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N-Representability Problem: Conditions on Geminals

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The N-representability problem is approached by considering geminal product expansions of symmetric and antisymmetric functions. The N-completeness problem, i.e., the problem of determining when a set of geminals is a suitable basis for expanding symmetric or antisymmetric N-particle functions, is considered. New necessary conditions are given for both N-completeness and N-representability. In some cases, one can also obtain sufficient conditions; examples of such cases are discussed. The circumstances under which a density matrix can be derived from two or more different functions are also treated. Finally, extensions to higher order are also mentioned.

I. INTRODUCTION

This paper is concerned with symmetric and antisymmetric geminal expansions and their relation to the N-representability problem[1,2] for the second-order density matrix. Attention is restricted to functions whose 2-rank is finite. When N is odd, this necessarily implies that the rank of the first-order density matrix is also finite.

An antisymmetric (symmetric) geminal product function is an antisymmetric (symmetric) function of the following form:

$$\Psi(1\cdots N)=\sum_{k_1\cdots k_\nu} c_{k_1\cdots k_\nu}\phi_{k_1}(12)\cdots\phi_{k_\nu}(N-1,N), \quad \text{when } N=2\nu \text{ is even;} \qquad (1a)$$

$$\Psi(1\cdots N)=\sum_{ik_1\cdots k_\nu} c_{ik_1\cdots k_\nu}f_i(1)\phi_{k_1}(23)\cdots\phi_{k_\nu}(N-1,N), \quad \text{when } N=2\nu \text{ is odd.} \qquad (1b)$$

These functions are antisymmetric (symmetric) in the form given above; it is not necessary to apply an antisymmetrizing (symmetrizing) operator to make them so. With no loss of generality, the geminals $\{\phi_p\}$ $(p=1\cdots M)$ can be assumed to be antisymmetric (symmetric) and orthonormal; when N is odd the associated orbitals $\{f_j\}$ $(j=1\cdots L)$ can also be taken to be orthonormal. The sum over $k_1\cdots k_\nu$ includes all combinations and permutations, including those with $k_i=k_j$ $(i\neq j)$. Thus there are M^ν such terms. Functions of the form (1) certainly exist. The expansion of a Slater determinant in terms of two-particle Slater determinants (i.e., the successive expansion in 2×2 minors and cofactors) is of this form. As will be shown later, the natural spin geminal (NSG) expansion of any function is of this form, although M may be infinite in the most general case. The problem of determining when a set of geminals forms an appropriate basis for such functions is considered.

Definition: When N is even, a set of orthonormal geminals $\{\phi_p\}$ $(p=1\cdots M)$ is said to be fermion (boson) N-complete if the following conditions hold:

(A) Each ϕ_p is antisymmetric (symmetric) in 1 and 2;

(B) There exists at least one antisymmetric (symmetric) N-particle function $\Psi(1\cdots N)$ which can be written in the form (1a) using the set $\{\phi_p\}$ as a basis.

When N is odd, a set of orthonormal geminals $\{\phi_p\}$ $(p=1\cdots N)$ is fermion or boson N complete if:

(A) Above holds;

(B′) There exists an orthonormal set of associated orbitals $\{f_j\}$ such that there exists at least one antisymmetric (symmetric) N-particle function $\Psi(1\cdots N)$ which can be written in the form (1b) using $\{\phi_p\}$ and $\{f_j\}$ as a basis.

If $\{\phi_p\}$ is given is it easy to find at least one set of associated orbitals $\{f_j\}$. The set of orbitals obtained by orthogonalizing the union of the sets of natural spin orbitals (NSO) of the geminals $\{\phi_p\}$ will satisfy (B′) if the geminals are actually N complete. A set of necessary conditions for both fermion and boson N-completeness is obtained. These conditions are not sufficient in themselves; however, in certain cases they lead to a procedure for finding all possible expansion coefficients

$$c_{k_1\cdots k_\nu} \quad \text{or} \quad c_{ik_1\cdots k_\nu}.$$

Then by checking whether or not Ψ given by (1) with these expansion coefficients is actually symmetric or antisymmetric one obtains sufficient conditions.

By applying these results to the geminals in which a second-order density matrix can be expanded one can obtain new formulation of the N-representability problem. In certain cases this leads to a solution of the problem. Necessary conditions for determining when the function from which a density matrix can be derived is unique are also given.

The next section contains the necessary background information on density matrices and N-representability. In Sec. III the so-called transposition matrices are defined and their properties are discussed. The N-completeness problem is considered in Sec. IV, and the N-representability problem in Sec. V. The question of uniqueness is discussed in Sec. VI, and an example is worked out in detail. Extensions to higher-order p-particle states and density matrices are considered in Sec. VII.

II. DENSITY MATRICES

General discussions of density matrices and N-representability have been given elsewhere.[1-3] Only those relations specifically needed in later sections will be given here.

If Ψ is of the form (1) the second-order density matrix is

$$\Gamma(1,2;1',2')=\sum_{pq} d_{pq}\phi_p(12)\phi_q^*(1'2'), \qquad (2)$$

where $d_{pq}=\sum_{k_2\cdots k_\nu} c_{pk_2\cdots k_\nu}c^*_{qk_2\cdots k_\nu}$,

if $N=2\nu$ is even, (3a)

and $d_{pq}=\sum_{ik_2\cdots k_\nu} c_{ipk_2\cdots k_\nu}c^*_{iqk_2\cdots k_\nu}$,

if $N=2\nu+1$ is odd. (3b)

When the $\{\phi_p\}$ are NSG's one has

$$d_{pq}=\lambda_p\delta_{pq} \quad (p=1\cdots M_0), \qquad (4)$$

where the $\{\lambda_p\}$ are the eigenvalues of Γ.

The p-rank of any function is the rank of its pth-order reduced density matrix. If N is odd, one can find the following relation between the 1-rank and 2-rank.

Theorem 1: If N is odd then the 2-rank of any function is finite if and only if the 1-rank is finite.

Proof: If $N=3$ the result follows directly from the fact that the first- and second-order density matrices of any three-particle function have the same nonzero eigenvalues.[1,4] Now suppose Ψ is given by (1b) with the range of k_j $(k_j=1\cdots M)$ finite. The range of i may be infinite. Let $K=\{k_2\cdots k_\nu\}$ $(K=1\cdots M^{\nu-1})$ denote a set of $\nu-1$ indices. Then one can define the following unnormalized symmetric or antisymmetric three-particle functions for each value of K.

$$\chi_K(1,2,3)=\sum_{ip} c_{ipK}f_i(1)\phi_p(2,3).$$

Since the number of ϕ_p is finite, the 2 rank of χ_K will be finite. Then the 1 rank of χ_K is also finite since it is a three-particle function. Now if the first-order density matrix of χ_K is γ_K and the first-order density matrix of Ψ is γ, then

$$\gamma=\sum_K\gamma_K.$$

Thus γ is the sum of a finite number of density matrices of finite rank. So γ must also have finite rank. Thus if Ψ has finite 2-rank, it must also have finite 1-rank. Conversely, if Ψ has finite 1-rank the second-order density matrix can be expanded in the 2-particle Slater determinants formed the NSO's of Ψ. Then Ψ clearly has finite 2-rank.

Theorem 2: Any symmetric or antisymmetric function $\Psi(1\cdots N)$ can be expanded in the form (1) using its NSG's as the geminal basis $\{\phi_p\}$.

Proof: According to the Carlson-Keller[1,4] theorem one can expand Ψ as

$$\Psi=\sum_p\lambda_p^{1/2}\phi_p(12)\Phi_p(3\cdots N). \qquad (5)$$

Now consider the ν pairs (12), (34), ..., $(2k-1, 2k)$, ..., $(2\nu-1, 2\nu)$. Ψ is symmetric with respect to interchange of any two such pairs. One now proceeds as in Coleman's[1] theorem 3.2 for symmetric particles to finish the proof by induction.

III. THE TRANSPOSITION MATRICES $\underline{T}$ and $\underline{\mathcal{T}}$

In order to treat fermions and bosons simultaneously, the following notation will be used. ϵ will be a two-valued parameter with

$$\epsilon=+1 \text{ for bosons}, \quad \epsilon=-1 \text{ for fermions}.$$

The projection operator onto the subspace of symmetric N-particle functions will be denoted $\mathcal{O}_{+1}$, and the projection operator onto the subspace of antisymmetric functions will be denoted $\mathcal{O}_{-1}$.

An antisymmetric function is symmetric with respect to interchange of any two pairs. Therefore the expansion coefficients

$$c_{k_1\cdots k_\nu} \quad \text{and} \quad c_{ik_1\cdots k_\nu}$$

must be symmetric in the indices $k_1k_2\cdots k_\nu$ for both symmetric and antisymmetric functions.

