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Approximating q-order reduced density matrices in terms of the lower-order ones. I. General relations

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The commutation-anticommutation relations of q-electron operators imply a set of N representability conditions [A. J. Coleman, Rev. Mod. Phys. **31**, 668 (1963)] for the corresponding q-order reduced density matrices (q-RDM) [C. Valdemoro, An. Fis. **79**, 95 (1983); in *Structure, Interaction and Reactivity*, edited by S. Fraga (Elsevier, Amsterdam, 1992)]. From these conditions, a general and closed-form relation is obtained here. In this equation the part involving RDM's has the same structure as that involving hole reduced density matrices. This relation is the basis of a method for approximating a q-RDM in terms of the r-RDM's [C. Valdemoro, Phys. Rev. A **45**, 4462 (1992)] with $r < q$. The derivation of this relation can be simplified significantly by employing a graph method which is described here. These graphs are in a one-to-one correspondence with the elements of the symmetric group of permutations.

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I. INTRODUCTION

Contracting a q-order reduced density matrix (q-RDM) into an r-RDM, where $q > r$, is a well-known and straightforward operation [1–6]. However, the information carried by the r-RDM is in general insufficient to determine the corresponding q-RDM in an unique way. Nevertheless, according to the central idea of the density-functional theorem [7–9] (DFT) the average local density $\rho(r)$ carries sufficient information about the ground state of the system to determine its energy. It is well known that the energy is the trace of the product of the reduced Hamiltonian [10–14] and the 2-RDM of the state of the system considered. Therefore, the DFT raises the question whether all the relevant information about the state of the system can be recovered from the 1-RDM. This question was studied in a previous work [15], where it was shown that from the knowledge of the 1-RDM an approximation to the 2-RDM could be obtained. This method was used for calculating the value of the energy of the three lower states of the beryllium atom, and it was found to be highly efficient.

The main purpose of this paper is to extend the results obtained in Ref. [15] to higher-order RDM's. Apart from its formal interest, a general algorithm for approximating a q-RDM from the knowledge of the r-RDM with $r < q$ may prove to be very useful. In particular, if good approximations to the 3-RDM and to the 4-RDM can be constructed from a 1-RDM and/or a 2-RDM, they can be used as initial data to build up a matrix representation of the contracted Schrödinger equation [16–21] (CSchE). In this way, the indeterminacy [20,22] of the CSchE can be removed [16] and it is reasonable to expect that by solving this new equation a better approximation to the exact 2-RDM can be obtained. This idea will be described in more detail in the following paper. Although the idea itself is straightforward, its practical implementation needs a careful study of the computational questions involved. This part of the study is still being developed.

The first step in attaining this practical aim is to derive the general relation linking the q-RDM with the q-order holes reduced density matrix (q-HRDM) in terms of the r-RDM's and r-HRDM's with $q > r$. This is needed in order to proceed in a similar way as in Ref. [15].

This paper is organized as follows. In Sec. II the notation, the basic relations, and the rules for a graphical representation are described. The 3-RDM N-representability conditions following from the anticommutation relation of 3-electron operators are derived in Sec. III. In this same section, the advantages of working with graphs which map the classes and operations of the symmetric group of permutations S_q are shown. Finally, the general and exact equation relating the q-HRDM with q-RDM in terms of the r-HRDM's and r-RDM's with $r < q$ is inferred from the lower-order relations (Sec. IV). In this general equation the part involving RDM's has the same structure as that involving HRDM's. In the following paper the relations reported here will be applied for approximating the 3-RDM and the 4-RDM in several test samples.

II. BASIC PROPERTIES OF THE REDUCED DENSITY MATRICES AND GRAPHICAL REPRESENTATION

A. Properties of the RDM's

When using a spin-free Hamiltonian operator it is advantageous to employ the following definition for the reduced density matrix of order q corresponding to a state $|\mathcal{L}\rangle$ of an N-electron system:

$$ {}^{q}D^{\mathcal{L}}_{i_1,i_2,\ldots,i_q;j_1,j_2,\ldots,j_q} = \frac{1}{q!} \langle \mathcal{L} | {}^{q}E^{i_1,i_2,\ldots,i_q}_{j_1,j_2,\ldots,j_q} | \mathcal{L} \rangle , \qquad (1) $$

where ${}^{q}E^{i_1,i_2,\ldots,i_q}_{j_1,j_2,\ldots,j_q}$ is the q-order replacement operator

(q −RO) [23–26] defined as

$$ {}^{q}E^{i_1,i_2,\dots,i_q}_{j_1,j_2,\dots,j_q} = \sum_{\sigma_1,\sigma_2,\dots,\sigma_q} b^{\dagger}_{i_1\sigma_1} b^{\dagger}_{i_2\sigma_2} \cdots b^{\dagger}_{i_q\sigma_q} b_{j_q\sigma_q} \times \cdots b_{j_2\sigma_2} b_{j_1\sigma_1} \; . \tag{2} $$

In relation (2) the indices i and j denote orbitals while $\sigma_1,\sigma_2,\dots,\sigma_q$ denote the spin functions.

