Grassmann products, cumulants, and two-electron reduced density matrices

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Some properties of Grassmann products of one-electron operators and of cumulants and related quantities for two-electron reduced density matrices (2-RDMs) are reported. The results suggest that any physical significance of the Grassmann product plus cumulant decomposition must be based on the physics of the system described, not just on the mathematical structure. The Grassmann product plus cumulant decomposition of the 2-RDM is resolved into components based on unitary invariants. Simple examples using mathematically acceptable but physically unlikely wave functions show that a Grassmann product differing from the usual one may better approximate the 2-RDM, and that the usual Grassmann product, cumulant, and 2-RDM can be mutually proportional.

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I. INTRODUCTION

Considerable attention has been given recently to the use of reduced density matrix (RDM) cumulants, which in the case of the two-electron RDM $\hat{\Gamma}$ give the part of $\hat{\Gamma}$ not expressible in terms of the one-electron RDM $\hat{\gamma}$ [1–8]. Alternative decompositions of $\hat{\Gamma}$ based on the introduction of transition RDMs have also been suggested [9]. Each of these has been characterized as the true two-electron part of $\hat{\Gamma}$. These papers deal with RDMs for various numbers of electrons, with particular attention to those appearing in contracted Schrödinger equations. Attention here will be concentrated on the one-and two-electron RDMs. It will be shown that $\hat{\gamma}\wedge\hat{\gamma}$ is not always the best Grassmann product approximation to $\hat{\Gamma}$, but that it is a better approximation than Valdemoro's [9] in the sense of distance between matrices. It will also be shown that there are cases in which the Grassmann product of $\hat{\gamma}$ with itself, $\hat{\Gamma}$, and the cumulant, are mutually proportional.

Questions addressed in this paper are the following: What are the functionals of $\hat{\gamma}$ that can be considered as part of $\hat{\Gamma}$? Which functional is the "closest" to $\hat{\Gamma}$? How can the set of Grassmann products be characterized, and what are the consequences for the set of cumulants? What are the consequences of integrating over spin variables or the coordinates of the second electron?

It should be noted that (except for a few examples) this paper is not concerned with the properties of a particular system or state, with energy minimization, or with other physical properties. Instead, it explores general mathematical relationships. To the extent that a property or relationship observed for a particular system or state follows from general considerations independent of that system and state, the property or relationship does not really tell us anything about that system or state. One should first identify such general features and then suppress them in concentrating on specific system or state features.

Among the ideas used here is that of RDMs and other operators as elements in vector spaces [10–12]. In the model problem defined by a finite spin-orbital basis, mathematical subtleties do not arise and simple geometric ideas can be used. In the following section some of the common definitions are reviewed in order to establish a consistent terminology and notation. Some properties of Grassmann products and cumulants are described in Secs. III and IV. Reduction behavior is discussed in Sec. V and the significance of new results is discussed in the concluding section.

II. BACKGROUND

An underlying finite, orthonormal set of spin orbitals $\{\phi_j, j=1,...,b\}$ will be assumed. These functions might be orthogonalized atomic-orbital basis functions, Fock operator eigenfunctions, natural spin-orbitals, or some other convenient set. Usual fermion creation and annihilation operators will be used with $\phi_j \leftrightarrow |j\rangle = \check{a}_j^\dagger|\,\rangle$, etc. Operators on Fock space are denoted here by symbols like $\check{a}$, while operators on a Hilbert space are denoted by symbols like $\hat{f}$. A corresponding basis for two-electron functions will be taken to be the $b(b-1)/2$ normalized determinantal functions $|jk\rangle \leftrightarrow \{\Phi_{jk}(1,2)=2^{-1/2}(1-\hat{P}_{1,2})\phi_j(1)\phi_k(2), j<k\}$, and for any $p\leqslant b$ there are $b!/[p!(b-p)!]$ orthonormal antisymmetrized products that span the p-electron Hilbert space for the model defined by the spin-orbital basis.

Reduced density matrices. Reduced density operators for a system of n electrons will be denoted here by $\hat{\Gamma}^{(p)}$, with $\hat{\gamma}=\hat{\Gamma}^{(1)}$ and $\hat{\Gamma}=\hat{\Gamma}^{(2)}$. They are normalized to $\mathrm{Tr}\,\hat{\Gamma}^{(p)} = n!/[p!(n-p)!]$, so in particular $\mathrm{Tr}\,\gamma=n$ and $\mathrm{Tr}\,\Gamma=n(n-1)/2$. A distinction between tensor components and the matrix elements will be made. They are essentially the same for $\hat{\gamma}$ but differ for $\hat{\Gamma}$. General one- and two-electron operators (not necessarily RDMs) can be expressed as

$$\hat{f}=\sum_{j,k} f_{j,k}|j\rangle\langle k|,$$

$$\hat{G}=\sum_{j<k,\ell<m} G_{jk,\ell m}|jk\rangle\langle \ell m\rangle, \qquad (1)$$

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where $f_{j,k}$ and $G_{jk,\ell m}$ are elements of matrices **f** and **G**. Alternatively, tensors f and G with components f^j_k and $G^{jk}_{\ell m}$ can be defined. The RDM tensor components are conveniently expressed in terms of creation and annihilation operators, as

$$\gamma^j_k = \langle \Psi | \check{a}^\dagger_j \check{a}_k | \Psi \rangle,$$

$$\Gamma^{jk}_{\ell m} = \frac{1}{2} \langle \Psi | \check{a}^\dagger_j \check{a}^\dagger_k \check{a}_m \check{a}_\ell | \Psi \rangle. \tag{2}$$

The *p*-electron RDM tensor component is denoted by ${}^p\Gamma^{j_1 \cdots j_p}_{k_1 \cdots k_p}$ and has a factor $1/p!$ multiplying the expectation value of the normal ordered product of creation and annihilation operators.

The operators $\hat{f}$ and $\hat{G}$ can also be expressed as integral operators with kernels

$$f(1;1') = \sum_{j,k} f_{j,k} \phi_j(1) \phi^*_k(1')$$

$$= \sum_{j,k} \mathsf{f}^j_k \phi_j(1) \phi^*_k(1'),$$

$$G(1,2;1',2') = \sum_{j<k,\ell<m} G_{jk,\ell m} \Phi_{jk}(1,2) \Phi^*_{\ell m}(1',2')$$

$$= \sum_{j,k,\ell,m} \mathsf{G}^{jk}_{\ell m} \phi_j(1) \phi_k(2) \phi^*_m(1') \phi^*_\ell(2'), \tag{3}$$

where, as usual, 1 represents the position and spin coordinates of electron 1, etc. In the case of **G**, summation indices are required to be ordered and the two-electron basis functions are antisymmetric. In the case of G, all orderings of the summation indices are included, the basis functions are simple products, and G will be antisymmetric in upper and in lower indices. It follows that

$$\mathsf{G}^{jk}_{\ell m} = -\mathsf{G}^{jk}_{m\ell} = -\mathsf{G}^{kj}_{\ell m} = \mathsf{G}^{kj}_{m\ell} = \frac{1}{2} G_{jk,\ell m}, \quad j<k,\ \ell<m. \tag{4}$$

Grassmann products. The Grassmann product of operators was introduced into the RDM community by Absar and Coleman [13–15] and used in connection with contracted Schrödinger equations by Mazziotti [16]. Expressions in terms of determinants that are equivalent to Grassmann products were used in the single determinant case by Löwdin [17]. The case of interest here is the Grassmann product of two one-electron operators

$$(\mathbf{f} \wedge \mathbf{g})^{jk}_{\ell m} = \frac{1}{4} (f^j_\ell g^k_m - f^k_\ell g^j_m - f^j_m g^k_\ell + f^k_m g^j_\ell) \tag{5}$$

or

$$(f \wedge g)(1,2;1'2') = \frac{1}{4} [f(1;1')g(2;2') - f(1;2')g(2;1') - f(2;1')g(1;2') + f(2;2')g(1;1')]. \tag{6}$$

It is obvious that $\mathbf{f} \wedge \mathbf{g}$ is antisymmetric in upper and in lower indices and that $f \wedge g$ is antisymmetric in unprimed and in primed variables. It can also be readily verified that they define Hermitian operators if $\hat{f}$ and $\hat{g}$ are Hermitian and that $\hat{f} \wedge \hat{g} = \hat{g} \wedge \hat{f}$.

