Construction of Approximately N-Representable Density Matrices*

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A method is given for obtaining the density matrix or matrices, expressible in terms of a given set of spin geminals, which are as nearly N representable as possible. A measure of N representability is introduced as the norm of the antisymmetric component of a normalized wave function leading to the density matrix. An error estimate is given for the maximum deviation of an energy calculated with the density matrix from that calculated with an antisymmetric wave function. Linear variational parameters may occur in the density matrix, and their number can be increased at the expense of N representability. Implementation of the method requires diagonalization of a large matrix, and the consequences of truncation are considered. The method is also related to the problem of the exact N representability of a given density matrix.

I. INTRODUCTION

The pth-order reduced density matrix,[1-6] or p matrix,[7] for a pure state of an N-fermion system can be obtained from the wave function Ψ as

$$D^{(p)}(1\cdots p;1'\cdots p') = \int \Psi(1\cdots p, p+1\cdots N) \times \Psi^*(1'\cdots p', p+1\cdots N)\, d\tau_{p+1}\cdots d\tau_N \ . \quad (1)$$

It has certain properties as immediate consequences of this definition: It is Hermitian, and if Ψ is a normalized, antisymmetric function, $D^{(p)}$ is antisymmetric with respect to permutations of the primed or of the unprimed variables, and is of trace 1. However, a proposed density matrix having these properties is not necessarily derivable from an antisymmetric N-particle wave function. The problem of determining conditions on a proposed density matrix such that there exists at least one antisymmetric function Ψ from which the given $D^{(p)}$ can be obtained according to Eq. (1) is known as the (pure state) N-representability problem.[7-17] It has received much attention in recent years but remains unsolved.

One reason for interest in this problem is that it would be easier to do a variational calculation with the 2-matrix directly than with a many-electron wave function.[10,18,19] This is particularly true when correlation effects are of interest, since they can be dealt with fairly well in two-electron systems. If a trial density matrix is not N representable, however, then the energy computed as the trace of the product of the density matrix and an appropriate reduced Hamiltonian matrix is not in general an upper bound to the ground-state energy of the system, as is a variational energy calculated from the wave function. The energy calculated from a non-N-representable density matrix is rigorously bounded below only by the lowest eigenvalue of the reduced Hamiltonian. This eigenvalue is also a lower bound for the ground-state energy of the system, and may be quite far below it. Unless N-representability constraints are imposed, a density-matrix calculation is thus of doubtful value.[20-23]

Although N-representability conditions for the 1-matrix can be stated entirely in terms of its eigenvalues, those for the 2-matrix necessarily involve not only the matrix elements but also the geminals in terms of which the matrix is expanded. One of the many problems associated with direct attacks on the N representability of the 2-matrix has been that the conditions on geminals seem to involve the very weakly occupied geminals to exactly the same extent as the most strongly occupied geminals.[13] This is unfortunate since the weakly occupied geminals have relatively little effect on calculated physical properties. It is a consequence of the statement of the N-representability question in "all or nothing" terms. We are thus led to consider the possibility of an *approximately* N-representable density matrix.

Some work has been done in which conditions which are known to be necessary, but not sufficient, for N representability are imposed and a variational calculation carried out. The results have been encouraging.[10,24,25] Perhaps if enough necessary conditions are imposed the resultant density matrices will not be too far from being N representable. It would clearly be more satisfactory, however, if some measure of deviation from N representability could be introduced and the consequences for calculation of properties such as the energy quantitatively estimated.

In this paper we will consider the following question, which is closely related to that of the N representability of a 2-matrix: Given a set of M orthonormal antisymmetric spin geminals $\{\phi_i(1,2), i=1,\ldots,M\}$ in terms of which 2-matrices can be

expressed as

$$D^{(2)}(1,2;1',2') = \sum_{i,j=1}^{M} d_{ij}\,\phi_i(1,2)\phi_j^*(1',2'), \qquad (2)$$

what are the restrictions on the coefficients d_{ij} such that $\underline{D}^{(2)}$ is as nearly N representable as possible? We find this problem to be somewhat more tractable than the N-representability problem itself. It will be of interest if we can establish a measure of the extent to which $\underline{D}^{(2)}$ is N representable, and an estimate of the maximum extent to which an energy calculated from $\underline{D}^{(2)}$ can fall below the ground-state energy of the system. Since we hope to do a variational calculation, we want to obtain a density matrix which has some free parameters in it. We will examine the way in which maximization of N representability interacts with minimization of the approximate energy.

As a first step in investigating the question posed above, we introduce in Sec. II a continuous measure of the N representability of a density matrix, and define a procedure which can in principle be used to obtain the density matrix or matrices of optimal N representability for a given geminal basis set. The method could easily be extended to consider a general p matrix, but we will confine our discussion to the 2-matrix, because of its physical interest for systems of pairwise interacting fermions. We find that the exact N-representability problem can be treated as a special case, but the solution which then results is not of great interest, leading in general to the equivalent of a complete configuration-interaction (CI) calculation.

In Sec. III we consider the effects of approximate N representability on variational energy calculations. We find that the maximum extent to which the calculated energy can go below the true ground-state energy can be related to our measure of N representability and to the eigenvalues of the reduced Hamiltonian in a greatly restricted basis set.

In Sec. IV we expand on methods of calculation which could be used in practice and consider the effects of truncation of certain expansions on our results. We also show how the geminal set can be systematically expanded to improve N representability and decrease maximum possible errors. We conclude with a discussion in Sec. V of the results which have been obtained, and a view to future efforts.

II. DEVELOPMENT OF FORMALISM

In this treatment we will assume that we have available a fixed set of orthonormal antisymmetric spin geminals $\{\phi_i\}$. They may be explicitly correlated or given as CI expansions in Slater geminals. Any member of the family of N-particle functions whose 2-matrix is expressible in terms of these spin geminals can be written as

$$\Psi(1\cdots N) = \sum_{i=1}^{M} \phi_i(1,2)\chi_i(3\cdots N)\,, \qquad (3)$$

where the χ_i are arbitrary $N-2$ particle functions. Of course, Ψ will not in general be antisymmetric in all particles. The 2-matrix of such a function is given by Eq. (2) with the coefficients d_{ij} determined by

$$d_{ij} = \int \chi_i(3\cdots N)\chi_j^*(3\cdots N)\,d\tau_3\cdots d\tau_N\,. \qquad (4)$$

It is clear that the matrix of coefficients $\underline{d}$ is Hermitian, positive semidefinite, and that $\mathrm{tr}\underline{d} = 1$, if Ψ is normalized to unity. (This will be assumed to be the case throughout what follows.) These are well known necessary conditions for N representability.

We now introduce as a measure of the antisymmetry of Ψ the norm of its antisymmetric component

$$\mu[\Psi] = \int |\mathcal{O}_{1\cdots N}\Psi|^2\,d\tau$$

$$= \int \Psi^*(1\cdots N)\mathcal{O}_{1\cdots N}\Psi(1\cdots N)d\tau_1\cdots d\tau_N\,, \qquad (5)$$

where $\mathcal{O}_{1\cdots N}$ is the N-particle antisymmetric projection operator

$$\mathcal{O}_{1\cdots N} = (N!)^{-1}\sum_{P\in S_N}(-1)^p P. \qquad (6)$$

The summation on P extends over all $N!$ permutations of the N space-spin variables, and p is the parity of P. Because $\mathcal{O}_{1\cdots N}$ is a projection operator and Ψ is normalized we know that $0 \le \mu[\Psi] \le 1$ and that $\mu = 0$ implies that $\mathcal{O}_{1\cdots N}\Psi = 0$, while $\mu = 1$ implies that $\mathcal{O}_{1\cdots N}\Psi = \Psi$. Substituting from Eq. (3) into Eq. (5), we obtain an expression for the measure of antisymmetry for any member of the desired class of functions:

$$\mu[\Psi] = \sum_{i,j=1}^{M} \int \phi_i^*(1,2)\chi_i^*(3\cdots N)\mathcal{O}_{1\cdots N}$$

$$\times\phi_j(1,2)\chi_j(3\cdots N)\,d\tau_1\cdots d\tau_N\,. \qquad (7)$$

This expression can be simplified somewhat when we realize that $\mathcal{O}_{1\cdots N}$ can be decomposed as

$$\mathcal{O}_{1\cdots N} = \binom{N}{2}^{-1}\mathcal{T}\mathcal{O}_{1,2}\mathcal{O}_{3\cdots N}\,. \qquad (8)$$

