja) s(q_1 b; p_1 a) \dots] \times \\
 &\quad \sum_{\substack{l, j \notin P_r \\ k, t \notin Q_r}} [O_{11}^{[1^r]} s(p_1 a; q_1 b) \dots] \\
 D_{ja, ia}^{ia, ia} &= - \sum_{r=1}^{\binom{n-1}{m}} \frac{(r!)^2}{\binom{n}{r}} \sum_{P_r, Q_r} \{ (ja, ia) O_{11}^{[1^r]} s(p_1 a; q_1 b) \dots \} \times \\
 &\quad \sum_{\substack{l \in P_r \\ j \notin P_r}} [O_{11}^{[1^r]} s(q_1 b; p_1 a) \dots] \\
 D_{ia, kb}^{ia, kb} &= \sum_{r=0}^{\binom{n-1}{m-1}} \frac{(r!)^2}{\binom{n}{r}} \sum_{P_r, Q_r} |O_{11}^{[1^r]} s(p_1 a; q_1 b) \dots|^2 \\
 &\quad \sum_{\substack{l \notin P_r \\ k \notin Q_r}} \\
 D_{ia, kb}^{ia, kb} &= \sum_{r=0}^{\binom{n-1}{m-1}} \frac{(r!)^2}{\binom{n}{r+1}} \sum_{P_r, Q_r} |O_{11}^{[1^r]} s(p_1 a; q_1 b) \dots|^2 \\
 &\quad \sum_{\substack{l \notin P_r \\ k \notin Q_r}} \\
 D_{ia, ja}^{ia, ja} &= \sum_{r=0}^{\binom{n-2}{m}} \frac{(r!)^2}{\binom{n}{r}} \sum_{P_r, Q_r} |O_{11}^{[1^r]} s(p_1 a; q_1 b) \dots|^2 \\
 &\quad \sum_{\substack{l, j \notin P_r}} \\
 D_{ia, kb}^{ia, ja} &= - \sum_{r=1}^{\binom{n-1}{m-1}} \frac{(r!)^2}{\binom{n}{r}} \sum_{P_r, Q_r} \{ (kb, jb) O_{11}^{[1^r]} s(p_1 a; q_1 b) \dots \} \times \\
 &\quad \sum_{\substack{l \notin P_r \\ k \in Q_r \\ j \notin Q_r}} [O_{11}^{[1^r]} s(q_1 b; p_1 a) \dots] \\
 D_{ia, ta}^{ia, ja} &= - \sum_{r=1}^{\binom{n-2}{m}} \frac{(r!)^2}{\binom{n}{r}} \sum_{P_r, Q_r} \{ (ja, ta) O_{11}^{[1^r]} s(p_1 a; q_1 b) \dots \} \times \\
 &\quad \sum_{\substack{s, t \notin P_r \\ j \notin P_r}} [O_{11}^{[1^r]} s(q_1 b; p_1 a) \dots] \\
 D_{ia, kb}^{ia, kb} &= \sum_{r=0}^{\binom{n-2}{m-2}} \frac{[(r+1)!]^2}{\binom{n}{r+1}} \sum_{P_r, Q_r} [O_{11}^{[1^{r+1}]} s(ja; kb) s(p_1 a; q_1 b) \dots] \times \\
 &\quad \sum_{\substack{l, j \notin P_r \\ k, t \notin Q_r}} [O_{11}^{[1^{r+1}]} s(tb; ia) s(q_1 b; p_1 a) \dots] \\
 D_{ia, ia}^{ia, ia} &= \sum_{r=0}^{\binom{n-2}{m-1}} \frac{r!(r+1)!}{\binom{n}{r+1}} \sum_{P_r, Q_r} [O_{11}^{[1^{r+1}]} s(ja; sb) s(p_1 a; q_1 b) \dots] \times \\
 &\quad \sum_{\substack{l, j \notin P_r \\ s, t \notin Q_r}} [O_{11}^{[1^{r+1}]} s(tb; ia) s(q_1 b; p_1 a) \dots]
 \end{aligned}$$

FIG. 2. The reduced spatial density matrices.

The τ here operates on the electrons $\tau\Phi(1, 2, 3, \dots) = \Phi(\tau(1), \tau(2), \tau(3), \dots)$ so that $\tau\phi_{i_1}(1)\phi_{i_2}(2)\dots = \phi_{i_1}(\tau(1))\phi_{i_2}(\tau(2))\dots = \phi_{i_{\tau^{-1}(1)}}(1)\phi_{i_{\tau^{-1}(2)}}(2)\dots$. Now we consider the various τ for which $\langle \Phi | \tau\Phi \rangle \neq 0$. Due to the orthogonality among the a states and among the b states, if $\langle \Phi | \tau\Phi \rangle \neq 0$ then either ϕ_{ia} is in the i position of $\Phi' = \tau\Phi$ or else it is in a position $> n$; similarly either ϕ_{ib} is in the $n+i$ position of Φ' or else it is in a position $\leq n$. If τ takes no element $\leq n$ to a position $> n$, then $\langle \Phi | \tau\Phi \rangle \neq 0$ only for $\tau = \epsilon$. If τ takes one element, say i , from a position $\leq n$ to a position $> n$, then it must take one element, say j , from a position $> n$ to a position $\leq n$; and $\langle \Phi | \tau\Phi \rangle \neq 0$ only for $\tau = (i, j)$. If τ takes two ele-