Similarly, the holes reduced density matrices (q-HRDM) are defined as

$$ {}^{q}\bar{D}^{\mathcal{L}}_{j_1,j_2,\dots,j_q;i_1,i_2,\dots,i_q} = \frac{1}{q!} \langle \mathcal{L} | {}^{q}\bar{E}^{j_1,j_2,\dots,j_q}_{i_1,i_2,\dots,i_q} | \mathcal{L} \rangle \; , \tag{3} $$

where

$$ {}^{q}\bar{E}^{j_1,j_2,\dots,j_q}_{i_1,i_2,\dots,i_q} = \sum_{\sigma_1,\sigma_2,\dots,\sigma_q} b_{j_q\sigma_q} \cdots b_{j_2\sigma_2} b_{j_1\sigma_1} b^{\dagger}_{i_1\sigma_1} b^{\dagger}_{i_2\sigma_2} \times \cdots b^{\dagger}_{i_q\sigma_q} \tag{4} $$

is the q-order holes replacement operator (q-HRO).

An important property of these RO's is that they are invariant when an upper index and its corresponding lower index changes simultaneously their place in the list, e.g.,

$$ {}^{q}E^{i_1,i_2,\dots,i_q}_{j_1,j_2,\dots,j_q} \equiv {}^{q}E^{i_2,i_1,\dots,i_q}_{j_2,j_1,\dots,j_q} \equiv {}^{q}E^{i_1,i_q,\dots,i_2}_{j_1,j_q,\dots,j_2} \equiv \cdots \tag{5} $$

and this also holds for the q-HRO's.

As is well known the RDM's (as well as the HRDM's) are positive, semidefinite matrices and our trace, in our convention, has the value

$$ \mathrm{Tr}({}^{q}\underline{D}^{\mathcal{L}}) = \sum_{i_1,i_2,\dots,i_q} {}^{q}D^{\mathcal{L}}_{i_1,i_2,\dots,i_q;i_1,i_2,\dots,i_q} = \begin{bmatrix} N \\ q \end{bmatrix} . \tag{6} $$

In what follows, the monoelectronic subspace is assumed to be finite and spanned by K orbitals. It follows that the trace of the q-HRDM is obtained by replacing N by $2K - N$ in relation (6).

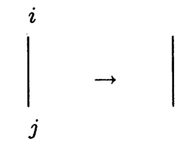
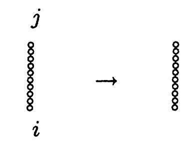
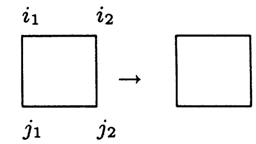
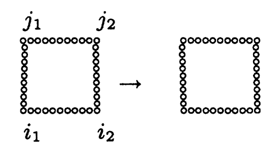
B. Graphical representation

A graphical method similar to that previously used [21,26] will be employed extensively in this work since it simplifies the algebraic derivations involving RO's in a significant way. The basic correspondences between the different operators and graphs are given in Table I.

Finally, each Krönecker δ function is represented by a *dotted line* and a product of n deltas is represented by a group of *n disjoint dotted lines.*

These graphs are very useful in order to visualize the structure of complicated algebraic expressions. Moreover, there are two kinds of operator multiplication which may be performed directly in graphical form. Namely, there is a general and simple graphical rule for multiplying two RO's [21,26] of arbitrary order and the same rule applies to multiply two HRO's. We have not yet been able to devise a general and sufficiently simple graphical rule for multiplying a p-RO and a q-HRO (or vice versa), which would complete the list of fundamental operations.

TABLE I. Graphs and operators correspondence.

Operators		Graphs
E^{i}_{j}	→	
$\bar{E}^{j}_{i}$	→	
${}^{2}E^{i_1 i_2}_{j_1 j_2}$	→	
${}^{2}\bar{E}^{j_1 j_2}_{i_1 i_2}$	→	

C. Graphical equations

Let us now consider the graph representations of two important relations.

