Geometry of density matrices. V. Eigenstates

John E. Harriman
Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706
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Constraints placed on a reduced density matrix or density by the requirement that it correspond to an eigenstate or ensemble of eigenstates of some operator are investigated. Linear conditions, including expectation value, commutator, hypervirial, and hierarchy equation conditions, may lead to linear constraints on lower-order reduced density matrices and densities or leave them unconstrained. A zero-dispersion condition for a p-electron operator defines a parabolic trough on which reduced density matrices of order $2p$ must lie, but usually does not restrict lower-order reduced density matrices or the density. Some properties of symmetrized and antisymmetrized matrix products, related to their reduction behavior, are also investigated.

I. INTRODUCTION

In the previous papers in this series[1–4] (referred to here as GDM I–IV) density matrices and densities defined with respect to a finite basis set have been treated as elements in Euclidean vector spaces. Various geometric properties,[1,2] spin properties,[3] and mappings from one space to another[2,4] have been considered. Other workers have emphasized group-theoretic aspects, treating the spaces of density matrices as carrier spaces for representations of the group of unitary transformations of the underlying spin-orbital basis.[5–8]

The present paper is concerned with properties of density matrices and densities resulting from the requirement that they correspond to an eigenstate of some operator, or to ensembles of such states. An eigenstate condition implies other, less stringent conditions involving expectation values and commutation or hypervirial relationships. Density matrix hierarchy equations also result.[9–12] It will be shown in what follows that these conditions place linear constraints on the density matrices, either fixing certain components or establishing linear relationships among components. A zero-dispersion condition $\langle \hat{A}^2 \rangle = \langle \hat{A} \rangle^2$ is well known in the pure-state case to be equivalent to an eigenstate condition, and this has been extended to density matrices.[13–15] This nonlinear condition defines a parabolic trough in the space of reduced density matrices.

The next section of this paper deals with mathematical background. Previous results are very briefly reviewed. Some new terminology, and some new results relating to matrix products, are presented. Subsequent sections deal with various sets of conditions and their consequences. Simple examples are provided by a consideration of spin eigenstates.

Conditions on density matrices also imply conditions on densities. These are complicated by the fact that they are in general basis-set dependent,[4] and a basis set chosen to simplify the relationships[16] may not be convenient for other purposes. Section VII is devoted to a discussion of eigenstate conditions on densities. The operator of greatest interest is of course the Hamiltonian, but the results of this paper are developed for general operators.

II. BACKGROUND

This paper investigates some of the properties of density matrices associated with *eigenstates* of some operator, $\hat{\Omega}$. If D is a pure-state density matrix projecting onto a wave function Ψ

$$D = \Psi\Psi^* , \tag{1}$$

then this refers to the fact that Ψ is an eigenfunction of $\hat{\Omega}$

$$\hat{\Omega}\Psi = \omega\Psi . \tag{2}$$

We will also consider *eigenensembles,* which are ensembles of eigenstates all associated with the same eigenvalue. If

$$\hat{\Omega}\Psi_\kappa = \omega\Psi_\kappa, \quad \kappa = 1, \ldots, d \tag{3}$$

and

$$D = \sum_\kappa \lambda_\kappa \Psi_\kappa \Psi_\kappa^* \tag{4}$$

with $0 \le \lambda_\kappa \le 1$, $\sum_\kappa \lambda_\kappa = 1$, then D is the density matrix for an eigenensemble. Finally, we will sometimes consider ensembles of eigenstates with different eigenvalues. These minimally constrained density matrices will be called *diagonal ensembles.*

As in previous papers in this series, especially GDM II, we assume a one-electron basis set consisting of r orthonormal spin-orbitals. An orthonormal basis for n-electron functions can then be taken to consist of the $\binom{r}{n}$ independent, normalized single-determinant functions. Although n could be as large as r, we can avoid a number of complications by requiring $r > 2n$.

We will speak of an operator being "restricted" to the space spanned by the relevant set of functions. More precisely, the domain of the operator is restricted to this space and its range is projected onto the space. Such a restricted operator can be represented by a finite-dimensional matrix, with each physical problem being replaced by the matrix, model problem. Some care is essential in specifying what fundamental operators are involved (the stage in a calculation at which the restriction to the finite space occurs) since in general the product of restricted operators differs from the restriction of the prod-

uct of the corresponding unrestricted operators.

Since there are $\binom{r}{n}$ n-electron basis functions, an operator acting on n-electron functions will be replaced by an $\binom{r}{n}\times\binom{r}{n}$ matrix. The real linear space of $\binom{r}{n}\times\binom{r}{n}$ Hermitian matrices is denoted by $\mathscr{E}_n$. The reduction operation $\hat{L}_n^p$, defined originally for density matrices,[17,18] can be applied to any matrix in $\mathscr{E}_n$ to give a matrix in $\mathscr{E}_p$. Each space $\mathscr{E}_p$ can be uniquely divided into orthogonal subspaces $\mathscr{E}_{p\pi}$, $0\le\pi\le p$. These are the invariant subspaces with respect to unitary transformations of the spin-orbital basis.[5-8] They have the further very important properties that if $\vec{V}^{(p,\pi)}$ is any element of $\mathscr{E}_{p\pi}$, then

$$\hat{L}_p^q\vec{V}^{(p,\pi)}=\vec{0},\quad q<\pi\ , \tag{5}$$

and that a one-to-one correspondence can be established between the elements of $\mathscr{E}_{p\pi}$ and those of $\mathscr{E}_{q\pi}$ for any $p,q\ge\pi$. (Since matrices are regarded here as elements in vector spaces, a vector notation is used.)

In the absence of a basis set we speak of an operator $\hat{\Omega}$ as a p-electron operator acting on n-electron functions if it is of the form

$$\hat{\Omega}=\sum_{\substack{k_1,\ldots,k_p=1\\ k_1<\cdots<k_p}}^{n}\hat{\Omega}(k_1,\ldots,k_p)\ . \tag{6}$$

An operator can have components associated with different values of p, the most important example being the Hamiltonian, with one-electron and two-electron parts. Such an operator can be written formally as having a single value of p. For example, the usual reduced Hamiltonian form[19]

$$\hat{\mathscr{H}}=\sum_{j=1}^{n}\hat{\mathscr{f}}(j)+\sum_{\substack{j,k=1\\ j<k}}^{n}\hat{g}(j,k)=\sum_{\substack{j,k=1\\ j<k}}^{n}\hat{h}(j,k)\ , \tag{7}$$

$$\hat{h}(j,k)=\frac{1}{n-1}[\hat{\mathscr{f}}(j)+\hat{\mathscr{f}}(k)]+\hat{g}(j,k)\ . \tag{8}$$

For matrices, a different decomposition is more fundamental. Any $\vec{V}^{(p)}\in\mathscr{E}_p$ can be divided into components $\vec{V}^{(p,\pi)}\in\mathscr{E}_{p\pi}$. We will refer to the component label π as the *reduction index* of $\vec{V}^{(p,\pi)}$ and p will be called the *order,* the latter being the conventional reduced-density matrix terminology. The matrix $\vec{\Omega}^{(n)}$ of the p-electron operator $\hat{\Omega}$, will in general have components of reduction index π for various values of π between 0 and p. We define the *degree* of the matrix as being equal to the maximum of the reduction indices of its nonvanishing components. A matrix of degree p can always be constructed as the matrix of a p-electron operator.