Here $\mathcal{O}_{1,2}$ and $\mathcal{O}_{3\cdots N}$ are the 2 particle and $N-2$ particle antisymmetric projection operators, respectively, and $\mathcal{T}$ is the sum of all signed transpositions between particles 1 and 2 and particles $3\cdots N$ [26]:

$$\mathcal{T} = 1 - \sum_{j=3}^{N}(P_{1j}+P_{2j}) + \sum_{j<k=3}^{N} P_{1j}P_{2k}\,. \qquad (9)$$

Our method of obtaining the density matrices which can be expanded in terms of the given set of spin geminals and which are as nearly N representable as possible will be to choose the functions $\{\chi_i\}$ so as to maximize $\mu[\Psi]$ and then to take $\underline{d}$ to be given by Eq. (4). In general we will not be able to attain the result $\mu = 1$, which would imply exact N representability. We can, however, interpret the maximum attainable value of μ as a measure of the N representability of the density matrix we have obtained.

The form of $\Theta_{1\cdots N}$ introduced in Eq. (8) makes it clear that in seeking a maximum value of μ for normalized Ψ we need consider only those functions $\chi_i(3\cdots N)$ which are antisymmetric in the $N-2$ particles. The spin geminals ϕ_i are also antisymmetric, by assumption, so that our expression for μ can be written as

$$\mu[\Psi] = \binom{N}{2}^{-1} \sum_{i,j=1}^{M} \int \phi_i^* \chi_i^* \mathcal{T} \phi_j \chi_j \, d\tau_1 \cdots d\tau_N \, . \quad (10)$$

If the antisymmetric functions χ_i are varied so as to make μ stationary subject to the normalization constraint

$$\int \Psi^* \Psi \, d\tau = \sum_{i=1}^{M} \int \chi_i^* \chi_i \, d\tau_3 \cdots d\tau_N = 1, \quad (11)$$

a set of equations satisfied by the optimum $\{\chi_i\}$ is obtained,

$$\sum_{j=1}^{M} \binom{N}{2}^{-1} \int \phi_i^*(1,2) \mathcal{T} \phi_j(1,2) \chi_j(3\cdots N) \, d\tau_1 d\tau_2 = \lambda \chi_i(3\cdots N), \quad i = 1\cdots M \, , \quad (12)$$

where λ is a Lagrange multiplier introduced to assure that Eq. (11) will be satisfied.

In order to make progress in using Eq. (12) to determine the optimum $\{\chi_i\}$, we introduce in Appendix A a set of R (perhaps infinite) orthonormal spin orbitals labeled by $\{\alpha_1, \alpha_2, \ldots, \alpha_R\}$ in terms of which all the $\{\phi_i\}$ can be expressed. For convenience we denote the spin orbitals themselves by the indices α_i. Then

$$\phi_i(1,2) = \sum_{\alpha_1 < \alpha_2 = 1}^{R} (i \mid \alpha_1 \alpha_2)[\alpha_1 \alpha_2] \, . \quad (13)$$

Here $(i \mid \alpha_1 \alpha_2)$ is an expansion coefficient and brackets denote a normalized Slater determinant

$$[\alpha_1 \alpha_2] = 2^{-1/2} \{\alpha_1(1)\alpha_2(2) - \alpha_2(1)\alpha_1(2)\} \, . \quad (14)$$

In general there will be

$$\binom{R}{2}$$

Slater determinants $[\alpha_i \alpha_j]$, but the number M of spin geminals used in the density matrix will be smaller, possibly much smaller, especially if the spin geminals are correlated.

It can also be shown that the *optimum* $\{\chi_i\}$ can be expressed exactly in terms of the

$$\binom{R}{N-2}$$

$N-2$ particle Slater determinants which can be formed from the α_i:

$$\chi_i(3\cdots N) = \sum_{\alpha_3 < \cdots < \alpha_N = 1}^{R} C_{i\alpha_3 \cdots \alpha_N} [\alpha_3 \cdots \alpha_N] = \sum_{\alpha=1}^{\binom{R}{N-2}} C_{i\alpha}[\alpha] \, , \quad (15)$$

where the set $\alpha_3 \cdots \alpha_N$ has been replaced by α for brevity. That this expansion is possible for the optimum $\{\chi_i\}$ can most readily be verified by examining the dependence of the terms in Eq. (12) on one particle, say particle 3, and making use of the antisymmetry of the functions.

Substitution of Eq. (15) into Eq. (10) gives

$$\mu[\Psi] = \binom{N}{2}^{1} \sum_{i,j=1}^{M} \sum_{\alpha,\beta=1}^{\binom{R}{N-2}} C_{i\alpha}^* \times \int \phi_i^*[\alpha]^* \mathcal{T} \phi_j[\beta] \, d\tau \, C_{j\beta} \, , \quad (16)$$

which is a Hermitian form in the coefficients $\{C_{i\alpha}\}$. In Appendix B we show that the integral appearing in Eq. (16) can be further reduced by use of the identity

$$\binom{N}{2}^{-1} \int \phi_i^*[\alpha]^* \mathcal{T} \phi_j[\beta] \, d\tau = \int \phi_i^*[\alpha]^* \hat{T} \phi_j[\beta] \, d\tau = \hat{T}_{i\alpha,j\beta}, \quad (17)$$

with[27,28]

$$\hat{T} = \binom{N}{2}^{-1} \{1 - 2(N-2)P_{13} + \tfrac{1}{2}[(N-2)(N-3)] P_{13} P_{24}\} \, . \quad (18)$$

Equation (16) can then be replaced by

$$\mu[\Psi] = \sum_{i,j=1}^{M} \sum_{\alpha,\beta=1}^{\binom{R}{N-2}} C_{i\alpha}^* \hat{T}_{i\alpha,j\beta} C_{j\beta} \, . \quad (19)$$

The functional $\mu[\Psi]$ is thus a weighted average of the eigenvalues of the matrix $\underline{\hat{T}}$ whose elements are given in Eq. (17). The maximum value of $\mu[\Psi]$ is equal to the largest eigenvalue of $\underline{\hat{T}}$, and occurs when the $\{C_{i\alpha}\}$ are the elements of an eigen-

vector of $\underline{\hat{T}}$ associated with this largest eigenvalue. Thus we are led to consider the eigenvalue equation

$$\sum_{j=1}^{M}\sum_{\beta=1}^{\binom{R}{N-2}} \hat{T}_{i\alpha,j\beta}C_{j\beta} = \lambda C_{i\alpha} \ . \tag{20}$$

The normalization condition on Ψ takes the form

$$\sum_{i=1}^{M}\int \chi_i^* \chi_i \, d\tau_3\cdots d\tau_N = \sum_{i=1}^{M}\sum_{\alpha=1}^{\binom{R}{N-2}} |C_{i\alpha}|^2 = 1 \ , \tag{21}$$

so the eigenvector should be taken to be normalized. We will denote the largest eigenvalue of $\underline{\hat{T}}$ by λ_0, and recall that it may be degenerate. Equation (20) is an eigenvalue equation which can in principle be solved directly, without requiring an iterative process. This reason alone may place the present method closer to being computationally useful than some previous schemes.[29] However, we must remember that the dimension of $\underline{\hat{T}}$ is

$$M\binom{R}{N-2},$$

which can be an extremely large number, or even infinite if R is infinite. In practice it would probably be necessary to choose some truncated set of spin orbitals $\{\alpha_i,\ i=1,\ldots,R'\}$ in terms of which to express the $N-2$ particle Slater determinants. Also, we have in mind a situation in which the number M of spin geminals ϕ_i is much less than

$$\binom{R}{2} \text{ and probably much less than } \binom{R'}{2}.$$

These approximations will be discussed in more detail in Sec. IV.

