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

$$(\alpha_T)_\text{chem} = \frac{1}{2}[\alpha_0(1-\alpha_0)](\Delta H/RT).$$

But, we find from Eq. (9), that the chemical part of $\alpha_T$ reduces to this form provided either $2D_3=D_4$ or $D_4=0$. 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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**INTRODUCTION**

In a previous paper referred to as 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 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.

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 paper we defined an operator $G^{\gamma}$ 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

$$\psi_{\text{exact}}^S,M(1, \ldots, N) = G\Phi\chi(1, \ldots, N),$$

where

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

$\alpha$ and $\beta$ are eigenfunctions of $\hat{S}_z$ with eigenvalues $+\frac{1}{2}$ and $-\frac{1}{2}$, respectively, and $\Phi$ is some function of the spatial coordinates of the $N$ electrons. In II we considered a function $G^{\nu}\Phi_x$, where $\Phi$ 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-electron theory.
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 $G_i^\gamma \Phi_X$ 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 $\hat{S}_f$. 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 $G_i^\gamma \Phi_X$ and derive the explicit coefficients for the equations which lead to the best such $G_i^\gamma \Phi_X$ 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

$$G_i^\gamma \Phi_X,$$

where $\chi$ is a product of one-electron spin functions as in (3), $\Phi$ is restricted to be a simple product of one-electron spatial functions (i.e., orbitals), the total spin projection is $S$, and $\gamma$ corresponds to the total spin.

The tableau $S_f^\gamma$ 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

$$\Phi(1 \cdots N) = \phi_{l_1}(1) \phi_{l_2}(2) \cdots \phi_{l_n}(n) \chi \phi_{o_1}(n+1) \phi_{o_2}(n+2) \cdots \phi_{o_m}(N),$$

where the set $\{ \phi_{l_a} \}$ is orthonormal as is the set $\{ \phi_{o_b} \}$.

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

$$E = \langle G_i^\gamma \Phi_X | H | G_i^\gamma \Phi_X \rangle / \langle G_i^\gamma \Phi_X | G_i^\gamma \Phi_X \rangle = \langle \Phi | H O_{ff}^\gamma | \Phi \rangle / \langle \Phi | O_{ff}^\gamma | \Phi \rangle$$

be stationary with respect to variation of any of the orbitals of $\Phi$. That is we require\footnote{We often omit the superscript $\gamma$ in the following.}

$$\delta \langle \Phi | (H - E) O_{ff} | \Phi \rangle = \sum_{i,j=1} e_{ij} \delta \langle \phi_{l_a} | \phi_{l_b} \rangle - \sum_{i,j=1} e_{ij} \delta \langle \phi_{o_b} | \phi_{o_b} \rangle = 0 \quad (6a)$$

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

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

$$\sum_{i,j=1} U_{ik}^a e_{ij} U_{jl}^a \delta \langle \phi_{l_b} | \phi_{l_b} \rangle,$$

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

$$\delta \langle \Phi | (H - E) O_{ff} | \Phi \rangle - \sum_k e_{kb} \delta \langle \phi_{o_b} | \phi_{o_b} \rangle = 0 \quad (6b)$$

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

$$\delta \langle \Phi | (H - E) O_{ff} | \Phi \rangle = \epsilon_{kb} \delta \langle \phi_{o_b} | \phi_{o_b} \rangle \quad (6c)$$

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

$$H^{ba} \phi_b = \epsilon_{ba} \phi_b \quad k = 1, 2, \cdots, n,$$

$$H^{kb} \phi_b = \epsilon_{kb} \phi_b \quad k = 1, 2, \cdots, m,$$

where $H^{ba}$ is given by Eqs. (11) of II (in this case the sums over $v$ and $u$ in II are for $v_b$ and $u_b$ since $v_a$ and $u_a$

\footnote{We use $\langle \phi | H | \phi \rangle$ merely to indicate the integral $\int \phi^* H \phi \ dx$. Whether the integral is $N$ dimensional or of some other dimension is determined by the dimension of $\phi$.}