If N is even and the coefficients are indeed symmetric, then a necessary and sufficient condition for antisymmetry or symmetry of a function of the form (1a) is:

$$\Psi(1\ 2\ 3\ 4\cdots N) = \epsilon\Psi(1\ 3\ 2\ 4\cdots N). \quad (6)$$

This is equivalent to:

$$\sum_{k_1\cdots k_\nu} c_{k_1k_2\cdots k_\nu}\phi_{k_1}(12)\phi_{k_2}(34)\cdots\phi_{k_\nu}(N-1,N)$$
$$= \epsilon \sum_{k_1\cdots k_\nu} c_{k_1k_2\cdots k_\nu}\phi_{k_1}(13)$$
$$\times\,\phi_{k_2}(24)\cdots\phi_{k_\nu}(N-1,N).$$

Now multiplying both sides by

$$\phi_p^*(12)\phi_q^*(34)\phi_{k_3}^*(56)\cdots\phi_{k_\nu}^*(N-1,N)$$

and integrating one gets:

$$\epsilon c_{pqk_3\cdots k_\nu} = \sum_{rs} t_{pq,rs}c_{rsk_3\cdots k_\nu}, \quad (7)$$

where

$$t_{pq,rs} = \int \phi_p^*(12)\phi_q^*(34)\phi_r(13)\phi_s(24). \quad (8)$$

Thus a necessary condition for N-completeness of $\{\phi_p\}$ is that $\underline{T} = \{t_{pq,rs}\}$ have ϵ as an eigenvalue.

If N is odd, a necessary and sufficient condition for antisymmetry or symmetry of a function of the form (1b) with symmetric coefficients is[5]:

$$\Psi(1\ 2\ 3\cdots N) = \epsilon\Psi(2\ 1\ 3\cdots N). \quad (9)$$

Proceeding as before, one sees that this implies

$$\epsilon\tilde{c}_{pik_2\cdots k_\nu} = \sum_{jq}\tau_{pi,qj}\tilde{c}_{qjk_2\cdots k_\nu}, \quad (10)$$

where

$$\tau_{pi,qj} = \int f_i^*(1)\phi_p^*(23)f_j(2)\phi_q(13) \quad (11)$$

and

$$\tilde{c}_{qjk_2\cdots k_\nu} = c_{jqk_2\cdots k_\nu}.$$

Thus a necessary condition for N-completeness is that $\underline{\mathcal{T}} = \{\tau_{pi,qj}\}$ have ϵ as an eigenvalue. These conditions on the eigenvalues of $\underline{T}$ and $\underline{\mathcal{T}}$ have been recognized previously.[6–8] It is the imposition of additional constraints on their eigenvectors which leads to new results.

The main properties of the transposition matrices are summarized below:

(a) Both $\underline{T}$ and $\underline{\mathcal{T}}$ are Hermitian

$$t_{pq,rs} = t^*_{rs,pq} \quad (12a)$$

$$\tau_{pi,qj} = \tau^*_{qj,pi}. \quad (12b)$$

(b) $\underline{T}$ is symmetric in each set of indices

$$t_{pq,rs} = t_{qp,rs} = t_{pq,sr}. \quad (13)$$

(c) It follows from (b) that 0 is an eigenvalue of $\underline{T}$ with degeneracy $\binom{M}{2}$.

(d) All diagonal elements of both $\underline{T}$ and $\underline{\mathcal{T}}$ are non-negative.

(e) The elements of $\underline{T}$ and $\underline{\mathcal{T}}$ are bounded in magnitude by $\frac{1}{2}$ when they are formed from antisymmetric geminals[8] and by 1 when they are formed from symmetric geminals.

(f) All eigenvalues of $\underline{T}$ and $\underline{\mathcal{T}}$ are bounded in magnitude by 1. The proof of this will be given later.

(g)
$$\sum_{rs}|t_{pq,rs}|^2 \leq 1 \quad (14)$$

$$\sum_{qj}|\tau_{pi,qj}|^2 \leq 1. \quad (15)$$

This property implies that all previous statements regarding $\underline{T}$ and $\underline{\mathcal{T}}$ make sense when the number of geminals is infinite.[9] The proof, which depends upon (f) is as follows:

$$\sum_{rs}|t_{pq,rs}|^2 = (\underline{T}\,\underline{T}^\dagger)_{pq,pq} = (\underline{T}^2)_{pq,pq}$$
$$\leq \text{maximum eigenvalue of } \underline{T}^2$$
$$= (\text{spectral radius of } \underline{T})^2 = 1^2 = 1.$$

(h) $\mathrm{Tr}\underline{\mathcal{T}} = M. \quad (16)$

To prove this, let γ_p be the first-order density matrix of ϕ_p. Then

$$\mathrm{Tr}\underline{\mathcal{T}} = \sum_{pi}\tau_{pi,pi} = \sum_{pi}\int f_i^*(1)\gamma_p(1,2)f_i(2)$$
$$= \sum_p \mathrm{Tr}\gamma_p = \sum_p 1 = M.$$

It follows from (d) and (e) that

$$0 < \mathrm{Tr}\underline{T} < \tfrac{1}{2}M^2 \quad \text{for fermions}, \quad (17)$$

and from (c), (d), and (f) that

$$0 < \mathrm{Tr}\underline{T} \leq \tfrac{1}{2}M(M+1) \quad \text{for bosons}, \quad (18)$$

A certain ambiguity exists regarding the eigenvectors of $\underline{T}$, $\underline{\mathcal{T}}$, and other such double index matrices. An eigenvector $\underline{A}$ is a column vector relative to the double index matrix. But since the elements of $\underline{A} = \{a_{pj}\}$ depend on two indices, they can also be arranged in a square array. Thus the eigenvector $\underline{A}$ itself can also be considered a (single index) matrix. The orthonormality condition on such a set of vectors, $\underline{A}^m$, can be written as

$$\mathrm{Tr}(\underline{A}^{m\dagger}\underline{A}^{n}) = \mathrm{Tr}(\underline{A}^{m}\underline{A}^{n\dagger}) = \delta_{mn} \; . \tag{19}$$

Any unitary transformation among the geminals induces a unitary transformation on $\underline{T}$ or $\underline{\mathcal{T}}$ as follows. Let $\{v_{\bar{p}p}\} = \underline{V}$ be a unitary transformation on the geminals ϕ_p, i.e.,

$$\theta_{\bar{p}} = \sum_p v_{\bar{p}p}\,\phi_p \,.$$

Then for even N one has in the $\theta_{\bar{p}}$ basis

$$t_{\bar{p}\bar{q},\bar{r}\bar{s}} = \sum_{pqrs} \sigma_{\bar{p}\bar{q},pq}\, t_{pq,rs}\, \sigma^{*}_{\bar{r}\bar{s},rs} \tag{20}$$

or
$$\underline{\bar{T}} = \underline{\Sigma}^{e}\,\underline{T}\,\underline{\Sigma}^{e\dagger} \,, \tag{20'}$$

where
$$\sigma_{\bar{p}\bar{q},pq} = v_{\bar{p}p}v_{\bar{q}q} \tag{21}$$

$\underline{\Sigma}^e$ is easily seen to be unitary. If N is odd let

$$\sigma_{\bar{p}i,pk} = \delta_{ik}v_{\bar{p}p} \,. \tag{22}$$

Then $\underline{\Sigma}^{o}$ is again unitary and $\underline{\mathcal{T}}$ in the $\theta_{\bar{p}}$ basis is given by

$$\underline{\bar{\mathcal{T}}} = \underline{\Sigma}^{o}\,\underline{\mathcal{T}}\,\underline{\Sigma}^{o\dagger} \,. \tag{23}$$

Thus the eigenvalues of both $\underline{T}$ and $\underline{\mathcal{T}}$ are invariant under any unitary transformation of the geminals. If $\underline{A}^m$ are the eigenvectors of $\underline{T}$ or $\underline{\mathcal{T}}$ the transformed eigenvectors $\underline{B}^m$ are given by

$$\underline{B}^{m} = \underline{V}\,\underline{A}^{m}, \quad \text{when } N \text{ is odd}, \tag{24a}$$

$$\underline{B}^{m} = \underline{V}\,\underline{A}^{m}\underline{\tilde{V}}, \text{ when } N \text{ is even}. \tag{24b}$$

Unitary transformations are not the most general transformations on the geminals which preserve N-completeness. In fact, certain classes of partial isometries[10] also preserve N completeness. In general, such partial isometries $\{v_{\bar{p}p}\}$ ($p = 1\cdots\bar{M}$; $q = 1\cdots M$; $\bar{M} < M$) will satisfy $\underline{V}\,\underline{V}^{\dagger} = \underline{I}_{\bar{M}}$ but $\underline{V}^{\dagger}\underline{V} \neq \underline{I}_{M}$, where $\underline{I}_J$ is the identity matrix of order $J\times J$. Any such partial isometry $\{v_{\bar{p}p}\}$ will induce a partial isometry on $\underline{T}$ and $\underline{\mathcal{T}}$ as in (20) to (23). But little is known about the transformation properties of matrices under partial isometries. They do not preserve eigenvalues in general, and (24) does not hold since $\underline{V}^{\dagger}\underline{V} \neq 1$. The connection between partial isometries and N-representability is discussed in Sec. V.

