Theoretical and Applicative Properties of the Correlation and *G*-Particle-Hole Matrices

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Received 27 October 2008; accepted 5 December 2008
Published online 14 April 2009 in Wiley InterScience (www.interscience.wiley.com).
DOI 10.1002/qua.22042

ABSTRACT: We have recently (Valdemoro et al., Sixth International Congress of the International Society for Theoretical Chemical Physics, 2008; Alcoba et al., Int J Quantum Chem, in press) reported the form of the *G*-particle-hole hypervirial equation, which can be identified with the anti-Hermitian part of the correlation contracted Schrödinger equation (Alcoba, Phys Rev A, 2002, 65, 032519), as a tool to obtain the second-order reduced density matrix of an *N*-electron system without previous knowledge of the wave-function. The results which have been obtained when solving the *G*-particle-hole hypervirial equation with an iterative method also described in (Valdemoro et al., Sixth International Congress of the International Society for Theoretical Chemical Physics, 2008; Alcoba et al., Int J Quantum Chem, in press) have been highly accurate. The convergence of these test calculations has been very smooth, though rather slow. One of the factors which determines the performance of the method is the accuracy with which the 3-order correlation matrices (3-CM) involved in the calculations are approximated. It is, therefore, necessary to optimize to the utmost the construction algorithms of these 3-order matrices in terms of the 2-CM. In this article, the main theoretical features of the *p*-CM are described. Also, some aspects of the correlation contracted Schrödinger equation and of the *G*-particle-hole hypervirial equation are revisited. A new theorem, concerning the sufficiency of the hypervirial of the 3-order correlation operator to guarantee a correspondence between its solution and that of the Schrödinger equation, and some preliminary results concerning the constructing algorithms of the 3-CM in terms of the 2-CM, are reported in the second part of this article. Int J Quantum Chem 109: 2622–2638, 2009

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Key words: correlation matrix; *G*-matrix, reduced density matrix; electronic correlation effects; contracted Schrödinger equation; anti-hermitian contracted Schrödinger equation; hypervirial of the *G*-matrix

1. Introduction

The direct search for the second-order reduced density matrix (2-RDM) corresponding to a given state of a N-electron system, without a previous determination of the corresponding wave function, has motivated a great deal of work. This line of research started more than 50 years ago with the seminal papers of Husimi [1], Löwdin [2], Ayres [3], and McWeeny [4]. In the sixties, several important results among which are the two outstanding contributions by Coleman [5] on the N-representability problem and the Garrod and Percus study on the so-called G-matrix [6] were published. The interested reader may find a comprehensive bibliography in the books by Davidson [7] and by Coleman and Yukalov [8] as well as in several excellent reviews [9–11] and, particularly, in the collective volume recently edited by Mazziotti [12] on the RDM theory.

In late years, important theoretical and applicative reports have shown that obtaining accurate results by looking directly for the 2-RDM is at present possible. One of these developments is based on the integro-differential equation, proposed in 1976 by Nakatsuji [13] and by Cohen and Frishberg [14]. A matrix equation, represented in the two-electron space and equivalent to these authors' integro-differential equation was reported later on [15]. This matrix equation was obtained by applying Valdemoro's matrix-contracting mapping [15–17] to the matrix representation of the Schrödinger equation (SE), to obtain its contracted form in the 2-electron space. In view of its derivation procedure, this equation was called contracted Schrödinger equation (2-CSE).

In 1976, Nakatsuji [13] reported an important property of his density equation which was later on confirmed in its matrix form by Mazziotti [18]. Thus, these authors proved that the 2-RDM which solves the 2-CSE equation coincides with that which would be obtained by integrating the N-electron density matrix over (N-2) electron variables. The drawback of this equation is that, besides its dependence on the 2-RDM, it is also an averaged function of the 3- and 4-RDMs, which renders it operationally indeterminate. A way out of this difficulty was to approximate the high-order RDMs in terms of the lower ones. Thus, Valdemoro's method for approximating the 2-RDM in terms of the 1-RDM [19] was generalized [20] so as to obtain the algorithms for constructing the 3- and the 4-RDM elements appearing in the 2-CSE. By proceeding in this way Colmenero and Valdemoro solved iteratively the 2-CSE in 1994 [21]. In the following years, the constructing algorithms, as well as the iterative solution procedure, underwent important optimizations, mostly through the work of the groups headed by Nakatsuji and coworkers [22–24], Mazziotti [18, 25, 26] and Valdemoro and coworkers [27–34].