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

\footnote{Equation (11) of $H$ is just the operator equivalent to the matrix $H^{ba}$ given in Eq. (10) below.}
are orthogonal to \( h k a \) and similarly for \( H^b_b \). Taking a Roothaan expansion

\[ \phi_{ba} = \sum_{\mu} \chi_\mu C_{\mu b}^a, \]

\[ \phi_{ib} = \sum_{\mu} \chi_\mu C_{\mu i}^b, \]

in terms of a finite basis set, we obtain\(^7\)

\[ H^a_{\mu b} = \{ \langle \mu | h | \nu \rangle \} D_{\mu b}^a + \sum_{\sigma \neq \mu} \{ \langle \mu | h | \sigma \rangle \} D_{\mu b}^{a, \sigma \mu} + \sum_{\mu} \{ \langle \mu | h | \nu \rangle \} D_{\mu b}^{a, b \nu}, \]

\[ H^b_{\mu b} = \{ \langle \mu | h | \nu \rangle \} D_{\mu b}^b + \sum_{\sigma \neq \mu} \{ \langle \mu | h | \sigma \rangle \} D_{\mu b}^{b, \sigma \mu} + \sum_{\mu} \{ \langle \mu | h | \nu \rangle \} D_{\mu b}^{b, b \nu}, \]

where \( \delta_{\mu \nu} = \langle \chi_\mu | \chi_\nu \rangle \) and\(^8\)

\[ H^a_{\mu b} = S_{\mu b} C_{\mu b}^a, \quad H^b_{\mu b} = S_{\mu b} C_{\mu b}^b, \]

The first- and second-order reduced spatial density matrices,\(^9\) \( D^j \) and \( D^{a j} \), are derived in Appendix B. Now it would appear that \( H^a_{\mu b} \) is a function of \( k \); however, we show in Appendix C that terms may be added to each \( H^a_{\mu b} \) to obtain a new function \( H^a_{\nu} \) 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

\[ H^a_{\nu} C_{\nu b} = S_{\nu b} C_{\nu b}^a, \]

\[ H^b_{\nu} C_{\nu b} = S_{\nu b} C_{\nu b}^b, \]

where \( H^a_{\nu} \) is defined as

\[ H^a_{\nu} = \{ \langle \mu | h | \nu \rangle \} D_{\nu b}^a + \sum_{\sigma \neq \mu} \{ \langle \mu | h | \sigma \rangle \} D_{\nu b}^{a, \sigma \nu} + \sum_{\mu} \{ \langle \mu | h | \nu \rangle \} D_{\nu b}^{a, b \nu}, \]

\[ H^b_{\nu} = \{ \langle \mu | h | \nu \rangle \} D_{\nu b}^b + \sum_{\sigma \neq \mu} \{ \langle \mu | h | \sigma \rangle \} D_{\nu b}^{b, \sigma \nu} + \sum_{\mu} \{ \langle \mu | h | \nu \rangle \} D_{\nu b}^{b, b \nu}, \]

and similarly for \( H^b_{\nu} \). The \( D \) matrices in (12) are derived in Appendix C in terms of the \( D \) matrices. This transformation of the \( H^a_{\nu} \) 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 \( H_{\nu}^a(k) \) for \( G^a \Phi^b \) can be transformed so that there is one \( H \) operator for each antisymmetric set of states in \( S^\nu \). Similarly, the integrodifferential Eqs. (7) can be transformed such that \( H^a \) and \( H^b \) are used rather than \( H^a \) and \( H^b \).

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

As discussed in II the Eqs. (7) defining the orbitals which when substituted in \( \Phi \) yield the lowest-energy \( G^a \Phi^b \) 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 \( \langle \alpha | h | \nu \rangle \) or \( \langle \mu | h | \sigma \rangle \) appear since \( \langle \alpha | h | \alpha \rangle = \delta_{\alpha \sigma} \) and hence these terms vanish from (5).