We assume that the degeneracy of the largest eigenvalue λ_0 is δ and denote the set of orthonormal eigenvectors associated with it by $\{C_{i\alpha}^{(a)},\ a=1,\ldots,\delta\}$. Any linear combination of these will provide a set of coefficients optimizing $\mu[\Psi]$:

$$C_{i\alpha} = \sum_{a=1}^{\delta} Y_a C_{i\alpha}^{(a)} \ , \tag{22}$$

in which the Y_a are arbitrary except for the normalization condition

$$\sum_{a=1}^{\delta} |Y_a|^2 = 1 \ , \tag{23}$$

will be an eigenvector of $\underline{\hat{T}}$ with eigenvalue λ_0 and thus with $\mu=\lambda_0$. The coefficients Y_a can be considered as variational parameters in the density matrix, which is given by Eq. (2) with

$$d_{ij} = \sum_{\alpha=1}^{\binom{R}{N-2}} C_{i\alpha}C_{j\alpha}^*$$

$$= \sum_{a,b=1}^{\delta} Y_a Y_b^* \sum_{\alpha=1}^{\binom{R}{N-2}} C_{i\alpha}^{(a)}C_{j\alpha}^{(b)*} \ . \tag{24}$$

This provides a solution in principle to the problem of constructing optimally N-representable 2-matrices. In practice there would remain problems associated with the construction of $\underline{\hat{T}}$ and the determination of the $\{C_{i\alpha}^{(a)}\}$. Except in simple cases, the large dimension of $\underline{\hat{T}}$ would probably make the time and effort required to carry out these steps prohibitively large. For this reason we will examine later the possibility of decreasing the dimension of $\underline{\hat{T}}$ by truncation of the set of determinants $[\alpha_3\ldots\alpha_N]$ used in the expansion of the optimum $\{\chi_i\}$.

If the $\{\phi_i\}$ were equivalent to the set of all Slater geminals $[\alpha_i\alpha_j]$, which requires that

$$M = \binom{R}{2},$$

then the largest eigenvalue λ_0 would be equal to 1 and its degeneracy δ would be

$$\binom{R}{N}.$$

This is just a restatement of the fact that

$$\binom{R}{N}$$

independent N-particle Slater determinants can be formed from N spin orbitals.[30,31] The present approach then reduces (or expands) to the equivalent of a conventional full CI calculation. In practice we hope to use a number M of spin geminals which is much smaller. The question of how this reduction will affect the value of λ_0 and its degeneracy is difficult to answer in general.

For such smaller sets of spin orbitals, λ_0 may be nondegenerate or the degeneracy may be low. There may, however, be other eigenvalues of $\underline{\hat{T}}$ nearly as large as λ_0. We can then gain more flexibility in the density matrix by including in the expansion of Eq. (22) eigenvectors associated with these slightly smaller eigenvalues. The result will, of course, be to decrease slightly the value of $\mu[\Psi]$, i.e., the N representability of the density matrix. The effects of such a decrease will be considered below, when we consider the error bounds which can be placed on energies calculated from the density matrix. It may be that a small loss of N representability is tolerable in order to gain variational flexibility.

To make more explicit this possibility, let us suppose that we have decided that there are $q+1$

different eigenvalues of $\hat{\underline{T}}$, $\lambda_0, \lambda_1, \ldots, \lambda_q$, with degeneracies $\delta_0, \delta_1, \ldots, \delta_q$, respectively, that are large enough to be included. The eigenvectors associated with them are added to the expansion, and Eq. (22) is replaced by

$$C_{i\alpha} = \sum_{t=0}^{q} \sum_{a=1}^{\delta_t} Y_{at} C_{i\alpha}^{(t,a)} \quad , \tag{25}$$

where $C_{i\alpha}^{(t,a)}$ is the ath eigenvector of $\hat{\underline{T}}$ associated with eigenvalue λ_t. The normalization condition then becomes

$$\sum_{t=0}^{q} \sum_{a=1}^{\delta_t} |Y_{at}|^2 = 1 \tag{26}$$

and the N representability is measured by

$$\mu[\Psi] = \sum_{t=0}^{q} \sum_{a=1}^{\delta_t} |Y_{at}|^2 \lambda_t \quad . \tag{27}$$

Before turning to a discussion of errors, methods, and approximations, we find it of interest to relate this treatment to the exact N-representability problem for a given density matrix. We note that the $\{C_{i\alpha}\}$ are not the only coefficients which will lead to the matrix $\underline{d}$. From the properties of $\underline{d}$ we know that there exists a square Hermitian matrix $\underline{d}^{1/2}$ such that

$$\sum_{k=1}^{M} d_{ik}^{1/2} d_{kj}^{1/2} = d_{ij} \quad . \tag{28}$$

To relate $\underline{d}^{1/2}$ to $\underline{C} = \{C_{i\alpha}\}$ we define the rectangular matrix $\underline{V}$ by

$$C_{i\alpha} = \sum_{j=1}^{M} d_{ij}^{1/2} V_{j\alpha} \quad . \tag{29}$$

It then follows from Eq. (28) and

$$d_{ij} = \sum_{\alpha=1}^{\binom{R}{N-2}} C_{i\alpha} C_{j\alpha}^*$$

$$= \sum_{k,l=1}^{M} \sum_{\alpha=1}^{\binom{R}{N-2}} d_{ik}^{1/2} V_{k\alpha} V_{l\alpha}^* d_{jl}^{1/2*} \tag{30}$$

that

$$\sum_{\alpha=1}^{\binom{R}{N-2}} V_{i\alpha} V_{j\alpha}^* = \delta_{ij} \quad . \tag{31}$$

However, it is not necessarily true that

$$\sum_{j=1}^{M} V_{j\alpha}^* V_{j\beta} = \delta_{\alpha\beta} \quad .$$

Matrices such as $\underline{V}$ are referred to as partial isometries.

To relate these partial isometries to the exact N-representability problem, let us suppose that we are given a Hermitian non-negative matrix $\underline{d}$ of unit trace, and a set of orthonormal antisymmetric spin geminals $\{\phi_i\}$. We can then use Eq. (29) to define a set of coefficients $\{C_{i\alpha}\}$ and thus a wave function Ψ, for *any* partial isometry $\underline{V}$. We substitute this expression for the coefficients into Eq. (19) and obtain

$$\mu[\Psi] = \sum_{k,l=1}^{M} \sum_{\alpha,\beta=1}^{\binom{R}{N-2}} V_{k\alpha}^* (\underline{d}^{1/2} \hat{\underline{T}} \underline{d}^{1/2})_{k\alpha,l\beta} V_{l\beta} \quad , \tag{32}$$

where

$$(\underline{d}^{1/2} \hat{\underline{T}} \underline{d}^{1/2})_{k\alpha,l\beta} = \sum_{i,j=1}^{M} d_{ki}^{1/2} \hat{T}_{i\alpha,j\beta} d_{jl}^{1/2} \quad .$$