One of the most fundamental facts of reduced density matrix theory is that the expectation value of a p-electron operator can be evaluated from the reduced density matrix of order p.[20] If $\hat{\Omega}$ is given by Eq. (6), then for density matrices normalized to unit trace

$$\langle\hat{\Omega}\rangle=\int'\hat{\Omega}D^{(n)}(1,\ldots,n;1',\ldots,n')dx_1\cdots dx_n=\binom{n}{p}\int'\hat{\Omega}(1,\ldots,p)D^{(p)}(1,\ldots,p;1',\ldots,p')dx_1\cdots dx_p,\quad p\le n\ . \tag{9}$$

(The prime on the integral sign is a reminder of the prescription that after the operator acts, on unprimed variables only, primes are dropped before integration.) In matrix form

$$\langle\Omega\rangle=\mathrm{tr}(\vec{\Omega}^{(n)}\vec{D}^{(n)}) \tag{10}$$

is the finite-basis approximation to $\langle\Omega\rangle$, but this is not equal to $\mathrm{tr}[\vec{\Omega}^{(p)}\vec{D}^{(p)}]$ where $\vec{\Omega}^{(p)}=\hat{L}_n^p\vec{\Omega}^{(n)}$. Instead, we can define an *effective reduced matrix,* $\vec{\Omega}_{\mathrm{eff}}^{(p)}$, by requiring that for any $\vec{V}^{(n)}\in\mathscr{E}_n$ and $\vec{V}^{(p)}=\hat{L}_n^p\vec{V}^{(n)}$,

$$\binom{n}{p}(\vec{\Omega}_{\mathrm{eff}}^{(p)},\vec{V}^{(p)})\equiv\binom{n}{p}\mathrm{tr}(\vec{\Omega}_{\mathrm{eff}}^{(p)}\vec{V}^{(p)})$$

$$=(\vec{\Omega}^{(n)},\vec{V}^{(n)})\equiv\mathrm{tr}(\vec{\Omega}^{(n)}\vec{V}^{(n)})\ , \tag{11}$$

where the trace scalar product has been introduced.[1]

The relationship between $\vec{\Omega}_{\mathrm{eff}}^{(p)}$ and $\hat{L}_n^p\vec{\Omega}^{(n)}$ is complicated by the fact that, although $\hat{L}_n^p$ provides a one-to-one linear map from $\mathscr{E}_{n\pi}$ onto $\mathscr{E}_{p\pi}$, it changes norms by a factor depending on π as well as on n and p:[21]

$$||\hat{L}_n^p\vec{V}^{(n,\pi)}||=\zeta(n,p,\pi)||\vec{V}^{(n,\pi)}||\ . \tag{12}$$

This is readily generalized to the scalar product

$$(\vec{\Omega}^{(p,\pi)},\vec{V}^{(p,\pi)})=(\hat{L}_n^p\vec{\Omega}^{(n,\pi)},\hat{L}_n^p\vec{V}^{(n,\pi)})$$

$$=[\zeta(n,p,\pi)]^2(\vec{\Omega}^{(n,\pi)},\vec{V}^{(n,\pi)})\ . \tag{13}$$

Since components with different reduction index are orthogonal,

$$(\vec{\Omega}^{(n)},\vec{V}^{(n)})=\sum_{\pi}(\vec{\Omega}^{(n,\pi)},\vec{V}^{(n,\pi)})$$

$$=\sum_{\pi}[\zeta(n,p,\pi)]^{-2}(\vec{\Omega}^{(p,\pi)},\vec{V}^{(p,\pi)})$$

$$=\left[\sum_{\pi}[\zeta(n,p,\pi)]^{-2}\vec{\Omega}^{(p,\pi)},\vec{V}^{(p)}\right]\ . \tag{14}$$

We can thus identify

$$\vec{\Omega}_{\mathrm{eff}}^{(p)}=\sum_{\pi}\chi(n,p,\pi)\vec{\Omega}^{(p,\pi)}\ , \tag{15}$$

where

$$\chi(n,p,\pi)=\binom{n}{p}^{-1}[\zeta(n,p,\pi)]^{-2}$$

$$=\frac{n!(n-p)!(r-n-\pi)!(p-\pi)!}{p!(n-\pi)!(r-p-\pi)!}\ . \tag{16}$$

Matrix products will also be of interest. The product of two Hermitian matrices will not in general be Hermitian. We could extend the real vector space $\mathscr{E}_p$ to a complex vector space $\mathscr{E}_p^*$ including all $\binom{r}{p}\times\binom{r}{p}$ matrices, but choose instead to deal with Hermitian matrices

$$(\vec{A}\,\vec{B})^{\pm}=\tfrac{1}{2}(\pm 1)^{1/2}(\vec{A}\,\vec{B}\pm\vec{B}\,\vec{A})\ . \tag{17}$$

The order superscript has been suppressed, but $\vec{A}$, $\vec{B}$, and $(\vec{A}\,\vec{B})^{\pm}$ are all of some particular order q. Introduce any orthonormal basis $\{\vec{Y}_k\}$ for $\mathscr{E}_q$. Then

$$\vec{A}=\sum_{\kappa} a_\kappa \vec{Y}_\kappa,\quad \vec{B}=\sum_{\kappa} b_\kappa \vec{Y}_\kappa\ , \tag{18}$$

and

$$(\vec{A}\vec{B})^{\pm}=\sum_{\kappa} c_\kappa^{\pm}\vec{Y}_\kappa\ . \tag{19}$$

The expansion coefficients are related by

$$c_\kappa^{\pm}=\sum_{\lambda,\mu} T^{\pm}_{\kappa\lambda\mu}a_\lambda b_\mu \tag{20}$$

with

$$T^{\pm}_{\kappa\lambda\mu}=\tfrac{1}{2}(\pm 1)^{1/2}[\mathrm{tr}(\vec{Y}_\kappa\vec{Y}_\lambda\vec{Y}_\mu)\pm\mathrm{tr}(\vec{Y}_\kappa\vec{Y}_\mu\vec{Y}_\lambda)]\ . \tag{21}$$

It follows from this definition and the invariance of the trace of a product under cyclic permutations of factors that the array T^{+} (T^{-}) is symmetric (antisymmetric) with respect to permutations of indices. Equations of this type are common for the commutator,[22,23] but not as usual for the symmetrized product.

This property of the products $(\vec{A}\,\vec{B})^{\pm}$ and the results presented above can be combined to establish the following.

Theorem. If $\vec{A}=\vec{A}^{(n,\pi_a)}$ and $\vec{B}=\vec{B}^{(n,\pi_b)}$, then if $(\vec{A}\,\vec{B})^{\pm}$ is nonzero it can be resolved into components with reduction indices between $|\pi_a-\pi_b|$ and $\pi_a+\pi_b$. If $\vec{A}$ is of degree p_a and $\vec{B}$ is of degree p_b, then the degree of $(\vec{A}\,\vec{B})^{\pm}$ does not exceed p_a+p_b and its minimum value is the smallest value of $|\pi_a-\pi_b|$ for which the product of components $(\vec{A}^{(n,\pi_a)}\vec{B}^{(n,\pi_b)})^{\pm}$ is nonzero.

An explicit proof of this theorem is given in the Appendix. The theorem will allow some simplifications which facilitate the interpretation of the eigenstate restrictions to follow.

III. EXPECTATION VALUES

For an eigenstate of $\vec{\Omega}$ associated with eigenvalue ω, the expectation value of $\vec{\Omega}$ will also be ω. In density matrix terms, if $\hat{\Omega}$ is a p-electron operator then

$$\begin{aligned}\langle\Omega\rangle=\omega&=\binom{n}{p}\mathrm{tr}(\vec{D}^{(p)}\vec{\Omega}^{(p)}_{\mathrm{eff}})\\&=\binom{n}{p}(\vec{D}^{(p)},\vec{\Omega}^{(p)}_{\mathrm{eff}})\end{aligned} \tag{22}$$

whenever $\vec{D}^{(p)}$ is associated with an eigenstate or eigenensemble with eigenvalue ω. The effect of specifying an expectation value is thus to fix one component (in the direction of $\vec{\Omega}^{(p)}_{\mathrm{eff}}$) of $\vec{D}^{(p)}$.

In general, even if $\vec{D}^{(n)}$ were known to be pure-state n representable, the expectation value condition does not ensure an eigenstate. If, however, the spectrum of $\vec{\Omega}^{(n)}$ is bounded and ω is an extreme value then the expectation value condition ensures that a reduced density matrix satisfying Eq. (22) comes from an eigenstate or eigenensemble with that eigenvalue.

If several operators commute, it is possible for them to have simultaneous eigenstates. For a specified set of expectation values to occur simultaneously, commutation of the operators involved is not required, and expectation-value conditions need not be related to eigenstate conditions. Let $\{\vec{\Omega}_\kappa,\ \kappa=1,\ldots,\nu\}$ be a set of operators. When is it possible to simultaneously satisfy the conditions $\langle\Omega_\kappa\rangle=\omega_\kappa$, $\kappa=1,\ldots,\nu$? Westhaus has suggested[24] extension of the term "n representable" to a set of expectation values which can be realized by an n-electron pure state. In the present context, it is convenient to extend this definition to include ensembles.