Recently, two important theoretical and applicative developments, closely connected to the 2-CSE, have been reported. Thus, Mazziotti [35, 36] proposed a method for solving the antihermitian part of the 2-CSE, the ACSE, which can be identified with the diagonal hypervirial of the 2-order density operator. An important feature of this method is that, contrary to the 2-CSE, it preserves the N-representability structure of the 2-RDM throughout the iterative process applied to solve the ACSE [34–37]. Another advantage of this equation is that it only involves 2- and 3-RDM elements because, when obtaining the anti-Hemitian part of the 2-CSE, the 4-RDM contribution cancels out. These two highly simplifying facts render this method very attractive . The other advance in this line of research is still more recent and concerns the hypervirial of the 2-order correlation operator or, equivalently, the G-particle-hole hypervirial equation (GHV) [38]. This equation can be identified with the antihermitian part of the 2-order correlation contracted Schrödinger equation (CCSE) [39]. The CCSE results from the application of a correlation contracting mapping to the matrix representation of the SE [38]. In 2002, Alcoba [39] demonstrated that a similar theorem to Nakatsuji's one for the 2-CSE is satisfied by the CCSE solution. Recently, a generalization of Mazziotti's method for solving the ACSE has been used for solving the GHV with very good results [38, 40]. Moreover, it has been shown that the hypervirial of the 2-order correlation operator originates an equation which, while retaining the main advantages of the ACSE, implies that a set of more demanding conditions are satisfied by its solution [38].

In the CCSE and GHV methodologies the correlation matrices (CM) [28, 30, 32, 34, 37–39, 41–49] or,

equivalently, the G-matrices play a central role similar to that played by the RDMs in the 2-CSE and ACSE theories.

To provide a clear outlook of the theory on which these developments are based as well as on the newly introduced concepts which are not yet familiar to most Quantum Chemists, the first part of this work is dedicated to describe the theoretical background which will be needed later on. Thus, it is shown in the following section how apparently abstract and complicated results follow easily from the application of the basic second quantization relations. The RDM's N-representability properties, the interconnection of the RDMs and the corresponding CMs, as well as the properties of these latter matrices, are also described in Section 2. Some aspects of the CCSE and of the GHV methodologies [38] are revisited in Section 3. A new relevant theorem, concerning the sufficiency of the 3-order GHV to guarantee a correspondence between its solution and that of the SE, is also reported in this section.

One of the critical questions which is a determining factor when optimizing the GHV method so as to render it competitive with other ab-initio approaches is the need for a set of sufficiently accurate algorithms for constructing the 3-order correlation matrices (3-CM) in terms of the 2-CM. Until now, and as a provisional solution, the 3-CM elements were evaluated indirectly [38] in terms of an approximated 3-order cumulant [28, 31–34, 37]. At present, to improve both the method accuracy as well as its performance rate, we deem necessary—although we realize that it is a complex and difficult task—to change the strategy used previously for constructing the different GHV terms and to attempt to evaluate directly the 3-CM in terms of the 2-CM.

At present, we can only claim to have achieved part of this task. Thus, we have started by limiting our study to evaluate the elements of the 3-CM spin-blocks with highest/lowest spin projection $\left(M_s = \pm\frac{3}{2}\right)$. Moreover, although the results are very encouraging, there are a few 3-CM elements where the accuracy must still be improved. In Section 4, we report those algorithms which we consider reliable and discuss the problems which are still under study. A significant sample of these algorithms performance is given here. The analysis of the results accuracy is carried out by having as reference the set of exact 3-CM elements obtained in a full configuration interaction (FCI) calculation of the ground-state of the BeH_2 linear molecule. Finally, in the Appendix, a summary of the graphs, which we find very helpful and which we currently use in this line of research, is given.