If operators are expanded as in Eq. (1), then

$$\hat{f} \wedge \hat{g} = \sum_{j<k,\ell<m} (f \wedge g)_{j,k;\ell,m} |jk\rangle\langle \ell m| . \tag{7}$$

Cumulants. Reduced density matrix tensor components can be expressed in terms of a generating ''function'' involving creation and annihilation operators. If this generating function is considered to be the exponential of another such function, that function is a generating function for the cumulants [3,5]. The cumulant part of a *p*-electron operator is commonly denoted by ${}^p\Delta$, and for $p=1$ and 2,

$${}^1\Delta = \gamma, \quad {}^2\Delta = \Gamma - \gamma \wedge \gamma. \tag{8}$$

Since these are the only cumulants of interest in this paper, ${}^1\Delta$ will be replaced by γ and ${}^2\Delta$ will be denoted simply by Δ. Use of cumulants avoids ''unlinked'' terms and leads to size-consistent results.

Correlation terms. Valdemoro and co-workers [9,18,19] decompose the two-electron RDM in a different way. For an *n*-electron state $|\Psi\rangle$, define projection operators $\hat{P} = |\Psi\rangle\langle\Psi|$ and $\hat{Q} = \hat{I}^{(n)} - \hat{P}$ where $\hat{I}^{(n)}$ is the identity operator on the *n*-electron Hilbert space and $\hat{Q}$ can be expressed as a sum of projectors onto the states other than $|\Psi\rangle$ in a complete set. The operator whose expectation value is $\Gamma^{\ell m}_{jk}$ [Eq. (2)] can be rearranged using the anticommutation properties of the creation and annihilation operators and the insertion of the identity operator:

$$\begin{aligned} \check{a}^\dagger_j \check{a}^\dagger_k \check{a}_m \check{a}_\ell &= -\check{a}^\dagger_j \check{a}^\dagger_k \check{a}_\ell \check{a}_m \\ &= -\check{a}^\dagger_j [\delta_{k\ell} - \check{a}_\ell \check{a}^\dagger_k] \check{a}_m \\ &= -\check{a}^\dagger_j \check{a}_m \delta_{k\ell} + \check{a}^\dagger_j \check{a}_\ell [\hat{P} + \hat{Q}] \check{a}^\dagger_k \check{a}_m . \end{aligned} \tag{9}$$

Taking the expectation value with respect to $|\Psi\rangle$ of the left and right sides gives

$$2\Gamma^{jk}_{\ell m} = -\gamma^j_m \delta_{k\ell} + \gamma^j_\ell \gamma^k_m + V^{jk}_{\ell m}, \tag{10}$$

where

$$V^{jk}_{\ell m} = -\langle \Psi | \check{a}^\dagger_j \check{a}_\ell \hat{Q} \check{a}^\dagger_k \check{a}_m | \Psi \rangle$$

$$= \sum_{\psi' (\neq \Psi)} \gamma(\Psi, \Psi')^j_\ell \gamma(\Psi', \Psi)^k_m \tag{11}$$

TABLE I. Components of one- and two-electron matrices.

Matrix	$\pi=0$	$\pi=1$	$\pi=2$
$\mathbf{f}^{(1,\pi)}$	$(\mathrm{Tr}\,\mathbf{f})\mathbf{X}$	$\mathbf{f}-\mathbf{f}^{(1,0)}$	
$\mathbf{F}^{(2,\pi)}$	$(\mathrm{Tr}\mathbf{F})\mathbf{X}^{(2)}$	$\frac{4b}{b-2}\mathbf{f}^{(1,1)}\wedge\mathbf{X}$	$\mathbf{F}-\mathbf{F}^{(2,0)}-\mathbf{F}^{(2,1)}$

is a sum of products of elements of one-electron reduced transition operators. Valdemoro *et al.* call these ''correlation terms,'' but to avoid possible confusion with other correlation functions they will here be referred to as Valdemoro matrices. This analysis has the advantage that, formally, only one-electron operators are involved, albeit they include transitions matrices from the state of interest to all other states.

Matrix spaces and reduction components. In the model defined by a set of b spin-orbitals a p-electron operator is equivalent to a $\binom{b}{p}$ by $\binom{b}{p}$ Hermitian matrix. Let $\mathcal{E}_p$ be the linear space of such matrices [11] and introduce the trace scalar product

$$(\mathbf{A}^{(p)},\mathbf{B}^{(p)})=\mathrm{Tr}\mathbf{A}^{(p)}\mathbf{B}^{(p)},\quad \mathbf{A}^{(p)},\mathbf{B}^{(p)}\in\mathcal{E}_p. \tag{12}$$

A partial trace defines a map from $\mathcal{E}_p$ to $\mathcal{E}_q$ with $q<p$ [20]. A reduction superoperator can be defined to also adjust the normalization of RDMs [12],

$$^{q}\mathsf{A}=\mathrm{Tr}_{q+1,\ldots,p}\,{}^{p}\mathsf{A},$$

$$^{q}\mathsf{A}^{j_1\ldots j_q}_{k_1\ldots k_q}=\sum_{j_{q+1}\ldots j_p}\mathsf{A}^{j_1\ldots j_q,j_{q+1}\ldots j_p}_{k_1\ldots k_q,j_{q+1}\ldots j_p},$$

$$\Gamma^{(q)}={}^{q}_{p}\!\downarrow\Gamma^{(p)}=\frac{p!(n-p)!}{q!(n-q)!}\mathrm{Tr}_{q+1,\ldots,p}\Gamma^{(p)}. \tag{13}$$

These maps define a decomposition of $\mathcal{E}_p$ into orthogonal subspaces [12] $\mathcal{E}_{p\pi}$ (with $\pi=0,\ldots,p$) such that for $\mathbf{A}^{(p,\pi)}\in\mathcal{E}_{p\pi}$,

$${}^{q}_{p}\!\downarrow\mathbf{A}^{(p,\pi)}=\begin{cases}\mathbf{A}^{(q,\pi)} & \text{if } q\geqslant\pi\\ 0 & \text{if } q<\pi.\end{cases} \tag{14}$$

The decomposition can also be defined in terms of components of particular matrices. It is convenient to introduce a multiple of the identity in each space scaled to trace 1, $\mathbf{X}^{(p)}=\binom{b}{p}^{-1}\mathbf{I}^{(p)}$. For $\mathbf{F}\in\mathcal{E}_2$ and $\mathrm{Tr}_2\mathbf{F}=\mathbf{f}\in\mathcal{E}_1$ [13,15],

$$\mathbf{f}=\mathbf{f}^{(1,0)}+\mathbf{f}^{(1,1)},\quad \mathbf{F}=\mathbf{F}^{(2,0)}+\mathbf{F}^{(2,1)}+\mathbf{F}^{(2,2)}. \tag{15}$$

These components are given in Table I. There and in what follows $\mathbf{X}$ is used for $\mathbf{X}^{(1)}$ and we note that $\mathrm{Tr}_2\mathbf{X}^{(2)}=\mathbf{X}$ and $\mathbf{X}\wedge\mathbf{X}=[(b-1)/2b]\mathbf{X}^{(2)}$. As in general for elements in these $\pi>0$ subspaces, $\mathrm{Tr}\mathbf{f}^{(1,1)}=\mathrm{Tr}\mathbf{F}^{(2,1)}=\mathrm{Tr}\mathbf{F}^{(2,2)}=0$, and $\mathrm{Tr}_2\mathbf{F}^{(2,2)}=0$. These decompositions are related to the behavior of the components or subspaces when the spin orbital basis is subjected to a unitary transformation. Each $\mathcal{E}_p$ is a carrier space for a representation of the group $\mathbb{U}(b)$ of such transformations, and the $\mathcal{E}_{p\pi}$ are the invariant subspaces [15,21–24].