To prove property (f) let f_i ($i = 1\cdots L < \infty$) be a set of one-particle states in which the geminals $\{\phi_p\}$ ($p = 1\cdots M$) can be expanded. Let υ_q ($q = 1\cdots M_S$) be the set of all Slater geminals formed from $\{f_i\}$, where $M_S = \binom{L}{2}$ for fermions and $M_S = \binom{L+1}{2}$ for bosons. The geminals $\{\phi_p\}$ are related to the Slater geminals by a partial isometry. One can construct a set of geminals $\{\tilde{\phi}_p\}$ ($p = 1\cdots M_S$) which are unitarily equivalent to the Slater geminals and identical to $\{\phi_p\}$ for $p = 1\cdots M < M_S$. Now the transposition matrices in the Slater geminal basis, $\underline{T}_S$ and $\underline{\mathcal{T}}_S$ have block diagonal form and can be obtained explicitly. It is easy to show that their eigenvalues are bounded in magnitude by 1. Since (20) to (23) imply that $\underline{\tilde{T}}$ and $\underline{\tilde{\mathcal{T}}}$ are unitarily equivalent to $\underline{T}_S$ and $\underline{\mathcal{T}}_S$, their eigenvalues are also bounded in magnitude by 1. Now $\underline{T}$ and $\underline{\mathcal{T}}$ are just truncations of $\underline{\tilde{T}}$ and $\underline{\tilde{\mathcal{T}}}$. Truncating a matrix always decreases the magnitude of its eigenvalues[11] so the eigenvalues of $\underline{T}$ and $\underline{\mathcal{T}}$ are also bounded in magnitude by 1. This proves (f) when L and M are finite. But then (g) implies that all operations make sense for infinite L and M, so the proof can be extended to those cases also.

According to (7) or (10) the expansion coefficients of Ψ form a set of eigenvectors of $\underline{T}$ or $\underline{\mathcal{T}}$. There are as many eigenvectors as there are sets $k_3\cdots k_\nu$ or $k_2\cdots k_\nu$. It is interesting to consider how many of these eigenvectors are linearly independent. Clearly if $k_3'\cdots k_\nu'$ is a permutation of $k_3\cdots k_\nu$ then the corresponding eigenvectors are equal, so that only distinct (i.e., permutationally inequivalent) sets $k_3\cdots k_\nu$ and $k_2\cdots k_\nu$ need to be considered. If $N=3$, $\nu=1$ and the set $k_2\cdots k_\nu$ does not exist; then $\underline{\mathcal{T}}$ need have only one eigenvector to eigenvalue ϵ. Similarly, when $N=4$, $\underline{T}$ need have only one eigenvector to eigenvalue ϵ. When $N=5,6$ the sets $k_2\cdots k_\nu$ and $k_3\cdots k_\nu$ consist of a single index $r = 1\cdots M$. In both cases, it can be shown [Eq. (41)] that if the $\{\phi_p\}$ are the NSG's of some function, then $\underline{T}$ and $\underline{\mathcal{T}}$ have at least M orthogonal eigenvectors to eigenvalue ϵ. Thus if $N=5,6$ and the $\{\phi_p\}$ are unitarily equivalent to the NSG's of some function, then the expansion coefficients form a set of M linearly independent eigenvectors to eigenvalue ϵ. Now suppose $N>8$. Then the number of distinct sets $k_3\cdots k_\nu$ is greater than $\frac{1}{2}M(M+1)$ which, according to (c), is the maximum number of nonzero eigenvalues of $\underline{T}$. So the expansion coefficients must form a linearly dependent set of eigenvectors of $\underline{T}$ when $N>8$. If $N=8$, and the geminals are antisymmetric, the preceding argument and the trace condition (17) imply that the expansion coefficients also form a linearly dependent set of eigenvectors.

IV. N-COMPLETENESS

Now suppose that a set of geminals $\{\phi_p\}$ is given and we want to determine whether or not they are N-complete. If N is odd, complete the definition of the $\underline{\mathcal{T}}$-matrix as the matrix given by (11) by choosing the one-particle states as $\{\hat{f}_i\}$, the orthogonalized NSO's of the geminals. The extension of all theorems to other one-particle bases should be obvious. The first step in testing for N-completeness is to form $\underline{T}$ and $\underline{\mathcal{T}}$ and find the eigenvectors to eigenvalue ϵ. In general, these eigenvectors will not be the expansion coefficients which appear in (7) and (10). One needs to find additional conditions under which the eigenvectors can be chosen as possible expansion coefficients.

$N = 3,4$

When $N=3$, $\nu=1$ and, as stated previously, $\underline{\mathcal{T}}$ need have only one eigenvector with eigenvalue ϵ. If it has only one such eigenvector, call it $\underline{A} = \{a_{pi}\}$, then a sufficient condition for N completeness is that $\mathcal{O}_\epsilon\Psi=\Psi$, where $\mathcal{O}_\epsilon$ is the symmetrizing or antisymmetrizing projection operator and Ψ is of the form (1b) with

$$c_{jk_1} = a_{pj} \quad (k_1 = p). \tag{25}$$

If ϵ is degenerate, with eigenvectors $\underline{A}^m = \{a_{pi}{}^m\}$ then one does not know, in general, which linear combinations $\underline{A}^m$ will lead to antisymmetric functions.[12]

The four-particle case can be treated similarly. If $\underline{A}$ is an eigenvector of $\underline{T}$ to eigenvalue ϵ then possible expansion coefficients in (1a) are given by

$$c_{k_1k_2} = a_{pq} \quad (k_1 = p, k_2 = q). \tag{26}$$

One can summarize N-completeness for $N=3,4$ in the following theorem.

Theorem 3: If $N=3,4$ a finite set of antisymmetric (symmetric) geminals is fermion (boson) N-complete if and only if the transposition matrix, $\underline{T}$ or $\underline{\mathcal{T}}$, has at least one eigenvector $\underline{A}$ corresponding to eigenvalue ϵ such that if Ψ is given by (1) with expansion coefficients determined by $\underline{A}$ according to (25) or (26) then $\mathcal{O}_\epsilon\Psi=\Psi$.

Odd N

Suppose $N=2\nu+1$ is odd and $\geqslant 5$. Let $\underline{A}^m = \{a_{pi}{}^m\}$ be the orthonormal eigenvectors of $\underline{\mathcal{T}}$ with eigenvalue ϵ. One wants to know whether or not there exist linear combinations of these $\underline{A}^m$ which give a new set of eigenvectors whose elements might be suitable expansion coefficients. This condition can be expressed in the following way. Let $K=\{k_3\cdots k_\nu\}$ $(K=1\cdots M^{\nu-2})$ denote all possible sets of $(\nu-2)$ indices $k_3\cdots k_\nu$. Then a necessary condition for N-completeness of a geminal basis $\{\phi_p\}$ is that there exists a linear transformation $\{u_{qK,m}\}$ $(q=1\cdots M; K=1\cdots M^{\nu-2}; m=1\cdots J)$ such that if

$$\hat{\underline{A}}^{qK} = \textstyle\sum_m u_{qK,m}\underline{A}^m, \tag{27}$$

then $\hat{a}_{pi}{}^{qK} = \hat{a}_{pi}{}^{qk_3\cdots k_\nu}$ is symmetric with respect to any permutation of the ν indices $pqk_3\cdots k_\nu$. In particular, this means that

$$\hat{a}_{pi}{}^{qK} = \hat{a}_{qi}{}^{pK} \tag{28}$$

or equivalently,

$$\textstyle\sum_m u_{qK,m}\, a_{pi}{}^m = \sum_n u_{pK,n}\, a_{qi}{}^n. \tag{28$'$}$$

Then multiplying by $(a_{pi}{}^{m'})^*$ and taking the sum over i and p one gets

$$u_{qK,m} = \sum_{pn} \omega_{qm,pn}\, u_{pK,n}, \tag{29}$$

where

$$\omega_{qm,pn} = \textstyle\sum_i a_{qi}{}^n (a_{pi}{}^m)^* = (\underline{A}^n \underline{A}^{m\dagger})_{qp} \tag{30}$$

or equivalently

$$\underline{\Omega}\,\underline{U}^K = +1\ \underline{U}^K, \tag{29$'$}$$

where $\underline{\Omega}$ is the $MJ\times MJ$ matrix with elements $\omega_{qm,pn}$. The eigenvectors $\underline{U}^K$ can be considered as $M\times J$ matrices with elements $u_{pm}{}^K = u_{pK,m}$. Thus $\underline{\Omega}$ must have $+1$ as an eigenvalue. $\underline{\Omega}$ is Hermitian since

$$\omega_{qm,pn} = (\underline{A}^n\underline{A}^{m\dagger})_{qp} = [(\underline{A}^n\underline{A}^{m\dagger})^{\sim}]_{pq}$$
$$= (\underline{A}^m\underline{A}^{n\dagger})^*_{pq} = \omega^*_{pn,qm}.$$

Now consider the structure of $\underline{\Omega}$ and $\underline{U}^K$. The elements of $\underline{\Omega}$, $\omega_{qm,pn}$, have the same dependence on the geminal indices p and q as the $\underline{\mathcal{T}}$ matrix. Further, a necessary condition for N-completeness of $\{\phi_p\}$ is that the eigenvectors

$$\underline{U}^K = \{u_{qm}{}^{k_3\cdots k_\nu}\},$$

are symmetric in $(\nu-1)$ indices $qk_3\cdots k_\nu$. But these are just the conditions which the $\underline{\mathcal{T}}$ matrix must satisfy for boson $(N-2)$-completeness.