2. Theoretical Background

In this section, an extended self-contained account of the main concepts which are at the base of the CCSE and GHV methodologies is given.

In our notation, the symbol N denotes the number of electrons of the system under study, and K is the finite number of real orthonormal orbitals of the one-electron basis set. Although, later on, when an explicit distinction of the spin-functions will be needed, the notation will change; here we will use the small latin letters to denote each of the different $2K$ spin-orbitals.

Let us now start by recalling the definitions of the basic matrices which are at the center of our theoretical developments. A p-order reduced density matrix (p-RDM) corresponding to an N-electron state Ψ [1–4], is defined, in the occupation number representation of second quantization, as:

$$
\begin{aligned}
{}^{p}\mathrm{D}_{i_1 i_2..i_p;j_1 j_2..j_p} &= \frac{1}{p!}\left\langle \Psi \left| a^{\dagger}_{i_1} a^{\dagger}_{i_2} \ldots . a^{\dagger}_{i_p} a_{j_p} \ldots . a_{j_2} a_{j_1} \right| \Psi \right\rangle \\
&\equiv \frac{1}{p!}\langle \Psi | {}^{p}\hat{\Gamma}_{i_1 i_2..i_p;j_1 j_2..j_p} | \Psi \rangle \qquad (1)
\end{aligned}
$$

where ${}^{p}\hat{\Gamma}$ is the p-electron density operator.

The properties of the p-RDM are generically called N-representability properties. The N-representability of a p-order matrix is an important concept defined in 1963 by John Coleman [5]. The properties (or conditions) that a p-order matrix must satisfy in order to be able to state that there exists an N-electron wave-function from which this p-matrix may be derived, by integrating over the variables of $N - p$ electrons, are called N-representability properties, or conditions, of a p-RDM. Thus, any p-order matrix must be N-representable if it is to be considered to be a p-RDM. We will now consider the main N-representability properties of the lower-order RDMs and inter-related matrices. More information about the 2-RDM theory and its methodology may be found in [7–12].

2.1. BASIC *N*-REPRESENTABILITY PROPERTIES OF THE TWO LOWER ORDER RDMs

In this paragraph a series of very well-known formulae are given explicitly, not because we assume

that the reader ignores them, but because we wish to stress that these simple relations are at the base of many subtle and not obvious developments which are later reported.

From the properties of the fermion operators, as well as from the definition of the *bra* and *ket* which appear in (1), one deduces that a *p*-RDM must be a Hermitian positive semi-definite matrix. Therefore, at the base of a *p*-RDM *N*-representability properties lies the fermion operators algebra. Two main types of operations can be distinguished in the fermion operators algebra. The anticommutator of two fermion operators and the sum relations describing that there is a finite number of electrons *N* in the system considered and that when the one-electron basis set is finite (as mentioned earlier), there is also a finite number of *holes* with respect to the bare vacuum. There are very good books [50–52], Quantum-Chemistry oriented, where the second quantization language and techniques are described in detail. However, to be self-contained, we are recalling here the five basic fermion relations which are repeatedly used in our developments:

$$\left[a_i^\dagger, a_j\right]_+ = \delta_{i,j} \tag{2}$$

where $\delta_{i,j}$ stands for the Krönecker delta,

$$\left[a_i^\dagger, a_j^\dagger\right]_+ = 0 = [a_i, a_j]_+, \tag{3}$$

$$\hat{N} = \sum_i^{2K} a_i^\dagger a_i, \tag{4}$$

and

$$(2K - \hat{N}) = \sum_i^{2K} a_i a_i^\dagger. \tag{5}$$

These basic operations determine, directly or indirectly, most of the RDM properties. The other basic relation, which plays a relevant role in RDM and CM theory is:

$$\hat{I} = |\Psi\rangle\langle\Psi| + \hat{\mathcal{Q}} \tag{6}$$

where Ψ is the N-electron state in which we are interested, $|\Psi\rangle\langle\Psi|$ is the projector operator into this state subspace, and $\hat{\mathcal{Q}}$ is the complementary projector operator corresponding to the states orthogonal to Ψ.