III. SOME PROPERTIES OF GRASSMANN PRODUCTS

Since $\mathbf{f}\wedge\mathbf{g}$ is Hermitian if $\mathbf{f}$ and $\mathbf{g}$ are, and it is antisymmetric, the Grassmann product defines a map from $\mathcal{E}_1\otimes\mathcal{E}_1$ to $\mathcal{E}_2$. Some properties of this map and of elements of $\mathcal{E}_2$ that are Grassmann products are developed in this section.

A necessary property of density matrices, including RDMs, is that they be positive. In the Hartree-Fock case, $\hat{\Gamma}=\hat{\gamma}\wedge\hat{\gamma}$, and this will be generalized to non-Hartree-Fock $\hat{\gamma}$'s. When is the result a positive matrix? Consider first a rather special case in which a and b in $\mathcal{E}_1$ can be simultaneously diagonalized so that the corresponding operators can be written

$$\hat{a}=\sum_j\alpha_j|j\rangle\langle j|,\quad \hat{b}=\sum_j\beta_j|j\rangle\langle j| \tag{16}$$

in the basis that simultaneously diagonalizes them. Then

$$\hat{a}\wedge\hat{b}=\sum_{j<k}\frac{\alpha_j\beta_k+\alpha_k\beta_j}{2}|jk\rangle\langle jk|. \tag{17}$$

One result follows immediately when $\mathbf{b}=\mathbf{a}$.

Theorem 1. If $\mathbf{a}$ is positive then $\mathbf{A}=\mathbf{a}\wedge\mathbf{a}$ is positive.

Without loss of generality we can choose the basis to consist of the eigenfunctions of the operator $\hat{a}$, and for a positive operator $\alpha_j\geqslant 0$ for each j. It follows that

$$\hat{a}\wedge\hat{a}=\sum_{j<k}\alpha_j\alpha_k|jk\rangle\langle jk| \tag{18}$$

is positive. The matrix $\mathbf{A}$ of $\hat{a}\wedge\hat{a}$ will thus be positive. ■

One might ask whether $\mathbf{\Gamma}$, or any other operator or matrix in the same space, can always be expressed as a Grassmann product. The answer is no. The Grassmann product map $\mathcal{E}_1\otimes\mathcal{E}_1\mapsto\mathcal{E}_2$ is into, not onto.

Theorem 2. Unless there are fewer than four basis spin orbitals, there are matrices $\mathbf{F}$ in $\mathcal{E}_2$ that cannot be expressed as $\mathbf{f}\wedge\mathbf{g}$ for any $\mathbf{f},\mathbf{g}\in\mathcal{E}_1$.

For simplicity, only real symmetric matrices will be treated in detail. The dimensions of $\mathcal{E}_1$ and $\mathcal{E}_2$ restricted to real symmetric matrices are

$$\dim\mathcal{E}_1=\frac{b(b+1)}{2},\quad \dim\mathcal{E}_2=\frac{1}{2}\binom{b}{2}\left[\binom{b}{2}+1\right]. \tag{19}$$

Consider general elements of $\mathcal{E}_1$ corresponding to operators

$$\hat{f}=\sum_{j,k=1}^{b}f_{j,k}|j\rangle\langle k|,\quad \hat{g}=\sum_{\ell,m=1}^{b}g_{\ell,m}|\ell\rangle\langle m|, \tag{20}$$

with $f_{k,j}=f_{j,k}$ and $g_{m,\ell}=g_{\ell,m}$. Using the definition of the Grassmann product we find that this general, real Grassmann product in $\mathcal{E}_2$ can be written as

$$\hat{f}\wedge\hat{g}=\sum_{p<q}\sum_{r<s}C_{pq,rs}|pq\rangle\langle rs|, \tag{21}$$

with

$$C_{pq,rs}=C_{rs,pq}=\langle pq|\hat{f}\wedge\hat{g}|rs\rangle$$
$$=\frac{1}{2}(f_{p,r}g_{q,s}-f_{q,r}g_{p,s}-f_{p,s}g_{q,r}+f_{q,s}g_{p,r}). \quad (22)$$

Now think of the C's as being given for a general element of $\mathcal{E}_2$ and try to solve for the f's and g's that will reproduce it as an element of the set of Grassmann products. The number of equations will be equal to the number of unknowns if $2\dim\mathcal{E}_1=\dim\mathcal{E}_2$, or

$$2\frac{b(b+1)}{2}=\frac{1}{2}\frac{b(b-1)}{2}\left[\frac{b(b-1)}{2}+1\right], \quad (23)$$

which has as its only real solution $b=3.92...$. For larger values of b, there will be more equations than unknowns and for general values of the C's there will be no solution.

For complex Hermitian matrices $\dim\mathcal{E}_1=b^2$ and $\dim\mathcal{E}_2=\binom{b}{2}^2$. The equation for the critical b is then $2b^2=b^2(b-1)^2/4$ leading to $b=\sqrt{8}+1\simeq 3.828$. ■

It is possible to define an algorithm for determining whether a given matrix in $\mathcal{E}_2$ can be expressed as a Grassmann product of a matrix in $\mathcal{E}_1$ with itself. Consider a general matrix in $\mathcal{E}_1$ corresponding to an operator $\hat{a}$, and choose as basis the eigenfunctions of $\hat{a}$, as in Eq. (16). Construct the Grassmann product of this operator with itself and take a partial trace,

$$\mathrm{Tr}_2\hat{a}\wedge\hat{a}=\frac{1}{2}(\mathrm{Tr}\ \mathbf{a})\hat{a}-\frac{1}{2}\hat{a}^2=\frac{1}{2}\sum_j\ [(\mathrm{Tr}\ \mathbf{a})\alpha_j-\alpha_j^2)]|j\rangle\langle j|. \quad (24)$$

It is apparent from either of these forms that $\mathrm{Tr}_2(\mathbf{a}\wedge\mathbf{a})$ is diagonal in the basis that diagonalized $\mathbf{a}$. We see from Eq. (18) that the eigenvectors of $\hat{a}\wedge\hat{a}$ are antisymmetrized products of the eigenvectors of $\hat{a}$, and that the eigenvalues of the former are products of those of the latter. This suggests the following procedure.

Given any $\mathbf{G}\in\mathcal{E}_2$, construct $\mathrm{Tr}_2\mathbf{G}$ and diagonalize it. Transform $\mathbf{G}$ to the basis of antisymmetrized products of the eigenvectors of $\mathrm{Tr}_2\mathbf{G}$. (Any vectors associated with eigenvalue 0 can be omitted.) A necessary condition for $\mathbf{G}$ to be expressible as $\mathbf{a}\wedge\mathbf{a}$ is that it be diagonal in this basis [cf. Eqs. (18) and (24)].

If this condition is satisfied, consider next the diagonal elements. They can be labeled as $g_{jk}=G_{jk,jk}$ and, from Eq. (18)

$$\frac{g_{j\not k}}{g_{k\not k}}=\frac{\alpha_j}{\alpha_k} \quad \text{or} \quad \frac{g_{j\not k}}{g_{\not k k}}=\frac{\alpha_j}{\alpha_k}, \quad (25)$$

etc., depending on the ordering of the indices; the ratio of any two g's sharing a common index will be the ratio of the α's with the remaining indices. Of course these ratios are not all independent, so, for example,

$$\frac{\alpha_j}{\alpha_k}\frac{\alpha_k}{\alpha_{\not k}}=\frac{g_{jm}}{g_{km}}\frac{g_{kn}}{g_{\not k n}}=\frac{\alpha_j}{\alpha_{\not k}}=\frac{g_{jp}}{g_{\not k p}},$$

$$\frac{g_{jm}}{g_{km}}=\frac{\alpha_j}{\alpha_k}=\frac{g_{jn}}{g_{kn}}, \quad m\neq n. \quad (26)$$

A necessary condition for $\mathbf{G}$ to be expressible as $\mathbf{a}\wedge\mathbf{a}$ is that its eigenvalues be related in this way.