Proceeding inductively, one can eventually reduce the N-completeness conditions to those for boson three-completeness. Denote the $\underline{\Omega}$ matrix defined by (30) as $\underline{\Omega}^{\nu-1}$ and its orthonormal eigenvectors to eigenvalue $+1$ by

$${}^{\nu-1}\underline{U}^{m_{\nu-1}} = \{\underline{u}_{pn}{}^{m_{\nu-1}}\}.$$

Then by applying the $(N-2)$-completeness conditions to $\underline{\Omega}^{\nu-1}$ one gets a matrix $\underline{\Omega}^{\nu-2}$, which must satisfy the conditions of boson $[2(\nu-2)+1]$-completeness. Continuing one gets a series of $\nu-1$ matrices $\underline{\Omega}^\mu$ $(\mu=\nu-1, \nu-2\cdots 1)$ with orthonormal eigenvectors

$$ {}^{\mu}\underline{U}^{m_\mu} = \{u_{pm_{\mu+1}}^{m_\mu}\}, \quad (\mu = \nu - 1 \cdots 2), $$

belonging to eigenvalue $+1$. $\underline{\Omega}^1$ must satisfy the conditions for boson three completeness. Let

$$ \underline{W}^l = \{w_{pm_2}^l\} $$

be the eigenvectors of $\underline{\Omega}^1$ to eigenvalue $+1$. Now let:

$$ c_{ik_1\cdots k_\nu} = \sum_n \sum_{m_\mu} a_{k_1 i}^{\ n}\, u_{k_2 n}^{\ m_{\nu-1}} \times u_{k_3 m_{\nu-1}}^{\ m_{\nu-2}} \cdots u_{k_{\nu-1} m_3}^{\ m_2}\, w_{k_\nu m_2}, \tag{31} $$

where $\underline{W}$ is some linear combination of the $\underline{W}^l$. A sufficient condition for N-completeness is that Ψ, given by (1b) with

$$ c_{ik_1\cdots k_\nu} $$

given by (31), satisfies $\mathcal{O}_\epsilon \Psi = \Psi$. One can summarize these results in the following theorem.

Theorem 4: If $N = 2\nu + 1$ is odd, then a finite set of antisymmetric (symmetric) geminals is fermion (boson) N-complete if and only if the following conditions are satisfied:

(a) The $\underline{\mathcal{T}}$ matrix defined by (11) has ϵ as an eigenvalue.

(b) If $\underline{\Omega}^{\nu-1}$ is formed from the eigenvectors of $\underline{\mathcal{T}}$ according to (30) then $\underline{\Omega}^{\nu-1}$ satisfies the conditions for boson $(N-2)$-completeness.

(c) If $\underline{\Omega}^\mu$ is defined inductively from $\underline{\Omega}^{\mu+1}$ then $\underline{\Omega}^1$ must have at least one eigenvector $\underline{W}$ belonging to eigenvalue $+1$ such that if Ψ is given by (1b) with expansion coefficients given by (31) then $\mathcal{O}_\epsilon \Psi = \Psi$.

Even N

Suppose $N = 2\nu$ is even and ≥ 6. Let $K = \{k_4 k_5 \cdots k_\nu\}$ $(K = 1 \cdots M^{\nu-3})$ denote all possible sets of $\nu - 3$ indices $k_4 \cdots k_\nu$. Let $\underline{A}^m = \{a_{pq}^{\ m}\}$ $(m = 1 \cdots J)$ be the orthonormal eigenvectors of $\underline{T}$ with eigenvalue ϵ. Then by (7) a necessary condition for N-completeness of a geminal basis $\{\phi_p\}$ is that there exists a linear transformation $\{u_{rK,m}\}$ $(r = 1 \cdots M; K = 1 \cdots M^{\nu-3}; m = 1 \cdots J)$ such that if

$$ \underline{\hat{A}}^{rK} = \sum_m u_{rK,m} \underline{A}^m \tag{32} $$

then $\hat{a}_{pq}^{\ rK} = \hat{a}_{pq}^{\ rk_4\cdots k_\nu}$

is symmetric with respect to any permutation of the indices $pqrk_4 \cdots k_\nu$. In particular one must have

$$ \hat{a}_{pq}^{\ rK} = \hat{a}_{pr}^{\ qK} \tag{33} $$

or equivalently

$$ \sum_m u_{rK,m}\, a_{pq}^{\ m} = \sum_n u_{qK,n}\, a_{pr}^{\ n}. \tag{33'} $$

Then by multiplying both sides by $(a_{pq}^{\ m'})^*$ and taking the sum over p and q one gets a condition on $u_{rK,m}$.

$$ u_{rK,m} = \sum_{qn} \omega_{rm,qn}\, u_{qK,n}, \tag{34} $$

where

$$ \omega_{rm,qn} = \sum_p a_{pr}^{\ n} (a_{pq}^{\ m})^* = (A^{m\dagger} A^n)_{qr} \tag{35} $$

or equivalently

$$ \underline{\Omega}\,\underline{U}^K = \underline{U}^K, \quad \text{for all } K, \tag{34'} $$

where $\underline{U}^K = \{u_{qm}^{\ K}\} = \{u_{qK,m}\}$.

Then $+1$ must be an eigenvalue of $\underline{\Omega}$.

Now consider Eq. (34) again. $\underline{\Omega}$ is a Hermitian $JM \times JM$ matrix with double indices $\omega_{rm,qn}$. Thus $\underline{\Omega}$ has the same dependence on geminal indices as $\underline{\mathcal{T}}$. Further, the eigenvectors

$$ \underline{U}^K = \{u_{rm}^{\ k_4\cdots k_\nu}\} $$

must be symmetric in the $(\nu - 2)$ indices $rk_4 \cdots k_\nu$. But these are exactly the conditions which the $\underline{\mathcal{T}}$ matrix must satisfy for boson $(N-3)$-completeness. Thus one gets an inductive set of necessary conditions similar to those for odd N. Let $\underline{\Omega}^{\nu-2}$ be the matrix defined by (35). Define $\underline{\Omega}^\mu (\mu = \nu - 2 \cdots 1)$, ${}^{\mu}\underline{U}^{m_\mu} (\mu = \nu - 2 \cdots 2)$ and $\underline{W}$ as in the previous section for odd N. Let

$$ c_{k_1\cdots k_\nu} = \sum_n \sum_{m_\mu} a_{k_1 k_2}^{n}\, u_{k_3 n}^{\ m_{\nu-2}} \cdots \cdots u_{k_{\nu-1} m_3}^{\ m_2}\, w_{k_\nu m_2}. \tag{36} $$

Then a sufficient condition for N-completeness is that Ψ given by (1a) and (36) satisfies $\mathcal{O}_\epsilon \Psi = \Psi$ for some $\underline{W}$.

Theorem 5: If $N = 2\nu$ is even, then a finite set of antisymmetric (symmetric) geminals is fermion (boson) N-complete if and only if the following conditions are satisfied:

(a) The $\underline{T}$-matrix, defined by (8), has ϵ as an eigenvalue.

(b) If $\underline{\Omega}^{\nu-2}$ is formed from the eigenvectors of $\underline{T}$ according to (35) then $\underline{\Omega}^{\nu-2}$ satisfies the conditions for boson $(N-3)$-completeness.

(c) If $\underline{\Omega}^{\mu}$ is defined inductively from the eigenvectors of $\underline{\Omega}^{\mu+1}$ then $\underline{\Omega}^{1}$ must have at least one eigenvector $\underline{W}$ belonging to eigenvalue $+1$ such that if Ψ is given by (1a) with expansion coefficients given by (36) then $\mathcal{O}_{\epsilon}\Psi=\Psi$.

TABLE I. Summary of matrix notation.

Matrix	Defining equation	Matrix elements	Description
$\underline{D}$	3, 37	d_{pq}	Matrix of expansion coefficients of the second-order density matrix in some geminal basis.
$\underline{T}$	8	$t_{pq,rs}$	Transposition matrix for even N; formed from some geminal basis.
$\underline{\mathcal{T}}$	11	$\tau_{pi,qj}$	Transposition matrix for odd N; formed from some geminal basis and an associated set of orbitals.
$\underline{A}^{m}$		a_{pq}^{m} or a_{pi}^{m}	Eigenvectors of $\underline{T}$ or $\underline{\mathcal{T}}$ corresponding to eigenvalue ϵ; orthonormal.
$\underline{\Omega}^{\mu_0}$ $\mu_0=\nu-1$, odd N $\mu_0=\nu-2$, even N	(30) (35)	$\omega_{qm,pn}$	Formed from $\underline{A}^{m}$.
$\underline{\Omega}^{\mu}$	inductive use of (30)	$\omega_{qm_{\mu+1},pn_{\mu+1}}$	Formed inductively from the eigenvectors of $\underline{\Omega}^{\mu+1}$ to eigenvalue $+1$.
${}^{\mu}\underline{U}^{m_\mu}$		$u_{p,m_{\mu+1}}^{m_\mu}$	Eigenvectors of $\underline{\Omega}^{\mu}$ to eigenvalue $+1$; orthonormal.
$\underline{W}$		w_{pm_2}	Eigenvectors of $\underline{\Omega}^{1}$.
$\underline{\mathcal{R}}$	(45)	$\rho_{pq,kl}$	Formed from $\underline{W}$.