Suppose that $\hat{\Omega}_\kappa$ is a p_κ-electron operator. If the p_κ are not all the same, define $p=\max\{p_\kappa\}$ and redefine each $\hat{\Omega}_\kappa$ as a p-electron operator [cf. Eq. (8)]. The normalization requirement also provides a constraint on the density matrix. It can be expressed as an expectation value if the unit matrix is introduced as $\vec{\Omega}^{(p)}_{\mathrm{eff},0}=\binom{r}{p}^{-1}\vec{1}$ and $\omega_0=1$. Then the conditions are

$$(\vec{D}^{(p)},\vec{\Omega}^{(p)}_{\mathrm{eff},\kappa})=\omega_\kappa,\quad \kappa=0,1,\ldots,\nu\ . \tag{23}$$

If an n-representable $\vec{D}^{(p)}$ can be found such that these equations are satisfied, then the set of expectation values $\{\omega_\kappa\}$ is n representable. There are two ways in which this can fail to be possible.

We will denote by $\mathscr{E}_p(\Omega)$ the subspace of $\mathscr{E}_p$ spanned by the set of vectors $\{\vec{\Omega}^{(p)}_{\mathrm{eff},\kappa}\}$. The orthogonal complement (with respect to the trace scalar product) of $\mathscr{E}_p(\Omega)$ in $\mathscr{E}_p$ will be denoted by $\mathscr{E}_p(\perp)$. Then any $\vec{D}^{(p)}$ can be resolved into components in $\mathscr{E}_p(\Omega)$ and $\mathscr{E}_p(\perp)$. The specification of a set of expectation values $\{\omega_\kappa\}$ determines a point in $\mathscr{E}_p(\Omega)$ and fixes the component in $\mathscr{E}_p(\Omega)$ of any $\vec{D}^{(p)}$ giving those expectation values. The component of $\vec{D}^{(p)}$ in $\mathscr{E}_p(\perp)$ is unrestricted by the expectation value conditions.

If the set of vectors $\{\vec{\Omega}^{(p)}_{\mathrm{eff},\kappa}\}$ is linearly dependent, the dimension of $\mathscr{E}_p(\Omega)$ will be less than $\nu+1$. The $\nu+1$ values of ω_κ are then not independent, and only consistent sets can be n representable. It is also obviously necessary that for each κ, ω_κ is neither greater than the largest eigenvalue nor smaller than the smallest eigenvalue of $\vec{\Omega}^{(n)}_\kappa$.

A point in $\mathscr{E}_p(\Omega)$ may be defined by an internally consistent set $\{\omega_\kappa\}$ which nevertheless does not define a permissible component in $\mathscr{E}_p(\Omega)$ for any n-representable reduced density matrix. If $\vec{D}^{(p)}(\Omega)\in\mathscr{E}_p(\Omega)$ is fixed by the expectation values, then for n representability there must be some $\vec{D}^{(p)}(\perp)\in\mathscr{E}_p(\perp)$ such that $\vec{D}^{(p)}=\vec{D}^{(p)}(\Omega)+\vec{D}^{(p)}(\perp)$ is in the set $\mathscr{P}^{(n)}_p$ of n-representable p matrices.

Equivalently, $\vec{D}^{(p)}(\Omega)$ must be in the (orthogonal) projection of $\mathscr{P}_p^{(n)}$ on to $\mathscr{E}_p(\Omega)$. Since $\mathscr{P}_p^{(n)}$ is convex and of finite extent, this projection image will also be convex and of finite extent.

Westhaus has also suggested[24] that the Levy condition[25] that a function Ψ yield a specified density ρ can be considered as fixing a nondenumerable set of expectation values. The condition has been generalized to ensembles by Valone.[26] For the finite basis set model, only a finite set of conditions are involved in fixing a density. They again have the effect of fixing certain components of the density matrix and may or may not be realizable. This situation has been discussed elsewhere.[4] It differs from the unrestricted (no basis set) case in which any density is n representable.[27,28]

As a simple example we consider the consequences of fixing expectation values of the spin operators $\mathscr{S}^2$ and $\mathscr{S}_z$. (The notation and normalization for spin components are those defined previously.[3]) Since $\mathscr{S}_z$ is a one-electron operator

$$\mu=\langle\mathscr{S}_z\rangle=n(\vec{\mathscr{s}}_z(1),\vec{D}^{(1)})=\tfrac{1}{2}n\,\mathrm{tr}\vec{\gamma}^z\,, \tag{24}$$

where γ^z is the spin-density matrix. For $\langle\mathscr{S}^2\rangle$ the two-matrix is required

$$\sigma=\langle\mathscr{S}^2\rangle=\tfrac{3}{4}n-\sqrt{3}\begin{bmatrix}n\\2\end{bmatrix}\mathrm{tr}\vec{\Upsilon}([1\bar{1}])\,. \tag{25}$$

This can be expressed as a condition on the permutationally symmetric and antisymmetric components of the two-electron charge-density matrix[3,29,30]

$$\begin{aligned}\mathrm{tr}\vec{\Gamma}^s&=\frac{n(n+2)-4\sigma}{8n(n-1)}\,,\\ \mathrm{tr}\vec{\Gamma}^a&=\frac{3n(n-2)+4\sigma}{8n(n-1)}\,.\end{aligned} \tag{26}$$

Since $\langle\mathscr{S}^2\rangle\geq 0$, a value $\sigma=0$ is sufficient to ensure a singlet eigenstate or eigenensemble.

IV. COMMUTATOR AND HYPERVIRIAL CONDITIONS

If $\vec{D}^{(n)}$ is an ensemble of eigenstates of $\vec{\Omega}^{(n)}$, not necessarily all with the same eigenvalue, then

$$[\vec{D}^{(n)},\vec{\Omega}^{(n)}]=0 \tag{27}$$

or, in terms of a matrix in $\mathscr{E}_n$,

$$(\vec{D}^{(n)}\vec{\Omega}^{(n)})^-=0\,. \tag{28}$$

The commutation of $\vec{D}^{(1)}$ with the Fock operator is well known in density-matrix Hartree-Fock theory[31] and properties of the commutator of $\vec{D}^{(2)}$ with the reduced Hamiltonian $\vec{h}^{(2)}$ have also been considered.[32] In the general case being treated here, Eq. (28) says that the matrix $(\vec{D}^{(n)}\vec{\Omega}^{(n)})^-$ is zero and thus that for any basis $\{\vec{\Upsilon}_\kappa^{(n)}\}$ for $\mathscr{E}_n$

$$\begin{aligned}0&=(\vec{\Upsilon}_\kappa^{(n)},(\vec{D}^{(n)}\vec{\Omega}^{(n)})^-)\\ &=\frac{i}{2}[\mathrm{tr}(\vec{\Upsilon}_\kappa^{(n)}\vec{D}^{(n)}\vec{\Omega}^{(n)})-\mathrm{tr}(\vec{\Upsilon}_\kappa^{(n)}\vec{\Omega}^{(n)}\vec{D}^{(n)})]\\ &=\frac{i}{2}[\mathrm{tr}(\vec{\Omega}^{(n)}\vec{\Upsilon}_\kappa^{(n)}\vec{D}^{(n)})-\mathrm{tr}(\vec{\Upsilon}_\kappa^{(n)}\vec{\Omega}^{(n)}\vec{D}^{(n)})]\\ &=((\vec{\Omega}^{(n)}\vec{\Upsilon}_\kappa^{(n)}),\vec{D}^{(n)})^-\,.\end{aligned} \tag{29}$$

Any matrix $\vec{D}^{(n)}$ *that commutes with* $\vec{\Omega}^{(n)}$ *must be orthogonal to all the vectors* $(\vec{\Omega}^{(n)}\vec{\Upsilon}_\kappa^{(n)})^-$.

The hypervirial theorem[33] states that for an eigenstate of the Hermitian operator $\hat{\Omega}$,

$$\langle[\hat{\Omega},\hat{A}]\rangle=0 \tag{30}$$

for *any* operator $\hat{A}$. The vanishing of $\langle[\hat{H},\hat{A}]\rangle$ for energy eigenstates has been used in density-matrix theory by Rosina *et al.*,[34] and a related condition has been used by Erdahl.[13] The expectation value is readily generalized to ensembles of eigenstates, not necessarily associated with the same eigenvalue. When a basis set is introduced, the general matrix $\vec{A}^{(n)}$ can be expanded in terms of the $\{\vec{\Upsilon}_\kappa^{(n)}\}$, and thus the matrix form of Eq. (30) will be satisfied for all $\vec{A}^{(n)}$ if and only if Eq. (29) is satisfied for all κ.