\(^9\) The spatial density matrices are \( D^j \) and \( D^{a j} \), where \( D \) is defined in Appendix B. Thus the \( D^j \) and \( D^{a j} \) are denoted as reduced spatial density matrices. If from the context it is clear that \( D^j \) and \( D^{a j} \) 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 $S^{AB}(i, j) \equiv \langle \phi_{ja} | \phi_{kb} \rangle$. By considering the Hermitian matrices $\sum_i S^{AB*}(i, j) S^{AB}(j, k)$ and $\sum_i S^{AB*}(i, j) S^{AB}(k, j)$, 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. This transformed set of orbitals is quite convenient because in the case of diagonal $S^{AB}$ the expressions for $D$ and $\Omega$ 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 one orbital, say $\phi_{ja}$, it involves a factor $\phi_{ja}^* \phi_{ja}$ and in every case there is a sum over all $j$. But

$$\sum_j \phi_{ja}^* \phi_{ja} = \sum_{kij} \phi_{ka}^* \phi_{la} U_{ki} I_{k}^a = \sum_j \phi_{ja}^* \phi_{ja}$$

is left invariant under unitary transformations. In addition those terms which involve two or more such factors, say $\phi_{ja}^* \phi_{ja} \phi_{lb}^* \phi_{lb}$, 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 quantities

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

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 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 $\Omega$ 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) method uses a single Slater determinant but allows the orbitals of $\alpha$ spin to be different than the orbitals of $\beta$ 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 \textit{ab initio} calculations; an approximate method which is important in considering $\pi$-electron systems in alternate hydrocarbons is the alternate molecular orbital (AMO)

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

12 P. O. Löwdin, J. Chem. Phys. 2, 207 (1959), has pointed out that for the case of a spin-projected Slater determinant the fundamental invariants are $\rho_a$ and $\rho_b$. 

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 ps 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 limited 15 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 \( G_i \Phi_X \) for one specific \( i \) (where \( \Phi \) is a complicated function of the spatial coordinates). Hence, 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 \( \Phi \) 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 \( G_i \Phi_X \), where \( \Phi \) 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.

\(^{14}\) (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 ps orbital on each carbon).
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 with the Hartree–Fock method is biased—it treats some states incorrectly in a way that increases the 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 demonstrated 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, $\{j_1, j_2, \ldots, j_n\}$ for which

$$O_{ij} = -O_{ji}$$

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 $\Phi$ corresponding to these indices,

$$\phi_r = \sum_k S_{kj} \phi'_{k_l}$$

then

$$O_{ji} \Phi = (\det S) O_{ji} \Phi'$$

where $\Phi'$ contains the primed orbitals in place of the unprimed ones.

The proof is as follows:

$$O_{ji} \Phi = \sum_{k_1, k_2, \ldots, k_n} S_{k_1j_1} S_{k_2j_2} \ldots S_{k_nj_n} \times X_{O_{ij} \phi'_{k_1} \phi'_{k_2} \ldots \phi'_{k_n} \phi_{n+1} \ldots \phi_N},$$

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

$$\phi'_{k_l} = \phi_{k_1} \phi_{k_2} \ldots \phi_{k_n} \phi_{n+1} \ldots \phi_N$$

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

$$O_{ij} \phi'_{k} = \frac{1}{2} O_{ij} \left[ \phi'_{k} + (\phi'_{k_1} + \phi'_{k_2} + \ldots + \phi'_{k_n}) \right] \phi'_{k} = 0;$$

hence, we can presume that each of the antisymmetric indices occurs once and only once in $k$ so that $\Phi'_{k} = \tau \phi'$ where $\phi' = \phi_{k_1} \phi_{k_2} \ldots \phi_{k_n} \phi_{n+1} \ldots \phi_N$ and $\tau$ operates on the first $n$ indices. But $O_{ij} \tau = \tau O_{ij}$ so that

$$O_{ij} \Phi = \sum_{\tau \in S_n} S_{1r(1)} S_{2r(2)} \ldots S_{nr(n)} O_{ij} \phi' = (\det S) O_{ij} \phi'$$

where

$$S_{1r(1)} S_{2r(2)} \ldots S_{nr(n)} = (\det S)^{1/2},$$

and hence the transformation in (A1) does not change expectation values since $G_{ij} \phi_x = (\det S) G_{ij} \phi_x$ 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 $G_{ij} \phi_x$ type wavefunctions. If $F$ is such an operator, then from I and II