V. N-REPRESENTABILITY

Suppose that a second-order density matrix Γ is given. Then Γ can be expanded in a geminal basis as:

$$\Gamma=\sum_{rs} d_{rs}\phi_r(12)\phi_s^*(1'2'). \tag{37}$$

Since the NSG's of Γ can be written as linear combinations of the ϕ_p, it follows from Theorem 2 that a necessary condition for N-representability is that the basis $\{\phi_p\}$ is N-complete. One can obtain additional necessary conditions on the matrices $\underline{\Omega}^{\mu}$ and their eigenvectors.

If Γ is N-representable, then $\underline{\Omega}^{1}$ will have at least one eigenvector $\underline{W}$, corresponding to the N-particle function from which Γ can be derived. Combining (3b) and (31) one obtains a condition on $\underline{W}$.

$$d_{pq}=\sum_{i,k_1\cdots k_{\nu-1}} c_{ik_1\cdots k_{\nu-1}p}\,c^*_{ik_1\cdots k_{\nu-1}q} \tag{3b$'$}$$

$$d_{pq}=\sum_{ik_1\cdots k_{\nu-1}}\ \sum_{\substack{nm_\mu\\ n'm'_\mu}} a_{k_1i}^{\ n}\,a_{k_1i}^{\ n'}\,u_{k_2n}^{\ m_{\nu-1}}\,u_{k_2n'}^{\ m'_{\nu-1}}\cdots u_{k_{\nu-1}m_3}^{\ m_2}\,u_{k_{\nu-1}m'_3}^{\ m'_2}\,w_{m_2p}\,w^*_{m'_2q}. \tag{38}$$

The orthogonality of $\underline{A}^{n}$ and $\underline{U}^{m_\mu}$ is used repeatedly to simplify (38) for example:

$$\sum_{m_{\mu+1}m'_{\mu+1}}\ \sum_k u_{k,m_{\mu+1}}^{m_\mu}\,u_{k,m'_{\mu+1}}^{m'_\mu}\,\delta_{m_{\mu+1}m'_{\mu+1}}=\delta_{m_\mu m'_\mu}.$$

Finally one gets:

$$d_{pq}=\sum_{m_2m'_2}\delta_{m_2m'_2}\,w_{pm_2}\,w^*_{qm'_2}=\sum_m w_{pm}\,w^*_{qm}=(\underline{W}\,\underline{W}^{\dagger})_{pq}. \tag{39}$$

If N is even a similar result can be obtained from (3a) and (36). Thus one can conclude that a necessary condition for N-representability is that

$$\underline{W}\,\underline{W}^{\dagger} = \underline{D} \;, \tag{39$'$}$$

where $\underline{D} = \{d_{rs}\}$ is the matrix of expansion coefficients of Γ. When $N = 3, 4$ this condition applies to the eigenvectors of $\underline{T}$ and $\underline{\mathcal{T}}$ belonging to eigenvalue ϵ.

In general it has not been possible to say anything about the degeneracy of $+1$ as an eigenvalue of $\underline{\Omega}^{\mu}$. However, one can obtain such a condition on $\underline{\Omega}^2$ in any basis unitarily equivalent to the NSG's. Let

$$\hat{u}_{pl}^{\ q} = \sum_m u_{pl}^{\ m}\, w_{qm} \qquad (q = 1 \cdots M_0)\,, \tag{40}$$

where $m = m_2$ and $l = m_3$, be the indicated linear combination of eigenvectors of $\underline{\Omega}^2$. Suppose $\underline{W}$ corresponds to the function for which the $\{\phi_p\}$ are NSG's. The $\underline{\hat{U}}^q$ then satisfy:

$$\begin{aligned}\mathrm{Tr}(\underline{\hat{U}}^q \underline{\hat{U}}^{r\dagger}) &= \sum_{pl} \hat{u}_{pl}^{\ q} (\hat{u}_{pl}^{\ r})^* = \sum_{lp} \sum_{mm'} u_{pl}^{\ m} (u_{pl}^{\ m'})^*\, w_{qm} w_{rm'}^* \,, \\ &= \sum_{mm'} \delta_{mm'}\, w_{qm} w_{rm'}^* = (\underline{W}\,\underline{W}^{\dagger})_{qr} = \lambda_r \delta_{qr} \;.\end{aligned} \tag{41}$$

Thus $\underline{\Omega}^2$ has at least M_0 orthogonal and therefore linearly independent eigenvectors. When $N = 5, 6$ $\underline{\Omega}^2$ is not defined, but the above results apply to the eigenvectors of $\underline{T}$ and $\underline{\mathcal{T}}$.

The N-representability problem for $N = 3, 4$ has been solved previously.[13,14] One can also treat these cases by defining $\underline{\Omega}^1$ to be $\underline{\mathcal{T}}$ when $N = 3$ and $\underline{T}$ when $N = 4$.

Theorem 6: A second-order density matrix, Γ, of finite rank is fermion or boson N-representable if and only if the following conditions are satisfied:

(a) Γ can be expanded in a fermion or boson N-complete geminal basis, $\{\phi_p\}$.

(b) $\underline{\Omega}^1$ has at least one eigenvector $\underline{W}$, belonging to eigenvalue $+1$ (ϵ if $N = 3, 4$) such that $\underline{W}\,\underline{W}^{\dagger} = \underline{D}$.

(c) If Ψ is given by (1) with expansion coefficients corresponding to the $\underline{W}$ which satisfies condition (b) then $\mathcal{O}_\epsilon \Psi = \Psi$.

This theorem reduces the N-representability problem to the problem of determining under what conditions one can choose a linear combination $\underline{W}$ of the eigenvectors, $\underline{W}^k$, of $\underline{\Omega}^1$ belonging to eigenvalue $+1$ such that $\underline{W}\,\underline{W}^{\dagger} = \underline{D}$.

If $+1$ is a nondegenerate eigenvalue of $\underline{\Omega}^1$ this problem is trivial. One can construct examples in which this actually occurs.[15] If the NSG's form such a basis then Theorem 6 solves the N-representability problem. Note that in this case the geminals completely determine the density matrix. This implies that NSG's and eigenvalues are not independent in general.

If the degeneracy of $+1$ is not too large then a linearization procedure can be used to test condition (b). The following theorem describes such a procedure.

Theorem 7: The equations

$$\underline{W} = \sum_k x_k \underline{W}^k \tag{42}$$

$$\underline{W}\,\underline{W}^{\dagger} = \underline{D} \tag{43}$$

have a solution $\underline{x} = \{x_k\}$ if and only if the following conditions are satisfied:

(a) The M^2 equations

$$d_{pq} = \sum_{kl} \rho_{pq,kl}\, z_{kl} \;, \tag{44}$$

where

$$\rho_{pq,kl} = (W^k W^{l\dagger})_{pq} \;, \tag{45}$$

have a solution $\{z_{kl}\}$ $(k, l = 1 \cdots J)$.

(b) If $\{z_{kl}\}$ is written as a $J \times J$ matrix, $\underline{Z}$, then $\underline{Z}$ is Hermitian, non-negative and of rank 1.

Proof: It is well known that $\underline{Z}$ is a Hermitian non-negative matrix of rank $= 1$ if and only if $\underline{Z}$ can be written

$$\underline{Z} = \underline{x}\,\underline{x}^{\dagger} \;, \tag{46}$$

where $\underline{x}$ is a column matrix. Let the $\{x_k\}$ of Eq. (42) be the elements of the column vector $\underline{x}$. The proof of the theorem is then trivial. If the $\underline{W}^k$ are chosen to be normalized then one must have $\underline{x}^{\dagger}\underline{x} = 1$ and $\underline{Z}$ satisfies $\underline{Z}^2 = \underline{Z}$. In some cases (44), $\underline{P}\,\underline{Z} = \underline{D}$, may have more than one solution. Then the homogeneous equation

$$\sum_{kl} \rho_{rs,kl}\, z_{kl} = 0, \quad \text{or} \quad \underline{P}\,\underline{Z} = \underline{O} \,, \tag{47}$$

must have a nontrivial solution. Since the dimension of $\underline{P}$ is $M^2 \times J^2$, this will always happen if $J > M$. If $J < M$ it can only happen if rank $\underline{P} < J^2$. In such cases the condition $\underline{Z}^2 = \underline{Z}$ may be useful in determining whether or not any solutions of (44) are acceptable, i.e., Hermitian, non-negative, and of rank 1. Let $\underline{Z}^i$ $(i = 1 \cdots I)$ be the linearly independent Hermitian[16] solutions of the homogeneous Eq. (47) and let $\underline{Z}^0$ be a solution of (44). Then every solution of (44) can be written in the form

$$\underline{Z} = \underline{Z}^0 + \sum_i \eta_i Z^i, \quad \eta_i \text{ real.} \tag{48}$$

If $\underline{Z}^2 = \underline{Z}$ then $\{\eta_i\}$ must satisfy

$$\underline{Z}^0 + \sum_i \eta_i \underline{Z}^i = (\underline{Z}^0)^2 + \sum_i \eta_i (\underline{Z}^i \underline{Z}^0 + \underline{Z}^0 \underline{Z}^i) + \sum_{ij} \eta_i \eta_j (\underline{Z}^i \underline{Z}^j). \tag{49}$$

This equation gives a complicated, nonlinear condition on the $\{\eta_i\}$. But in many cases one will have $I \ll J$. Then it should be easy to check for solutions.