If the eigenvalues are related in this way, then the independent ratios can be used to express all of the α_j as multiples of one α, say α_1, with coefficients given in terms of the g's. The full trace of $\mathbf{G}$ can be expressed as

$$\mathrm{Tr}\ \mathbf{G}=\mathrm{Tr}\ \mathbf{a}\wedge\mathbf{a}=\sum_{j,k}\ \alpha_j\alpha_k-\sum_j\ \alpha_j^2. \quad (27)$$

Substitution of other α's in terms of α_1 gives an equation that can be solved for α_1^2. The sign of α_1, which determines the signs of all other α's, is necessarily indeterminate, since $(-\mathbf{a})\wedge(-\mathbf{a})=\mathbf{a}\wedge\mathbf{a}$. If $\mathbf{a}$ is to be a density matrix, α_1 should be chosen to be positive. The remaining α's are then obtained from the ratios and $\mathbf{a}$ is determined. A $\mathbf{G}=\mathbf{a}\times\mathbf{a}$ will be a Grassmann product of one-electron RDMs if and only if the eigenvalues of $\mathbf{a}$ satisfy the Coleman conditions [25] $0\leqslant\alpha_j\leqslant 1$ for each j.

An important property of the set of all density matrices for a given number of electrons is that it is convex. The set of n-representable reduced density matrices is also convex. This is not the case for Grassmann products.

Theorem 3. The set of Grassmann products $\{\mathbf{f}\wedge\mathbf{f},\mathbf{f}\in\mathcal{E}_1\}$ is not convex.

This negative result can be established by a simple example. A set $\mathbb{C}$ of matrices is convex if, for any $\mathbf{a}$, $\mathbf{b}\in\mathbb{C}$, $(1-\mu)\mathbf{a}+\mu\mathbf{b}\in\mathbb{C}$ for any μ, $0\leqslant\mu\leqslant 1$. If $\mathbf{a}$ and $\mathbf{b}$ are in $\mathcal{E}_1$ then $\mathbf{a}\times\mathbf{a}$ and $\mathbf{b}\times\mathbf{b}$ are in the set of Grassmann products. Consider a convex combination of them, $\mathbf{G}=(1-\mu)\mathbf{a}\wedge\mathbf{a}+\mu\mathbf{b}\wedge\mathbf{b}$. Suppose that $\mathbf{a}$ and $\mathbf{b}$ are diagonal in the same basis, $\{|k\rangle\}$, but have different eigenvalues $\{\alpha_k\}$ and $\{\beta_k\}$, respectively. Then $\mathbf{G}$ will have eigenvalues $g_{jk}=(1-\mu)\alpha_j\alpha_k+\mu\beta_j\beta_k$. The criterion in Eq. (26) becomes, for example,

$$\frac{(1-\mu)\alpha_1\alpha_3+\mu\beta_1\beta_3}{(1-\mu)\alpha_2\mu_3+\mu\beta_2\beta_3}=\frac{(1-\mu)\alpha_1\alpha_4+\mu\beta_1\beta_4}{(1-\mu)\alpha_2\alpha_4+\mu\beta_2\beta_4}. \quad (28)$$

This condition reduces to an identity when $\mu=0$ or $\mu=1$, but for intermediate values of μ it requires

$$\alpha_1\alpha_3\beta_2\beta_4+\alpha_2\alpha_4\beta_1\beta_3=\alpha_2\alpha_3\beta_1\beta_4+\alpha_1\alpha_4\beta_2\beta_3, \quad (29)$$

which will not be satisfied for general values of the α's and β's. It follows that $\mathbf{G}\neq\mathbf{f}\wedge\mathbf{f}$ for any $\mathbf{f}$, so the set is not convex. ■

Some formal results that are required for the geometric interpretation will next be established. Consider an element of $\mathcal{E}_1$,

$$\mathbf{g}=\mathbf{g}(\lambda)=(1-\lambda)\mathbf{a}+\lambda\mathbf{b}, \quad (30)$$

where $\mathbf{a}$ and $\mathbf{b}$ are two fixed elements of $\mathcal{E}_1$, possibly n-representable RDMs, and λ varies between 0 and 1. Then

$$\mathbf{G}(\lambda)=\mathbf{g}\wedge\mathbf{g}=(1-\lambda)^2\mathbf{a}\wedge\mathbf{a}+2(1-\lambda)\mathbf{a}\wedge\mathbf{b}+\lambda^2\mathbf{b}\wedge\mathbf{b} \quad (31)$$

is a combination of three vectors in $\mathcal{E}_2$. Except in special cases these vectors span a three-dimensional subspace of $\mathcal{E}_2$ containing any linear combination of them, but considered as points in $\mathcal{E}_2$ they define a plane. Note that

Theorem 4. For any linearly independent $\underline{U}$, $\underline{V}$, and $\underline{W}$ defining a three-dimensional subspace of the vector space of which they are elements, the combination $\underline{G}=(1-\lambda)^2\underline{U}+2\lambda(1-\lambda)\underline{V}+\lambda^2\underline{W}$ is in the plane determined by the points $\underline{U}$, $\underline{V}$, and $\underline{W}$.

Introduce any orthonormal set of three vectors in the subspace and take them to define a Cartesian coordinate system in terms of which $\underline{U}\leftrightarrow\vec{a}=(a_x,a_y,a_z)$, $\underline{V}\leftrightarrow\vec{b}=(b_x,b_y,b_z)$, and $\underline{W}\leftrightarrow\vec{c}=(c_x,c_y,c_z)$. The general equation for a plane in a three-dimensional space is $Ax+By+Cz+D=0$. In this case the plane does not contain the origin so $D\neq 0$ and the equation can be divided by $-D$ to give $A'x+B'y+C'z=1$. Defining $\vec{T}=(A',B',C')$ we have

$$\vec{T}\cdot\vec{a}=1,\quad \vec{T}\cdot\vec{b}=1,\quad \vec{T}\cdot\vec{c}=1 \tag{32}$$

as the equations determining A', B', and C'. A point $\vec{p}$ is in the plane if and only if $\vec{T}\cdot\vec{p}=1$, and we see that

$$\begin{aligned}\vec{V}\cdot\vec{G}&=(1-\lambda)^2\vec{V}\cdot\vec{a}+2\lambda(1-\lambda)\vec{V}\cdot\vec{b}+\lambda^2\vec{V}\cdot\vec{c}\\&=(1-\lambda)^2+2\lambda(1-\lambda)+\lambda^2\\&=[(1-\lambda)+\lambda]^2=1,\end{aligned} \tag{33}$$

so $\vec{G}$ is in the plane. ■

We can introduce two independent vectors in the plane defined by $\underline{U}\leftrightarrow\mathbf{a}\wedge\mathbf{a}$, $\underline{V}\leftrightarrow\mathbf{a}\wedge\mathbf{b}$, and $\underline{W}\leftrightarrow\mathbf{b}\wedge\mathbf{b}$ as

$$\vec{u}=\underline{U}-\underline{W},\quad \vec{v}=\underline{V}-\frac{1}{2}(\underline{U}+\underline{W}). \tag{34}$$

They are not in general orthogonal or normalized, but any point in the plane can be expressed as

$$\vec{p}=\vec{w}+\xi\vec{u}+\eta\vec{v}, \tag{35}$$

where $\vec{w}=(\vec{a}+\vec{b})/2$ is a fixed point corresponding to the origin of a two-dimensional coordinate system in the plane. It follows that $\vec{a}=\vec{w}+\vec{u}/2$, $\vec{b}=\vec{w}+\vec{v}$, and $\vec{c}=\vec{w}-\vec{u}/2$ so

$$\vec{G}=\vec{w}+\left(\frac{1}{2}-\lambda\right)\vec{u}+2\lambda(1-\lambda)\vec{v}. \tag{36}$$

As $\mathbf{g}(\lambda)$ moves linearly from $\mathbf{a}$ to $\mathbf{b}$, $\mathbf{G}(\lambda)$ moves along a parabolic path from $\mathbf{a}\wedge\mathbf{a}$ to $\mathbf{b}\wedge\mathbf{b}$. This path is in the plane determined by these end points and $\mathbf{a}\wedge\mathbf{b}$.