$$\langle F \rangle = \langle \Phi | F \Theta O_{ij} \phi | \Phi \rangle / \langle \Phi | \Theta O_{ij} \phi | \Phi \rangle,$$

where from I

$$\hat{H} = \langle 1/\theta^2 \rangle \sum_{r \in S_n} U_{fr} \phi_r$$

and the tableau $S_{ij}$ is given in Fig. 1. We need to know the general form for $U_{fr}$. From Appendix E of I we can always write $\tau = \tau_{1} \tau_{2} \tau_{3}$ where $\tau_{1}$ permutes letters $\leq n$, $\tau_{2}$ permutes letters $> n$, and $\tau_{3}$ is a product of $\tau$ 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,

$$U_{fr} = \xi_{r} S_{n} \left( \frac{n!}{r!} \right)^{-1},$$

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

A. The Denominator $D$

We define

$$D = \theta^{\tau} \langle \Phi | O_{ij} \phi | \tau \phi \rangle = \sum_{r \in S_n} U_{fr} \langle \Phi | \tau \phi \rangle.$$
The $\tau$ here operates on the electrons $\tau\Phi(1, 2, 3, \cdots) = \Phi(\tau(1), \tau(2), \tau(3), \cdots)$ so that $\tau\phi_{i_1}(1)\phi_{i_2}(2)\cdots = \phi_{\tau^{-1}(1)}(\tau^{-1}(2))\cdots = \phi_{i_1}(\tau(1))\phi_{i_2}(\tau(2))\cdots$. Now we consider the various $\tau$ 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 $\tau\phi_{i_1}$ is in the $i_1$ position of $\Phi$ or else it is in a position $> n$; similarly either $\phi_{i_2}$ is in the $n+i_1$ position of $\Phi$ or else it is in a position $> n$. If $\tau$ takes no element $\leq n$ to a position $> n$, then $\langle \Phi | \tau\Phi \rangle \neq 0$ only for $\tau = (i, j)$. If $\tau$ takes two elements, say $p$ and $q$, from positions $> n$ to positions $\leq n$; 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 if $\tau = (p, q)$ and $\rho = (p', q')$. If $\tau$ takes three elements, say $p$, $q$, and $r$, from positions $> n$ to positions $\leq n$; then it must take three elements, say $p'$, $q'$, and $r'$, from positions $> n$ to positions $\leq n$; and $\langle \Phi | \tau\Phi \rangle \neq 0$ only if $\tau = (p, q, r)$ and $\rho = (p', q', r')$. The choice of the specific set of $r$ disjoint transpositions for $\tau$ is arbitrary, the permutations $\tau$ and $\rho$ take $\tau$ through the $(r!)$ different such
permutations for which \( \langle \Phi | \tau \Phi \rangle \neq 0 \). Hence,

\[
D = \Theta^\tau (\Phi | O_{ff} \Phi) = \sum_{r=0}^N \sum_{1 \leq p_1 < \cdots < p_r \leq n \leq q_1 < \cdots < q_r} \sum_{T_1, \ldots, T_r} \langle \Phi_{p_1a} \cdots \Phi_{p_ra} | \tau_{T_1} \cdots \tau_{T_r} | \Phi_{q_1b} \cdots \Phi_{q_rb} \rangle.
\]

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

\[
\langle \Phi_{p_1a} \cdots \Phi_{p_ra} | \tau_{a} | \Phi_{q_1b} \cdots \Phi_{q_rb} \rangle = S(p_1a; q_1^{-1}(b)) \cdots S(p_r; q_r^{-1}(b)),
\]

otherwise we would obtain zero since we integrate over \( dx_{ia} \). In addition, since the \( \phi_{ia} \) 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 \( \tau_{1} \). Furthermore, there might be \( r-1 \) other transfers between \( a \) and \( b \) sets where \( 1 \leq r \leq m \). If \( r > 1 \) then \( \phi_{ab} \) need not end up in the \( ia \) position and \( \phi_{ia} \) need not end up in the \( sb \) position; thus \( \tau_{r} \) might change these and other states which were involved in \( \tau_{r-1} \). We have left \( \phi_{ja} \) 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 \( \tau \) 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 \( D_{ia}^{ab} \) as in Fig. 2, where the \(-1\) is due to \( \xi_{r} = -1 \) and \( (ia, ja) \) transposes \( ia \) and \( ja \) (replaces \( ia \) by \( ja \) since \( j \notin P_{r} \)).