If we now vary the $\{V_{i\alpha}\}$ to make $\mu[\Psi]$ stationary, subject to the constraints

$$\sum_{\alpha=1}^{\binom{R}{N-2}} V_{i\alpha} V_{j\alpha}^* = d_{ij}, \quad i,j = 1, \ldots, M, \tag{33}$$

we obtain the set of equations

$$\sum_{l=1}^{M} \sum_{\beta=1}^{\binom{R}{N-2}} (\underline{d}^{1/2} \hat{\underline{T}} \underline{d}^{1/2})_{k\alpha,l\beta} V_{l\beta} = \sum_{l=1}^{M} \epsilon_{kl} V_{l\alpha} \quad . \tag{34}$$

The ϵ_{kl} are Lagrange multipliers associated with the constraints of Eq. (33). Since we initially know neither the elements of the optimum $\underline{V}$ nor the Lagrange multipliers $\underline{\epsilon}$, Eq. (34) would have to be solved iteratively, if at all. If this can be done, we obtain

$$\mu[\Psi] = \sum_{k,l=1}^{M} \sum_{\alpha=1}^{\binom{R}{N-2}} \epsilon_{kl} V_{l\alpha} V_{k\alpha}^*$$

$$= \sum_{k,l=1}^{M} \epsilon_{kl} \delta_{kl} = \sum_{k=1}^{M} \epsilon_{kk} = \mathrm{tr}\underline{\epsilon} \quad . \tag{35}$$

We conclude that if the trace of the Lagrange multiplier matrix $\underline{\epsilon}$ is 1, then the given density matrix is exactly N representable. When $\mathrm{tr}\underline{\epsilon} < 1$, we interpret its value as a measure of how nearly N representable the density matrix is. Because of the large dimension of $\underline{d}^{1/2} \hat{\underline{T}} \underline{d}^{1/2}$, and because we

do not know that Eq. (34) can in fact be solved, there is little hope that this method will be computationally useful. This discussion has been presented only to establish the connection between our approach and the exact N-representability problem for a given density matrix.

There is another formulation of the exact N-representability problem for a given density matrix which avoids the difficulties associated with Eq. (34), although again the solution provided is one in principle rather than one of practical utility. Given a Hermitian non-negative matrix $\underline{d}$ of unit trace and a set of orthonormal antisymmetric spin geminals $\{\phi_i\}$, we first construct the matrix $\underline{\hat{T}}$ and find the δ different eigenvectors associated with the largest eigenvalue λ_0. If λ_0 is not unity, the density matrix cannot be N representable, so the question is answered. If λ_0 is equal to 1, we must determine whether the parameters $\{Y_a\}$ of Eq. (22) can be chosen so the Eq. (24) yields the *given* values of the d_{ij}. The density matrix will be N representable if and only if such coefficients can be found. If we define

$$P_{ij,ab} = \sum_{\alpha=1}^{\binom{R}{N-2}} C_{i\alpha}^{(a)} C_{j\alpha}^{(b)*} \tag{36}$$

and

$$Z_{ab} = Y_a Y_b^* , \tag{37}$$

Eq. (24) can be rewritten as

$$\sum_{a,b=1}^{\delta} P_{ij,ab} Z_{ab} = d_{ij} , \quad i,j = 1, \ldots, M . \tag{38}$$

This can be thought of as M^2 linear equations in the δ^2 unknowns Z_{ab}, of which only δ are independent. That is, if we know $Y_1 Y_1^*$, $Y_1 Y_2^*$, ..., $Y_1 Y_\delta^*$ we can determine all of the coefficients to within a single arbitrary phase factor. As in all systems of linear equations, the existence of solutions is governed by the rank of the matrix $\underline{P}$ and the rank of the augmented matrix which is formed by adjoining the "column vector" $\underline{d}$ to $\underline{P}$,

$$\underline{P}^a = \begin{pmatrix} d_{11} & P_{11,11} & \cdots & P_{11,\delta\delta} \\ d_{12} & P_{12,11} & & P_{12,\delta\delta} \\ \cdots & \cdots & & \cdots \\ \cdots & \cdots & & \cdots \\ \cdots & \cdots & & \cdots \\ d_{MM} & P_{MM,11} & & P_{MM,\delta\delta} \end{pmatrix} . \tag{39}$$

From the ranks of $\underline{P}$ and $\underline{P}^a$ we can in principle learn how many, if any, of the unknowns Z_{ab} are determined and how many are arbitrary. If the density matrix is to be N representable there must be a nontrivial solution to Eq. (38) having the further property that

$$Z_{ab} = Z_{ba}^* . \tag{40}$$

Methods, and even computational procedures, exist by which Eq. (38) can be solved and the solutions tested to see if the necessary conditions are satisfied. We are thus able in principle to test the N representability of a given density matrix. Because of the large dimensions of $\underline{\hat{T}}$ and $\underline{P}$, however, this approach is not useful, and is perhaps better characterized as a restatement rather than a solution of the N-representability problem.

Let us review what we have found in this section. To construct optimally N-representable 2-matrices from a given set of orthonormal antisymmetric spin geminals, we must find the eigenvectors associated with the largest eigenvalue λ_0 of the

$$M \binom{R}{N-2}$$

dimensional matrix $\underline{\hat{T}}$. The required coefficient matrix is then given by Eq. (24), and λ_0 is a measure of how N representable the resultant density matrix is, with the value 1 corresponding to exact N representability. Additional eigenvectors of $\underline{\hat{T}}$ associated with eigenvalues nearly as large as λ_0 may also be included to increase the variational freedom, with some loss of N representability. This approach can also be related to the exact N-representability problem for a given density matrix, but the resultant equations are not practical to work with.

III. CONSEQUENCES OF APPROXIMATE N REPRESENTABILITY

As we remarked earlier, one reason for interest in the N-representability problem is the desire to do variational calculations directly with the reduced density matrix, which is a potentially simpler thing than the wave function. If the Hamiltonian for the system is of the form

$$\mathcal{H} = \sum_{i=1}^{N} f(i) + \sum_{i>j=1}^{N} g(ij) , \tag{41}$$

then a *reduced* Hamiltonian may be defined as[32]

$$\mathcal{K} = \tfrac{1}{2} N [f(1) + f(2) + (N-1)\, g(1,2)] , \tag{42}$$

such that for an antisymmetric wave function Ψ

$$\tilde{E} \equiv \mathrm{tr}(\underline{K}\,\underline{d}) = \int \Psi^* \mathcal{H} \Psi \, d\tau , \tag{43}$$

where $\underline{K}$ is the matrix of $\mathcal{K}$ in the $\{\phi_i\}$ basis:

$$K_{ij} = \int \phi_i^*(1,2)\, \mathcal{K}\, \phi_j(1,2)\, d\tau_1\, d\tau_2 . \tag{44}$$

If Ψ is not antisymmetric the two expressions for $\tilde{E}$ are not equivalent, and $\tilde{E}$ calculated from $\underline{d}$ is

not an upper bound to E_0, the ground-state energy of a fermion system defined by $\mathcal{K}$.[33] Since $\underline{d}$ is in any case so defined as to be a non-negative Hermitian matrix, it will be true that

$$\tilde{E} \geq \epsilon_0 , \tag{45}$$

where ϵ_0 is the lowest eigenvalue of $\mathcal{K}$. However, ϵ_0 is a *lower* bound to the ground-state energy of the N electron system. In this section we will consider the errors which can arise from the use of a density matrix that is only approximately N representable. We will show that the extent to which $\tilde{E}$ can fall below the ground-state energy is related to μ, the measure of N representability introduced in Sec. II, and approaches zero as μ approaches 1.