(i) When using graphs, the fermion anticommutation relation

$$ \sum_{\sigma} [b_{j\sigma}, b^{\dagger}_{i\sigma}]_{+} = \bar{E}^{j}_{i} + E^{i}_{j} = 2\delta_{ij} \tag{7} $$

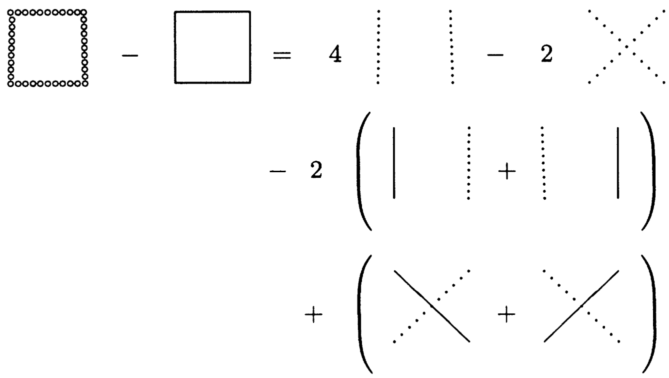
becomes

. (8)

(ii) The algebraic development of the commutation relation between pairs of fermion operators is already slightly long to write, thus

$$ \sum_{\sigma_1,\sigma_2} [b_{j_2\sigma_2} b_{j_1\sigma_1}, b^{\dagger}_{i_1\sigma_1} b^{\dagger}_{i_2\sigma_2}]_{-} = {}^{2}\bar{E}^{j_1 j_2}_{i_1 i_2} - {}^{2}E^{i_1 i_2}_{j_1 j_2} $$
$$ = 4\delta_{i_1 j_1}\delta_{i_2 j_2} - 2\delta_{i_1 j_2}\delta_{i_2 j_1} - 2(\delta_{i_2 j_2} E^{i_1}_{j_1} + \delta_{i_1 j_1} E^{i_2}_{j_2}) + (\delta_{i_1 j_2} E^{i_2}_{j_1} + \delta_{i_2 j_1} E^{i_1}_{j_2}) \; . \tag{9} $$

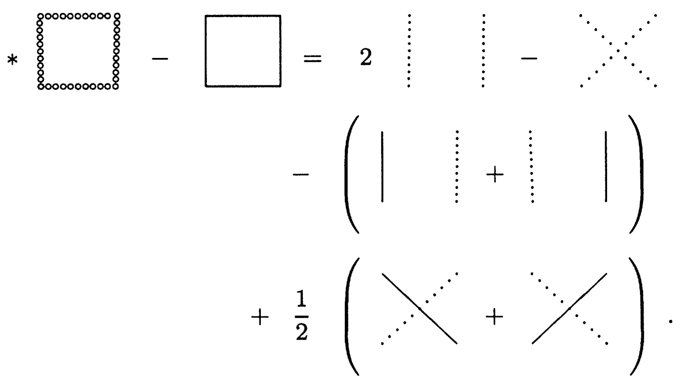
When the graph language is employed Eq. (9) becomes



(10)

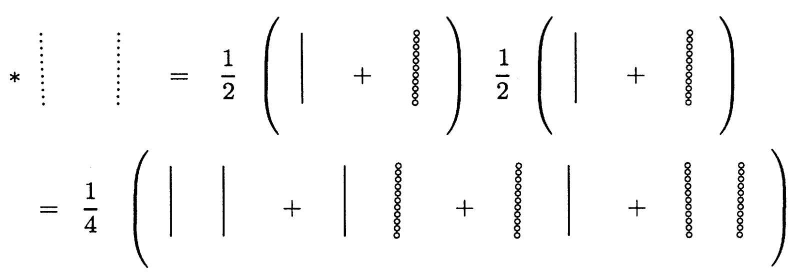
and the symmetry of the relation can be easily recognized.

Although operators and their corresponding expectation values are different concepts, the graphs just described are useful for representing both the RO's and the RDM's. To avoid confusion, an asterisk placed in front of a relation indicates that the relation concerns RDM's (and HRDM's). That is, the expectation value of the corresponding operator has been taken and the normalizing factor $1/q!$ has been applied. When these two operations have been performed relation (10) becomes



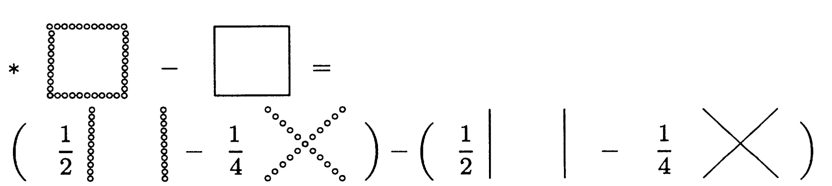
(11)