Although the $\{\vec{\Upsilon}_\kappa^{(n)}\}$ form a basis for $\mathscr{E}_n$, the vectors $\{(\vec{\Omega}^{(n)}\vec{\Upsilon}_\kappa^{(n)})^-\}$ will not be linearly independent and some of them may be 0. [If $\vec{\Omega}^{(n)}$ is taken as the unit matrix, $(\vec{\Omega}^{(n)}\vec{\Upsilon}_\kappa^{(n)})^-=0$ for all κ.] The situation is really very simple. Although the n-electron function basis is often best taken to consist of single determinants, it need not be. The basis functions can be taken to be eigenfunctions of the restriction of the operator $\hat{\Omega}$. Then both $\vec{\Omega}^{(n)}$ and the density matrix for any ensemble of eigenstates will be diagonal.

When the basis is chosen so that $\vec{\Omega}^{(n)}$ is diagonal

$$\Omega_{KL}^{(n)}=\omega_K\delta_{KL} \tag{31}$$

and the basis for $\mathscr{E}_n$ is taken to be the $\{\vec{A}^K,\vec{B}^{KL},\vec{C}^{KL}\}$ basis defined in GDM I, then

$$\begin{aligned}(\vec{\Omega}^{(n)}\vec{A}^K)^-&=0\,,\\ (\vec{\Omega}^{(n)}\vec{B}^{KL})^-&=\tfrac{1}{2}(\omega_K-\omega_L)\vec{C}^{KL}\,,\\ (\vec{\Omega}^{(n)}\vec{C}^{KL})&=-\tfrac{1}{2}(\omega_K-\omega_L)\vec{B}^{KL}\,.\end{aligned} \tag{32}$$

If $\vec{\Omega}^{(n)}$ has no degenerate eigenvalues any $\vec{D}^{(n)}$ which satisfies Eqs. (29) must be diagonal. For any degenerate eigenvalues $\omega_K=\omega_L$, $\vec{D}^{(n)}$ may have components in the $\vec{B}^{KL}$ and $\vec{C}^{KL}$ directions. (It could be diagonalized by a transformation leaving $\vec{\Omega}^{(n)}$ diagonal, but different transformations might be required for different $\vec{D}^{(n)}$.)

Another possibility is the use of a reducing basis[2] for $\mathscr{E}_n$. If $\vec{\Omega}$ is a q-electron operator, then for a $\vec{\Upsilon}_\kappa^{(n)}$ of reduction index π_κ the matrix $(\vec{\Omega}^{(n)}\vec{\Upsilon}_\kappa^{(n)})^-$ will be of order (at most) $q+\pi_\kappa$. To determine the consequences for density-matrix components of low reduction index of commutation of the density matrix with a few-electron

operator, only the basis elements with low reduction indices need be considered. We have seen that *the constraints of Eq. (29) will be satisfied for all κ if and only if $\vec{D}^{(n)}$ is the density matrix for a diagonal ensemble.* A combination of these constraints with an eigenvalue constraint severely restricts $\vec{D}^{(n)}$, but is still not sufficient in general to guarantee an eigenensemble.

Spin operators can again provide illustrative examples. The n electron

$$\hat{\mathscr{S}}_z=\sum_{j=1}^{n}\hat{s}_z(j) \tag{33}$$

can be taken as $\hat{\Omega}$. If a basis set is chosen in the usual way, where each orbital can be combined with either of the spin functions α or β, then $\mathrm{tr}\hat{\mathscr{S}}_z^{(1)}=0$ and $\hat{\mathscr{S}}_z^{(p)}$ will have reduction index 1 for each p. In the spin operator notation of GDM III, $\hat{s}_z=[1]_0/\sqrt{2}$ and the one-electron commutators are

$$[\hat{s}_z,[1]_m]=m[1]_m,\quad [\hat{s}_z,[s]_0]=0\ . \tag{34}$$

From this it can be shown that

$$\begin{aligned}&[\hat{\mathscr{S}}_z,\{n,j,u\}_0]=0\ ,\\ &[\hat{\mathscr{S}}_z,\{n,j,u\}_m]\propto\{n,j,u\}_m,\quad m\neq 0\end{aligned} \tag{35}$$

so that Eq. (29) leads to the well-known result that a density matrix for an ensemble of $\hat{\mathscr{S}}_z$ eigenstates will include only spin components of the form $\{p,j,u\}_0$.

Commutators involving $\hat{\mathscr{S}}^2$ are readily evaluated but the interpretation of the resulting conditions is quite complicated. A treatment of the consequences of the requirement $[(\hat{\mathscr{S}}^2)^{(n)},D^{(n)}]=0$ will therefore be postponed to a future paper.

V. HIERARCHY EQUATIONS

We begin this section with a generalization of the hierarchy equations[9,10] which differs from that of Schlosser.[11] The derivation closely parallels that of Nakatsuji[10] but the notation and normalization conventions differ from his. If $\vec{D}^{(n)}$ is an eigenensemble of $\vec{\Omega}^{(n)}$, then

$$\vec{\Omega}^{(n)}\vec{D}^{(n)}=\omega\vec{D}^{(n)},\quad \vec{D}^{(n)}\vec{\Omega}^{(n)}=\omega\vec{D}^{(n)}\ . \tag{36}$$

These equations can be combined and reduced. Defining

$$\vec{G}^{(p)}=\hat{L}_n^p(\vec{\Omega}^{(n)}\vec{D}^{(n)})^+ \tag{37}$$

we find that Eqs. (36) imply

$$\vec{G}^{(p)}=\omega\vec{D}^{(p)} \tag{38}$$

for any p, $0\le p\le n$.

Now suppose that $\vec{D}^{(p)}$ is a reduced density matrix (ensemble) n-representatable by $\vec{D}^{(n)}$, such that Eqs. (37) and (38) are satisfied. Consider

$$\begin{aligned}\eta&=\mathrm{tr}[(\vec{\Omega}^{(n)})^2\vec{D}^{(n)}]=\mathrm{tr}(\vec{\Omega}^{(n)}\vec{G}^{(n)})\\ &=(\vec{\Omega}^{(n)},\vec{G}^{(n)})\ .\end{aligned} \tag{39}$$

If $\vec{\Omega}^{(n)}$ is of degree q, the matrix $\vec{\Omega}_{\mathrm{eff}}^{(q)}$ defined previously can be introduced and

$$\eta=(\vec{\Omega}_{\mathrm{eff}}^{(q)},\vec{G}^{(q)})\ . \tag{40}$$

Since by assumption Eq. (38) is satisfied,

$$\eta=\omega(\vec{\Omega}_{\mathrm{eff}}^{(q)},\vec{D}^{(q)})=\omega^2\ . \tag{41}$$

This means that for expectation values computed with respect to $\vec{D}^{(n)}$, $\langle\Omega^2\rangle=\langle\Omega\rangle^2$ and thus $\vec{D}^{(n)}$ is an eigenensemble.[13] *It has been established that an eigenensemble density matrix satisfies Eqs. (36)—(38) and that an n-representable reduced density matrix satisfying these equations is associated with an eigenensemble.*

For a given value of ω, the linear equations

$$\hat{L}_n^p(\vec{\Omega}^{(n)}\vec{D}^{(n)})^+=\omega\vec{D}^{(p)}=\omega\hat{L}_n^p\vec{D}^{(n)} \tag{42}$$

place conditions on the components of $\vec{D}^{(p)}$ in a way which has been discussed elsewhere[12] for the Hamiltonian and is readily generalized. In the absence of n-representability constraints, these equations do not provide for a determination of the eigenvalue ω. A nonlinear condition not involving ω explicitly will be given in the next section.

In the case of spin operators, the eigenvalue is usually known. It is not easy to obtain useful information from the hierarchy equations, even for $\hat{\mathscr{S}}_z$, however. The effect of $\hat{\mathscr{S}}_z$ acting on $\vec{D}^{(n)}$ is to modify the spin operators. The orthogonality of these operators can then be used to obtain from the hierarchy equation at each order a set of equations relating various spatial components of the reduced density matrices. One would like to further reduce these to obtain constraints on the components of $\vec{D}^{(1)}$ and $\vec{D}^{(2)}$. This requires a knowledge of the partial traces of spatial components, which is beyond the scope of the present paper.

VI. DISPERSIONLESS ENSEMBLES

We have already made use of the fact that $\langle\Omega^2\rangle=\langle\Omega\rangle^2$ if and only if the expectation values are computed with respect to an eigenensemble. A density matrix $\vec{D}^{(n)}$ such that

$$\begin{aligned}\langle\Omega^2\rangle&=\mathrm{tr}[(\vec{\Omega}^{(n)})^2\vec{D}^{(n)}]=[\mathrm{tr}(\vec{\Omega}^{(n)}\vec{D}^{(n)})]^2\\ &=\langle\Omega\rangle^2\end{aligned} \tag{43}$$

will be referred to as dispersionless.[35] We take q to be the degree of $\vec{\Omega}^{(n)}$ and investigate the geometric consequences in $\mathscr{E}_{2q}$ of Eq. (43).