We begin by introducing a *remainder function* $\Omega(1, 2, \ldots, N)$ defined for any Ψ of the type in Eq. (3) by

$$\Omega(1, \ldots, N) = [\mathcal{O}_{1\ldots N} - \mu]\Psi , \tag{46}$$

with μ determined from Ψ by Eq. (5). This function is antisymmetric in the first two particles, and if only antisymmetric χ's are considered, it is also antisymmetric in the last $N-2$ particles:

$$\mathcal{O}_{1,2}\Omega = \mathcal{O}_{3\ldots N}\Omega = \Omega . \tag{47}$$

If the optimum χ' s are used, corresponding to $\mu = \lambda_0$, then it also follows from Eq. (12) that Ω is orthogonal to all of the ϕ_i:

$$\int \phi_i^*(1, 2)\Omega(1, 2, 3\cdots N)\, d\tau_1\, d\tau_2 = 0 . \tag{48}$$

The square of the norm of Ω is

$$\begin{aligned} ||\Omega||^2 &= \int |\Omega|^2\, d\tau \\ &= \int [(\mathcal{O}_{1\ldots N} - \mu)\Psi]^* (\mathcal{O}_{1\ldots N} - \mu)\Psi\, d\tau \\ &= \mu - 2\mu^2 + \mu^2 = \mu(1-\mu) . \end{aligned} \tag{49}$$

For an antisymmetric function such as $\mathcal{O}\psi$ it is readily shown by relabeling variables of integration that[34]

$$\begin{aligned} \hat{E} &= \int (\mathcal{O}\Psi)^* \mathcal{K}\mathcal{O}\Psi\, d\tau / \int |\mathcal{O}\Psi|^2\, d\tau \\ &= \int (\mathcal{O}\Psi)^* \mathcal{K}\mathcal{O}\Psi\, d\tau / \int |\mathcal{O}\Psi|^2\, d\tau . \end{aligned} \tag{50}$$

It is clear also, by the variation principle, that $\hat{E} > E_0$. We will consider the possible difference between $\hat{E}$ and $\tilde{E}$ defined in terms of the density matrix. Of course, any other symmetric one- or two-electron operator can be substituted for the Hamiltonian if an appropriate reduced operator is also defined, but the comparison with E_0 has an analogy only for operators that are bounded below.

We look first at the expectation value of $\mathcal{K}$ with respect to Ω

$$\begin{aligned} \langle\Omega|\mathcal{K}|\Omega\rangle &= \langle\mathcal{O}\Psi - \mu\Psi|\mathcal{K}|\mathcal{O}\Psi - \mu\Psi\rangle \\ &= \langle\Psi|\mathcal{O}\mathcal{K}\mathcal{O}|\Psi\rangle - \mu[\langle\Psi|\mathcal{K}|\mathcal{O}\Psi\rangle \\ &\quad + \langle\mathcal{O}\Psi|\mathcal{K}|\Psi\rangle] + \mu^2\langle\Psi|\mathcal{K}|\Psi\rangle . \end{aligned} \tag{51}$$

Making use of $\mathcal{O}\Psi = \Omega + \mu\Psi$ and the definitions of μ and Ω, we rewrite this as

$$\begin{aligned} \langle\Omega|\mathcal{K}|\Omega\rangle = \mu\, &\frac{\langle\Psi|\mathcal{O}\mathcal{K}\mathcal{O}|\Psi\rangle}{\langle\Psi|\mathcal{O}\Psi\rangle} + \mu^2\, \frac{\langle\Psi|\mathcal{K}|\Psi\rangle}{\langle\Psi|\Psi\rangle} \\ &- \mu\left(2\mu\, \frac{\langle\Psi|\mathcal{K}|\Psi\rangle}{\langle\Psi|\Psi\rangle} + \langle\Psi|\mathcal{K}|\Omega\rangle + \langle\Omega|\mathcal{K}|\Psi\rangle\right) \end{aligned} \tag{52}$$

or

$$\langle\Omega|\mathcal{K}|\Omega\rangle + \mu[\langle\Psi|\mathcal{K}|\Omega\rangle + \langle\Omega|\mathcal{K}|\Psi\rangle] = \mu\hat{E} - \mu^2\tilde{E} , \tag{53}$$

since

$$\langle\Psi|\mathcal{K}|\Psi\rangle / \langle\Psi|\Psi\rangle = \langle\Psi|\mathcal{K}|\Psi\rangle = \mathrm{tr}(\underline{d}\,\underline{K}) = \tilde{E} . \tag{54}$$

Then using the triangle inequality we find

$$|\mu\hat{E} - \mu^2\tilde{E}| \leq |\langle\Omega|\mathcal{K}|\Omega\rangle| + 2\mu\,|\langle\Omega|\mathcal{K}|\Psi\rangle| . \tag{55}$$

A more useful relationship can be obtained by using bounds for the terms on the right-hand side. By the Schwarz inequality,

$$|\langle\Psi|\mathcal{K}|\Omega\rangle|^2 \leq ||\Omega||^2 ||\mathcal{K}\Psi||^2 = \mu(1-\mu)\langle\Psi|\mathcal{K}^2|\Psi\rangle . \tag{56}$$

It should be noted that $\mathcal{K}^2$, the square of a two-electron operator, is itself a two-electron operator. It follows that

$$\langle\Psi|\mathcal{K}^2|\Psi\rangle = \mathrm{tr}(\underline{K}^2\,\underline{d}) . \tag{57}$$

The remaining term can be bounded as

$$|\langle\Omega|\mathcal{K}|\Omega\rangle| \leq \langle\Omega|\Omega\rangle\, |e|_{\max} = \mu(1-\mu)\,|e|_{\max} , \tag{58}$$

where $|e|_{\max}$ is the eigenvalue of maximum absolute value associated with $\mathcal{K}$ in the space spanned by the Slater spin geminals $[\alpha_i\alpha_j]$. This follows from the expansion of Eq. (15).

We have seen earlier that in the case of the optimum $\{\chi_i\}$ when $\mu = \lambda_0$, Ω is orthogonal to all the spin geminals ϕ_i. In this case it follows that

$$|\langle\Omega|\mathcal{K}|\Omega\rangle| \leq \mu(1-\mu)\,|e'|_{\max} , \tag{59}$$

where $|e'|_{\max}$ is the eigenvalue of maximum absolute value associated with $\mathcal{K}$ in the difference space between that spanned by all the Slater geminals and that spanned by the ϕ_i. The dimension of this difference space is

$$\binom{R}{2} - M .$$

Our bound on the energy difference is thus

$$\begin{aligned} &|\hat{E} - \mu\tilde{E}| \\ &\quad \leq (1-\mu)\,|e|_{\max} + 2[\mu(1-\mu)]^{1/2}[\mathrm{tr}(\underline{K}^2\,\underline{d})]^{1/2} , \end{aligned} \tag{60}$$

and if the optimum χ_i are used, $|e|_{\max}$ can be replaced by $|e'|_{\max}$. The occurrence of μ multiply-

ing $\tilde{E}$ is somewhat unfortunate, but not really serious since presumably $\mu \sim 1$ in cases of interest.

Since both terms on the right-hand side of Eq. (60) contain $(1-\mu)$, the bound can be improved by modifying the spin geminal set to increase μ. In the limit when μ becomes equal to 1 the bound goes to zero and $\hat{E} = \tilde{E}$. For μ's somewhat less than 1, if the optimum χ_i have been used and the term involving $|e'|_{\max}$ makes a significant contribution, the bound can be reduced by a particular augmentation of the spin geminal basis. We add to the set $\{\phi_i\}$ the eigenfunctions of $\mathcal{K}$, within the difference space, which are associated with large eigenvalues. Because the new difference space which remains does not contain these high-energy functions, the effect of this procedure will be to reduce $|e'|_{\max}$ and thus to improve our bound. Such an augmentation will clearly not decrease the optimum value of μ.

Of course, we could augment the spin geminal basis by adding *all* of the functions in the difference space. We would then have to deal with a set of

$$\binom{R}{2}$$

functions equivalent to the full set of Slater geminals $[\alpha_i\alpha_j]$, and would again be in effect doing a complete CI calculation.