The mathematical form of relation (11) was transformed in Ref. [15] into an equivalent but more useful one, at least for our purpose, by replacing the value of the Krönecker δ functions by the expectation value of Eq. (8). The equation



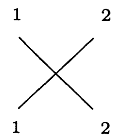
(12)

shows an example of how such a transformation can be performed graphically. When all the δ's in (11) have been replaced accordingly, it takes the following form:



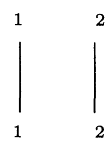
(13)

Note that in relations (11) and (13) the terms appearing on the right-hand side (rhs) can be associated with one of the two classes, each with a single operation, of the symmetric group S_2. This correspondence between graphs and the operations of the symmetric group of permutations can be easily seen. Indeed, let us number the points of the graph



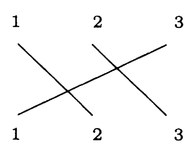
Let us now consider the upper point of index 1 and follow the line starting there. This line ends at the lower point of number 2; that is, 1 is changed into 2. The following step is to go to the upper number, i.e., to upper 2, and follow the line starting there. It ends at the lower point of number 1 and thus closes a cycle. The graph therefore maps the transposition (12) (expressed in standard cyclic notation [27,28]) and corresponds to class [2].

When the same procedure is applied to the graph,



the lines go from 1 to 1 and from 2 to 2, both closing a cycle. As a consequence, this graph maps the unit operation and corresponds to class $[1^2]$.

In the case of the more complex graph



the lines leading from 1 to 2, from 2 to 3, and from 3 to 1 close the cycle. Hence, this graph maps the permutation (123) corresponding to class [3] of S_3. (Note that the convention chosen in this work is that the lower indices are the ones which are permuted).

In Sec. III similar graph expressions linking the 3-RDM with the 3-HRDM will be given. These graphical relations will be used to obtain a general closed-form expression in Sec. IV.

It is interesting to note that the scheme of orbital indices appearing in the graph equation (13) is the familiar Coulomb and exchange one. This is due to the antisymmetry of the wave function or equivalently to the fermion statistics described by the anticommuting rules of fermion operators. Therefore, provided that the state function is antisymmetrical this equation will be fulfilled independently of the form of the state.

A particularly interesting case arises when the 1-RDM is diagonal (i.e., represented in its natural orbital basis). Indeed, when the off-diagonal elements of the 1-RDM are null, the matrix equation (13) has only the following nonvanishing elements:

$$\bar{D}_{ij,ij}-D_{ij,ij}=\left[\frac{\bar{d}_{ii}\bar{d}_{jj}}{2}-0\right]-\left[\frac{d_{ii}d_{jj}}{2}-0\right] \tag{14}$$

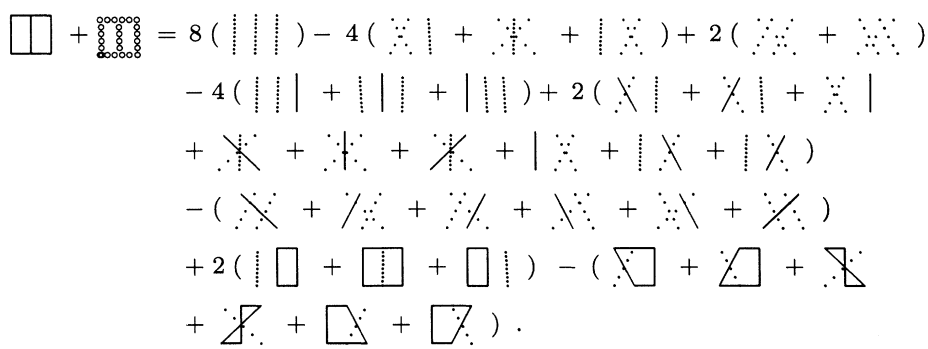
and

$$\bar{D}_{ij,ji}-D_{ij,ji}=\left[0-\frac{\bar{d}_{ii}\bar{d}_{jj}}{4}\right]-\left[0-\frac{d_{ii}d_{jj}}{4}\right] \tag{15}$$

independently of the quality of the state of reference considered, that is, of the quality of the 1-RDM.