ments, i and j , from positions $\leq n$ to positions $> n$; then it must take two elements, say p and q , from positions $> n$ to positions $\leq n$; and $\langle \Phi | \tau\Phi \rangle \neq 0$ only for $\tau = (i, p)(j, q); (i, j)(i, p)(j, q); (p, q)(i, p)(j, q);$ and $(i, j)(p, q)(i, p)(j, q) = (i, q)(j, p)$. If τ takes r elements (p_1, p_2, \dots, p_r) from positions $\leq n$ to positions $> n$, then it must take r elements (say q_1, q_2, \dots, q_r) from positions $> n$ to positions $\leq n$; and $\langle \Phi | \tau\Phi \rangle \neq 0$ only if $\tau = \tau_a \tau_b \tau_r$ where $\tau_r = (p_1, q_1)(p_2, q_2)\dots(p_r, q_r)$ and τ_a is any permutation of $\{p_1, p_2, \dots, p_r\}$ and τ_b is any permutation of $\{q_1, q_2, \dots, q_r\}$. [The choice of the specific set of r disjoint transpositions for τ_r is arbitrary, the permutations τ_a and τ_b take τ_r through the $(r!)^2$ different such

permutations for which $\langle \Phi | \tau \Phi \rangle \neq 0$.] Hence,

$$D = \Theta^\gamma \langle \Phi | O_{ff} \tau \Phi \rangle = \sum_{r=0}^m \binom{n}{r}^{-1} \sum_{p_1 < p_2 < \dots < p_r; q_1 < q_2 < \dots < q_r} \sum_{\tau_a \tau_b} \zeta_{\tau_a} \zeta_{\tau_b} \langle \phi_{p_1 a} \dots \phi_{p_r a} \phi_{q_1 b} \dots \phi_{q_r b} | \tau_a \tau_b | \phi_{q_1 b} \dots \phi_{q_r b} \phi_{p_1 a} \dots \phi_{p_r a} \rangle.$$

But the integral factors into two integrals, one of which is

$$\langle \phi_{p_1 a} \phi_{p_2 a} \dots \phi_{p_r a} | \tau_a | \phi_{q_1 b} \phi_{q_2 b} \dots \phi_{q_r b} \rangle = S(p_1 a; q_{r-1} b) \dots S(p_r a; q_{r-1} b),$$

where $S(i, j) = \langle \phi_i | \phi_j \rangle$. The sum $\sum_{\tau_a} \zeta_{\tau_a}$ times the above factor is recognized as the determinant of the r -dimensional matrix $S(p_i a; q_j b)$ which from I is written as $r! O_{11}^{r-1} S(p_1 a; q_1 b) \dots S(p_r a; q_r b)$. Thus D is as in Fig. 2. The P_r is an abbreviation for the sum of the p_i from 1 to n such that $p_1 < p_2 < \dots < p_r$ and similarly for Q_r , where a standard order of the p_i and of the q_i is presumed to have been defined. Since $S(i a; j b) = S^*(j b; i a)$ each term in the above sum is real and positive.

B. The First-Order Reduced Spatial Density Matrices D_j^i

We define the coefficient of $\phi_i^*(i) \phi_j(i)$ in¹⁷

$$\Theta^\gamma \int \Phi^*(1, \dots, N) O_{ff} \Phi(1, \dots, N) (dx'_i)$$

as D_j^i and call the resulting matrix the first-order reduced spatial density matrix.⁹ Hence,

$$\Theta^\gamma \int \Phi^* O_{ff} \Phi (dx'_i) = \sum_j \phi_i^*(i) \phi_j(i) D_j^i.$$

The diagonal element D_{ia}^{ia} is derived exactly as was $D = \Theta^\gamma \langle \Phi | O_{ff} \Phi \rangle$ except that the orbital ϕ_{ia} cannot be involved in any of the permutations. The upper limit on r in D_{ia}^{ia} (see Fig. 2) is determined by the maximum sizes of P_r and Q_r which in this case are $n-1$ and m , respectively, since P_r cannot contain i ; the $[\cdot^i]$ indicates that the lower of i and j is to be used as the upper limit of the sum. Now consider D_{ja}^{ia} where $i \neq j$; the general permutation τ for which $\tau \Phi$ has ϕ_{ja} in the ia position and for which $\int \Phi^* \tau \Phi (dx'_{ia}) \neq 0$ can be written $\tau = \tau_2 \tau_a \tau_b \tau_{r-1} \tau_1$, where¹⁸ $\tau_1 = (ia, sb)$ for any s , $\tau_2 = (ia, ja)$, τ_{r-1} does not involve ia, ja , or sb , τ_a may involve i but not j , and τ_b may involve s . It is easy to construct such a general τ by just considering what it must accomplish. Thus, we obtain

$$\begin{array}{cccccc} ia & sb & sb & tb & ja & \\ \vdots & \vdots & \vdots & \vdots & \vdots & \\ ja & \xrightarrow{\tau_1} ja & \xrightarrow{\tau_{r-1}} ja & \xrightarrow{\tau_a \tau_b} ja & \xrightarrow{\tau_2} tb & \\ \vdots & \vdots & \vdots & \vdots & \vdots & \\ sb & ia & ia & ua & ua & \end{array} \quad (B2)$$

since $\tau \Phi$ must put ϕ_{ja} in the ia position and since the final state in the ja position must be a b -type state

¹⁷ $(dx'_i) = dx_1 dx_2 \dots dx_{i-1} dx_{i+1} \dots dx_N$ and similarly for (dx''_{ij}) .
¹⁸ Note that we denote the electron number by the orbital in the unpermuted Φ corresponding to it [see (4)].