IV. METHODS OF CALCULATION AND EFFECTS OF TRUNCATION

Clearly, the possible practical utility of the method described above for the construction of optimally N-representable density matrices is dependent on our ability to construct the

$$M\binom{R}{N-2}$$

dimensional matrix $\underline{\hat{T}}$ and to find the eigenvectors $\{C_{i\alpha}^{(a)}\}$ associated with the largest eigenvalue λ_0. Let us first turn our attention to the evaluation of the elements of $\underline{\hat{T}}$. The operator $\hat{T}$ is defined in Eq. (18) and the matrix elements of interest are those of Eq. (17). Using the well-known rules for evaluating matrix elements of one- and two-particle operators between Slater determinants, we obtain the following expressions for contributions to $\hat{T}_{i\alpha,j\beta}$:

$$\int \phi_i^*[\alpha]^*\,\phi_j[\beta]\,d\tau = \delta_{ij}\delta_{\alpha\beta} \quad , \tag{61}$$

$$\int \phi_i^*[\alpha]^* P_{13}\,\phi_j[\beta]\,d\tau$$

$$= (N-2)^{-1}\sum_{k=3}^{N}\int \phi_i^*(1,2)\alpha_k^*(3)\phi_j(3,2)\alpha_k(1)\,d\tau \qquad \text{if } \alpha=\beta$$

$$= (N-2)^{-1}(-1)^{k+m}\int \phi_j(1,2)\alpha_k^*(3)\phi_j(3,2)\beta_m(1)\,d\tau \qquad \text{if } \alpha=\alpha_k=\beta-\beta_m$$

$$= 0 \qquad \text{otherwise} \tag{62}$$

$$\int \phi_i^*[\alpha]^* P_{13}P_{24}\phi_j[\beta]\,d\tau$$

$$= \binom{N-2}{2}^{-1}\sum_{k<l=3}^{N}\int \phi_i^*(1,2)[\alpha_k\alpha_l](1,2)\,d\tau \times\int[\alpha_k\alpha_l]^*(3,4)\phi_j(3,4)\,d\tau \quad \text{if } \alpha=\beta$$

$$= (-1)^{k+m}\binom{N-2}{2}^{-1}\sum_{l=3}^{N}\int \phi_i^*(1,2)[\beta_m\alpha_l](1,2)\,d\tau \times\int[\alpha_k\alpha_l]^*(3,4)\phi_j(3,4)\,d\tau \quad \text{if } \alpha-\alpha_k=\beta-\beta_m$$

$$= (-1)^{k+l+m+n}\binom{N-2}{2}^{-1}\int \phi_i^*(1,2)[\beta_m\beta_n](1,2)\,d\tau \times\int[\alpha_k\alpha_l]^*(3,4)\phi_j(3,4)\,d\tau \quad \text{if } \alpha-\alpha_k-\alpha_l=\beta-\beta_m-\beta_n$$

$$= 0 \qquad \text{otherwise.} \tag{63}$$

The notation $\alpha=\beta$ means that the two sets $\{\alpha_3\ldots\alpha_N\}$ and $\{\beta_3\ldots\beta_N\}$ are identical; $\alpha-\alpha_k=\beta-\beta_m$ means that the two sets differ only in the unequal indices α_k and β_m, the other indices in the α set being the same as the other indices in the β set; and $\alpha-\alpha_k-\alpha_l=\beta-\beta_m-\beta_n$ means that the two sets differ in the two indices α_k, α_l and β_m, β_n only. If strongly orthogonal geminals[35] are used, all the integrals are zero except in Eq. (61) and the third case in Eq. (63). Since the spin geminals $\{\phi_i\}$ can also be expanded in terms of the spin-orbital set $\{\alpha\}$, these results can be expressed entirely in terms of the expansion coefficients of Eq. (13), which are determined by

$$(i|\alpha_1\alpha_2) = \int[\alpha_1\alpha_2]^*\phi_i\,d\tau \ . \tag{64}$$

It should be noted that only the coefficients with $\alpha_1<\alpha_2$ are required in Eq. (13). It is convenient for the expressions we now want, and consistent with Eqs. (13) and (64), to allow either order with $(i|\alpha_2\alpha_1) = -(i|\alpha_1\alpha_2)$. The expressions for the integrals can then be written

$$\int \phi_i^*[\alpha]^*\phi_j[\beta]\,d\tau = \delta_{ij}\delta_{\alpha\beta} \ , \tag{65}$$

$$\int \phi_i^*[\alpha]^* P_{13}\phi_j[\beta]\,d\tau$$

$$= \tfrac{1}{2}(N-2)^{-1}\sum_{k=3}^{N}\sum_{\alpha_1=1}^{R}(i\,|\,\alpha_k\alpha_1)^*(j\,|\,\alpha_k\alpha_1) \qquad \text{if } \alpha=\beta$$

$$= \tfrac{1}{2}(-1)^{k+m}(N-2)^{-1}\sum_{\alpha_1=1}^{R}(i\,|\,\beta_m\alpha_1)^*(j\,|\,\alpha_k\alpha_1)$$

if $\alpha - \alpha_k = \beta - \beta_k$

$= 0$ otherwise, (66)

$$\int \phi_i^*[\alpha]^* P_{13} P_{24} \phi_j[\beta]\, d\tau$$

$$= \binom{N-2}{2}^{-1} \sum_{k<l=3}^{N} (i|\alpha_k\alpha_l)^*(j|\alpha_k\alpha_l)$$

if $\alpha = \beta$

$$= (-1)^{k+m}\binom{N-2}{2}^{-1} \sum_{l=3}^{N} (i|\beta_m\alpha_l)^*(j|\alpha_k\alpha_l)$$

if $\alpha - \alpha_k = \beta - \beta_m$

$$= (-1)^{k+l+m+n}\binom{N-2}{2}^{-1} (i|\beta_m\beta_n)^*(j|\alpha_k\alpha_l)$$

if $\alpha - \alpha_k - \alpha_l = \beta - \beta_m - \beta_n$

$= 0$ otherwise . (67)

These integrals provide all the information we need to evaluate the elements of $\underline{\hat{T}}$. Because of the large dimension of $\underline{\hat{T}}$ it will be difficult, or at least time consuming, to find the largest eigenvalue and the eigenvectors associated with it. Many of the matrix elements are zero, but even though the matrix is quite sparse it does not appear to have any block structure which might aid in the diagonalization.

The trace of $\underline{\hat{T}}$ is of some interest. Since the positive quantity $\mu[\Psi]$ is expressed in Eq. (19) as a potentially arbitrary weighted average of the eigenvalues of $\underline{\hat{T}}$, all the eigenvalues must be nonnegative, and $\lambda_0\delta$ thus cannot exceed the trace of $\underline{\hat{T}}$. This quantity can be evaluated from the diagonal matrix element expressions included above. It is found that the expansion coefficients occur only in sums that can be put in the form

$$\sum_{\alpha_1<\alpha_2=1}^{R} |(i|\alpha_1\alpha_2)|^2 ,$$

which is 1 if ϕ_i is normalized. The trace is thus independent of the expansion coefficients. It is

$$\mathrm{Tr}\underline{\hat{T}} = 2M(R-2)!/[N!(R-N)!] . \quad (68)$$

We note that it is simply proportional to M, the number of spin geminals in the set.

If $M = \binom{R}{2}$, then the trace is $\binom{R}{N}$.

We expect that in this case the eigenvalue 1 will occur with

degeneracy $\binom{R}{N}$.

If $M < \binom{R}{2}$ then $\mathrm{Tr}\underline{\hat{T}} < \binom{R}{N}$.

We have noted previously that the number R of spin orbitals $\{\alpha_i\}$ may be very large or even, if correlated geminals are used, infinite. It may thus be necessary to truncate the set, using only some smaller number R'. In addition, we may find it a practical necessity to use only

$$S < \binom{R'}{N-2}$$

of the possible $N-2$ particle determinants made up from these spin orbitals. Either of these truncations will affect our estimation of μ and also the elements d_{ij} which we ascribe to the optimally N-representable density matrix.