Let us now see which are the direct implications of the relations just given when considering specifically the 1-, 2-, and 3-RDMs.

2.1.1. 1-RDM and the First-Order Fermion Relation

When taking the expectation value of Eq. (2) one obtains:

$${}^1\mathrm{D}_{i;j} + {}^1\bar{\mathrm{D}}_{i;j} = \delta_{i,j} \tag{7}$$

where ${}^1\bar{\mathrm{D}}_{i;j} = \langle\Psi|a_j a_i^\dagger|\Psi\rangle$ is the $(i;j)$ element of the first-order *hole*-RDM (1-HRDM). Since the 1-RDM as well as the 1-HRDM are positive semi-definite matrices, relation (7) tells us that both the 1-RDM and 1-HRDM eigenvalues are constrained to lie between 0 and 1. This is a very important ensemble *N*-representability condition reported by Coleman [5]. Also, when taking the expectation value of (4) and of (5) one obtains the trace of the 1-RDM

$$N = \sum_i \left\langle \Psi \left| a_i^\dagger a_i \right| \Psi \right\rangle \equiv tr({}^1\underline{\mathrm{D}}) \tag{8}$$

and of the 1-HRDM

$$(2K - N) = \sum_i \left\langle \Psi \left| a_i a_i^\dagger \right| \Psi \right\rangle \equiv tr({}^1\underline{\bar{\mathrm{D}}}) \tag{9}$$

respectively.

2.1.2. The 2-RDM and the Second-Order Fermion Relation

The so-called D *N*-representability condition [5, 6, 53, 54] states that the 2-RDM is a positive semi-definite matrix. Another basic property of the 2-RDM is that when permuting two indices, either of column or row labels, the sign of the element changes. Obviously, this property follows from relation (3). Let us now reorder the string of operators $a_{i_1}^\dagger a_{i_2}^\dagger a_{j_2} a_{j_1}$, which defines the 2-order density operator ${}^2\hat{\Gamma}_{i_1 i_2; j_1 j_2}$, into the ordering $a_{j_2} a_{j_1} a_{i_1}^\dagger a_{i_2}^\dagger$, which is the 2-order *hole*-density operator ${}^2\hat{\bar{\Gamma}}_{i_1 i_2; j_1 j_2}$, through a repeated application of (2). The expectation value of this last chain of operators is 2! times the value of an element of the 2-HRDM.

When taking the expectation value of the relation resulting from the reordering just described, one obtains the second-order fermion relation which interrelates the 1-RDM, the 2-RDM, and the 2-HRDM,

$$2!\,{}^2\bar{\mathrm{D}}_{i_1 i_2; j_1 j_2} - 2!\,{}^2\mathrm{D}_{i_1 i_2; j_1 j_2} = \delta_{i_1, j_1} \wedge \delta_{i_2, j_2} - \delta_{i_1, j_1} \wedge {}^1\mathrm{D}_{i_2, j_2} \tag{10}$$

where the symbol $\wedge$ denotes a Grassman, or antisymmetrized product [18, 55], of the terms linked by it. The 2-HRDM is also a positive semi-definite matrix: this is the so-called QN-representability condition [5, 6, 53, 54] which can be derived from (10) when knowing the 2-RDM.

2.1.3. The 2-RDM and 2-HRDM Contractions

Let us consider now the 2-RDM and 2-HRDM properties which follow respectively from relations (4) and (5). Thus, because of relation (4) one first obtains the 1-RDM

$$2!\sum_i {}^2\mathrm{D}_{mi;li} = \sum_i \left\langle \Psi \left| a_m^\dagger a_i^\dagger a_i a_l \right| \Psi \right\rangle = {}^1\mathrm{D}_{m;l}(N-1) \tag{11}$$

and, contracting a second time, one obtains the 2-RDM trace

$$2!\sum_{i,m} {}^2\mathrm{D}_{mi;mi} = \sum_{i,m} \left\langle \Psi \left| a_m^\dagger a_i^\dagger a_i a_m \right| \Psi \right\rangle = 2!\binom{N}{2} \equiv 2!tr({}^2\underline{\mathrm{D}}) \tag{12}$$

The 2-HRDM contraction into the 1- and 0-body spaces is carried out by applying relation (5) and following a similar reasoning as previously.