When geometric aspects are considered scalar products are sometimes involved. A useful result is the following.

Theorem 5. Scalar products of Grassmann products in $\mathcal{E}_2$ can be expressed in terms of scalar products in $\mathcal{E}_1$.

This is readily verified from the definitions of scalar and Grassmann products. Suppose that $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$, and $\mathbf{d}$ are elements of $\mathcal{E}_1$. Then

$$\begin{aligned}(\mathbf{a}\wedge\mathbf{b},\mathbf{c}\wedge\mathbf{d})&=\sum_{j,k,\ell,m}(\mathbf{a}\wedge\mathbf{b})^{\ell m}_{jk}(\mathbf{c}\wedge\mathbf{d})^{jk}_{\ell m}\\&=\frac{1}{4}[(\mathbf{a},\mathbf{c})(\mathbf{b},\mathbf{d})-(\mathbf{ac},\mathbf{bd})\\&\quad+(\mathbf{a},\mathbf{d})(\mathbf{b},\mathbf{c})-(\mathbf{ad},\mathbf{bc})].\end{aligned} \tag{37}$$

Note that some of the scalar products involve matrices that are matrix products. ■

The vast majority of operators of interest, including nearly all molecular electronic Hamiltonians, are spin free. It is thus appropriate to work with the spinless or charge density components of the one- and two-electron reduced density matrices, obtained by integrating over the spin variables. The complete one-matrix can be expressed in terms of spin-up and spin-down components or in terms of charge-density and spin-density components

$$\begin{aligned}\gamma(x;x')&=\gamma^{(0)}(\vec{r};\vec{r}')[\alpha(\xi)\alpha^\dagger(\xi')+\beta(\xi)\beta^\dagger(\xi')]/2+\gamma^{(z)}\\&\quad\times(\vec{r};\vec{r}')[\alpha(\xi)\alpha^\dagger(\xi')-\beta(\xi)\beta^\dagger(\xi')].\end{aligned} \tag{38}$$

It is well known that $\Gamma^{(0)}$, the two-electron charge-density matrix or spinless component of Γ, can be divided into permutationally symmetric and antisymmetric parts [26], and this property is not limited to $\Gamma^{(0)}$. Suppose that $\mathbf{G}$ is any element of $\mathcal{E}_2$. The kernel of the corresponding integral operator can be expanded as in Eq. (3) in terms of antisymmetrized products of the basis spin-orbitals, but these spin geminals can be replaced by a unitarily equivalent set consisting of singlet and triplet spin geminals. Integration over the spin variables will eliminate any singlet-triplet cross products, and the remaining spatial functions are permutationally symmetric (for singlet) or antisymmetric (for triplet). For the RDM,

$$\Gamma^{(0)}(\vec{r}_1,\vec{r}_2;\vec{r}_1',\vec{r}_1')=\Gamma^a(\vec{r}_1,\vec{r}_2;\vec{r}_1',\vec{r}_1')+\Gamma^s(\vec{r}_1,\vec{r}_2;\vec{r}_1',\vec{r}_1'). \tag{39}$$

and there will be similar decompositions for $\gamma\wedge\gamma$ and Δ.

Expressions originally obtained for single determinant density matrices [27] are valid for more general Grassmann products of one-electron RDMs as well. It is convenient to define a symmetrized product analogous to the antisymmetrized, Grassmann product,

$$(\mathbf{a}\vee\mathbf{b})^{jk}_{\ell m}=\frac{1}{4}(a^j_\ell b^k_m+a^j_m b^k_\ell+a^k_\ell b^j_m+a^k_m b^j_\ell),$$

$$\begin{aligned}(a\vee b)(1,2;1',2')&=\frac{1}{4}[a(1;1')b(2;2')+a(1;2')b(2,1')\\&\quad+a(2;1')b(1;2')+a(2;2')b(1;1')].\end{aligned} \tag{40}$$

By inserting the spin components of γ into $\gamma\wedge\gamma$, expanding and integrating over spin variables we obtain the spinless

component $(\gamma\wedge\gamma)^{(0)}$. Application of the projection operators $(1\pm\hat{P}_{1,2})/2$ extracts the symmetric or antisymmetric component. The results are

$$(\gamma\wedge\gamma)^a=\frac{3}{8}\gamma^{(0)}\wedge\gamma^{(0)}+\frac{1}{8}\gamma^{(z)}\wedge\gamma^{(z)},$$

$$(\gamma\wedge\gamma)^s=\frac{1}{8}\gamma^{(0)}\vee\gamma^{(0)}-\frac{1}{8}\gamma^{(z)}\vee\gamma^{(z)}. \tag{41}$$

For a singlet (or other spin eigenstate having $M_S=0$) $\gamma^{(z)}\equiv 0$.

IV. CUMULANTS AND VALDEMORO MATRICES

Note that Δ and $\mathbf{V}$ can be expressed as linear combinations of $\hat{\Gamma}$ and Grassmann products of Hermitian matrices. They are thus antisymmetric and Hermitian. When the wave function is a single determinant $\hat{\Gamma}=\hat{\gamma}\wedge\hat{\gamma}$ the cumulant is zero. A Hartree-Fock single determinant is often a good initial approximation, so one might expect that $\hat{\gamma}\wedge\hat{\gamma}$ provides a good approximation to $\hat{\Gamma}$ in general. It is not always the best Grassmann product approximation, however. A measure of how closely one matrix approximates another is the norm of their difference, which is the distance between them, $d(\mathbf{A},\mathbf{B})=\|\mathbf{A}-\mathbf{B}\|=(\mathbf{A}-\mathbf{B},\mathbf{A}-\mathbf{B})^{1/2}$.

Theorem 6. There are n-representable two-electron RDMs $\boldsymbol{\Gamma}$ and one-electron RDMs $\gamma'\neq\gamma={}^2_1\downarrow\boldsymbol{\Gamma}$ for which

$$\|\boldsymbol{\Gamma}-\gamma'\wedge\gamma'\|<\|\boldsymbol{\Gamma}-\gamma\wedge\gamma\|=\|\Delta\|. \tag{42}$$

The possibility can be established by a simple example. Consider a two-electron system with four basis functions $|1\rangle$, $|2\rangle$, $|3\rangle$, $|4\rangle$. Take a wave function $\Psi=C_n[|1,2\rangle+0.1|3,4\rangle+0.01(|1,4\rangle-|2,3\rangle)]$ where C_n is chosen so that Ψ is normalized. For this case γ has eigenvalues 0.990 123 and 0.009 877, each doubly degenerate, and $\|\Gamma-\gamma\wedge\gamma\|=0.141\,89$. With $\gamma'=1.015\,0859\gamma-0.015\,085\,9X$, where X is the diagonal matrix with all diagonal elements 1/2, $\|\Gamma-\gamma'\wedge\gamma'\|=0.140\,37$. This γ' has doubly degenerate eigenvalues 0.997 517 and 0.002 483 12, so it satisfies the Coleman criteria for ensemble n representability. ■

Although a single example serves to establish the result, the difference in norms is quite small. Another example, although not corresponding to a physically likely state, provides a somewhat larger reduction in the norm. Let $\Psi_2=(|1,2\rangle+|3,4\rangle)/\sqrt{2}$. This leads to a diagonal γ with all four eigenvalues 1/2. In this case $\|\Gamma-\gamma\wedge\gamma\|=0.935\,414$, but for a diagonal γ' with doubly degenerate eigenvalues 0.788 675 and 0.211 325 the norm becomes 0.912 871. It is straightforward in principle, although challenging computationally, to find the one matrix that gives a best fit to a given two matrix. It seems likely that still smaller values for $\|\Gamma-f\wedge f\|$ could be obtained for matrices (kernels) $f\in\mathcal{E}_1$ that are not required to be n-representable reduced density matrices.