(otherwise we would obtain zero since we integrate over dx_{ja}). In addition, since the ϕ_{ia} state will not be in the ia position we must place it in one of the b positions, thus we must have at least one transfer between a and b states which for definiteness can be taken as τ_1 . Furthermore, there might be $r-1$ other transfers between a and b sets where $1 \leq r \leq m$. If $r > 1$ then ϕ_{ab} need not end up in the ia position and ϕ_{ia} need not end up in the sb position; thus $\tau_a \tau_b$ might change these and other states which were involved in τ_{r-1} . We have left ϕ_{ja} in the ia position so that we can now ensure that it ends up in the ia position. This same general procedure can be used to obtain the general τ for any of the density matrices; in the following we will just show the diagram as in (B2) and even that only for the cases which are less obvious. Using the permutation indicated in (B2) we obtain D_{ja}^{ia} as in Fig. 2, where the -1 is due to $\zeta_{\tau_2} = -1$ and (ia, ja) transposes ia and ja (replaces ia by ja since $j \notin P_r$).

For D_{jb}^{ia} , $\tau = \tau_a \tau_b \tau_r \tau_1$, where $\tau_1 = (ia, jb)$:

$$\begin{array}{cccc} ia & jb & jb & jb \\ \vdots & \vdots & \vdots & \vdots \\ jb & \xrightarrow{\tau_1} ia & \xrightarrow{\tau_r} ia & \xrightarrow{\tau_a \tau_b} sa. \end{array}$$

Thus D_{ja}^{ia} becomes as in Fig. 2, where the (τ_{r-1}) occurs above because of the $r+1$ transpositions between sets a and b . The above equations determine the first-order spatial density matrix. Note that D_j^i is Hermitian.

C. The Second-Order Reduced Spatial Density Matrices, D_{ki}^{ij}

We define the second-order density matrix D_{ki}^{ij} as the coefficient of $\phi_i^*(i) \phi_j^*(j) \phi_k(i) \phi_l(j)$ in

$$\Theta^\gamma \int \Phi^*(1 \dots N) O_{ff} \Phi(1 \dots N) (dx''_{ij}).$$

The same approach as was used for the first-order density matrices is again appropriate. The results are given in Fig. 2, where indices are equal only if the same letter is used (i.e., $i \neq j \neq k \neq l$). For $D_{ab,ia}^{ia,jb}$ we used $\tau = \tau_2 \tau_a \tau_b \tau_r \tau_1$ and $\tau_2 = (jb, tb)$:

$$\begin{array}{cccccc} ia & tb & ib & tb & tb & \\ \vdots & \vdots & \vdots & \vdots & \vdots & \\ jb & \xrightarrow{\tau_1} jb & \xrightarrow{\tau_r} sa & \xrightarrow{\tau_a \tau_b} ua & \xrightarrow{\tau_2} ia. & \\ \vdots & \vdots & \vdots & \vdots & \vdots & \\ tb & ia & ia & ia & ua & \end{array}$$

For $D_{ja,ib}^{ia,kb}$ we used $\tau = \tau_2\tau_a\tau_b\tau_r\tau_1$:

$$\begin{array}{cccccc}
 ia & kb & kb & ub & ja & \\
 ja & ja & ja & ja & ub & \\
 kb \xrightarrow{\tau_1} ia \xrightarrow{\tau_r} ia \xrightarrow{\tau_a\tau_b} va \xrightarrow{\tau_2} lb. & & & & & \\
 lb & lb & lb & lb & va &
 \end{array}$$

Note that the D_{kl}^{ij} matrices have the following symmetries

$$\begin{aligned}
 D_{ks_3,ls_4}^{is_1,js_2} &= (D_{is_1,js_2}^{ks_3,ls_4})^* = D_{ls_4,ks_3}^{js_2,is_1} \\
 D_{ks_3,ls_4}^{is_1,js_1} &= -D_{ks_3,ls_4}^{js_1,is_1}.
 \end{aligned} \tag{B3}$$

Using these relations all other D_{kl}^{ij} can be obtained from the formulas in Fig. 2. If we now define D_{kl}^{ij} for the case $i=j$ in such a way that it has the properties (B3), then $D_{k,i}^{ia,ia} = -D_{k,i}^{ia,ia} = 0$ and we can write

expectation values for two-electron operators without the primes on the sum over i and j and over k and l .