2.2. THE 2-RDM DECOMPOSITION AND THE 2-CM DEFINITION

The orderings $a_{i_1}^\dagger a_{i_2}^\dagger a_{j_2} a_{j_1}$ and $a_{j_2} a_{j_1} a_{i_1}^\dagger a_{i_2}^\dagger$ are not the only possible orderings of a creator pair and an annihilator pair of fermion operators. Thus, through the use anew of relation (2) one may also obtain

$$\begin{aligned} 2!\,{}^2\mathrm{D}_{i_1 i_2;j_1 j_2} &\equiv \left\langle \Psi \left| a_{i_1}^\dagger a_{i_2}^\dagger a_{j_2} a_{j_1} \right| \Psi \right\rangle \\ &= -\delta_{i_2,j_1} \left\langle \Psi \left| a_{i_1}^\dagger a_{j_2} \right| \Psi \right\rangle + \left\langle \Psi \left| a_{i_1}^\dagger a_{j_1} a_{i_2}^\dagger a_{j_2} \right| \Psi \right\rangle. \end{aligned} \tag{13}$$

Inserting relation (6) into the second term of the previous equation, one obtains:

$$\begin{aligned} 2!\,{}^2\mathrm{D}_{i_1 i_2;j_1 j_2} \equiv {}^1\mathrm{D}_{i_1;j_1}\,{}^1\mathrm{D}_{i_2;j_2} - \delta_{i_2,j_1}\,{}^1\mathrm{D}_{i_1;j_2} \\ + \left\langle \Psi \left| a_{i_1}^\dagger a_{j_1} \hat{\mathcal{Q}} a_{i_2}^\dagger a_{j_2} \right| \Psi \right\rangle. \end{aligned} \tag{14}$$

The last term is an element of the 2-CM which may be also denoted in the following equivalent ways:

$$\left\langle \Psi \left| {}^1\hat{\Gamma}_{i_1;j_1} \hat{\mathcal{Q}}\, {}^1\hat{\Gamma}_{i_2;j_2} \right| \Psi \right\rangle \equiv \left\langle \Psi \left| {}^2\hat{C}_{i_1 i_2;j_1 j_2} \right| \Psi \right\rangle \equiv {}^2C_{i_1 i_2;j_1 j_2}. \tag{15}$$

That is, Eq. (14) describes the decomposition of the 2-RDM into three types of matrices [28, 30, 32, 33, 41–45, 47–49]:

- The matrix $Z^{(1)}$

$$Z^{(1)}_{i_1 i_2;j_1 j_2} = {}^1\mathrm{D}_{i_1;j_1}\,{}^1\mathrm{D}_{i_2;j_2} \tag{16}$$

  describes two density charges whose interaction will yield a Coulomb term.
- The matrix $Z^{(2)}$

$$Z^{(2)}_{i_1 i_2;j_1 j_2} = -\delta_{i_2,j_1}\,{}^1\mathrm{D}_{i_1;j_2} \tag{17}$$

  describes the exchange and the particle-hole polarization effect. The interpretation of this term becomes clear when replacing δ_{i_2,j_1} by relation (7)

$$Z^{(2)}_{i_1 i_2;j_1 j_2} \equiv -{}^1\mathrm{D}_{i_2;j_1}\,{}^1\mathrm{D}_{i_1;j_2} - {}^1\bar{\mathrm{D}}_{i_2;j_1}\,{}^1\mathrm{D}_{i_1;j_2}. \tag{18}$$