In the RDM cumulant literature it is suggested that $\boldsymbol{\Gamma}$ be decompoesed into a part determined by $\boldsymbol{\gamma}$ and a "true" two-electron part. It is not clear that this is always meaningful. Another simple example establishes the following.

Theorem 7. There are functions $\boldsymbol{\Psi}$, not single determinants, leading to RDMs $\boldsymbol{\Gamma}$ and $\boldsymbol{\gamma}$ and cumulant Δ for which

$$\Delta\propto\gamma\wedge\gamma\propto\boldsymbol{\Gamma}. \tag{43}$$

Consider a model with b basis spin orbitals for a system of n electrons and some number r between n and b. Let $J_r=\{j_1,\ldots,j_r\}$ be some set of r distinct indices each between 1 and b and define

$$\Psi(J_r)=\binom{r}{n}^{-1}\sum_{K_n\subset J_r}|K_n\rangle, \tag{44}$$

where $|K_n\rangle$ is the normalized, antisymmetrized product of the n spin orbitals indexed by $k_1<\cdots<k_n$, and the sum is over all subsets of n indices chosen from among those in J_r. Although unlikely to correspond to a physically interesting state, this is a legitimate n-electron wave function. It treats all spin orbitals with indices in J_r equivalently, and without actually doing the reductions we can conclude that the one matrix and two matrix also treat these spin orbitals equivalently so they must be

$$\hat{\gamma}(J_r)=\frac{n}{r}\sum_{t=1}^{r}|j_t\rangle\langle j_t|.$$

$$\hat{\Gamma}(J_r)=\binom{n}{2}\binom{r}{2}^{-1}\sum_{t<u,=1}^{r}|j_tj_u\rangle\langle j_tj_u|. \tag{45}$$

These operators are proportional to the projection operators but are not idempotent (they might be called "portiopotent")

$$[\hat{\gamma}(J_r)]^2=\frac{n}{r}\hat{\gamma}(J_r),\quad[\hat{\Gamma}(J_r)]^2=\binom{n}{2}\binom{r}{2}^{-1}\hat{\Gamma}(J_r). \tag{46}$$

Using Eq. (18) with $\alpha_j=n/r$ for each j we find

$$\hat{\gamma}(J_r)\wedge\hat{\gamma}(J_r)=\frac{n^2}{r^2}\sum_{j<kj,=1}^{b}|j_tj_u\rangle\langle j_tj_u|=\frac{n(r-1)}{r(n-1)}\hat{\Gamma}(J_r). \tag{47}$$

The cumulant will thus also just be a multiple of $\hat{\Gamma}$,

$$\Delta(J_r)=\hat{\Gamma}(J_r)-\frac{n(r-1)}{r(n-1)}\hat{\Gamma}(J_r)=\frac{n-r}{r(n-1)}\hat{\Gamma}(J_r). \tag{48}$$

The proportionality constant is negative, so $\Delta(J_r)$ is in fact negative semidefinite. ■

When $r=n$, $\hat{a}=\hat{\gamma}$, and $\hat{\Gamma}=\hat{\gamma}\wedge\hat{\gamma}$, the well-known single determinant case. If we forego n-representability and define $\hat{a}=[r(n-1)/n(r-1)]^{1/2}\hat{\gamma}$, then $\hat{a}\wedge\hat{a}=\hat{\Gamma}$.

Tracing or integrating over spin variables in the cumulant gives its spinless part, which can be separated into symmetric and antisymmetric components. They are related to the components of Γ and $\gamma\wedge\gamma$ by [cf. Eqs. (41)]

$$\Delta^a=\Gamma^a-(\gamma\wedge\gamma)^a=\Gamma^a-\frac{3}{8}\gamma^{(0)}\wedge\gamma^{(0)}-\frac{1}{8}\gamma^{(z)}\wedge\gamma^{(z)},$$

$$\Delta^s=\Gamma^s-(\gamma\wedge\gamma)^s=\Gamma^s-\frac{1}{8}\gamma^{(0)}\vee\gamma^{(0)}+\frac{1}{8}\gamma^{(z)}\wedge\gamma^{(z)}\vee\gamma^{(z)}. \tag{49}$$

Equation (10) can be rewritten with permuted indices and the results added, with appropriate signs, to give

$$\mathbf{\Gamma}=\boldsymbol{\gamma}\wedge\boldsymbol{\gamma}+\boldsymbol{\gamma}\wedge\mathbf{I}+\mathbf{V}, \tag{50}$$

where the matrix elements are labeled by ordered pairs of spin-orbital indices. [See Eq. (4).] We see that in the case of a single determinant wave function $\mathbf{V}=-\boldsymbol{\gamma}\wedge\mathbf{I}$, so $\mathbf{V}$ by itself is not a measure of the difference between $\mathbf{\Gamma}$ and $\boldsymbol{\gamma}\wedge\boldsymbol{\gamma}$. An analog of Theorem 6 is thus not particularly interesting. For the portiopotent RDMs considered in connection with Theorem 7, $\boldsymbol{\gamma}\wedge\mathbf{I}$ is not proportional to $\mathbf{\Gamma}$ or $\boldsymbol{\gamma}\wedge\boldsymbol{\gamma}$ and thus $\mathbf{V}$ will also differ by more than a proportionality factor.

It is straightforward to show that when $\boldsymbol{\gamma}\wedge\mathbf{I}$ is traced over spin variables the result is

$$(\gamma\wedge I)^{(0)}=\frac{3}{2}\gamma^{(0)}\wedge I^{(0)}+\frac{1}{2}\gamma^{(0)}\vee I^{(0)}, \tag{51}$$

where $I^{(0)}$ is the identity operator or matrix on the orbital space. There is no contribution from $\gamma^{(z)}$. Assuming that the spin-orbital basis consists of $b/2$ orbitals χ_j, each multiplied by α for one spin orbital and by β for another, then the kernel for $I^{(0)}$ is

$$I^{(0)}(\vec{r};\vec{r}\,')=\sum_{j=1}^{b/2}\chi_j(\vec{r})\chi_j^*(\vec{r}\,'). \tag{52}$$

The two terms on the right-hand side in Eq. (51) are obviously the antisymmetric and symmetric components, respectively. Combining these with previous results, the components of $\mathbf{V}$ can be constructed,

$$\begin{aligned}\mathbf{V}^a&=\Gamma^a-(\gamma\wedge\gamma)^a-(\gamma\wedge\mathbf{X})^a\\&=\Gamma^a-\frac{3}{8}\gamma^{(0)}\wedge\gamma^{(0)}-\frac{1}{8}\gamma^{(z)}\wedge\gamma^{z}-\frac{3}{2}\gamma^{(0)}\wedge I^{(0)},\\ \mathbf{V}^s&=\Gamma^s-(\gamma\wedge\gamma)^s-(\gamma\wedge\mathbf{X})^s\\&=\Gamma^s-\frac{1}{8}\gamma^{(0)}\vee\gamma^{(0)}+\frac{1}{8}\gamma^{(z)}\vee\gamma^{(z)}-\frac{1}{2}\gamma^{(0)}\vee I^{(0)}.\end{aligned} \tag{53}$$

V. REDUCTION BEHAVIOR AND GEOMETRY

Except in the single determinant case, the reduction of $\boldsymbol{\gamma}\wedge\boldsymbol{\gamma}$ is not $\boldsymbol{\gamma}$ and its trace is not that of $\mathbf{\Gamma}$. For the Grassmann product of any $\mathbf{a}$ and $\mathbf{b}$ in $\mathcal{E}_1$ it is readily verified that

$$\mathrm{Tr}_2(\mathbf{a}\wedge\mathbf{b})=\frac{1}{4}[(\mathrm{Tr}\ \mathbf{b})\mathbf{a}+(\mathrm{Tr}\ \mathbf{a})\mathbf{b}-\mathbf{ab}-\mathbf{ba}],$$

$$\mathrm{Tr}(\mathbf{a}\wedge\mathbf{b})=\frac{1}{2}[(\mathrm{Tr}\ \mathbf{a})(\mathrm{Tr}\ \mathbf{b})-\mathrm{Tr}(\mathbf{ab})]. \tag{54}$$

It will be convenient to have a compact notation for the traceless part of a matrix. Define

$$\begin{aligned}\overline{\mathbf{f}}&=\mathbf{f}^{(1,1)}=\mathbf{f}-(\mathrm{Tr}\ \mathbf{f})\mathbf{X},\\ \overline{\mathbf{F}}&=\mathbf{F}^{(2,1)}+\mathbf{F}^{(2,2)}=\mathbf{F}-(\mathrm{TrF})\mathbf{X}^{(2)},\end{aligned} \tag{55}$$

for any $\mathbf{f}\in\mathcal{E}_1$ and $\mathbf{F}\in\mathcal{E}_2$.