To avoid excessive writing of sub- and superscripts we define

$$\vec{F}=\vec{\Omega}_{\mathrm{eff}}^{(2q)} \tag{44}$$

and

$$\vec{G}=[(\vec{\Omega}^{(n)})^2]_{\mathrm{eff}}^{(2q)} \tag{45}$$

so that

$$\langle\Omega\rangle=(\vec{F},\vec{D}),\quad \langle\Omega^2\rangle=(\vec{G},\vec{D})\ , \tag{46}$$

where $\vec{D}=\vec{D}^{(2q)}$. The theorem of Sec. II ensures that if $\vec{\Omega}^{(n)}$ is of degree q, $(\vec{\Omega}^{(n)})^2$ will be of degree not greater than $2q$, so the effective reduced operator $\vec{G}$ can be defined in $\mathscr{E}_{2q}$. Let $\hat{A}_0$ be the normalized basis element of $\mathscr{E}_{2q,0}$.

$$\hat{A}_0=\begin{bmatrix} r \\ 2q \end{bmatrix}^{-1/2} \vec{1}^{(2q)} . \tag{47}$$

Then $\vec{F}$ can be written as

$$\vec{F}=\begin{bmatrix} r \\ 2q \end{bmatrix}^{1/2} \bar{f}\,\hat{A}_0+\phi\hat{F} \tag{48}$$

where

$$\bar{f}=\begin{bmatrix} r \\ 2q \end{bmatrix}^{-1/2} (\vec{F},\hat{A}_0)=\begin{bmatrix} r \\ 2q \end{bmatrix}^{-1} \mathrm{tr}\vec{F} \tag{49}$$

is the average of the eigenvalues of $\vec{F}$, and $\hat{F}$ is a unit vector in $\mathscr{E}_{2q}$ orthogonal to $\hat{A}_0$

$$(\hat{A}_0,\hat{F})=0, \quad (\hat{F},\hat{F})=1 . \tag{50}$$

Explicitly,

$$\vec{F}=(\vec{F}-\bar{f}\,\vec{1}^{(2q)})/||\vec{F}-\bar{f}\,\vec{1}^{(2q)}|| , \tag{51}$$

and

$$\phi=(\hat{F},\vec{F})>0 . \tag{52}$$

In a similar way $\vec{G}$ can have components along $\hat{A}_0$, along $\hat{F}$, and orthogonal to both of these

$$\vec{G}=\begin{bmatrix} r \\ 2q \end{bmatrix}^{1/2} \bar{g}\hat{A}_0+\lambda\hat{F}+\gamma\hat{G} , \tag{53}$$

where

$$\bar{g}=\begin{bmatrix} r \\ 2q \end{bmatrix}^{-1/2} (\hat{A}_0,\vec{G})=\begin{bmatrix} r \\ 2g \end{bmatrix}^{-1} \mathrm{tr}\vec{G} \tag{54}$$

is the average of the eigenvalues of $\vec{G}$,

$$\lambda=(\hat{F},\vec{G}) \tag{55}$$

and

$$\hat{G}=\frac{\vec{G}-\bar{g}\,\vec{1}^{(2q)}-\lambda\hat{F}}{||\vec{G}-\bar{g}\,\vec{1}^{(2q)}-\lambda\hat{F}||} ,$$
$$\gamma=(\hat{G},\vec{G})\geq 0 . \tag{56}$$

Except in the trivial case where $\vec{F}$ is proportional to the unit matrix, which we exclude, ϕ cannot be zero. Further, λ and γ can both be zero only in trivial cases, but we cannot exclude cases in which one of them is zero or in which λ is negative.

Any reduced density matrix in $\mathscr{E}_{2q}$ can be resolved into components along $\hat{A}_0$, $\hat{F}$, and $\hat{G}$, and a remainder orthogonal to all of them. The component along $\hat{A}_0$ is fixed by the normalization condition, so

$$\vec{D}=\begin{bmatrix} r \\ 2q \end{bmatrix}^{-1/2} \hat{A}_0+y\hat{F}+z\hat{G}+\vec{D}(\perp) ,$$
$$(\vec{D}(\perp),\hat{A}_0)=(\vec{D}(\perp),\hat{F})=(\vec{D}(\perp),\hat{G})=0 . \tag{57}$$

Any reduced density matrix satisfying the zero dispersion condition must have coefficients y and z such that

$$(\vec{F},\vec{D})^2=(\bar{f}+\phi y)^2=(\vec{G},\vec{D})=\bar{g}+\lambda y+\gamma z \tag{58}$$

or

$$\gamma z=\phi^2y^2+(2\bar{f}\phi-\lambda)y+\bar{f}^2-\bar{g} . \tag{59}$$

This defines a parabola in the y-z (i.e., $\hat{F},\hat{G}$) plane and leaves other components of $\vec{D}$ restricted only by normalization and n-representability constraints.

As a first step in characterizing the meaning of Eq. (59), we relate the eigenvalue averages $\bar{f}$ and $\bar{g}$ to the eigenvalues ω_j of $\vec{\Omega}^{(n)}$. We introduce the unit-trace element of $\mathscr{E}_{2q}$, $\vec{X}^{(2q)}=\binom{r}{2q}^{-1}\vec{1}^{(2q)}=\binom{r}{2q}^{-1/2}\hat{A}_0$. It is related to the corresponding element $\vec{X}^{(n)}$ of $\mathscr{E}_{n,0}$ by $\vec{X}^{(2q)}=\hat{L}_n^{2q}\vec{X}(n)$. It follows from the definition of $\vec{F}$ that

$$(\vec{\Omega}^{(n)},\vec{X}^{(n)})=\begin{bmatrix} r \\ n \end{bmatrix}^{-1} \mathrm{tr}\vec{\Omega}^{(n)}=\begin{bmatrix} r \\ n \end{bmatrix}^{-1} \sum_{j=1}^{\binom{r}{n}} \omega_j$$
$$=(\vec{F},\vec{X}^{(2q)})=\begin{bmatrix} r \\ 2q \end{bmatrix}^{-1} \mathrm{tr}\vec{F}=\bar{f} \tag{60}$$

and similarly

$$((\vec{\Omega}^{(n)})^2,\vec{X}^{(n)})=\begin{bmatrix} r \\ n \end{bmatrix}^{-1} \mathrm{tr}[(\vec{\Omega}^{(n)})^2]$$
$$=\begin{bmatrix} r \\ n \end{bmatrix}^{-1} \sum_{j=1}^{\binom{r}{n}} \omega_j^2$$
$$=(\vec{G},\vec{X}^{(2q)})=\begin{bmatrix} r \\ 2q \end{bmatrix}^{-1} \mathrm{tr}\vec{G}=\bar{g} . \tag{61}$$

Since for any set of numbers (not all zero) the average of the squares is greater than the square of the average,

$$\bar{f}^2-\bar{g}<0 . \tag{62}$$

The parameters ϕ, λ, and γ are also determined, for any fixed $\vec{\Omega}^{(n)}$. It is a consequence of their definitions that $\phi>0$ (in nontrivial cases) and that $\gamma\geq 0$. We will initially assume that $\gamma>0$ as well. Equation (59) can then be written in the standard form

$$z=ay^2+by+c \tag{63}$$

with

$$a=\phi^2/\gamma>0, \quad b=(2\bar{f}\phi-\lambda)/\gamma ,$$
$$c=(\bar{f}^2-\bar{g})/\gamma<0 . \tag{64}$$

Since $d^2z/dy^2=2a>0$, the parabola in the y-z plane defined by Eq. (59) or (63) is concave up. Further

$$b^2-4ac>b^2>0 \tag{65}$$

so the equation $z=0$ has two real roots of opposite sign. The origin $y=z=0$ is thus "inside" the parabola.

If $\gamma=0$, which occurs if $\vec{G}-\bar{g}\vec{1}^{(2q)}$ lies along $\vec{F}-\bar{f}\vec{1}^{(2q)}$, then Eq. (59) becomes

$$a'y^2+b'y+c'=0 \tag{66}$$

with

$$a'=\phi^2>0,\quad b'=(2\bar{f}\phi-\lambda),\quad c'=\bar{f}^2-\bar{g}>0\ . \tag{67}$$

The z, or $\hat{G}$, component is unrestricted (and in fact $\hat{G}$ is undefined). There are two possible real values of y on opposite sides of $y=0$.