For \( D_{ia}^{ab} \), \( \tau = \tau_{r} \tau_{r} \tau_{r-1}, \) where \( \tau_{1} = (ia, ja) \):

\[
\begin{align*}
&ia \quad jb \quad ja \quad jb \\
&\cdots \quad \cdot \quad \cdot \quad \cdot \\
&ja \rightarrow ia \rightarrow ja \rightarrow ja \rightarrow jb \\
&\begin{array}{c}
\vdots \\
\vdots \\
\vdots \\
\vdots \\
\vdots
\end{array}
\end{align*}
\]

Thus \( D_{ia}^{ab} \) becomes as in Fig. 2, where the \( (\ast \ast_{1}) \) 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 \( D_{i}^{j} \) is Hermitian.

C. The Second-Order Reduced Spatial Density Matrices, \( D_{ik}^{ij} \)

We define the second-order density matrix \( D_{ik}^{ij} \) as the coefficient of \( \phi_{i}^{*}(i) \phi_{j}^{*}(j) \phi_{k}(i) \phi_{l}(j) \) in

\[
\Theta^\tau \langle \Phi^{*}(1 \cdots N) O_{ff} \Phi^{*}(1 \cdots N) (dx'_{ij}) \rangle.
\]

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., \( i \neq j, k \neq l \)). For \( D_{\theta_{ia}^{ab}, \theta_{ia}^{ab}} \) we used \( \tau = \tau_{r} \tau_{r} \tau_{r-1} \) and \( \tau_{1} = (jb, lb) \):

\[
\begin{align*}
&ia \quad lb \quad ib \quad lb \\
&\cdots \quad \cdot \quad \cdot \quad \cdot \\
&ja \rightarrow jb \rightarrow sa \rightarrow ua \rightarrow ia \\
&\begin{array}{c}
\vdots \\
\vdots \\
\vdots \\
\vdots \\
\vdots
\end{array}
\end{align*}
\]

\[\text{Note that we denote the electron number by the orbital in the unpermuted } \Phi \text{ corresponding to it [see (4)].}\]
For $D_{sa,ka}^{ab}$ we used $\tau = \tau_0 \tau_0 \tau_1$:
\[
\begin{array}{cccccc}
  ia & kb & kb & ub & ja \\
  ja & ja & ja & ja & ub \\
  \tau_1 & \tau & \tau_0 & \tau_0 & \tau_2 \\
  kb & \rightarrow & ia & \rightarrow & ia & \rightarrow & va & \rightarrow & tb.
\end{array}
\]

Note that the $D_{kii}$ matrices have the following symmetries
\[
D_{k_{12},l_{12}}^{(1)} = (D_{k_{11},l_{11}}^{1})^{*} = D_{k_{21},l_{21}}^{(2)},
\]
\[
D_{k_{21},l_{21}}^{(1)} = -D_{k_{12},l_{12}}^{(1)}.
\]

Using these relations all other $D_{kii}$ can be obtained from the formulas in Fig. 2. If we now define $D_{kii}$ for the case $i = j$ in such a way that it has the properties (B3), then $D_{k,ia,ia,va} = 0$ 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
\[
\langle F \rangle = \sum_{i,j} \langle \psi_i \mid f \mid \psi_j \rangle D_{ij}/D.
\]

Similarly for the two-electron spatial operator $G = \sum_{i,j} g(i,j)$ we obtain
\[
\langle G \rangle = \sum_{i,j} \langle \psi_i \mid \psi_j \rangle D_{kii}/D.
\]

Thus the total energy for the Hamiltonian given in (1) is
\[
E = \sum_{i,j} \langle i \mid h \mid j \rangle D_{ij} + \frac{1}{2} \sum_{i,j} \langle ij \mid g \mid kl \rangle D_{kii}/D.
\]

**APPENDIX C**

Here we show that the solutions of Eqs. (9) are also solutions of (11). To do this we need to show that $H_{\mu}^{k_{1},c_{1}} = H_{\mu}^{k_{2},c_{2}}$ where $H_{\mu}^{k_{1},c_{1}}$ is defined in (10) and $H_{\mu}^{k_{2},c_{2}}$ in (12).