D. Expectation Values

The expectation value for the one-electron spatial operator $F = \sum_i f(i)$ is

$$\langle F \rangle = \sum_{i,j} \langle \phi_i | f | \phi_j \rangle D_j^i / D.$$

Similarly for the two-electron spatial operator $G = \sum_{i>j} g(i,j)$ we obtain

$$\langle G \rangle = \frac{1}{2} \sum_{ijkl} \langle \phi_i \phi_j | g | \phi_k \phi_l \rangle D_{kl}^{ij} / D.$$

Thus the total energy for the Hamiltonian given in (1) is

$$E = \left[\sum_{i,j} \langle i | h | j \rangle D_j^i + \frac{1}{2} \sum_{ijkl} \langle ij | g | kl \rangle D_{kl}^{ij} \right] D^{-1}.$$

APPENDIX C

Here we show that the solutions of Eqs. (9) are also solutions of (11). To do this we need to show that $H_{\mu\nu}^{ka} C_{\nu k}^a = H_{\mu\nu}^a C_{\nu k}^a$ where $H_{\mu\nu}^{ka}$ is defined in (10) and $H_{\mu\nu}^a$ in (12).

Consider the following term of $H_{\mu\nu}^{ka} C_{\nu k}^a$:

$$\sum_{\nu} \langle \mu | h | sa \rangle \langle vb | ka \rangle D_{sa,ka}^{ka,vb}.$$

From Appendix B¹⁹

$$D_{sa,ka}^{ka,vb} = - \sum_{r=0}^{\lfloor \frac{n-2}{m-1} \rfloor} \left[r!(r+1)! / \binom{n}{r+1} \right] \sum_{P_r, Q_r; k, s \notin P_r; v \notin Q_r} [O_{11}^{[1r+1]} S(sa; vb) S(p_1a; q_1b) \dots] [O_{11}^{[1r]} S(q_1b; p_1a) \dots]$$

Now define

$$\begin{aligned}
 f_{sa,ka}^{ka,vb}(ka) &= - \sum_{r=0}^{\lfloor \frac{n-2}{m-1} \rfloor} \left[r!(r+1)! / \binom{n}{r+1} \right] \\
 &\quad \times \sum_{P_r, Q_r; s \notin P_r; k \in P_r; v \notin Q_r} [O_{11}^{[1r+1]} S(sa; vb) S(p_1a; q_1b) \dots] [O_{11}^{[1r]} S(q_1b; p_1a) \dots].
 \end{aligned}$$

That is, $f(ka)$ is defined just as is D except that the restrictions in D which prohibit ka (i.e., $k \notin P_r$) are replaced by inclusions (i.e., $k \in P_r$). We now define $\mathfrak{D}_{sa,a}^{a,vb} \equiv D_{sa,ka}^{ka,vb} + f_{sa,ka}^{ka,vb}(ka)$ and obtain

$$\mathfrak{D}_{sa,a}^{a,vb} = - \sum_{r=0}^{\lfloor \frac{n-2}{m-1} \rfloor} \left[r!(r+1)! / \binom{n}{r+1} \right] \sum_{P_r, Q_r; s \notin P_r; v \notin Q_r} [O_{11}^{[1r+1]} S(sa; vb) S(p_1a; q_1b) \dots] [O_{11}^{[1r]} S(q_1b; p_1a) \dots]$$

which is independent of k .

Using (D2) we see that

$$\sum_{\nu=1}^m \langle vb | ka \rangle f_{sa,ka}^{ka,vb}(ka) \tag{C1}$$

contains a factor like $[O_{11}^{[1r+1]} S(q_1b; ka) S(q_2b; p_2a) \dots]$ where $k \in P_r$. Hence, since the same column is contained twice, each of these terms is zero and (C1) is zero. Therefore

$$\sum_{\nu} \langle vb | ka \rangle D_{sa,ka}^{ka,vb} = \sum_{\nu} \langle vb | ka \rangle \mathfrak{D}_{sa,a}^{a,vb}.$$

¹⁹ See Appendix B for definitions of P_r and the other symbols.

In a similar way each term in $H_{\mu\nu}^{ka}$ which has a factor of type $\langle vb | ka \rangle$ can have the D matrix with ka indices replaced by the \mathfrak{D} matrix with a indices, where in each case the $\mathfrak{D}_{s,a,t,\dots}^{a,i,j,\dots}$ is defined as $D_{s,ka,t,\dots}^{ka,i,j,\dots}$ except that the sum over $P(r)$ contains no restriction on ka . Thus,