Slater Determinants

It may be of some interest to apply the preceding theorems on N-completeness and N-representability to Slater determinants.[17] Suppose $\{\phi_p\}$ is the set of all Slater geminals formed from some orthonormal set of L orbitals $\{f_j\}$ $(j = 1 \cdots L)$. Then one has $M = \binom{L}{2}$. One can choose the eigenvectors of $\underline{\Omega}^1$ so that each $\underline{W}^K$ corresponds to a single N-particle Slater determinant formed from the $\{f_j\}$. Then every linear combination $\underline{W} = \sum_K x_K \underline{W}^K$ corresponds to some configuration-interaction type function formed from the orbitals $\{f_i\}$. Since there are $\binom{L}{N}$ orthonormal N-particle Slater determinants, there will be at least $\binom{L}{N}$ orthonormal $\underline{W}^K$, i.e., $J \geq \binom{L}{N}$. One has $J = M$ only if $L = N + 2$. It is interesting to note that every N-representable density matrix with 1-rank $= N + 2$ corresponds to a unique N-particle function.[18] If L is large, then

$$\binom{L}{N} = J \gg M = \binom{L}{2},$$

and the procedure described in Theorem 7 does not seem practical. In fact, $(\underline{W}^K \underline{W}^{L\dagger})$ corresponds to the transition density matrix between the corresponding Slater determinants and the $\{x_K\}$ are just expansion coefficients when the N-particle function is expanded in N-particle Slater determinants. Thus Theorems 6 and 7 merely represent a restatement of the N-representability problem. It follows from (20) to (23) that $\underline{T}$, $\underline{\Upsilon}$, and $\underline{\Omega}^\mu$ all transform unitarily under unitary transforms of the geminals, so that similar considerations apply to any geminal basis unitarily equivalent to such a Slater geminal basis.

NSG's and Partial Isometries

Let L_0 and M_0 be the 1-rank and 2-rank of some second-order density matrix. If

$$M_0 < \binom{L_0}{2}$$

then the NSG's are not unitarily equivalent to the Slater geminal basis and the above considerations do not apply. In these cases it is important to emphasize the difference between unitary transformations and partial isometries. When working with the density matrix or wave function one can make a partial isometry into a unitary transformation by adding on additional orthonormal geminals. All expansion coefficients involving these geminals are zero so nothing is changed. However, no weighting factors appear in the $\underline{T}$ and $\underline{\Upsilon}$ matrices. Therefore partial isometries not only reduce the dimension of $\underline{T}$ and $\underline{\Upsilon}$, but can also change the eigenvalues and their degeneracies. In general J decreases as M decreases, so that an appropriate choice of geminal basis may make J quite small. Then Theorems 6 and 7 may give a complete solution to the N-representability problem. In general, (44) is more restrictive as J decreases. In the most extreme case $J = 1$, and (44) is trivial.

An example of some practical interest in which $M_0 < \binom{L}{2}$ can be obtained from Ref. 2.[19] Consider the "r blocks" occurring in (34). Each block has dimension $P \times P$, i.e., is formed from the P Slater geminals $[i, r]$ $(i = 1 \cdots P)$. Now this block can be diagonalized in the nonorthogonal basis

$$h_K = \sum_i c_{iK} [i, r],$$

where there are as many h_K as there are nonzero b_K with K containing r. Let the number of h_K be I_r. The number of NSG's corresponding to that r block must be less than I_r. So if I_r is less than P the number of NSG's will be less than the number of Slater geminals,[20] $[i, r]$.

The most interesting situation would occur if L_0 were infinite and M_0 finite. Theorem 2 says that this cannot happen if N is odd. Whether or not it is possible when N is even is not known. It can be shown that the following special functions[21] have infinite 2-rank if they have infinite 1-rank: antisymmetrized geminal power; antisymmetrized product of strongly orthogonal geminals; disjoint pair functions. Thus if any functions exist with finite 2-rank and infinite 1-rank they will have a rather complicated form.

Summary

The results of this section will now be summarized by giving a possible testing procedure for N-representability.

(A) Determine the rank of Γ. If it is infinite, or equal to the number of Slater geminals formed from NSO's, Theorem 6 and 7 can give no further information.

(B) If the rank is less than the number of Slater geminals, form the $\underline{T}$ or $\underline{\mathcal{T}}$ matrix in an appropriate geminal basis. Theorem 7 will probably be most useful if the NSG basis is used.

(C) Find the $\underline{\Omega}^{\mu}$ matrices and note the degeneracy of $+1$ as an eigenvalue of Ω^2. If this is less than the number of NSG's, Γ is not N representable.

(D) Find $\underline{\Omega}^1$ and the degeneracy, J, of $+1$. The usefulness of Theorem 7 depends upon the relative size of M and J.

(E) If J is not too large, find $\underline{P}$ and apply Theorem 7 to test for N-representability.

(F) If $\underline{P}\,\underline{Z}=0$ has a solution, apply (49) to select acceptable solutions of $\underline{P}\,\underline{Z}=\underline{D}$.

(G) Find the N-particle function Ψ and test for antisymmetry or symmetry.

This procedure depends critically on the number of eigenvectors $\underline{W}^k$ $(k=1\cdots J)$ of $\underline{\Omega}^1$ to $+1$. Therefore all geminal bases are not equivalent when testing for N-representability – some are more suitable than others. When this procedure solves the N-representability problem, it also determines the N-particle function from which Γ can be derived. All known solutions[2,13,14,18] of the N-representability problem for the second-order density matrix have this property, i.e., solving the problem determines the N-particle function.

VI. UNIQUENESS

There has been some interest in determining for which second-order density matrices the functions, from which the density matrix can be derived, are not unique.[22] It follows from condition (b) of Theorem 6 that a necessary condition for nonuniqueness is that $+1$ is a degenerate eigenvalue of $\underline{\Omega}^1$ in any geminal basis in which Γ can be expanded. Let $\underline{P}$ be the matrix $\underline{P}=\{\rho_{pq,kl}\}$ defined by (45). Then, as shown previously, a necessary condition for nonuniqueness is that the equation

$$\underline{P}\,\underline{Z}=\underline{D} \tag{44$'$}$$

have at least two solutions $\underline{Z}=\{z_{kl}\}$ which are Hermitian, non-negative matrices of rank one. This can only occur if the homogeneous equation

$$\underline{P}\,\underline{Z}=\underline{0}. \tag{47}$$

has a nontrivial solution. To illustrate this condition and the use of Theorems 5, 6, and 7, an example is worked out for $N=6$.

Let Ψ_1 and Ψ_2 be antisymmetric six-particle functions. Let $\{\phi_p\}$ $(p=1\cdots M_1)$ and $\{\bar{\phi}_{\bar{p}}\}$ $(\bar{p}=1\cdots M_2)$ be the NSG's of Ψ_1 and Ψ_2, respectively. Γ_1 and Γ_2 are the corresponding second-order density matrices; $\underline{T}_1$ and $\underline{T}_2$ the corresponding transposition matrices. Now assume that ϕ_p and $\bar{\phi}_q$ are strongly orthogonal for all p,q, i.e.,

$$\int \phi_p(12)\bar{\phi}_q^*(12)\,d1=0.$$

Now let

$$\Psi_\alpha=2^{-1/2}(\Psi_1+e^{i\alpha}\Psi_2). \tag{50}$$

All Ψ_α and $\Psi_{\alpha'}$ are linearly independent if $\alpha\neq\alpha'$, but

$$\Gamma_\alpha=\tfrac{1}{2}(\Gamma_1+\Gamma_2)=\Gamma \tag{51}$$

is the same for all α and α'. Thus one has an uncountably infinite number of distinct functions with the same Γ. The NSG's of Γ are those of Γ_1 and Γ_2. Thus $\underline{T}$ is independent of α and has the form:

$$\underline{T}=\begin{array}{c} \begin{array}{cccc} pq & p\bar{q} & \bar{p}q & \bar{p}\bar{q} \end{array} \\ \begin{pmatrix} \underline{T}_1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \underline{T}_2 \end{pmatrix} \end{array} \begin{array}{c} \\ pq \\ p\bar{q} \\ \bar{p}q \\ \bar{p}\bar{q} \end{array}. \tag{52}$$

The nonzero eigenvalues of $\underline{T}$ are those of $\underline{T}_1$ and $\underline{T}_2$. The eigenvectors belonging to ϵ clearly have the form:

$$\underline{A}^m=\begin{array}{c} \begin{array}{cc} p & \bar{p} \end{array} \\ \begin{pmatrix} \underline{A}_1{}^m & 0 \\ 0 & 0 \end{pmatrix} \end{array} \begin{array}{c} \\ p \\ \bar{p} \end{array}, \quad \underline{A}^{\bar{m}}=\begin{array}{c} \begin{array}{cc} p & \bar{p} \end{array} \\ \begin{pmatrix} 0 & 0 \\ 0 & \underline{A}_2{}^m \end{pmatrix} \end{array} \begin{array}{c} \\ p \\ \bar{p} \end{array}, \tag{53}$$

where $\underline{A}_1{}^m$ and $\underline{A}_2{}^m$ are the eigenvectors of $\underline{T}_1$ and $\underline{T}_2$, respectively. Note that

$$\underline{A}^{\bar{m}\dagger}\underline{A}^n=\underline{A}^\dagger\underline{A}^{\bar{n}}=0 \quad \text{for all } r,s$$

$$\underline{A}^{m\dagger}\underline{A}^n=\begin{pmatrix} (\underline{A}_1{}^{m\dagger}\underline{A}_1{}^n) & 0 \\ 0 & 0 \end{pmatrix},$$

$$\underline{A}^{\bar{m}\dagger}\underline{A}^{\bar{n}}=\begin{pmatrix} 0 & 0 \\ 0 & (\underline{A}_2{}^{m\dagger}\underline{A}_2{}^n) \end{pmatrix}.$$