III. THE EQUATION LINKING THE 3-RDM WITH THE 3-HRDM

The graph form of the relation linking the 3-RO and the 3-HRO may be obtained by anticommuting three fermion annihilators with three fermion creators and by replacing the algebraic symbols in this relation by the corresponding graphs. The result is



(16)

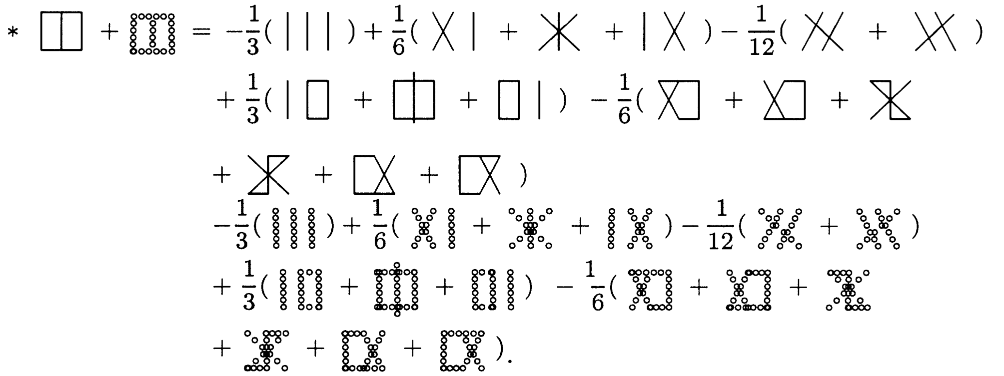
Let us analyze the structure of the right-hand side of relation (16). Observe that there are graphs including three, two, or one δ functions. Grouping the graphs having the same number of Krönecker δ functions into one set, three different sets are obtained. These sets may be classified according to the order of the RO's as, none, 1-RO, and 2-RO, since the sum of the number of δ functions and the order of the RO's must be three. Considering now, either the three-δ (no RO) set or the two-δ (1-RO) set, it can be seen that the graphs map the operations of the symmetric group S_3 and graphs belonging to the same class have the same coefficients. It should be noted that the product of two Krönecker δ functions and an operator gives rise to a number of graphs which may be considered as degenerate since they arise from the same topological graph but any of the lines may represent the operator. The same effect is encountered when taking the product of a Krönecker δ function and a 2-RO. Indeed, this happens whenever the graph represents a product of symbols of different nature.

It may seem puzzling that the single δ set has only two classes of graphs ($[1^3]$ and $[2,1]$) and that some terms corresponding to the class $[2,1]$ do not appear in Eq. (16). The explanation can be found from the analysis of the missing terms,

(17)

The first of these graphs represents $\delta_{i_3 j_3}\,{}^2E^{i_1 i_2}_{j_2 j_1}$. By comparing it with the 3-RO operator ${}^3E^{i_1 i_2 i_3}_{j_1 j_2 j_3}$, from which it must arise, one sees that there is an incorrect matching of the spin variables on which the sum is performed. Therefore, this term must be a forbidden one. The same mismatching of spin variables can be found in the other missing terms. This point will be discussed in more detail below.

Let us now take the expectation value of Eq. (16) in order to obtain the relation linking the 3-RDM to the 3-HRDM. By replacing the δ functions according to relation (8) one does not yet obtain an expression in which the hole part has the same structure as the particle one. Indeed, mixed particle and hole terms do appear. Nevertheless, when the value of the 2-RDM is replaced, according to relation (13), in the terms which are the products of a 1-HRDM element and a 2-RDM element, the following final expression is obtained:



(18)

Equation (18) shows clearly that, similarly to the two-electron case [15], the particle graphs have a symmetric counterpart in the hole graphs (the coefficients, the graphs symmetry, and the number of graphs are the same in the hole part of the equation as in the particle one). Let us examine how the structure of this equation can be classified according to the S_3 group. As the holes part is similar to the particles part, only this part will be considered. Two main type of graphs may be distinguished.

(i) The graphs involving a product of three 1-RDM elements which map the classes $[1^3]$, $[2,1]$, and $[3]$ with the coefficients $-\frac{1}{3}, \frac{1}{6}$, and $-\frac{1}{12}$, respectively.

(ii) The graphs involving the product of a 1-RDM element and a 2-RDM element. Here class [3] is spin-forbidden and the two other classes have coefficients with opposite signs but with the same absolute value as in the previous case. Since a 2-RDM element may, in principle, involve any of the three possible pairs formed with the supraindices and any of the three possible pairs of the subindices, a structural degeneracy follows and the number of terms increases accordingly.

IV. THE GENERAL CASE

The cases $q=2$ (Sec. II), $q=3$ just described, and $q=4$ (which is not given here) can be generalized to any value of q. Thus, from these particular cases it can be inferred that the addition or subtraction of the q-RDM to or from q-HRDM (for q odd or even) will give rise to an equation which can be exactly expressed in terms of the r-RDM's and r-HRDM's with $r=1,\ldots,q-1$. Moreover, in this expression the holes part will have the same form as the particles one.