If $\gamma\neq 0$ and $\vec{D}$ is a matrix satisfying the zero-dispersion condition, then its component amplitudes y and z must satisfy Eq. (63). The $\hat{A}_0$ component is fixed by the normalization condition, but the components orthogonal to $\hat{A}_0$, $\hat{F}$, and $\hat{G}$, making up $\vec{D}(\perp)$, are unrestricted.

The set of $\underline{\underline{\vec{D}}}=\vec{D}-\vec{X}^{(2q)}\in\mathcal{N}_{2q}$ (Ref. 1) for which $\vec{D}$ satisfies Eq. (59) is thus a parabolic trough, with a parabolic cross section in the $\hat{F},\hat{G}$ plane and linear in other directions.

This set depends, of course, on $\vec{\Omega}^{(n)}$. The corresponding set in $\mathscr{C}_{2q}$ will be denoted by $\mathscr{T}_{2q}(\vec{\Omega}^{(n)})$. In the special cases when $\gamma=0$, $\mathscr{T}_{2q}(\vec{\Omega}^{(n)})$ consists not of a parabolic trough but of two parallel hyperplanes defined by $y=[-b'\pm(b'^2-4a'c')^{1/2}]/2a'$.

The point $\vec{X}^{(2q)}$ in $\mathscr{C}_{2q}$, which corresponds to the origin in $\mathscr{N}_{2q}$, is known to lie in the interior of the set $\mathscr{P}_{2q}^{(n)}$ of n-representable $2q$ matrices. A pure-state n-representable reduced density matrix corresponding to an eigenvector of $\vec{\Omega}^{(n)}$ must lie in both $\mathscr{T}_{2q}(\Omega^{(n)})$ and $\mathscr{P}_{2q}^{(n)}$; in fact, the set of all such reduced density matrices is just $\mathscr{P}_{2q}^{(n)}\cap\mathscr{T}_{2q}(\Omega^{(n)})$. If $\vec{\Omega}^{(n)}$ has no degenerate eigenvalues, this intersection consists of a set of discrete points. The intersection corresponding to a degenerate eigenvalue will be a convex set of dimension one less than the degeneracy. Related results have been obtained in a different context by Erdahl.[13,14] As different matrices $\vec{\Omega}^{(n)}$ are considered, different $\mathscr{T}_{2q}(\Omega^{(n)})$ result. For each of them the set $\mathscr{P}_{2q}^{(n)}$ must be inside the trough (or between the parallel hyperplanes) and intersect $\mathscr{T}_{2q}(\Omega^{(n)})$ in points which are pure state reduced-density matrices corresponding to eigenstates (or possibly eigenensembles) of $\vec{\Omega}^{(n)}$. Each $\mathscr{T}_{2q}(\Omega^{(n)})$ is a hypersurface which divides $\mathscr{C}_{2q}$ into two regions: an "inside" denoted by $\mathscr{I}_{2q}(\Omega^{(n)})$ and an "outside" $\mathscr{O}_{2q}(\Omega^{(n)})$. [When $\mathscr{T}_{2q}(\Omega^{(n)})$ consists of parallel hyperplanes, $\mathscr{I}_{2q}(\Omega^{(n)})$ is the region betwen them and $\mathscr{O}_{2q}(\Omega^{(n)})$ consists of two disjoint parts.] The dividing hypersurface itself is taken to be part of the inner region. Since $\mathscr{P}_{2q}^{(n)}\subset\mathscr{I}_{2q}(\Omega^{(n)})$ for each choice of $\vec{\Omega}^{(n)}$, it will also be true that

$$\mathscr{P}_{2q}^{(n)}\subset\mathscr{I}_{2q}\equiv\bigcap_{\{\Omega^{(n)}\}}\mathscr{I}_{2q}(\Omega^{(n)})\ ,$$

where the intersection is taken over all the $\Omega^{(n)}$ being considered. The boundary of $\mathscr{P}_{2q}^{(n)}$ will also include points that are in the boundary of $\mathscr{I}_{2q}$. The picture provided by parabolic troughs intersecting in a convex set provides one way of looking at the nature of that set, and each trough provides a way of expressing a zero dispersion condition in convenient geometric terms. The utility of this approach lies in the information it provides about the restriction placed on density matrices by physically interesting eigenstate conditions, rather than as a means of characterizing $\mathscr{P}_{2q}^{(n)}$. It certainly provides some information about $\mathscr{P}_{2q}^{(n)}$, but at best a very large set of $\Omega^{(n)}$ would be required, so that there is likely to be little practical utility.

We can again look to spin operators for a simple, if quite atypical, example. The zero dispersion condition for $\hat{\mathscr{S}}_z$ appears as an equation relating components of $\vec{D}^{(2)}$. It can be written in terms of traces of spatial components as

$$\begin{aligned}\langle\mathscr{S}_z\rangle^2&=\binom{n}{2}^2\{\mathrm{tr}\Upsilon([1s])+\mathrm{tr}\Upsilon([s\,1])\}^2\\&=\langle\mathscr{S}_z^2\rangle=\frac{n}{4}+\frac{n(n-1)}{24}\{\tfrac{1}{12}\mathrm{tr}\Upsilon([1\bar{1}]_0)\\&\quad+\frac{1}{\sqrt{6}}\mathrm{tr}\Upsilon([1^2]_0)\}\ .\end{aligned} \tag{68}$$

The directions involved are those of the appropriate spin operators time unit spatial operators.

VII. EFFECTS OF REDUCTION OR COLLAPSE

In the preceding sections we have considered various constraints imposed on a density matrix by eigenstate-related conditions. The order (particle number) of the density matrix involved must be equal to at least p for a p-electron operator, and in some cases twice that. In this section we will investigate how these constraints may impose constraints on a lower-order density matrix obtained by reduction or a density obtained by collapse.[36] For brevity and generality in notation, the order index will be suppressed when not critical.

We will use $\mathscr{C}$ to denote the space of matrices to which the original constraints apply. It can be divided into two orthogonal subspaces, $\mathscr{C}'$ and $\mathscr{C}''$. The elements of $\mathscr{C}'$ are in one-to-one correspondence with those of the space of lower-order reduced density matrices or densities of interest. Any element of $\mathscr{C}''$ will be annihilated by the relevant density matrix reduction or collapse to a density.[2,4] Single and double primes on matrices will be used to distinguish elements of these two subspaces.

Consider first a single expectation-value constraint. If both $\vec{D}$ and $\vec{\Omega}_{\mathrm{eff}}$ are divided into components in the orthogonal subspaces, the constraint equation becomes

$$(\vec{D}',\vec{\Omega}'_{\mathrm{eff}})+(\vec{D}'',\vec{\Omega}''_{\mathrm{eff}})=\omega\ . \tag{69}$$

It is possible that $\vec{\Omega}''_{\mathrm{eff}}$ is zero. This will happen, for example, whenever $\mathscr{C}'$ corresponds to the space of densities and $\hat{\Omega}$ is a multiplicative, one-electron operator such as the dipole moment or an external potential. In such a case the equation is already a constraint simply on $\vec{D}'$ (thus on the density). It would also be possible in princi-

ple that $\vec{\Omega}'_{\text{eff}}$ be zero, but it seems unlikely that any physically interesting operator would have this property.

When $\vec{\Omega}''_{\text{eff}}$ is nonzero, Eq. (69) places no restrictions on $\vec{D}'$ by itself, in the absence of n-representability constraints: for any choice of $\vec{D}'$, a $\vec{D}''$ can be found such that the equation will be satisfied. The constraint may, however, interact with n-representability conditions to restrict $\vec{D}'$. For example, $||\vec{D}||$ is certainly bounded. Not only is $||\vec{D}'||$ similarly bounded, but for any given $\vec{D}'$, Eq. (69) may mandate a nonzero $\vec{D}''$, thereby reducing the bound on $||\vec{D}'||$. Because of the complexity and incompleteness of known n-representability conditions, these interactions cannot be effectively explored here.