$$\begin{aligned}
 H_{\mu\nu}(ka)C_{\nu k}^a = & \{ \langle \mu | h | ka \rangle [D_{ka}^{ka} - \sum_p \langle vb | ka \rangle \mathfrak{D}_{ka,a}^{a,vb}] + \sum_{s,v} \langle \mu | h | s \rangle \langle vb | ka \rangle \mathfrak{D}_{s,a}^{a,vb} \\
 & + \sum_{i,u} \langle \mu | ub \rangle \langle i | h | ka \rangle [D_{ub,ka}^{ka,i} - \sum_p \langle vb | ka \rangle \mathfrak{D}_{ub,ka,a}^{a,i,vb}] + \sum_{i,u,v;s} \langle \mu | ub \rangle \langle i | h | s \rangle \langle vb | ka \rangle \mathfrak{D}_{ub,s,a}^{a,i,vb} \\
 & + \sum_{i,v;s,t} \langle \mu, i | g | s, t \rangle \langle vb | ka \rangle \mathfrak{D}_{s,t,a}^{a,i,vb} + \sum_{i,s} \langle \mu, i | g | ka, s \rangle [D_{ka,s}^{ka,i} - \sum_p \langle vb | ka \rangle \mathfrak{D}_{ka,s,a}^{a,i,vb}] \\
 & + \sum_{i,s} \langle \mu, i | g | s, ka \rangle [D_{s,ka}^{ka,i} - \sum_p \langle vb | ka \rangle \mathfrak{D}_{s,ka,a}^{a,i,vb}] \\
 & + \sum_{u,v} \langle \mu | ub \rangle \langle vb | ka \rangle^{\frac{1}{2}} \sum_{i,j;s,t} \langle i, j | g | s, t \rangle \mathfrak{D}_{ub,a,s,t}^{a,vb,i,j} + \sum_{i,j,t;u} \langle \mu | ub \rangle \langle i, j | g | ka, t \rangle \\
 & \times [D_{ub,ka,t}^{ka,i,j} - \sum_p \langle vb | ka \rangle \mathfrak{D}_{ub,a,ka,t}^{a,vb,i,j}] + -E \sum_{u,v} \langle \mu | ub \rangle \langle vb | ka \rangle \mathfrak{D}_{ub,a}^{a,vb} \}, \tag{C2}
 \end{aligned}$$

where terms have been added and subtracted so that all sums over i, j, s, t are over all states (i.e., none are restricted to be different than ka). Now note that

$$\begin{aligned}
 - \sum_p \langle vb | ka \rangle \mathfrak{D}_{ka,a}^{a,vb} & = + \sum_p \langle vb | ka \rangle \mathfrak{D}_{a,ka}^{a,vb} \\
 & = \sum_p \langle vb | ka \rangle \sum_{r=1}^{[n-1]} \left[r!(r-1)! / \binom{n}{r} \right] \sum_{P'r,Q'r; k \in P'r; v \in Q'r} [O_{11}^{[r]} S(ka, vb) S(p_2a; q_2b) \dots] [O_{11}^{[1-r-1]} S(q_2b; p_2a) \dots] \\
 & = \sum_{r=1}^{[n-1]} \left[r!r! / \binom{n}{r} \right] \sum_{P_r, Q_r; k \in P_r} [O_{11}^{[r]} S(p_1a; q_1b) \dots] [O_{11}^{[r]} S(q_1b; p_1a) \dots],
 \end{aligned}$$

where Theorem 2 of Appendix D has been used. Thus

$$D_{ka}^{ka} - \sum_p \langle vb | ka \rangle \mathfrak{D}_{ka,a}^{a,vb} = \sum_{r=0}^{[n-1]} \left[(r!)^2 / \binom{n}{r} \right] \sum_{P_r, Q_r} [O_{11}^{[r]} S(p_1a; q_1b) \dots] [O_{11}^{[r]} S(q_1b; p_1a) \dots] \equiv \mathfrak{D}_a^a$$

which is independent of k .

Similarly using Appendix D we see that each of the other terms in brackets in (C2) may be replaced by a \mathfrak{D} matrix in which each of the ka indices of the first term is replaced by an a . Thus, we obtain

$$H_{\mu\nu}^{ka}C_{\nu k}^a = H_{\mu\nu}^aC_{\nu k}^a,$$

where $H_{\mu\nu}^a$ is given in (12).

APPENDIX D

Here we develop two theorems required in Appendix C.

Theorem 1:

$$r! [O_{11}^{[r]} S(ka; q_1b) S(p_2a; q_2b) \dots] = (r-1)! \sum_{u=q_1}^{q_r} \zeta_{(q_1,u)} S(ka; ub) [(q_1b; ub) O_{11}^{[r-1]} S(p_2a; q_2b) \dots], \tag{D1}$$

where²⁰ the O_{11} operates on the subscripts of the q 's. This is equivalent to expressing the determinant in terms of minors.

Proof: Write

$$\sum_{\tau \in S_r} = \sum_{\tau(1)=1}^r \sum_{\tau(2)=1; \tau(2) \neq \tau(1)}^r \dots \sum_{\tau(r)=1; \tau(r) \neq \tau(r-1), \dots, \tau(1)}^r = \sum_{\tau(1)=1}^r \sum_{\sigma \in S_{r-1}},$$

²⁰ Recall that $O_{11}^{[r]} = r!^{-1} \sum_{\tau \in S_r} \zeta_{\tau, \tau}$; that is, $r! O_{11}^{[r]}$ is the determinant operator.

where S_{r-1} contains elements 1 through r except for $\tau(1)$. Then $\tau = [1, \tau(1)]\sigma$ and

$$\begin{aligned} r! [O_{11}^{[1r]} S(ka; q_1b) S(p_2a; q_2b) \dots] &= \sum_{\tau \in S_r} \zeta_\tau S(ka; q_{\tau(1)}b) S(p_2a; q_{\tau(2)}b) \dots \\ &= \sum_{u=q_1}^{q_r} \zeta_{(q_1, u)} S(ka; ub) \sum_{\sigma \in S_{r-1}} \zeta_\sigma S(p_2a; q_{\sigma^{-1}[1, \tau(1)](2)}b) \dots \\ &= (r-1)! \sum_{u=q_1}^{q_r} \zeta_{(q_1, u)} S(ka; ub) [(q_1b; ub) O_{11}^{[1r-1]} S(p_2a; q_2b) \dots]. \end{aligned}$$