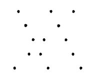
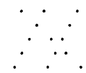
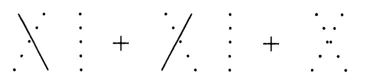
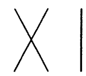
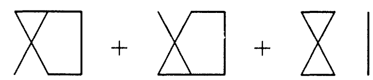
The derivation of the general expression may be decomposed into the two following steps.

(1) The derivation of the anticommutation-commutation relations of q-electron operators, whose expectation value generates the equation linking the q-RDM and the q-HRDM in terms of Krönecker δ functions and r-RDM's with $r<q$.

(2) The Krönecker δ functions are replaced by their values given in terms of the 1-RDM and the 1-HRDM. Then, the expression thus obtained is transformed by using lower-order equations into the final equation where the part involving HRDM's has the same structure as that involving the RDM's.

In order to express the equations resulting from steps 1 and 2 in a compact form, it is useful to introduce two new symbols, ${}^qG^{i}_{\hat{P}_{C_q}}$ and ${}^q\mathcal{F}^{i}_{\hat{P}_{C_q}}$. These symbols are associated with a graph or in most cases with a sum of graphs. The meaning of these symbols is described in detail in the fol-

TABLE II. Graphs and symbols correspondence.

Symbols		Graphs
${}^{3}G^{0}_{(123)} \equiv {}^{3}G^{0}_{(12)(23)}$	$\rightarrow$	* 
${}^{3}G^{0}_{(132)} \equiv {}^{3}G^{0}_{(13)(23)}$	$\rightarrow$	* 
${}^{3}G^{1}_{(12)}$	$\rightarrow$	* 
${}^{3}\mathcal{F}^{0}_{(12)}$	$\rightarrow$	* 
${}^{3}\mathcal{F}^{2}_{(12)}$	$\rightarrow$	* 

lowing subsections and may become clear by examining the examples given in Table II.

As can be observed the graphs involving Krönecker δ functions are denoted by the letter G, while those which are products of RDM elements correspond to the symbol $\mathcal{F}$. The asterisk placed in front of the graphs has the same meaning as previously, i.e., the symbols G and $\mathcal{F}$ represent RDM terms, not operators. Note that the last diagram of ${}^{3}\mathcal{F}^{0}_{(12)}$ is spin forbidden.

A. The general anticommutation-commutation relation

Let us start by considering the first two lines in Table II. According to our notation, the general order of the term (q) is given by a left-side superscript, i.e., ${}^{3}G$. The right-side superscript (i) indicates the order of the RDM appearing in the term. Since these two particular examples involve only Krönecker δ functions, the order i of the RDM must be zero. The lower index, which generically is denoted $\hat{P}_{C_q}$, represents the permutation ($\hat{P}$) of the indices belonging to class (C_q) of the group S_q. Thus, the permutations applied to the lower indices in these examples are the two different permutations belonging to class [3] of the S_3 group.

The third line of Table II shows a slightly more complex case. As before, the general order of the term is three but here, the right-side superscript specifies that the term involves a 1-RDM element [consequently it involves (3-1) δ functions]. As has already been discussed, the line representing the 1-RDM may be any one of the three graph lines and hence three graphs appear in this term.

Using this notation the general expression for $q>1$ may be written as

$$
{}^{q}\bar{D}_{i_1 i_2,\ldots,i_q;j_1 j_2,\ldots,j_q} \pm {}^{q}D_{i_1 i_2,\ldots,i_q;j_1 j_2,\ldots,j_q} = \frac{2^q}{q!}\left[\sum_{i=0}^{q-1}(-1)^i\left[\frac{i!}{2^i}\right]\sum_{C_q}\Gamma_{C_q}\sum_{\hat{P}_{C_q}}{}^{q}G^{i}_{\hat{P}_{C_q}}\right], \tag{19}
$$

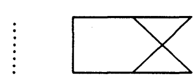
where

$$
\Gamma_{C_q} = (-1)^{p_{C_q}}\left[\frac{1}{2^{p_{C_q}}}\right]. \tag{20}
$$

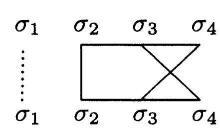
The index p_{C_q} denotes the parity of the permutations belonging to class C_q (i.e., their resolution in terms of transpositions).

Thus, in the general case this addition or subtraction is partitioned into terms with q δ functions, terms with $q-1$ δ functions and an element of the 1-RDM, terms with $q-2$ δ functions and an element of the 2-RDM, ..., terms with a single δ function and an element of the $(q-1)$-RDM. It can be observed that for an even q (therefore, the equation derives from a commutator), the sign of the left-hand side (lhs) of relation (19) is negative. In this case, the highest value of i is odd and then the last value of the factor $(-1)^i$ appearing in the rhs is negative. For an odd q (the equation derives from an anticommutator) the sign of the lhs is positive and that of the rhs factor $(-1)^i$ for the highest value of i is positive.