Consider the following term of $H_{\mu}^{k_{1},c_{1}}$:
\[
\sum_{\tau} \langle \mu \mid h \mid sa \rangle \langle vb \mid ka \rangle D_{sa,ka}^{sa,va}.
\]

From Appendix B\(^{19}\)
\[
D_{sa,ka}^{ka,va} = -\sum_{r=0}^{n-2} \left[ r!(r+1)! \left( \begin{array}{c} n \\ r+1 \end{array} \right) \right] \sum_{P_{r},Q_{r},P_{r+1},Q_{r+1}} [O_{H}^{1+r+1} S(sa; vb) S(p_{r}a; q_{r}b) \cdots] [O_{H}^{1+r} S(q_{r}b; p_{r}a) \cdots]
\]

Now define
\[
f_{sa,ka}^{ka,va}(ka) = -\sum_{r=0}^{n-2} \left[ r!(r+1)! \left( \begin{array}{c} n \\ r+1 \end{array} \right) \right] \times \sum_{P_{r},Q_{r},P_{r+1},Q_{r+1}} [O_{H}^{1+r+1} S(sa; vb) S(p_{r}a; q_{r}b) \cdots] [O_{H}^{1+r} S(q_{r}b; p_{r}a) \cdots].
\]

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 $D_{sa,ka}^{a,b} = D_{sa,ka}^{a,b} + f_{sa,ka}^{a,b}(ka)$ and obtain
\[
D_{sa,ka}^{a,b} = -\sum_{r=0}^{n-2} \left[ r!(r+1)! \left( \begin{array}{c} n \\ r+1 \end{array} \right) \right] \sum_{P_{r},Q_{r},P_{r+1},Q_{r+1}} [O_{H}^{1+r+1} S(sa; vb) S(p_{r}a; q_{r}b) \cdots] [O_{H}^{1+r} S(q_{r}b; p_{r}a) \cdots]
\]

which is independent of $k$.

Using (D2) we see that
\[
\sum_{r=1}^{n} \langle vb \mid ka \rangle f_{sa,ka}^{a,b}(ka)
\]
contains a factor like $[O_{H}^{1+r+1} S(q_{r}b; ka) S(q_{r}b; p_{r}a) \cdots]$ where $k \in P_{r}$. Hence, since the same column is contained twice, each of these terms is zero and (C1) is zero. Therefore
\[
\sum_{r} \langle vb \mid ka \rangle D_{sa,ka}^{a,b} = \sum_{r} \langle vb \mid ka \rangle D_{sa,ka}^{a,b}.
\]

\(^{19}\) See Appendix B for definitions of $P_{r}$ and the other symbols.
In a similar way each term in $H_{\mu}^{ka}$ which has a factor of type $\langle vb \mid ka \rangle$ can have the $D$ matrix with $ka$ indices replaced by the $D$ matrix with $a$ indices, where in each case the $D_{\alpha,\alpha',t,\ldots,a_1,i_1,j_1,\ldots}$ is defined as $D_{\alpha,i_1,\ldots,a_1,i_1,j_1,\ldots}$ except that the sum over $P(r)$ contains no restriction on $ka$. Thus,

$$H_{\mu}^{ka}(ka)C_{\nu a} = \{ \langle \mu \mid h \mid ka \rangle \} D_{\alpha}^{ka} - \sum_s \langle \nu \mid h \mid ka \rangle D_{\alpha}^{ka} \sum_s \langle \nu \mid h \mid ka \rangle D_{\alpha}^{ka}$$