As an initial step in the estimation of the consequences of such truncations, we note that much of what we have done above is in fact valid for any choice of basis set. The particular choice $\{\alpha_i, i = 1 \cdots R\}$ is merely one which is convenient and is capable of leading to optimum results. Equation (7) defines $\mu[\Psi]$ for any $\{\chi_i\}$, and so long as these functions are antisymmetric, the expression of Eq. (10) follows. If the χ_i are expanded in terms of some set of Slater determinants built up from orthonormal spin orbitals, we can arrive at Eq. (19) and the optimum expansion coefficients are obtained from Eq. (20). The optimum density matrix has $\underline{d}$ given by Eq. (24). None of this requires that the set of spin orbitals be complete for the expansion of the spin geminals ϕ_i or that the sum over the $N-2$ particle determinants include all possible choices. If these conditions are not met, we will not be able in general to attain the truly optimum μ or find the truly best $\underline{d}$ possible for the given set $\{\phi_i\}$. This loss of complete optimization may be offset by gains in convenience, however. We will still be able to estimate the consequences of only approximate N representability and thus to decide in a given case if the results are good enough.

In deciding which spin orbitals and which determinants to include in the truncated sets we must be guided by the following considerations: We want the largest eigenvalue of $\underline{\hat{T}}$, λ_0, to be close to unity and its degeneracy (or the number of other eigenvalues nearly degenerate with it) to be sufficiently large to give good variational freedom, but not so large as to return us effectively to the CI problem. It is difficult to formulate specific criteria in the general case. The fact that we are trying to make Ψ as nearly antisymmetric as possible, together with the effect that various functions have in attaining this goal as indicated by the results above, suggests certain features of the criteria, however. Those spin orbitals which figure significantly in the $\{\phi_i\}$ must be included. For a general set of spin orbitals $\{\alpha_i'\}$, we can say that

α_i' and α_j' must be included in any truncated set if $\int [\alpha_i' \alpha_j']^* \phi_k \, d\tau$ is large for any k. Similarly, the determinants which are most important to include are those containing the greatest numbers of the most important spin orbitals.

Let us consider finally the problem of using the density matrices resulting from the above procedures to calculate properties of our system. We suppose that we have chosen not only the set of spin geminals $\{\phi_i\}$, but also a set of spin orbitals $\{\alpha_i', i = 1 \cdots R'\}$ and selected some S of the $N-2$ particle determinants made up from them. We suppose that $\underline{\hat{T}}$ has been formed and the $q+1$ largest eigenvalues, $\lambda_0, \ldots, \lambda_q$, together with their associated eigenvectors $\{C_{i\alpha'}^{(t,a)}, \; t = 0, \ldots, q, \; a = 1 \ldots \delta_t\}$ have been found. The 2-matrix is then given by Eq. (2) with

$$d_{ij} = \sum_{\alpha'=1}^{\delta} \sum_{t,u=0}^{q} \sum_{a=1}^{\delta_t} \sum_{b=1}^{\delta_u} Y_{at} Y_{bu}^* \times C_{i\alpha'}^{(t,a)} C_{j\alpha'}^{(u,b)*} . \tag{69}$$

The expectation value of a two-particle operator G can be written as

$$\langle G \rangle = \binom{N}{2} \sum_{i,j=1}^{M} d_{ij} G_{ji} = \sum_{t,u=0}^{q} \sum_{a=1}^{\delta_t} \sum_{b=1}^{\delta_u} Y_{bu}^* \overline{G}_{bu,at} Y_{at} \; , \tag{70}$$

with

$$G_{ji} = \int \phi_j^*(1,2) g_{12} \phi_i(1,2) \, d\tau_1 \, d\tau_2 \tag{71}$$

or

$$\overline{G}_{bu,at} = \binom{N}{2} \sum_{i,j=1}^{M} \sum_{\alpha'=1}^{S} C_{j\alpha'}^{(u,b)*} G_{ji} C_{i\alpha'}^{(t,a)} \; . \tag{72}$$

When our interest is in the energy of the system we introduce the reduced Hamiltonian $\mathcal{K}$, as in Sec. III. We seek to make the value of $\tilde{E}$ stationary, subject to the normalization constraint of Eq. (26). We obtain in the usual way an eigenvalue equation

$$\sum_{t=0}^{q} \sum_{a=1}^{\delta_t} K_{bu,at} Y_{at} = E Y_{bu} \; . \tag{73}$$

The dimension of the matrix $\underline{K}$ which must be considered is the sum of the degeneracies of the eigenvalues which have been included:

$$\text{dimension } (\underline{K}) = \sum_{t=0}^{q} \delta_t \; . \tag{74}$$

The lowest eigenvalue in Eq. (73) is our approximation to the ground-state energy of the system. Its associated normalized eigenvector can be substituted into Eq. (69) to determine an approximation to the 2-matrix for the system in its ground state, and from this, other properties can be determined. In the same way, higher eigenvalues and their associated eigenvectors can be used to approximate properties of excited states of the system. We would expect the approximation to get progressively worse as we go higher, and it is obvious that to obtain a full description we would have to work with a matrix of infinite dimension.

For the ground state, where our approximation should be the best, we can calculate μ from Eq. (27) and bound $|\hat{E} - \mu \tilde{E}|$ by using Eq. (60). Since $\hat{E}$ is an upper bound to the true ground-state energy, this establishes a maximum on the extent to which our estimate may fall below the true value. Of course, if the $\{\phi_i\}$ are poorly chosen or we have too few linear variational parameters our value may be far above the true value. This is common to all variational calculations, however.

V. DISCUSSION OF RESULTS

We have proposed here a method whereby, given some set of spin geminals, we can find the 2-matrices expressible in terms of them which are as nearly N representable as possible. We introduce a family of wave functions, not necessarily antisymmetric, which lead to 2-matrices involving only the given set of spin geminals. The norm of the antisymmetric component of such a normalized wave function is taken as a measure of the N representability of the corresponding density matrix. The wave functions are then varied to maximize this quantity, and thus to obtain the most nearly N-representable density matrix. The wave function itself need not appear explicitly at any stage, however. The measure of N representability and the density matrix are determined from the eigenvalues and eigenvectors of a matrix $\underline{\hat{T}}$. We have given explicit expressions for the elements of this matrix.

If the largest eigenvalue of $\underline{\hat{T}}$ is degenerate, then variational parameters occur in the density matrix. If there is no degeneracy, or if more parameters are desired, other large eigenvalues of $\underline{\hat{T}}$ may be included. Variational freedom is then gained at the expense of N representability. Of course, the spin geminals themselves can be varied, but each change in the spin geminals requires a reevaluation of N representability. We have also investigated the N representability of a density matrix for which both spin geminals and expansion coefficients are given. The problem here is more difficult and although a new restatement of the exact N-representability problem results, it is doubtful that practical utility will be found in this case. The treatment for a given density matrix is thus

of interest primarily in relating the present treatment to other attacks on the N-representability problem. This is not a severe limitation, however, since we are less interested in testing a *given* density matrix than in obtaining density matrices with embedded variational parameters, such that exact or approximate N representability is maintained as the parameters are adjusted to minimize the energy of the system.

Because the energy calculated from a non-N-representable density matrix is not an upper bound to the true ground-state energy of the system, it is necessary to estimate the consequences for such a calculation of having only approximate N representability. We have obtained a bound on the difference between $\tilde{E}$, an energy determined from the density matrix, and $\hat{E}$, determined from an antisymmetric wave function. Since $\hat{E}$ is an upper bound to the true energy, this establishes a limit on how far $\tilde{E}$ could possibly be below the true energy. The difference between these two energies can be reduced in a systematic way by expanding the basis set, and becomes zero as exact N representability is approached.