Thus $\underline{\Omega}^1$ has the form:

$$\underline{\Omega}=\underline{\Omega}^1=\begin{array}{c} \begin{array}{cccc} pm & \bar{p}m & p\bar{m} & \bar{p}\bar{m} \end{array} \\ \begin{pmatrix} \underline{\Omega}_1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \underline{\Omega}_2 \end{pmatrix} \end{array} \begin{array}{c} \\ pm \\ \bar{p}m \\ p\bar{m} \\ \bar{p}\bar{m} \end{array}. \tag{54}$$

The nonzero eigenvalues of $\underline{\Omega}$ are just those of $\underline{\Omega}_1$ and $\underline{\Omega}_2$. Suppose $+1$ is a nondegenerate eigenvalue of each, with eigenvectors $\underline{G}_1$ and $\underline{G}_2$. Then the eigenvectors of $\underline{\Omega}$ can be chosen as

$$\underline{W}^1 = \begin{pmatrix} \underline{G}_1 & 0 \\ 0 & 0 \end{pmatrix}, \quad \underline{W}^2 = \begin{pmatrix} 0 & 0 \\ 0 & \underline{G}_2 \end{pmatrix}. \tag{55}$$

Now one wants to find x_1 and x_2 such that if $\underline{W} = x_1\underline{W}^1 + x_2\underline{W}^2$, then

$$\underline{W}\,\underline{W}^\dagger = \underline{D} = \tfrac{1}{2}\begin{pmatrix} \underline{D}_1 & 0 \\ 0 & \underline{D}_2 \end{pmatrix}. \tag{56}$$

But from (55),

$$\underline{W}\,\underline{W}^\dagger = |x_1|^2\,\underline{W}^1\underline{W}^{1\dagger} + |x_2|^2\,\underline{W}^2\underline{W}^{2\dagger}$$

and

$$\underline{W}^1\underline{W}^{1\dagger} = \begin{pmatrix} \underline{D}_1 & 0 \\ 0 & 0 \end{pmatrix}, \quad \underline{W}^2\underline{W}^{2\dagger} = \begin{pmatrix} 0 & 0 \\ 0 & \underline{D}_2 \end{pmatrix}.$$

Then any x_1 and x_2 for which $|x_1|^2 = |x_2|^2 = \frac{1}{2}$ will do. One can also use Theorem 7 to find x_1 and x_2. Combining (55) and (45) one gets:

$$\begin{array}{ccccc} & 11 & 12 & 21 & 22 \\ \underline{P} = \Big[& \begin{pmatrix} \underline{D}_1 & 0 \\ 0 & 0 \end{pmatrix} & 0 & 0 & \begin{pmatrix} 0 & 0 \\ 0 & \underline{D}_2 \end{pmatrix} \Big] \end{array}$$

One needs to find solutions to:

$$\underline{P}\,\underline{Z} = \underline{D} = \frac{1}{2}\begin{pmatrix} \underline{D}_1 \\ 0 \\ 0 \\ \underline{D}_2 \end{pmatrix} \begin{array}{c} 11 \\ 12 \\ 21 \\ 22 \end{array}. \tag{57}$$

This has the particular solution

$$\begin{pmatrix} \frac{1}{2} \\ 0 \\ 0 \\ \frac{1}{2} \end{pmatrix} \text{ or } \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$$

The homogeneous equation

$$\underline{P}\,\underline{Z} = 0 \tag{58}$$

has two solutions:

$$\begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} \text{ and } \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}.$$

Thus the general Hermitian solution can be written in matrix form as:

$$\underline{Z} = \begin{pmatrix} \frac{1}{2} & \sigma \\ \sigma^* & \frac{1}{2} \end{pmatrix}. \tag{59}$$

It is of rank 1 if and only if $\underline{Z}^2 = \underline{Z}$, i.e.,

$$\begin{pmatrix} \frac{1}{2} & \sigma \\ \sigma^* & \frac{1}{2} \end{pmatrix} = \begin{pmatrix} \frac{1}{4} + |\sigma|^2 & \sigma \\ \sigma^* & \frac{1}{4} + |\sigma|^2 \end{pmatrix}.$$

This implies $|\sigma|^2 = \frac{1}{4}$ or $\sigma = \frac{1}{2}e^{-i\beta}$ $(0 \leqslant \beta \leqslant 2\pi)$. Then $\underline{Z}$ can be written

$$\underline{Z} = \frac{1}{2}\begin{pmatrix} 1 & e^{+i\beta} \\ e^{-i\beta} & 1 \end{pmatrix} \quad \text{or} \quad \underline{Z} = \underline{x}\,\underline{x}^\dagger, \tag{60}$$

where

$$\underline{x} = 2^{-1/2}\begin{pmatrix} 1 \\ e^{-i\beta} \end{pmatrix}. \tag{61}$$

Then $\underline{W}$ is given by

$$\underline{W} = 2^{-\frac{1}{2}}(\underline{W}^1 + e^{-i\beta}\underline{W}^2) \tag{62}$$

and satisfies $\underline{W}\,\underline{W}^\dagger = \underline{D}$. Since $\underline{G}_1$ and $\underline{G}_2$ are the matrices which give the correct expansion coefficients for Ψ_1, and Ψ_2, $\underline{W}$ will correspond to the function

$$\Psi = 2^{-\frac{1}{2}}(\Psi_1 + e^{-i\beta}\Psi_2). \tag{63}$$

If β is chosen so that $(\beta = 2\pi - \alpha)$ then $e^{-i\beta} = e^{i\alpha}$ and (63) is just Ψ_α, as expected.

VII. HIGHER-ORDER DENSITY MATRICES

These results can be extended to higher-order density matrices. Let $N = (\nu p + \kappa)$ $(1 \leqslant \kappa \leqslant p)$. One can expand Ψ in p-particle and κ-particle states as:

$$\Psi = \sum_i \sum_{k_1\cdots k_\nu} c_{ik_1\cdots k_\nu}\chi_i(1\cdots\kappa) \times \phi_{k_1}(\kappa+1\cdots\kappa+p)\cdots\phi_{k_\nu}(N-p+1\cdots N). \tag{64}$$

The $\{\chi_i\}$ and $\{\phi_\gamma\}$ are assumed to be orthonormal and appropriately symmetric or antisymmetric.

With respect to permutations of $k_1k_2\cdots k_\nu$, the coefficients

$$c_{ik_1\cdots k_\nu}$$

are symmetric for bosons, and symmetric or antisymmetric for fermions as p is even or odd. If $\kappa = p$ they must also be symmetric or antisymmetric with respect to interchange of i and k_j. One can generalize Theorem 1 to show that the p rank of Ψ is finite if and only if the κ rank is finite. The generalized $\underline{\Upsilon}(p,\kappa)$ matrix is defined by

$$\tau_{ri,sj} = \int \chi_i^*(1\cdots\kappa-1,\kappa)\phi_\gamma^*(\kappa+1\cdots\kappa+p) \times \chi_j(1\cdots\kappa-1,\kappa+1)\phi_s(\kappa,\kappa+2\cdots\kappa+p). \tag{65}$$

Then the expansion coefficients must satisfy

$$\sum_{sj} \tau_{ri,sj}\tilde{c}_{sjk_2\cdots k_\nu} = \epsilon\tilde{c}_{rik_2\cdots k_\nu}, \tag{66}$$

where $\tilde{c}_{rik_2\cdots k_\nu} = c_{irk_2\cdots k_\nu}$.

Let $\underline{A}^m = \{a_{pi}{}^m\}$ be the eigenvectors of $\underline{\mathcal{T}}$ to eigenvalue ϵ; and let $\underline{\Omega}^{\nu-1}$ be given by

$$\omega_{rm,sn} = \sum_i a_{ri}{}^n (a_{si}{}^m)^* . \tag{67}$$

Then $\underline{\Omega}^{\nu-1}$ must satisfy the same conditions as $\underline{\mathcal{T}}(p, \kappa)$ does for fermion or boson $[(\nu-1)p+1]$-completeness. Boson conditions are necessary when symmetric functions are considered or when p is even; fermion conditions are necessary when antisymmetric functions are considered and p is odd. One can inductively define $\underline{\Omega}^{\mu}$ and $^{\mu}\underline{U}^{m\mu}$ as before. Then let

$$c_{ik_1\cdots k_\nu} = \sum_n \sum_{m_\mu} a_{k_1 i}{}^n u_{k_2 n}{}^{m_{\nu-1}} \cdots$$

$$\cdots u_{k_{\nu-1} m_3}{}^{m_2} w_{k_\nu m_2} , \tag{68}$$

where $\underline{W}$ is an eigenvector of $\underline{\Omega}^1$ to eigenvalue ϵ^p. One can then state the analog of Theorem 4 for any $p \geq 2$.