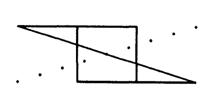
It must be stressed that relation (19) includes the spin-forbidden terms which must be removed from it. This can be done easily by analyzing the graph structure. Let us consider an example in detail,

 $\equiv \delta_{i_1 j_1}\,{}^{3}D^{i_2 i_3 i_4}_{j_2 j_4 j_3}$

The spin variables associated to this graph are



Since in the 3-RO generating the 3-RDM element appearing in this term the upper and lower spin indices should be ordered in the same way and they are permuted, this term is forbidden. Let us now consider



Here, the spin mismatching is only apparent because the δ requires that σ_1 and σ_4 be equal and therefore the 3-RDM element has the right order of spins. As a consequence, this term is allowed.

The need to remove the spin-forbidden terms from (19) complicates slightly the procedure since, with the exception of the 1-RDM graphs, all the other graphs should be analyzed. Fortunately, only a simple inspection of the graph is required. Indeed, one must just consider the i-RDM lines of a graph (for $i>1$) and verify that the partners of the vertices joined by an oblique line do not take part in the i-RDM graph (which is only a part of the complete graph).

The application to the case $q=4$ of Eq. (19) is given in the Appendix.

B. Transformation of Eq. (19)

In Table II two examples of the new symbol ${}^q\mathcal{F}^i_{\hat{P}_{C_q}}$ are given. These symbols represent the sum of products of $(q-i)$ 1-RDM elements and an element of the i-RDM. The graphs represented by this symbol are associated with the permutation $\hat{P}_{C_q}$ (belong to class C_q of the S_q group).

Having replaced the Krönecker δ functions by Eq. (8) in relation (19), the mixed holes-particles products can be eliminated by substituting the 2-RDM elements, the 3-RDM elements, . . . , the $(q-1)$-RDM elements by their values deduced from the lower-order equations in which no δ functions appear. In the resulting expression the form of the holes part is the same as that of the particle part (i.e., the holes part has the same coefficients with the same or opposite sign depending on whether q is odd or even, and the same symmetry of the graphs as those in the particle part). Although up to $q=4$ it is still simple to perform all the graphical operations, for higher orders it is more convenient to use the generalized closed-form expression which may be inferred from the four lower-order cases,

$$
\begin{aligned}
{}^qD_{i_1i_2,\ldots,i_q;j_1j_2,\ldots,j_q} \pm {}^q\bar{D}_{i_1i_2,\ldots,i_q;j_1j_2,\ldots,j_q} = (-1)^q \left[\frac{q-1}{q!}\right] \sum_{C_q} \Gamma_{C_q} \sum_{\hat{P}_{C_q}} {}^q\mathcal{F}^0_{\hat{P}_{C_q}} \\
+\sum_{i=2}^{q-1}(-1)^{q-i+1}\left[\frac{i!}{q!}\right]\sum_{C_q}\Gamma_{C_q}\sum_{\hat{P}_{C_q}}{}^q\mathcal{F}^i_{\hat{P}_{C_q}} \pm (\text{hole part}) \, . \qquad (21)
\end{aligned}
$$

The spin-forbidden terms must be eliminated from (21). This can be done in the same way as Eq. (19) but now the 1-RDM elements assume the role that is played by the δ functions in Eq. (19). The "hole part" is a sum of terms which are identical to the particle one [given explicitly in (21)] except that each q $-$RDM element is replaced by a q-HRDM one. The application of Eq. (21) to the case $q=4$ is given in the Appendix.

In Ref. [15] the formal similarity of the holes and the particle parts was studied for $q=2$ and exploited in order to approximate the 2-RDM when knowing the 1-RDM. The discussion on how Eq. (21), which after removal of the spin-forbidden terms is exact, may be used to approximate higher-order RDM matrices is the subject of the following paper.

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APPENDIX: DERIVATION OF FOURTH-ORDER RELATIONS

Table III summarizes the most relevant information for our purposes about the symmetric group S_4 and the values of the coefficients Γ_{C_4}. By taking into account the data given in this table, it is now an easy matter to obtain the fourth-order relations according to (19) and (21).

Let us consider the commutation relation of the four-electron operators or equivalently its expectation value divided by 4!. According to (19) it can be expressed as (only the terms corresponding to the first permutation of

TABLE III. Classes, parities, and permutations of the symmetric S_4 group. The coefficients Γ_{C_4} are also given.