The principal difficulty with our approach lies in the large size of the matrix $\underline{\hat{\Gamma}}$. It can be comparable in size to the full CI matrix for the problem of interest, for a basis set of a given size. We have thus considered the possibility of truncating the set of spin orbitals and the set of $N-2$ particle determinants which are used in estimating N representability and in determining the optimum density matrix. Such truncations are possible and the calculation can be carried through, although the optimum results potentially available for the given spin geminal set will then not be obtained.

We have neglected the consequences of symmetry, other than permutational, in the density matrix or in the wave function. It is well known that symmetry restrictions on the wave function lead to certain limitations on N-representable density matrices.[2,36–45] These restrictions should probably be imposed if we want satisfactory descriptions of the physical system of interest. We have not included them in the present discussion because of the additional complications they would add to an already difficult problem. The consequences of symmetry should be further investigated.

It is clear that the method proposed here cannot be properly evaluated until an attempt has been made to actually apply it to a calculation. We have considered some model problems in an attempt to investigate and illustrate the features of the method, but we find that if the model is simple enough to be easily treated it does not fully reproduce the interesting parts of the problem. We are continuing to investigate more extensive models, and hope also to apply the method to an actual problem, probably the lithium atom. When this has been done we will be better able to assess the practical utility of the method. Even if it should prove to be comparable in difficulty to a conventional CI calculation, however, we feel that the concept of approximate N representability is a useful one, and that this investigation has increased our understanding of the properties of reduced density matrices.

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APPENDIX A: SPIN-ORBITAL EXPANSION OF SPIN GEMINALS

The spin geminals with which we work are orthonormal and antisymmetric. Each such two-particle function can be expanded in terms of an orthonormal set of spin orbitals as

$$\phi_i(1,2) = \sum_{k<l=1}^{r_i} F^i_{kl}\ 2^{-1/2}[\xi^i_k(1)\xi^i_l(2) - \xi^i_l(1)\xi^i_k(2)] \ .$$

There are well-known advantages to taking the ξ^i_k to be eigenfunctions of the 1-matrix associated with ϕ_i. They are the natural spin orbitals of ϕ_i and the pseudo-natural-spin orbitals of the full problem. The number of spin orbitals required, r_i, is the 1-rank of ϕ_i and may be infinite.

To choose a spin-orbital basis for the whole problem we first form the space which is the union of the spaces spanned by the spin orbitals associated with the various spin geminals. We then find some orthonormal basis for this space. It might be convenient to start with the $\{\xi^1_k\}$ associated with ϕ_1, which we take to be the spin geminal we expect to be most important in the final density matrix. Any of the $\{\xi^2_l\}$ associated with the next spin geminal which cannot be expanded in terms of the $\{\xi^1_k\}$ are then orthogonalized to all the $\{\xi^1_k\}$ and added to the set. Any independent $\{\xi^3_j\}$ are then orthogonalized and added to the set, and this process continued until the set is sufficient to expand all the $\{\xi^i_k\}$. This final set will be labeled by $\{\alpha_i, i = 1 \circ\circ\circ R\}$. Clearly,

$$R \leq \sum_{i=1}^{M} r_i \ ,$$

and we expect that R will be much less than the sum unless strongly orthogonal spin geminals are used, in which case the equality holds. The expansion of Eq. (13) is clearly possible because of the way in which the $\{\alpha_i\}$ have been chosen.

APPENDIX B: RELATIONSHIP BETWEEN $\mathcal{T}$ AND $\hat{T}$

We want to show that the operators

$$\binom{N}{2}^{-1}\mathcal{T} \text{ and } \hat{T},$$

defined by Eqs. (9) and (18), respectively, have the same matrix elements in the $\{\phi_i \chi_i\}$ basis.

The common constant factor

$$\binom{N}{2}^{-1}$$

and the initial term 1 are clearly the same for both operators. The second terms in $\mathcal{T}$ are of the form $P_{1j} + P_{2j}$ and have matrix elements

$$\int \phi_k^*(12)\chi_k^*(3\cdots j\cdots N)[P_{1j}+P_{2j}]\phi_i(1,2)\chi_i(3\cdots j\cdots N)\, d\tau_1\cdots d\tau_N$$

$$= \int \phi_k^*(1,2)\chi_k^*(j\cdots 3\cdots N)P_{13}\phi_i(1,2)\chi_i(j\cdots 3\cdots N)\, d\tau_1\cdots d\tau_N$$
$$+ \int \phi_k^*(2,1)\chi_k^*(j\cdots 3\cdots N)P_{13}\phi_i(2,1)\chi_i(j\cdots 3\cdots N)\, d\tau_1\cdots d\tau_N$$
$$= 2\int \phi_k^*(1,2)\chi_k^*(3\cdots j\cdots N)P_{13}\phi_i(1,2)\chi_i(3\cdots j\cdots N)\, d\tau_1\cdots d\tau_N \quad .$$

The first transformation is obtained by relabeling the dummy variables of integration, and the second follows from the antisymmetry of ϕ_k, ϕ_i, χ_k, and χ_i. There are $N-2$ terms in the sum for $3 \le j \le N$, so the second terms of

$$\binom{N}{2}^{-1}\mathcal{T} \text{ and } \hat{T}$$

are equivalent.

The third terms in $\mathcal{T}$ are of the form $P_{1j}\,P_{2k}$, $j<k$, and have matrix elements

$$\int \phi_l^*(1,2)\chi_l^*(3\cdots j,k\cdots N)P_{1j}P_{2k}\phi_i(1,2)\chi_i(3\cdots j,k\cdots N)\, d\tau_1\cdots d\tau_N$$

$$= \int \phi_l^*(1,2)\chi_l^*(j,k\cdots 3,4\cdots N)P_{13}P_{24}\phi_i(1,2)\chi_i(j,k\cdots 3,4\cdots N)\, d\tau_1\cdots d\tau_N$$
$$= \int \phi_l^*(1,2)\chi_l^*(3,4\cdots j,k\cdots N)P_{13}P_{24}\phi_i(1,2)\chi_i(3,4\cdots j,k\cdots N)\, d\tau_1\cdots d\tau_N \quad .$$

Use has again been made of relabeling and of the antisymmetry of χ_k and χ_l. There are

$$\binom{N-2}{2}$$

terms in this sum, corresponding to $j<k$ between 3 and N. The final terms in the two operators are thus also equivalent.

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[4]A collection of papers including both original work and reviews will be found in *Reduced Density Matrices with Applications to Physical and Chemical Applications*, edited by A. J. Coleman and R. M. Erdahl (Queen's University, Kingston, Ontario, 1968), No. 11 of Queen's Papers on Pure and Applied Mathematics.

[5]Cf. also the reports of the 1968 and 1969 density-matrix conferences at Queen's University (unpublished).

[6]An extensive bibliography and review of the field as of early 1969 is included in the Ph. D. thesis of M. B. Ruskai, University of Wisconsin, 1969 (unpublished).

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$$\tfrac{1}{2}\sum_{j,k=3}^{N}{}' P_{1j}P_{2k}.$$

The equivalence of the two forms in the present context is readily established.
[27]Alternatively, one could relate these expressions to the operator $\frac{1}{2}(1+P_{13})$ and seek to *minimize* $\int \Psi^* \frac{1}{2}(1+P_{13}) \times \Psi \, d\tau$. However, it is not clear that the error bounds which we obtain later can be derived if the theory is formulated in terms of this operator.
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[32]The constants appearing in the reduced Hamiltonian depend on the normalization of the 2-matrix. Cf. Ref. 21.
[33]If Ψ is totally symmetric the two expressions are again equivalent but the description is one of boson states, so $\tilde{E}$ is still not in general an upper bound to E_0, the fermion ground-state energy.
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