We consider next a set of simultaneous linear constraints. Such constraints can be expressed as linear, inhomogeneous equations which the expansion coefficients of $\vec{D}$ must satisfy. They will be written in general form here as

$$A\vec{D}=\vec{\alpha}\ , \tag{70}$$

where A is a rectangular matrix with fewer rows than columns. The relevant theorems of linear algebra state that (i) this system of equations will have no solutions (be inconsistent) if $\vec{\alpha}$ is not an element of the vector space $\mathscr{C}(A)$ spanned by the columns of A; and (ii) if $\vec{\alpha}\in\mathscr{C}(A)$ and the rank of A [the dimension of $\mathscr{C}(A)$] is less than the number of columns of A [the number of elements of $\vec{D}$] then there are an infinite number of solutions differing from one another by any solution of the homogeneous equations $A\vec{D}=\vec{0}$. The usually interesting case where A is square and nonsingular will not be considered here since we assume we have too few constraints to completely determine $\vec{D}$. Case (i) can also be excluded if we assume that only consistent sets of constraints will be treated.

The column labels of A correspond to elements of $\vec{D}$ so, for an appropriate ordering of the basis, the division of $\vec{D}$ into $\vec{D}'$ and $\vec{D}''$ will correspond to a partitioning of A as (A',A'') and Eq. (70) becomes

$$A'\vec{D}'+A''\vec{D}''=\vec{\alpha}\ . \tag{71}$$

We want to know whether these equations place any restrictions on $\vec{D}'$, considered by itself. They do if and only if there are some choices of $\vec{D}'$ for which no choice of $\vec{D}''$ can lead to a solution of Eq. (71). The equations can be rewritten as

$$A''\vec{D}''=\vec{\alpha}-A'\vec{D}'\equiv\vec{\beta} \tag{72}$$

and for a solution to exist $\vec{\beta}$ must be within $\mathscr{C}(A'')$, the space spanned by the columns of A''.

Let $\mathscr{C}(\vec{\alpha},A')$ be the space spanned by $\vec{\alpha}$ and the columns of A'. Clearly $\vec{\beta}$ is an element of this space. We further define an orthogonal decomposition of this space as

$$\mathscr{C}(\vec{\alpha},A')=\mathscr{C}''+\mathscr{C}_\perp \tag{73}$$

where

$$\mathscr{C}''=\mathscr{C}(\vec{\alpha},A')\cap\mathscr{C}(A'') \tag{74}$$

and $\mathscr{C}_\perp$ is the orthogonal complement of $\mathscr{C}''$ in $\mathscr{C}(\vec{\alpha},A')$, and introduce orthonormal bases $\{\vec{u}_j\}$ and $\{\vec{v}_k\}$ for $\mathscr{C}''$ and $\mathscr{C}_\perp$, respectively. Then $\vec{\alpha}$, the columns of A, and $\vec{\beta}$ can all be expressed as linear combinations of $\{\vec{u}_j\}$ and $\{\vec{v}_k\}$:

$$\begin{aligned}\vec{\alpha}&=\sum_j U_{j0}\vec{u}_j+\sum_k V_{k0}\vec{v}_k\ ,\\ \vec{a}_i&=\sum_j U_{ji}\vec{u}_j+\sum_k V_{ki}\vec{v}_k\ ,\end{aligned} \tag{75}$$

and

$$\begin{aligned}\vec{\beta}&=\sum_j U_{j0}\vec{u}_j+\sum_k V_{k0}\vec{v}_k-\sum_i\left[\sum_j U_{ji}\vec{u}_j+\sum_k V_{ki}\vec{v}_k\right]d'_i\\ &=\sum_j\left[U_{j0}-\sum_i U_{ji}d'_i\right]\vec{u}_j+\sum_k\left[V_{k0}-\sum_i V_{ki}d'_i\right]\vec{v}_k\ ,\end{aligned} \tag{76}$$

where d'_i is the ith element of $\vec{D}'$. If $\vec{\beta}$ is to be in $\mathscr{C}(A'')$, the coefficients of all $\vec{v}_k$ must vanish in Eq. (76), so that

$$V_{k0}-\sum_i V_{ki}d'_i=0\ \text{ for all } k \tag{77}$$

or

$$V\vec{D}'=\vec{v}_0\ . \tag{78}$$

This is again a set of linear constraints, now applying to $\vec{D}'$. The elements of V and $\vec{v}_0$ are determined by those of A and $\vec{\alpha}$. It is possible that $\mathscr{C}(\vec{\alpha},A')\subset\mathscr{C}(A'')$. In such a case there are no $\vec{v}$'s and no constraints on $\vec{D}'$. The greater the dimension of $\mathscr{C}_\perp$, the more constraints on $\vec{D}'$.

The zero-dispersion condition imposes a nonlinear constraint, Eq. (59) or equivalent. To investigate the effect of reduction or collapse on this constraint we must begin by dividing the matrices involved into components in $\mathscr{E}'$ and $\mathscr{E}''$. Note that $\hat{A}_0\in\mathscr{E}'$, since it survives all reductions and corresponds to the "average density"[4] component of the density. Unit vectors can be introduced in the appropriate orthogonal directions so that

$$\vec{F}=\begin{bmatrix}r\\2q\end{bmatrix}\bar{f}\hat{A}_0+\phi'\hat{F}'+\phi''\hat{F}''\ , \tag{79}$$

where $\hat{F}'\in\mathscr{E}'$ is orthogonal to $\hat{A}_0$ and $\hat{F}''\in\mathscr{E}''$,

$$\vec{G}=\begin{bmatrix}r\\2q\end{bmatrix}\bar{g}\hat{A}_0+\lambda'\hat{F}'+\gamma'\hat{G}'+\lambda''\hat{F}''+\gamma''\hat{G}'' \tag{80}$$

with $\hat{G}'\in\mathscr{E}'$ orthogonal to $\hat{A}_0$ and $\hat{F}'$ and $\hat{G}''\in\mathscr{E}''$ orthogonal to $\hat{F}''$, and

$$\begin{aligned}\vec{D}=\begin{bmatrix}r\\2q\end{bmatrix}^{-1/2}&\hat{A}_0+y'\hat{F}'+z'\hat{G}'+\vec{D}'(\perp)\\ &+y''\hat{F}''+z''\hat{G}''+\vec{D}''(\perp)\end{aligned} \tag{81}$$

with $\vec{D}'(\perp)$ and $\vec{D}''(\perp)$ being the components of $\vec{D}$ in $\mathscr{E}'$ and $\mathscr{E}''$, respectively, orthogonal to previously defined directions in these spaces. Equations (43) and (46) then lead to

$$[\bar{f}^2-\bar{g}+(2\bar{f}\phi'-\lambda')y'+\phi'^2y'^2-\gamma'z']+[(2\bar{f}\phi''-\lambda'')+2\phi'\phi''y']y''+\phi''^2y''^2=\gamma''z'' \ . \tag{82}$$

We must learn what constraints this equation places on $\vec{D}'$.

As in the linear case, if there are to be any constraints on $\vec{D}'$, there must be choices of its components such that no choice of $\vec{D}''$ can result in the equation being satisfied. The coefficients in the expansion of $\vec{D}'$ which might be constrained are y' and z'. Suppose first that $\gamma''\neq 0$. Then for any choice of y' and z' (and indeed for any y'' as well), a z'' can be found such that Eq. (82) will be satisfied. The zero-dispersion condition thus places no constraint on $\vec{D}'$ if $\gamma''\neq 0$.

If both γ' and γ'' are zero, we have the $\gamma=0$ case considered in Sec. VI. In this case the condition becomes linear and can be examined by the techniques above. There remains the possibility $\gamma''=0$, $\gamma'\neq 0$. In this case, for given y' and z', Eq. (82) is a quadratic in y''. The discriminant will be non-negative so that a real solution exists if and only if

$$(\lambda''^2-4\bar{f}\phi''\lambda'')+(4\phi''\lambda'-4\phi'\phi''\lambda'')y'+(4\phi''^2\gamma')z'\geq 0 \tag{83}$$

This requires the component of $\vec{D}'$ in the $\hat{F}'$-$\hat{G}'$ plane to be in a specified half-plane.

VIII. DISCUSSION

We have considered a number of conditions which must be satisfied by density matrices or densities corresponding to eigenstates, eigenensembles, or diagonal ensembles associated with one or more operators. Each of these conditions is necessary, but in the absence of n-representability constraints none is sufficient (except possibly in special cases), to guarantee an eigenstate or eigenensemble. Some are linear and some are nonlinear; some involve a specification of the eigenvalue and others do not. The consequences for reduced density matrices of lower order also vary.

The expectation value constraints are the least restrictive, and require a knowledge of the eigenvalue sought. They are linear, simply expressed, and multiple conditions can be combined subject only to consistency conditions. These conditions are readily stated in terms of the linear dependency of certain vectors and provide a generalization of the n-representability criterion of Westhaus.