$$+ \sum_{i_1} \langle \mu \mid ub \rangle \langle i_1 \mid h \mid ka \rangle [D_{\alpha,\alpha_1}^{ka} - \sum_s \langle \nu \mid h \mid ka \rangle D_{\alpha,\alpha_1}^{ka} \sum_s \langle \nu \mid h \mid ka \rangle D_{\alpha,\alpha_1}^{ka}] + \sum_{i_1} \langle \mu \mid ub \rangle \langle i_1 \mid h \mid ka \rangle [D_{\alpha,\alpha_1}^{ka} - \sum_s \langle \nu \mid h \mid ka \rangle D_{\alpha,\alpha_1}^{ka} \sum_s \langle \nu \mid h \mid ka \rangle D_{\alpha,\alpha_1}^{ka}$$

$$+ \sum_{i_1} \langle \mu \mid g \mid ka \rangle [D_{\alpha,\alpha_1}^{ka} - \sum_s \langle \nu \mid h \mid ka \rangle D_{\alpha,\alpha_1}^{ka} \sum_s \langle \nu \mid h \mid ka \rangle D_{\alpha,\alpha_1}^{ka}]$$

$$+ \sum_{i_1} \langle \mu \mid ub \rangle \langle i_1 \mid g \mid ka \rangle [D_{\alpha,\alpha_1}^{ka} - \sum_s \langle \nu \mid h \mid ka \rangle D_{\alpha,\alpha_1}^{ka} \sum_s \langle \nu \mid h \mid ka \rangle D_{\alpha,\alpha_1}^{ka}]$$

$$+ \sum_{i_1} \langle \mu \mid ub \rangle \langle i_1 \mid g \mid ka \rangle [D_{\alpha,\alpha_1}^{ka} - \sum_s \langle \nu \mid h \mid ka \rangle D_{\alpha,\alpha_1}^{ka} \sum_s \langle \nu \mid h \mid ka \rangle D_{\alpha,\alpha_1}^{ka}]$$

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

$$- \sum_{i_1} \langle \nu \mid h \mid ka \rangle D_{\alpha,\alpha_1}^{ka}$$

$$= \sum_{i_1} \langle \nu \mid h \mid ka \rangle \sum_{r_1} \left[ \begin{array}{c} r_1 \\ r_1 \end{array} \right] \sum_{P_{r_1},Q_{r_1},k_{r_1}} O_{a_1}^{[r_1]} S(ka; q_{xb}) S(p_{xa}; q_{yb}) \cdots$$

$$\cdot [O_{n_{r_1}^{[r_1]}} S(ka; q_{xb}) S(p_{xa}; q_{yb}) \cdots] = 5)_{a_1}^{[r_1]}$$

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 $D$ matrix in which each of the $ka$ indices of the first term is replaced by an $a$. Thus, we obtain

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

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

**APPENDIX D**

Here we develop two theorems required in Appendix C.

**Theorem 1:**

$$r! [O_{n_{r}^{[r]}} S(ka; q_{xb}) S(p_{xa}; q_{yb}) \cdots] = (r-1)! \sum_{u=1}^{g_{r}} \xi_u S(ka; ub) [O_{n_{r}^{[r]}} S(q_{xb}; p_{ya}) \cdots]$$

**Proof:** Write

$$\sum_{r=1}^{\infty} \sum_{d=1}^{r-1} \sum_{r' \neq r} \cdots = \sum_{r=1}^{\infty} \sum_{r' \neq r} \cdots$$

Recall that $O_{1}^{[r]} = r! \sum_{\delta} \delta_{\delta}^{(r)}$; that is, $r! O_{a}^{[r]}$ is the determinant operator.
where \( S_{r-1} \) contains elements 1 through \( r \) except for \( \tau(1) \). Then \( r! [O_{1}^{[r]} S(\sigma; \tau) S(\rho; \varsigma) \ldots] = \sum_{\tau \in \sigma} \sigma_{r} S(\sigma; \tau) S(\rho; \varsigma) \ldots \)

\[
= \sum_{u \in q_{1}} \sum_{\tau \in \sigma_{r}} \tau_{u} S(\sigma; \tau) S(\rho; \varsigma) \ldots = (r-1) \sum_{u \in q_{1}} \sum_{\tau \in \sigma_{r}} \tau_{u} S(\sigma; \tau) S(\rho; \varsigma) \ldots \]