C_4	p_{C_4}	$\hat{P}_{C_4}$	Γ_{C_4}
$[1^4]$	0	e	1
$[2,1^2]$	1	(12), (13), (14), (23), (24), (34)	$-\frac{1}{2}$
$[2^2]$	2	(12)(34), (13)(24), (14)(23)	$\frac{1}{4}$
$[3,1]$	2	(12)(23), (13)(23), (12)(24) (14)(24), (13)(34), (14)(34), (23)(34), (24)(34)	$\frac{1}{4}$
$[4]$	3	(12)(23)(34), (12)(24)(34), (13)(23)(24), (13)(34)(24), (14)(24)(23), (14)(34)(23)	$-\frac{1}{8}$

each class are shown)

$$\begin{aligned}
&{}^4\bar{D}_{i_1i_2i_3i_4;j_1j_2j_3j_4} - {}^4D_{i_1i_2i_3i_4;j_1j_2j_3j_4} \\
&\quad = +\tfrac{2}{3}{}^4G_e^0 - \tfrac{1}{3}({}^4G^0_{(12)} + \cdots) + \tfrac{1}{6}({}^4G^0_{(12)(34)} + \cdots) + \tfrac{1}{6}({}^4G^0_{(12)(23)} + \cdots) - \tfrac{1}{12}({}^4G^0_{(12)(23)(34)} + \cdots) \\
&\qquad - \tfrac{1}{3}{}^4G_e^1 + \tfrac{1}{6}({}^4G^1_{(12)} + \cdots) - \tfrac{1}{12}({}^4G^1_{(12)(34)} + \cdots) - \tfrac{1}{12}({}^4G^1_{(12)(23)} + \cdots) + \tfrac{1}{24}({}^4G^1_{(12)(23)(34)} + \cdots) \\
&\qquad + \tfrac{1}{3}{}^4G_e^2 - \tfrac{1}{6}({}^4G^2_{(12)} + \cdots) + \tfrac{1}{12}({}^4G^2_{(12)(34)} + \cdots) + \tfrac{1}{12}({}^4G^2_{(12)(23)} + \cdots) \\
&\qquad - \tfrac{1}{2}{}^4G_e^3 + \tfrac{1}{4}({}^4G^3_{(12)} + \cdots) , \qquad\qquad (\mathrm{A1})
\end{aligned}$$

where the symbols G have been explicitly written.

Finally, let us consider the equation relating the 4-HRDM and the 4-RDM where the terms involving HRDM elements have a symmetric counterpart in the terms involving RDM elements. According to (21) it can be expressed as (only the particle terms corresponding to the first permutation of each class are developed)

$$\begin{aligned}
&{}^4D_{i_1i_2i_3i_4;j_1j_2j_3j_4} - {}^4\bar{D}_{i_1i_2i_3i_4;j_1j_2j_3j_4} \\
&\quad = +\tfrac{1}{8}{}^4\mathcal{F}_e^0 - \tfrac{1}{16}({}^4\mathcal{F}^0_{(12)} + \cdots) + \tfrac{1}{32}({}^4\mathcal{F}^0_{(12)(34)} + \cdots) + \tfrac{1}{32}({}^4\mathcal{F}^0_{(12)(23)} + \ldots) - \tfrac{1}{64}({}^4\mathcal{F}^0_{(12)(23)(34)} + \cdots) \\
&\qquad - \tfrac{1}{12}{}^4\mathcal{F}_e^2 + \tfrac{1}{24}({}^4\mathcal{F}^2_{(12)} + \cdots) - \tfrac{1}{48}({}^4\mathcal{F}^2_{(12)(34)} + \cdots) - \tfrac{1}{48}({}^4\mathcal{F}^2_{(12)(23)} + \cdots) \\
&\qquad + \tfrac{1}{4}{}^4\mathcal{F}_e^3 - \tfrac{1}{8}({}^4\mathcal{F}^3_{(12)} + \cdots) - (\text{hole part}) . \qquad\qquad (\mathrm{A2})
\end{aligned}$$

When the structure of the permutations becomes complicated and the order of the RDM's is large, the number of spin-forbidden terms increases appreciably. It can be shown that in this example all the 2-RDM terms of the class [4] and all the 3-RDM terms of the classes [2^2], [3,1], and [4] are spin forbidden. These spin-forbidden classes have been omitted in (A1) and (A2). In the remaining classes some of the terms are also spin forbidden and therefore the corresponding graphs must be analyzed and spin-forbidden terms must also be eliminated.

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