  The first term of this equation, where the indices appear interchanged, describes the exchange effects, and it vanishes when the two spin-functions involved are different. The second term describes the particle-hole polarization effect. Although this term can be considered to be a two-body correlation one, it must be underlined that it is a product of two one-body factors and because of (7) it is fully determined by the 1-RDM. Therefore, it is not a connected term. This polarization term also vanishes when the two electrons have different spin-functions.
- The matrix $Z^{(3)}$ is the third matrix in the 2-RDM decomposition. It is the genuine two-body part of the 2-RDM. Let us rewrite the $\hat{\mathcal{Q}}$ operator appearing in the 2-CM definition in terms of the states which are orthonormal to Ψ,

$${}^2C_{i_1 i_2;j_1 j_2} = \sum_{\Psi' \neq \Psi} \left\langle \Psi \left| a_{i_1}^\dagger a_{j_1} \right| \Psi' \right\rangle \left\langle \Psi' \left| a_{i_2}^\dagger a_{j_2} \right| \Psi \right\rangle. \tag{19}$$

  This matrix may be interpreted as describing the virtual excitation transitions of two electrons when avoiding each other. It is a correlation matrix which depends on the complete spectrum of the system (or, equivalently, carries information about it). Note, that the 2-CM is not determined by the 1-RDM of the state considered Ψ and, hence, it is what constitutes the kernel of the two-body problem.

It is interesting to realize that the elementary building-blocks of the 2-CM are the 1-order transition reduced density matrices (1-TRDM) corresponding to the one body excitations between the state Ψ under study and the rest of the spectrum states.

To broaden further our insight about the 2-CM it is useful to rewrite relation (19) as follows:

$$
\begin{aligned}
{}^2C_{i_1 i_2;j_1 j_2} &\equiv \sum_{\Psi' \neq \Psi} \langle \Psi' | a_{i_2}^\dagger a_{j_2} | \Psi \rangle \langle \Psi | a_{i_1}^\dagger a_{j_1} | \Psi' \rangle \\
&\equiv \sum_{\Psi' \neq \Psi} \langle \Psi' | \hat{\mathcal{T}} | \Psi' \rangle \qquad (20)
\end{aligned}
$$

where $\hat{\mathcal{T}} = a_{i_2}^\dagger a_{j_2} |\Psi\rangle\langle\Psi| a_{i_1}^\dagger a_{j_1}$. That is, the information about the action of the particle-hole excitations on the state considered is averaged over the whole spectrum.

The last paragraph of this introductory section will be entirely dedicated to developing the lower-order CMs theory, since they are at the center of the CCSE and the GHV methodologies.

2.3. THE CORRELATION AND THE *G*-PARTICLE-HOLE MATRICES

2.3.1. The *G*-Particle-Hole Matrix

The *G*-particle-hole matrix is directly related with the 2-CM. This matrix is formed by the same numbers as the 2-CM although located at different (row, column) positions. Thus,

$$
{}^2C_{i_1 i_2;j_1 j_2} = \sum_{\Psi' \neq \Psi} \langle \Psi | a_{i_1}^\dagger a_{j_1} | \Psi' \rangle \langle \Psi' | a_{i_2}^\dagger a_{j_2} | \Psi \rangle \equiv {}^2G_{i_1 j_1;j_2 i_2} \qquad (21)
$$

Note, that while the 2-CM elements have the same labels as those of the 2-RDM from which they derive, this is not the case for the *G*-matrix. Thus, while a 2-RDM row/column label refers to a pair of particles, in the *G*-matrix case, its row/column label refers to a particle-hole pair, which is why it is denoted *G*-particle-hole matrix.

The properties of the *G*-matrix, which was first defined and studied by Garrod and Percus [6], are extremely important. It is a symmetric, positive semi-definite matrix and, when contracting it, one obtains the following relations [47, 56, 57]:

$$
\begin{aligned}
\sum_i {}^2G_{ij;il} &= \sum_{\Psi' \neq \Psi} \langle \Psi | a_i^\dagger a_j | \Psi' \rangle \langle \Psi' | a_l^\dagger a_i | \Psi \rangle \\
&= N(\delta_{l,j} - {}^1\mathrm{D}_{l;j}) + ({}^1\mathrm{D} - {}^1\mathrm{D}^2)_{l;j} \qquad (22)
\end{aligned}
$$

and

$$
\sum_i {}^2G_{ji;li} = (2K - N)\ {}^1\mathrm{D}_{j;l} + ({}^1\mathrm{D} - {}^1\mathrm{D}^2)_{j;l}. \qquad (23)
$$