Theorem 8: If $N = (\nu p + \kappa)$ then a finite set of antisymmetric (symmetric) p-particle functions is fermion (boson) N-complete if and only if the following conditions are satisfied:

(a) The $\underline{\mathcal{T}}(p, \kappa)$ matrix, defined by (65) has ϵ as an eigenvalue.

(b) If $\underline{\Omega}^{\nu-1}$ is formed from the eigenvectors of $\underline{\mathcal{T}}$ according to (67) then $\underline{\Omega}^{\nu-1}$ satisfies the conditions of $[(\nu-1)p+1]$-completeness corresponding to ϵ^p.

(c) If Ω^{μ} is defined inductively from the eigenvectors of $\underline{\Omega}^{\mu+1}$ then Ω^1 must have at least one eigenvector $\underline{W}$ belonging to eigenvalue ϵ^p such that if Ψ is given by (64) with expansion coefficients given by (68), then $\mathcal{O}_{\epsilon} \Psi = \Psi$.

Theorem 6 can now be applied to p-particle states if condition (b) is replaced by:

(b′) Ω^1 has at least one eigenvector $\underline{W}$, belonging to eigenvalue ϵ^p such that $\underline{W}\,\underline{W}^\dagger = \underline{D}$. If ϵ^p is a degenerate eigenvalue of $\underline{\Omega}^1$ then Theorem 7 can be used to determine which linear combinations may satisfy condition (b′).

Although the N-representability conditions given in Sec. V can be extended to higher-order reduced density matrices, they cannot be extended to first-order density matrices. This is because the conditions on $\underline{T}$, $\underline{\mathcal{T}}$, and $\underline{\Omega}^{\mu}$ involve the p-particle states in which $\underline{\Gamma}^{(p)}$ is expanded. The N-representability problem for the first-order density matrix depends only on its eigenvalues and N;[1] it is independent of the NSO's.

VIII. DISCUSSION

The N-completeness conditions given in the preceding sections have exploited the symmetry of the expansion coefficients with respect to interchange of any two indices in $k_1 \cdots k_\nu$. Different sets of conditions can be obtained by exploiting other symmetry properties. For example, when $N \geq 8$ one could require only symmetry with respect to pairs of indices. Then the conditions on $\underline{\hat{A}}^m$ for $N = 8$ would be

$$\hat{a}_{pq}{}^{rs} = \hat{a}_{rs}{}^{pq} , \tag{69}$$

$$\text{where} \quad \underline{\hat{A}}^{rs} = \sum_m u_{rs,m} \underline{A}^m$$

for some linear transformation $\{u_{rs,m}\}$. This would reduce the problem more quickly than the method given in Sec. IV; on the other hand, it might lead to extra degeneracy and spurious solutions whose elimination would actually be more work. When N is odd, one could impose simultaneous conditions on the $\underline{T}$ and $\underline{\mathcal{T}}$ matrices. If N is 5 and the eigenvectors to eigenvalue ϵ of $\underline{\mathcal{T}}$ are $\underline{A}^m = \{a_{pi}{}^m\}$ and those of $\underline{T}$ are $\underline{B}^l = \{b_{pq}{}^l\}$ one could require

$$\hat{a}_{pi}{}^q = \hat{b}_{pq}{}^i , \tag{70}$$

$$\text{where} \quad \underline{\hat{A}}^q = \sum_k u_{qm} \underline{A}^m , \quad \underline{\hat{B}}^i = \sum_l v_{il} \underline{B}^l . \tag{71}$$

For some linear transformations $\{u_{qm}\}$ and $\{v_{il}\}$. Note that since $\underline{B}$ is symmetric, (28) will be satisfied whenever (70) is. Whether or not there is any practiced advantage to any of these methods is not known.

N-representability conditions can be used in three ways:

(1) As a testing procedure for determining whether or not a density matrix is actually N representable;

(2) As a constraint in variational calculations using the density matrix directly;

(3) As a means of writing down some general form for an N-representable density matrix.

The conditions presented here do give a testing procedure in some cases but it seems to be too complicated for practical use. If a particular geminal basis is given, one can obtain the general form of all N-representable density matrices, which can be expanded in that basis. It is simply

$$\underline{D} = \sum_{kl} y_k y_l^* \underline{W}^k \underline{W}^{l\dagger} . \tag{72}$$

where the $\{y_k\}$ are subject only to a normalization condition. At present, nothing is known about choosing a geminal basis for which (72) might be useful.

It has been known that geminal expansions cannot be truncated in the same way that NSO expansions can.[23] Even if all expansion coefficients involving a particular geminal ϕ_{p_0} are small, it may still be necessary to include ϕ_{p_0} in the set of N-complete geminals. This is reflected in the fact that all ϕ_p occur in $\underline{T}$ and $\underline{\mathcal{T}}$ with equal weight. Thus one cannot arbitrarily truncate a set of geminals and still retain N-completeness.

The results of this paper give procedures for testing for N-completeness and N-representability, which are applicable to geminal bases for which the degeneracy of $\underline{\Omega}^1$ is not too large. The procedures, if successful, also provide a method for constructing the corresponding N-particle function. Therefore they do not appear to have much practical use, unless they simplify in special cases. These results have raised several new questions which have not yet been answered: If N is even, can one construct an antisymmetric or symmetric N-particle function which has finite 2-rank and infinite 1-rank? Can one characterize those sets of geminals for which the degeneracy of $\underline{\Omega}^1$ is small in some simple manner? If a set of geminals is not N-complete, how can one choose additional geminals which will make them N-complete? Can one ever find a set of sufficient conditions for N-representability of the second-order density matrix which do not also generate the corresponding N-particle function?

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[1]A. J. Coleman, Rev. Mod. Phys. 35, 668 (1963).

[2]M. B. Ruskai and J. E. Harriman, Phys. Rev. 169, 101 (1968).

[3]"Proceedings of a Conference at Queen's University, Kingston, Ontario, 1967," Queen's Papers in Pure and Applied Mathematics, No. 11, edited by A. J. Coleman and R. M. Erdahl (Queen's University Press, Kingston, Ontario, 1967). See, in particular, the paper by A. J. Coleman, pp. 2–19.

[4]B. C. Carlson and J. M. Keller, Phys. Rev. 121, 659 (1961).

[5]It is not necessary to also require $\Psi(12345\cdots N) = \epsilon\Psi(12435\cdots N)$ since the functions under consideration satisfy: $\psi(12345) = \epsilon\psi(13245) = \psi(31245) = \psi(34512) = = \epsilon\psi(43512) = \epsilon\psi(41235) = \psi(14235) = \epsilon\psi(12435)$.

[6]A. J. Coleman, Abstract of a lecture given at the Symposium on Quantum Chemistry, Sanibel Island, Florida, January 17, 1964 (unpublished).

[7]M. Girardeau, J. Math. Phys. 4, 1096 (1963).

[8]F. D. Peat, Ref. 3, p. 315.

[9]N. I. Akhiezer and I. M. Glazman, Theory of Linear Operators in Hilbert Space (Frederick Ungar Publishing Co., New York, 1961), Vol. I, p. 102, Theorem 4. Since property (f) implies that the transposition matrices are bounded, they correspond to bounded Hermitian operators.

[10]A partial isometry is a linear transformation which is isometric on the orthogonal complement of its null space. An equivalent definition is that $\underline{U}$ is a partial isometry if and only if $\underline{UU}^\dagger$ is a projection.

[11]This follows from the fact that the spectral radius of any matrix $\underline{A}$ is sup $(|\underline{x}^\dagger \underline{Ax}| / \underline{x}^\dagger \underline{x})$, which clearly decreases if $\underline{A}$ is truncated.

[12]Of course, if all $\underline{A}^m$ yield antisymmetric functions then any linear combination will also.

[13]D. W. Smith, J. Chem. Phys. 43, S 258 (1965).

[14]D. W. Smith, Ref. 3, p. 247.

[15]The functions considered by M. B. Ruskai in Sec. VII of University of Wisconsin Theoretical Chemistry Institute Technical Note No. 190G 1966 (unpublished) have this property, i.e., if $\underline{\Omega}^1$ is obtained from their NSG's then +1 is a nondegenerate eigenvalue of $\underline{\Omega}^1$.

[16]If $\underline{Z}$ is a solution of (47) then $\underline{Z}^\dagger$ is also. Thus one can always choose as $\underline{Z}^i$ the Hermitian solutions $\underline{Z} + \underline{Z}^\dagger$ and $i(\underline{Z} - \underline{Z}^\dagger)$.

[17]The author would like to thank the referee for some helpful comments on Slater determinants.

[18]M. B. Ruskai, unpublished solution of the N-representability problem for functions whose 1 rank is $N+2$.

[19]In this paragraph the notation and equation numbers of Ref. 2 will be used without further explanation. Note that r refers to a paired NSO, not to a geminal in this reference.

[20]Following (38b) it is shown that these NSG's can all be written as single Slater determinants in some one-particle basis. However, this one-particle basis will be different for every r, so the simple results on Slater geminals given in the preceding section do not apply.

[21]For definitions, see Ref. 3, pp. 16 and 237.

[22]The only result known to the author is an unpublished theorem by R. M. Erdahl concerning three- and four-particle functions.

[23]See, for example, G. P. Barnett and H. Shull, Phys. Rev. 153, 61 (1967).