As noted above, the partial trace or reduction maps define a decomposition of an operator into orthogonal components, or of a matrix space into orthogonal subspaces

$$\mathcal{E}_1=\mathcal{E}_{1.0}\oplus\mathcal{E}_{1,1},\quad \mathcal{E}_2=\mathcal{E}_{2,0}\oplus\mathcal{E}_{2,1}\oplus\mathcal{E}_{2,2}. \tag{56}$$

The matrix space $\mathcal{E}_2$ is a carrier space for a representation of the unitary group $\mathbb{U}(b)$ of unitary transformations of the spin- orbital basis, and the $\mathcal{E}_{2,\pi}$ are the invariant subspaces. Expressions for the components of a matrix in these subspaces were given in Table I. Note that if $\mathbf{g}=\mathrm{Tr}_2\mathbf{G}$ then $\mathrm{Tr}\ \mathbf{g}=\mathrm{Tr}\,\mathbf{G}$ and $\overline{\mathbf{g}}=\mathrm{Tr}_2\overline{\mathbf{G}}$. The components of $\mathbf{G}$ can then be expressed as

$$\begin{aligned}\mathbf{G}^{(2,0)}&=(\mathrm{Tr}\ \mathbf{G})^{(2)}\mathbf{X},\\ \mathbf{G}^{(2,1)}&=\frac{4b}{b-2}\overline{\mathbf{g}}\wedge\mathbf{X},\\ \mathbf{G}^{(2,2)}&=\overline{\mathbf{G}}-\frac{4b}{b-2}\overline{\mathbf{g}}\wedge\mathbf{X}.\end{aligned} \tag{57}$$

Specialize now to the case of reduced density matrices. The components of various Grassmann products are summarized in Table II. The (2,2) components indicated in the table by * are given by the third of Eqs. (57) but there is no cancellation to give short expressions. The notation $\nu_k=\mathrm{Tr}(\gamma^k)$ has been introduced, with $\nu_1=n$. Note that $\overline{\gamma}\wedge\mathbf{X}$ is entirely in $\mathcal{E}_{2,1}$ and that the (2,1) components of $\gamma\wedge\gamma$ and $\gamma\wedge\mathbf{X}$ are the same as those of $\overline{\gamma}\wedge\overline{\gamma}$ and $\overline{\gamma}\wedge\mathbf{X}$, respectively. The norm is that defined by the trace scalar product $\|\mathbf{G}\|^2=(\mathbf{G},\mathbf{G})$. Since $\|\mathbf{X}^{(2)}\|=2/b(b-1)\|G^{(2,0)}\|$, it is readily determined from the entry in the second column in each case.

We can, without loss of generality, choose the spin orbital basis to be the natural spin orbitals (NSOs) so that $\hat{\gamma}$ is diagonal. Denote the diagonal elements by $\{\lambda_j\}$ and note that the diagonal elements of $\mathbf{X}$ are all $1/b$ so those of $\overline{\gamma}$ are λ_j-n/b. Recall that $\mathrm{Tr}\boldsymbol{\gamma}=n$ and $\mathrm{Tr}\ \mathbf{\Gamma}=n(n-1)/2$ for a system of n electrons, and $\gamma=\begin{smallmatrix}2\\1\end{smallmatrix}\downarrow\ \mathbf{\Gamma}=[2/(n-1)]\mathrm{Tr}_2\mathbf{\Gamma}$. In the NSO basis, all off-diagonal elements of $\mathbf{\Gamma}$ are associated exclusively with Δ or $\mathbf{V}$ and contribute to $\hat{\Gamma}^{(2,2)}$. The Grassmann products $\hat{\gamma}\wedge\hat{\gamma}$ and $\hat{\gamma}\wedge\mathbf{X}$ are diagonal, and the diagonal elements of Δ and $\mathbf{V}$ are determined by these and the diagonal elements of $\mathbf{\Gamma}$. The square of the norm of any matrix is the sum of the squared magnitudes of all its matrix elements, and the scalar product of two matrices is the sum of products of corresponding matrix elements. If $\mathbf{G}_d^{NSO}$ and $\mathbf{G}_{od}^{NSO}$ denote

TABLE II. Components of some Grassmann products.

G	$\mathbf{G}^{(2,0)}$	$\mathbf{G}^{(2,1)}$	$\|\mathbf{G}^{(2,1)}\|^2$	$\mathbf{G}^{(2,2)}$
$\gamma\wedge\gamma$	$\frac{n^2-\nu}{2}\mathbf{X}^{(2)}$	$\frac{2b}{b-2}(n\overline{\gamma}-\nu\overline{\gamma^2})\wedge\mathbf{X}$	$\frac{4b}{(b-1)^2}(-n^4+n^2b\,\nu_2-2nb\,\nu_2+2n\,\nu_2^2\nu_4-\nu_4^2)$	*[a]
$\overline{\gamma}\wedge\overline{\gamma}$	$\frac{n^2-\nu b}{2b}\mathbf{X}^{(2)}$	$\frac{2b}{b-2}(n\overline{\gamma}-\nu\overline{\gamma^2})\wedge\mathbf{X}$	same	*
$\gamma\wedge\mathbf{X}$	$\frac{n(b-1)}{2b}\mathbf{X}^{(2)}$	$\overline{\gamma}\wedge\mathbf{X}$	$\frac{1}{b^3}[2n^2-b(b-2)\nu_2]$	0
$\overline{\gamma}\wedge\mathbf{X}$	0	$\overline{\gamma}\wedge\mathbf{X}$	same	0

[a]See text.

the diagonal and off-diagonal parts of **G** in the NSO basis, then $(\mathbf{G}_{od}^{NSO},\mathbf{G}_{d}^{NSO})=0$ and $\|G\|^2=\|\mathbf{G}_{d}^{NSO}\|^2+\|\mathbf{G}_{od}^{NSO}\|^2$. In addition, $(\mathbf{G}^{(2,\pi)},\mathbf{G}^{(2,\pi')})=0$ if $\pi'\neq\pi$. The diagonal elements of the Grassmann products are given in Table III.

If Γ and $\gamma\wedge\gamma$ are divided into components, then Δ and **V** will be similarly divided. The relevant relationships are obviously

$$\Delta^{(2,\pi)}=\Gamma^{(2,\pi)}-(\gamma\wedge\gamma)^{(2,\pi)},$$

$$\mathbf{V}^{(2,\pi)}=\Gamma^{(2,\pi)}-(\gamma\wedge\gamma)^{(2,\pi)}-\frac{b(b-1)}{2}(\gamma\wedge\mathbf{X})^{(2,\pi)} \quad (58)$$

for $\pi=0,1,2$. While readily evaluated, they do not appear to be expressible in a more condensed form,

From the definitions of Δ and **V**, $\mathbf{V}=\Delta-b\,\boldsymbol{\gamma}\wedge\mathbf{X}$ and it follows that $\|\mathbf{V}\|^2=\|\Delta\|^2+b^2\|\boldsymbol{\gamma}\wedge\mathbf{X}\|^2-2b(\Delta,\boldsymbol{\gamma}\wedge\mathbf{X})$. The norms are necessarily positive but the scalar product could have either sign. It will be shown, however, that $(\Delta,\boldsymbol{\gamma}\wedge\mathbf{X})$ is negative and thus that $\|\mathbf{V}\|>\|\Delta\|$. This means that adding a $\boldsymbol{\gamma}\wedge\mathbf{I}$ term does not improve the approximation to $\boldsymbol{\Gamma}$.