Theorem 2:

$$\begin{aligned} r! \sum_{Q_r} [O_{11}^{[1r]} S(ka; q_1b) S(p_2a; q_2b) \dots] [O_{11}^{[1r]} S(q_1b; p'_1a) S(q_2b; p'_2a) \dots] \\ = (r-1)! \sum_{u=1}^m S(ka, ub) \sum_{Q_{r-1}; u \notin Q_{r-1}} [O_{11}^{[1r-1]} S(p_2a; q_2b) \dots] [O_{11}^{[1r]} S(ub; p'_1a) S(q_2b; p'_2a) \dots]. \end{aligned} \quad (D2)$$

Proof:

$$\begin{aligned} r! \sum_{Q_r} [O_{11}^{[1r]} S(ka; q_1b) S(p_2a; q_2b) \dots] [O_{11}^{[1r]} S(q_1b; p'_1a) \dots] \\ = (r-1)! \sum_{Q_r} \sum_{u=q_1}^{q_r} \zeta_{(q_1, u)} S(ka; ub) [(q_1b; ub) O_{11}^{[1r-1]} S(p_2a; q_2b) \dots] [O_{11}^{[1r]} S(q_1b; p'_1a) \dots] \\ = (r-1)! \sum_{Q_r} \sum_{u=q_1}^{q_r} S(ka; ub) [(q_1b; ub) O_{11}^{[1r-1]} S(p_2a; q_2b) \dots] [(q_1b; ub) O_{11}^{[1r]} S(q_1b; p'_1a) \dots] \\ = (r-1)! \sum_{u=1}^m S(ka; ub) \sum_{Q_{r-1}; u \notin Q_{r-1}} [O_{11}^{[1r-1]} S(p_2a; q_2b) \dots] [O_{11}^{[1r]} S(ub; p'_1a) S(q_2b; p'_2a) \dots], \end{aligned}$$

where in the last equation for each u we have relabeled Q_r such that $u = q_1$.

APPENDIX E

In this section all the D and \mathfrak{D} matrices are evaluated explicitly. These formulas are valid for any number of electrons, N , and any total spin, S . We take the Young shape to have two columns of length n and $m \leq n$, respectively, so that $N = n + m$ and $S = \frac{1}{2}(n - m)$ (see Fig. 1). We presume that the orbitals have been transformed so that $S^{AB}(i, j) = \langle \phi_{ia} | \phi_{jb} \rangle$ is diagonal,

$$S^{AB}(i, j) = \lambda_i \delta_{ij}.$$

In order for $D_{ja^{ia}}$, $D_{jb^{ia}}$, or $D_{jb^{ib}}$ to be nonzero we must have $i = j$ since there will be a factor like $\langle ja | ia \rangle$, $\langle jb | ia \rangle$, or $\langle jb | ib \rangle$ in D which would otherwise yield zero. Similarly, $D_{k_3, l_4^{i_3, j_4}}$ is nonzero only if $\{i, j\} = \{k, l\}$, i.e., the same indices apart from the a or b must appear as subscripts as appear as superscripts. The same result applies to the \mathfrak{D} matrices. The λ usually appear as products of squares; a typical factor is $\lambda_{j_1}^2 \lambda_{j_2}^2 \dots \lambda_{j_r}^2$ which we denote as $\Lambda_{j_1 j_2 \dots j_r}$. A general factor which occurs in each term in the D or \mathfrak{D} matrix is of the form²¹

$$T I_{m-j}^{n-K}(j_1, j_2) \equiv \sum_{r=0}^{\lfloor \frac{n-K}{m-j} \rfloor} \binom{n}{r+I}^{-1} \sum_{P_r; j_1, j_2 \notin P_r} \Lambda_{P_r}, \quad (E1)$$

where I, J , and K are nonnegative integers, $\binom{n}{r+I}$ is a binomial coefficient, $\lfloor \frac{n-K}{m-j} \rfloor$ denotes that the lower of the two numbers is to be used as the upper limit on the sum, and there can be from zero to three indices such as j_1 and j_2 excluded.²² If the upper limit on the sum is less than zero the whole term is taken to be zero. Since $n \geq m$

²¹ Recall that

$$\lfloor \frac{n}{m} \rfloor$$

as an upper limit implies that the lower of i and j is to be used as the upper limit.

²² Let

$$S_{SQ}(r, M, j_1, \dots, j_M) \equiv \sum_{P_r; i_1, \dots, i_M \notin P_r} \Lambda_{P_r}$$

then $S_{SQ} = 1$ if $r = 0$. Also if two or more j_i are equal or if any $j_i > m$, we can delete some j_i and decrease M accordingly to obtain M' . Then $S_{SQ} = 0$ if $r + M' > m$.