**Theorem 2:**

\[
(r-1)! \sum_{q_{r}} [O_{1}^{[r]} S(\sigma; \tau) S(\rho; \varsigma) \ldots] [O_{1}^{[r]} S(\sigma; \tau) S(\rho; \varsigma) \ldots] = (r-1)! \sum_{u \in q_{1}} \sum_{\tau \in \sigma_{r}} \tau_{u} S(\sigma; \tau) S(\rho; \varsigma) \ldots \]

**Proof:**

\[
= (r-1) \sum_{u \in q_{1}} \sum_{\tau \in \sigma_{r}} \tau_{u} S(\sigma; \tau) S(\rho; \varsigma) \ldots \]

\[
= (r-1)! \sum_{q_{r}} [O_{1}^{[r]} S(\sigma; \tau) S(\rho; \varsigma) \ldots] [O_{1}^{[r]} S(\sigma; \tau) S(\rho; \varsigma) \ldots] \]

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 \( \Sigma \) 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 \( S_{A}(i, j) = \langle \phi_{i A} | \phi_{j A} \rangle \) is diagonal.

\[
S_{A}(i, j) = \delta_{ij} \]

In order for \( D_{A}(a^{*}, b^{*}) \) or \( D_{B}(b^{*}) \) to be nonzero we must have \( i = j \) since there will be a factor like \( \langle j a | i a \rangle \) or \( \langle j b | i b \rangle \) in \( D \) which would otherwise yield zero. Similarly, \( D_{n}^{[i_{1}, \ldots, i_{n}]} \) 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 \( \Sigma \) matrices. The \( \lambda \) usually appear as products of squares; a typical factor is \( \lambda_{ij}^{2} \cdots \lambda_{r}^{2} \) which we denote as \( \Lambda_{ij \ldots r} \). A general factor which occurs in each term in the \( D \) or \( \Sigma \) matrix is of the form.

\[
T_{I m-J m} = \sum_{I} \sum_{J} \sum_{K} \sum_{\tau = 0}^{I} \sum_{\sigma = 0}^{J} \sum_{r = 0}^{K} \Lambda_{\tau \sigma r} \]

(E1)

where \( I, J, \) and \( K \) are nonnegative integers, \( \left( \begin{array}{c} I \cr J \end{array} \right) \) is a binomial coefficient, \( [m, K] \) 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.\(^{20}\) 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

\( [\cdot] \)

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

\(^{22}\) Let

\[
S_{Q Q}(r, M; i_{1}, \ldots, j_{M}) = \sum_{\tau = 0}^{I} \sum_{\sigma = 0}^{J} \sum_{r = 0}^{K} \Lambda_{\tau \sigma r}
\]

then \( S_{Q Q} = 1 \) 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 \( S_{Q Q} = 0 \) if \( r + M' > m \).
then if \( K \leq J \) we know that the upper limit is \( m - J \). In such a case (E1) is denoted by \( TII \ (j_1, j_2) \). Thus

\[
T_{0m}^{-1}(j) = \sum_{r=0}^{n-1} \binom{n}{r}^{-1} \sum_{P} \Lambda_P,
\]

and

\[
T_{23}(i, j) = \sum_{r=0}^{n+1} \binom{n}{r+2}^{-1} \sum_{P} \Lambda_P.
\]

Of course, if \( J > m \) then \( TII = 0 \).

The \( D \) and \( \mathcal{D} \) matrices are all derived 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., \( D_{ab}^{i,j} \) and \( D_{uv}^{i,j} \). In such cases only the one of these with fewer permutations (e.g., \( D_{ab}^{i,j} \) 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 \( D_{ab}^{i,j} \) is not valid for \( i = j \).

![Fig. 3. The \( D \) and \( \mathcal{D} \) matrices for diagonal \( S^{AB} \).](http://jcp.aip.org/jcp/copyright.jsp)