Theorem 8. The scalar product $(\Delta,\boldsymbol{\gamma}\wedge\mathbf{X})$ is negative.

Since all off-diagonal matrix elements of the Grassmann product are zero,

$$(\Delta,\boldsymbol{\gamma}\wedge\mathbf{X})=\sum_{j<k}\boldsymbol{\Gamma}_{\mathbf{jk},jk}(\boldsymbol{\gamma}\wedge\mathbf{X})_{jk,jk}$$

$$=2\sum_{j,k}\Delta_{jk}^{jk}(\boldsymbol{\gamma}\wedge\mathbf{X})_{jk}^{jk}$$

$$=2\sum_{j,k}\left[\boldsymbol{\Gamma}_{jk}^{jk}-\frac{1}{2}(\lambda_j+\lambda_k)\right]\frac{1}{2b}(\lambda_j+\lambda_k). \quad (59)$$

TABLE III. Diagonal matrix elements in NSO basis.

G	$G_{jk,jk}$
$\hat{\gamma}\wedge\hat{\gamma}$	$\lambda_j\lambda_k$
$\hat{\gamma}\wedge\hat{\gamma}$	$(\lambda_j-n/b)(\lambda_k-n/b)$
$\hat{\gamma}\wedge\mathbf{X}$	$(\lambda_j+\lambda_k)/(2b)$
$\hat{\overline{\gamma}}\wedge\mathbf{X}$	$(\lambda_j+\lambda_k)/(2b)-n/b^2$

Note that $\Sigma_k\Gamma_{jk}^{jk}=[(n-1)/2]\lambda_j$ in the NSO basis and similarly when j and k are interchanged, so

$$\sum_{j,k}\boldsymbol{\Gamma}_{jk}^{jk}(\lambda_j+\lambda_k)=(n-1)\sum_j\lambda_j^2 \quad (60)$$

and

$$(\Delta,\boldsymbol{\gamma}\wedge\mathbf{X})=\frac{1}{2}\sum_j\gamma_j^2-\frac{1}{2b}\left(\sum_j\lambda_j^2\sum_k\lambda_k+\sum_j\lambda_j\sum_k\lambda_k^2\right) \quad (61)$$

$$=\frac{1}{b}\left(\sum_j\lambda_j^2\right)(1-n), \quad (62)$$

which is clearly negative. ■

VI. DISCUSSION

Cumulants, Valdemoro correlation matrices, and reduction components provide different ways of dividing the two-electron reduced density matrix into contributions involving Grassmann products of one-electron matrices and a remainder. In this paper some relevant properties of the Grassmann products have been reported and the information they provide about Δ and **V** has been investigated.

The set of *n*-representable two-electron RDMs includes some that are Grassmann products, corresponding to single determinant wave functions. Since the Hartree-Fock single determinant is often a good initial approximation to the wave function, it can be expected that $\boldsymbol{\gamma}\wedge\boldsymbol{\gamma}$ might be a reasonable approximation to $\boldsymbol{\Gamma}$ and the two-electron cumulant Δ small. It has been shown by simple examples that $\boldsymbol{\gamma}\wedge\boldsymbol{\gamma}$ with $\boldsymbol{\gamma}$ the reduction of $\boldsymbol{\Gamma}$ is not necessarily the Grassmann product of a one-electron operator **f** with itself giving the largest fraction of $\boldsymbol{\Gamma}$ of this form.

The Valdemoro correlation matrix **V** involves the Grassmann product of $\boldsymbol{\gamma}$ with the unit matrix as well as with itself, and does not vanish in the single determinant case. It thus cannot be expected to provide a small correction to $\boldsymbol{\Gamma}$ in the same sense that Δ does. It has been shown here that the norm of **V** is always greater than that of Δ.

Since most interesting operators are independent of spin,

the spinless components of $\boldsymbol{\gamma}$ and $\boldsymbol{\Gamma}$ are also of interest. It is not surprising that the permutationally antisymmetric spatial component of $\boldsymbol{\gamma}\wedge\boldsymbol{\gamma}$ can be expressed as a linear combination of Grassmann products of the one-electron charge- and spin-density matrices with themselves. For any spin eigenstate with $M_S=0$, the spin-density matrix vanishes so that this spinless component has a simplicity like that of the case including spin. The permutationally symmetric spatial component of $\boldsymbol{\gamma}\wedge\boldsymbol{\gamma}$ can be expressed as a linear combination of symmetrized products analogous to the antisymmetrized, Grassmann product. Since $\boldsymbol{\Gamma}$ is also the sum of symmetric and antisymmetric parts, Δ and $\mathbf{V}$ will be similarly divided, and in the case of Δ corresponding components of $\boldsymbol{\gamma}\wedge\boldsymbol{\gamma}$ should normally provide reasonable first approximations.

Any density matrix is positive, in the matrix or operator sense, and the sets of density matrices and of *n*-representable reduced density matrices are convex. While $\boldsymbol{\gamma}\wedge\boldsymbol{\gamma}$ is positive, the set of such Grassmann products is not convex. A linear interpolation between two two-electron RDMs will give, on reduction, a similar linear interpolation between the corresponding one-electron RDMs, but $\boldsymbol{\gamma}\wedge\boldsymbol{\gamma}$ will follow a parabolic path in a two-dimensional subspace of the two-electron matrix space $\mathcal{E}_2$. As a consequence, Δ must also follow a nonlinear path.

Both Δ and $\mathbf{V}$ have been suggested to be the ''two-electron part'' of $\boldsymbol{\Gamma}$. An alternative characterization of the zero-, one-, and two-electron parts of Γ is based on invariant subspaces with respect to unitary transformations of the spin-orbital basis. The map from a subspace $\mathcal{E}_{2,\pi}$ of the two-electron matrix space to the corresponding subspace $\mathcal{E}_{1,\pi}$ of the one-electron matrix space is linear, so convexity is preserved. The components of the Grassmann products $\boldsymbol{\gamma}\wedge\gamma$ and $\boldsymbol{\gamma}\wedge\mathbf{X}$ in these subspaces have been determined. It is found that the nonlinear Grassmann product map from $\mathcal{E}_2$ to $\mathcal{E}_1$ does not preserve the reduction index (irreducible representation label) π. In particular, even $\overline{\boldsymbol{\gamma}}\wedge\overline{\boldsymbol{\gamma}}$, with $\overline{\boldsymbol{\gamma}}$ purely $\pi=1$, has components with $\pi=0$, 1, and 2.

It has been shown by a simple example that there are pure-state *n*-representable RDMs for which $\boldsymbol{\gamma}\wedge\boldsymbol{\gamma}$, Δ, and $\boldsymbol{\Gamma}$ are all proportional. This, as well as the fact that $\boldsymbol{\gamma}\wedge\boldsymbol{\gamma}$ is not in general the best Grassmann product approximation to $\boldsymbol{\Gamma}$, indicates that any discussion of the physical significance of the decomposition of $\boldsymbol{\Gamma}$ into pieces determined and not determined by $\boldsymbol{\gamma}$ must be based on considerations such as size consistency, or a perturbation series or other expansion of the wave function, and not on abstract properties of reduced density matrices and Grassmann products. Similarly, more exploration of the physical significance of $\mathbf{V}$ would be desirable.

The results presented in this paper are limited to the relationship between one- and two-electron RDMs. A similar analysis of Grassmann products, cumulants, and related quantities for three and four electrons will clearly be desirable but will require techniques in addition to those used here. Reduction behavior of the Grassmann products involved has been investigated [28].

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