$D = T_{00}$

$D_{ja}^{ja} = T_0^{n-1}(j)$	$\mathcal{D}_{ja}^{ja} = T_{01}(j)$	$\mathcal{D}_{ja}^{ia} = \lambda_j T_{12}$	$\mathcal{D}_{ub}^{va} = \lambda_u \lambda_v T_{m-2}^{n-4}$	$\mathcal{D}_{ua}^{vb} = \lambda_u \lambda_v T_{24}$
$D_{jb}^{jb} = T_{01}(j)$	$\mathcal{D}_{ja}^{ib} = T_{11}(j)$	$\mathcal{D}_{jb}^{ia} = \lambda_j T_{12}$	$\mathcal{D}_{ub}^{va} = \lambda_u \lambda_v \lambda_1 T_{m-3}^{n-4}$	$\mathcal{D}_{ua}^{vb} = \lambda_u \lambda_v \lambda_1 T_{34}$
$D_{jb}^{ja} = \lambda_j T_{11}(j)$	$\mathcal{D}_{ia}^{ib} = -\lambda_1 T_{m-1}^{n-3}$	$\mathcal{D}_{vb}^{ia} = T_{m-1}^{n-3}$	$\mathcal{D}_{ub}^{va} = -\lambda_u T_{m-2}^{n-3}$	$\mathcal{D}_{ua}^{vb} = -\lambda_u T_{23}$
$D_{ia}^{ja} = T_0^{n+2}(i, j)$	$\mathcal{D}_{ib}^{ib} = -\lambda_1 T_{13}$	$\mathcal{D}_{vb}^{ia} = \lambda_j T_{m-2}^{n-3}$	$\mathcal{D}_{ub}^{va} = -\lambda_u \lambda_1 T_{33}$	$\mathcal{D}_{ua}^{vb} = -\lambda_u \lambda_1 T_{33}$
$D_{ia}^{ja} = \lambda_j T_{m-1}^{n-2}(i, j)$	$\mathcal{D}_{ib}^{ia} = \lambda_j T_{22}$	$\mathcal{D}_{vb}^{ia} = \lambda_j \lambda_1 T_{33}$	$\mathcal{D}_{ub}^{va} = \lambda_u \lambda_v \lambda_1 T_{m-3}^{n-4}$	$\mathcal{D}_{ua}^{vb} = \lambda_u \lambda_v \lambda_1 T_{34}$
$D_{ib}^{ja} = \lambda_j \lambda_1 T_{22}(i, j)$	$\mathcal{D}_{ib}^{ib} = \lambda_j T_{22}$	$\mathcal{D}_{vb}^{ia} = T_{12}$	$\mathcal{D}_{ub}^{va} = \lambda_u \lambda_v T_{23}$	$\mathcal{D}_{ua}^{vb} = \lambda_u \lambda_v T_{23}$
$D_{ia}^{jb} = T_{01}(i, j)$	$\mathcal{D}_{ia}^{ib} = -\lambda_1 \lambda_j T_{m-2}^{n-3}$	$\mathcal{D}_{vb}^{ia} = \lambda_j \lambda_1 T_{23}$	$\mathcal{D}_{ub}^{va} = \lambda_u \lambda_v T_{33}$	$\mathcal{D}_{ua}^{vb} = \lambda_u \lambda_v T_{33}$
$D_{ja}^{jb} = \lambda_j \lambda_1 T_{12}(i, j)$	$\mathcal{D}_{ib}^{ia} = -\lambda_1 \lambda_j T_{23}$	$\mathcal{D}_{vb}^{ia} = \lambda_j \lambda_1 T_{33}$	$\mathcal{D}_{ub}^{va} = -\lambda_u \lambda_1 T_{33}$	$\mathcal{D}_{ua}^{vb} = -\lambda_u \lambda_1 T_{33}$
$D_{ib}^{jb} = \lambda_j \lambda_1 T_{22}(i, j)$	$\mathcal{D}_{ib}^{ib} = T_{12}$	$\mathcal{D}_{vb}^{ia} = T_{22}$	$\mathcal{D}_{ub}^{va} = -\lambda_u \lambda_1 T_{23}$	$\mathcal{D}_{ua}^{vb} = -\lambda_u \lambda_1 T_{23}$
$D_{ib}^{ja} = T_{11}(i, j)$	$\mathcal{D}_{ib}^{ia} = T_{m-1}^{n-2}$	$\mathcal{D}_{vb}^{ia} = \lambda_j T_{23}$	$\mathcal{D}_{ub}^{va} = -\lambda_u T_{23}$	$\mathcal{D}_{ua}^{vb} = -\lambda_u T_{m-2}^{n-3}$
$D_{ib}^{jb} = \lambda_j T_{12}(i, j)$	$\mathcal{D}_{ia}^{ib} = -\lambda_1 \lambda_j T_{m-2}^{n-3}$	$\mathcal{D}_{vb}^{ia} = T_{13}$	$\mathcal{D}_{ub}^{va} = -\lambda_u \lambda_1 T_{33}$	$\mathcal{D}_{ua}^{vb} = -\lambda_u \lambda_1 T_{33}$
$D_{ib}^{jb} = T_{02}(i, j)$	$\mathcal{D}_{ib}^{ib} = -\lambda_1 \lambda_j T_{23}$	$\mathcal{D}_{va}^{ia} = T_{m-1}^{n-3}$	$\mathcal{D}_{ub}^{va} = -\lambda_u T_{23}$	$\mathcal{D}_{ua}^{vb} = -\lambda_u T_{m-2}^{n-3}$
$\mathcal{D}_a^a = T_0^{n-1}$	$\mathcal{D}_{ib}^{ia} = T_{m-1}^{n-2}$	$\mathcal{D}_{va}^{ia} = \lambda_j T_{m-2}^{n-3}$	$\mathcal{D}_{ub}^{va} = -\lambda_u T_{23}$	$\mathcal{D}_{ua}^{vb} = -\lambda_u T_{m-2}^{n-3}$
$\mathcal{D}_b^b = T_{01}$	$\mathcal{D}_{ib}^{ib} = T_{12}$	$\mathcal{D}_{va}^{ia} = \lambda_j \lambda_1 T_{33}$	$\mathcal{D}_{ub}^{va} = -T_{13}$	$\mathcal{D}_{ua}^{vb} = -T_{m-1}^{n-3}$
$\mathcal{D}_a^{ja} = T_0^{n-2}(j)$	$\mathcal{D}_{ia}^{ib} = -\lambda_1 T_{12}$	$\mathcal{D}_{va}^{ia} = T_{12}$	$\mathcal{D}_{ub}^{va} = -T_{12}$	$\mathcal{D}_{ua}^{vb} = -T_{12}$
$\mathcal{D}_a^{ja} = \lambda_j T_{m-1}^{n-2}(j)$	$\mathcal{D}_{ib}^{ib} = -\lambda_1 T_{12}$	$\mathcal{D}_{va}^{ia} = \lambda_j \lambda_1 T_{23}$	$\mathcal{D}_{ub}^{va} = -\lambda_u T_{23}$	$\mathcal{D}_{ua}^{vb} = -\lambda_u T_{m-2}^{n-3}$
$\mathcal{D}_a^{jb} = T_{01}(j)$	$\mathcal{D}_{ib}^{ib} = -\lambda_1 T_{22}$	$\mathcal{D}_{va}^{ia} = \lambda_j \lambda_1 T_{33}$	$\mathcal{D}_{ub}^{va} = -T_{22}$	$\mathcal{D}_{ua}^{vb} = -T_{22}$
$\mathcal{D}_a^{jb} = T_{11}(j)$	$\mathcal{D}_{ja}^{ib} = -\lambda_1 T_{22}$	$\mathcal{D}_{va}^{ia} = T_{22}$	$\mathcal{D}_{ub}^{va} = -\lambda_u T_{m-2}^{n-3}$	$\mathcal{D}_{ua}^{vb} = -\lambda_u T_{23}$
$\mathcal{D}_b^{jb} = T_{02}(j)$	$\mathcal{D}_{ib}^{ib} = \lambda_j T_{22}$	$\mathcal{D}_{va}^{ia} = \lambda_j T_{23}$	$\mathcal{D}_{ub}^{va} = -\lambda_u \lambda_1 T_{33}$	$\mathcal{D}_{ua}^{vb} = -\lambda_u \lambda_1 T_{33}$
$\mathcal{D}_b^{jb} = \lambda_j T_{12}(j)$	$\mathcal{D}_{ia}^{ib} = \lambda_j T_{22}$	$\mathcal{D}_{va}^{ia} = T_{13}$	$\mathcal{D}_{ub}^{va} = -\lambda_u \lambda_1 T_{23}$	$\mathcal{D}_{ua}^{vb} = -\lambda_u \lambda_1 T_{23}$