Commutator and hypervirial conditions are essentially equivalent. One such condition is much more restrictive than a single expectation value condition. These constraints are linear and do not require knowledge of an eigenvalue.

Density hierarchy equations also provide linear constraints. A knowledge of the eigenvalue is required; it is not provided by the equations themselves. If combined with n-representability conditions, these constraints would provide necessary and sufficient conditions for an eigenensemble.

These linear constraints apply to density matrices or to reduced density matrices of different order. If the operator of interest is a p-electron operator acting on n-electron functions, then the expectation value condition is defined in $\mathscr{E}_p$, the hierarchy equation conditions in $\mathscr{E}_{2p}$, and commutator or hypervirial conditions in $\mathscr{E}_n$. It has been shown that linear constraints in any $\mathscr{E}_q$ may imply linear constraints in spaces $\mathscr{E}_{q'}$, $q'<q$. The number of such constraints will depend on the operator involved, and there may be none at all. A determination of the constraints on a density when the operator is not just one-electron multiplicative depends also on the basis set being used.

The zero-dispersion condition is nonlinear, but does not require a knowledge of the eigenvalue. It defines a parabolic trough in $\mathscr{E}_{2p}$ and, if combined with n-representability constraints, would provide necessary and sufficient conditions for an eigenensemble. Unfortunately, except in special cases, no constraints will be placed on lower-order reduced density matrices or on the density.

A number of the conditions could be applied simultaneously to further restrict acceptable density matrices. It is not suggested, however, that a practical method for obtaining an eigenstate density matrix of, e.g., the Hamiltonian will result. It is rather to be hoped that the constraints presented here will assist us in obtaining as much useful information as possible from a reduced density matrix and in distinguishing between truly informative results for a particular problem and those facts which could have been predicted in advance.

The theorem stated in Sec. II and developed in the Appendix provides triangle-inequality conditions on the reduction index of symmetrized or antisymmetrized matrix products. These conditions can be used to reduce the number of components which need be considered, even for a condition in $\mathscr{E}_n$. For example, if we are interested in the effect on $\vec{D}^{(2)}$ of the requirement that $\vec{D}^{(n)}$ commute with a matrix, $\vec{\Omega}^{(n)}$, of degree 2 (the matrix of a two-electron operator) then we need consider only components $\vec{D}^{(n,0)}, \ldots, \vec{D}^{(n,4)}$ of $\vec{D}^{(n)}$. The convenient properties of the products $(\vec{A}\vec{B})^{\pm}$ (as compared with the simple products $\vec{A}\vec{B}$ and $\vec{B}\vec{A}$) and the triangle condition on reduction indices are likely to be of use in other applications.

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APPENDIX

If $\hat{A}$ is a p-electron operator and $\hat{B}$ is a q-electron operator then when $p,q<n/2$ it is obvious that $\hat{A}\hat{B}$ is at most a $(p+q)$-electron operator. In this appendix related results for matrices (summarized in the theorem of Sec. II) are obtained. The argument will be presented as a

series of lemmas, theorems, and proofs, to exhibit the logical structure involved.

Lemma 1. (a) The matrix of a p-electron operator can be resolved into components with $0 \le \pi \le p$; and (b) the component with reduction index π of any matrix can be reproduced as the matrix of a π-electron operator.

Part (a) is established in GDM II and equivalent treatments. The proof of (b) depends on the observation that the operator $\hat{\Omega}(k_1, \ldots, k_p)$ in Eq. (6), when regarded as acting on n-electron functions, corresponds to a matrix $\hat{\Gamma}^n_p \vec{\Omega}^{(p)}$ (Refs. 2 and 17) or $\vec{\Omega}^{(p)} \wedge \vec{1}^{(n-p)}$ (Refs. 5–7). Given a matrix component $\vec{\Omega}^{(n,\pi)}$ with reduction index π, a matrix in $\mathscr{E}_\pi$ is determined. Its matrix elements provide expansion coefficients, in terms of the p-electron function basis, for an integral-operator kernel

$$\Omega^{(p)}(1, \ldots, p; 1', \ldots, p') = \sum_{K,L} \Omega^{(p)}_{KL} \Phi_K(1, \ldots, p) \Phi^*_L(1', \ldots, p') \tag{A1}$$

and the n-electron kernel is

$$\Omega^{(n)}(1, \ldots, n; 1', \ldots, n') = \Omega^{(p)}(1, \ldots, p; 1', \ldots, p') \prod_{k=p+1}^{n} \delta(k - k') \,. \tag{A2}$$

The various terms on the right-hand side of Eq. (6) are integral operators with kernels obtained from this one by permutations of indices. The operator $\hat{\Omega}$ defined in this way by Eq. (6) will have $\vec{\Omega}^{(n,\pi)}$ as its matrix.

Lemma 2. If $\vec{A} \in \mathscr{E}_{n,\pi_a}$ and $\vec{B} \in \mathscr{E}_{n,\pi_b}$ then $(\vec{A}\vec{B})^{\pm}$ has degree not exceeding $\pi_a + \pi_b$.

Construct a π_a-electron integral operator corresponding to $\vec{A}$ and a π_b-electron operator corresponding to $\vec{B}$, as described above. The product of these operators will also be a sum of integral operators, with kernels expressed as integrals of products. In each such term the "A" factor will involve $n - \pi_a$ delta functions and the "B" factor will involve $n - \pi_b$ delta functions. In the product, then, there must be least $n - \pi_a - \pi_b$ products of delta functions involving the same variables. Integration of such a product will produce a delta function, so this term in the expansion of $(\vec{A}\vec{B})^{\pm}$ involves at least $n - \pi_a - \pi_b$ delta functions. It is one of the terms in a $(\pi_a + \pi_b)$-electron operator. Other p-electron operators with $p < \pi_a + \pi_b$ may also occur, due to additional corresponding variables in the delta functions, with the minimum value of p being the larger of π_a and π_b. A value of p greater than $\pi_a + \pi_b$ is not possible. Since we have defined the degree of a matrix as the maximum reduction index occurring, the lemma is established.

Theorem 1. If $\vec{A} \in \mathscr{E}_{n,\pi_a}$ and $\vec{B} \in \mathscr{E}_{n,\pi_b}$ then $\vec{C} = (\vec{A}\vec{B})^{\pm}$ is resolvable into components with reduction indices π_c such that $\pi_c \le \pi_a + \pi_b$, and if $\vec{C}$ is nonzero, $\pi_c \ge |\pi_a - \pi_b|$.

The upper limit on π_c is just that established by Lemma 2. To establish the lower limit we introduce a reducing basis[2] and make use of the symmetry of the array $T^{\pm}$. Each basis matrix has a well-defined reduction index. Let π_κ be the reduction index of $\vec{Y}_\kappa$, etc. Then by Lemma 2 $T^{\pm}_{\kappa\lambda\mu} = 0$ if $\pi_\kappa > \pi_\lambda + \pi_\mu$. Because of the symmetry of $T^{\pm}$, this means that $T^{\pm}_{\kappa\lambda\mu} = 0$ if $\pi_\lambda > \pi_\mu + \pi_\kappa$ or $\pi_\mu > \pi_\kappa + \pi_\lambda$. These conditions establish that for each nonzero term the π's satisfy the triangle condition, which is equivalent to the statement of the theorem. Note that we have only established that components with π_c outside the allowed range vanish; it is also possible that all components vanish. A relevant example is the case when $\vec{A}$ and $\vec{B}$ are pure state density matrices projecting onto orthogonal states.

Theorem 2. If $\vec{A}^{(n)}$ is of degree p_a and $\vec{B}^{(n)}$ is of degree p_b, then the degree of $(\vec{A}^{(n)}\vec{B}^{(n)})^{\pm}$ does not exceed $p_a + p_b$. Its minimum value is the smallest value of $|\pi_a - \pi_b|$ for which the product of components $(\vec{A}^{(n,\pi_a)}\vec{B}^{(n,\pi_b)})^{\pm}$ is nonzero.

The maximum follows immediately from Theorem 1 and our definition of "degree." Since the conditions of the theorem imply nonvanishing components $\vec{A}^{(n,p_a)}$ and $\vec{B}^{(n,p_b)}$ the rank of $(\vec{A}\vec{B})^{\pm}$ is at least $|p_a - p_b|$ unless $(\vec{A}^{(n,p_a)}\vec{B}^{(n,p_b)})^{\pm} = 0$. This possibility cannot be excluded so we work our way down the components until a nonvanishing product is found, and then apply Theorem 1. The results established above are equivalent to the theorem of Sec. II.

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