FIG. 3. The D and \mathcal{D} matrices for diagonal S^{AB} .

then if $K \leq J$ we know that the upper limit is $m - J$. In such a case (E1) is denoted by $TIJ (j_1, j_2)$. Thus

$$T_{0m}^{n-1}(j) = \sum_{r=0}^{[n-1]} \binom{n}{r}^{-1} \sum_{P; r; j_1, j_2} \Delta_P,$$

and

$$T_{23}(i, j) = \sum_{r=0}^{m-3} \binom{n}{r+2}^{-1} \sum_{P; i, j; P_r} \Delta_P.$$

Of course, if $J > m$ then $TIJ = 0$.

The D and \mathcal{D} matrices are all derived²³ in the same way as in Appendix B except that since S^{AB} is diagonal the final expressions are all simpler. These are listed in Fig. 3, where we take i, j, u, v to all be different unless explicitly stated otherwise. Often two matrices which have different off-diagonal elements become identically the same element in the diagonal case, e.g., D_{iajb}^{iajb} and D_{jiaib}^{iajb} . In such cases only the one of these with fewer permutations (e.g., D_{iajb}^{iajb} above) is used since otherwise these terms would be counted twice in summing over all i and j and since the formula for those of type D_{jiaib}^{iajb} is not valid for $i = j$.

²³ For the case of an even number of electrons, the general expression for the energy of the alternate orbital wavefunction with different mixing parameters for each pair has been obtained by de Heer (Ref. 14b). In order to do this he evaluated the equivalent (for even N) to the D, D_i^i , and D_{ii}^{ii} derived here and given in Fig. 3.