These *G*-particle-hole matrix properties play a relevant role in the 2-RDM theory. In fact, the positive semi-definiteness of this matrix is one of the most important *N*-representability conditions, which is the so-called G *N*-representability condition [9]. It must be noted that, from relations (22) and (23), one can obtain the 1-RDM and, therefore, the 2-RDM and the 2-HRDM. It then follows that the 2-RDM *N*-representability problem may be equivalently studied by focusing on the *N*-representability conditions for the *G*-matrix [47–49].

Another feature of interest is the set of the following equalities:

$$
\begin{aligned}
&\sum_{\Psi' \neq \Psi} \langle \Psi | a_{i_1}^\dagger a_{j_1} | \Psi' \rangle \langle \Psi' | a_{i_2}^\dagger a_{j_2} | \Psi \rangle \\
&\qquad = -\sum_{\Psi' \neq \Psi} \langle \Psi | a_{j_1} a_{i_1}^\dagger | \Psi' \rangle \langle \Psi' | a_{i_2}^\dagger a_{j_2} | \Psi \rangle \\
&\qquad = -\sum_{\Psi' \neq \Psi} \langle \Psi | a_{i_1}^\dagger a_{j_1} | \Psi' \rangle \langle \Psi' | a_{j_2} a_{i_2}^\dagger | \Psi \rangle \\
&\qquad = \sum_{\Psi' \neq \Psi} \langle \Psi | a_{j_1} a_{i_1}^\dagger | \Psi' \rangle \langle \Psi' | a_{j_2} a_{i_2}^\dagger | \Psi \rangle
\end{aligned}
$$

These equalities result from applying the anticommutation relation of the fermion operators and from the orthonormality of the Ψ and Ψ' states.

This last set of relations completes the family of second-order matrices which can be constructed by taking the expectation value of two creator and two annihilators in all the possible ordering of these operators when they appear in combination with the $\hat{Q}$ operator. Concerning this point, it should be mentioned that other authors [58] prefer to consider just the different possible orderings of the fermion operators by themselves. All the relations interlinking the elements of these matrices are necessary *N*-representability conditions.

2.3.2. The Higher-Order Correlation Matrices

Relations similar to Eq. (14) would yield an entire family of *p*-CM. While in the two-electron space

one may define only one 2-CM and one *G*-particle-hole matrix, when considering the 3- and 4-electron spaces, the situation is more complex.

The set of 3-CM which may be derived when decomposing the 3-RDM are:

$$^{(3;2,1)}C_{ijl;pqr} = \left\langle \Psi \right| {}^{2}\hat{\Gamma}_{ij;pq}\hat{\mathcal{Q}}\,{}^{1}\hat{\Gamma}_{l;r}\left| \Psi \right\rangle \tag{24}$$

$$^{(3;1,2)}C_{ijl;pqr} = \left\langle \Psi \right| {}^{1}\hat{\Gamma}_{i;p}\hat{\mathcal{Q}}\,{}^{2}\hat{\Gamma}_{jl;qr}\left| \Psi \right\rangle \tag{25}$$

$$^{(3;1,1,1)}C_{ijl;pqr} = \left\langle \Psi \right| {}^{1}\hat{\Gamma}_{i;p}\hat{\mathcal{Q}}\,{}^{1}\hat{\Gamma}_{j;q}\hat{\mathcal{Q}}\,{}^{1}\hat{\Gamma}_{l;r}\left| \Psi \right\rangle \equiv {}^{(3;1,1,1)}G_{ipj;rlq} \tag{26}$$

All these matrices are 3-CM, since they may be obtained by decomposing the 3-RDM, but only the $^{(3;1,1,1)}C$ has a symmetric positive semi-definite counterpart, the $^{(3;\bar{1},1,1)}G$. In the Appendix, the decomposition of the 3-RDM which generates the $^{(3;2,1)}C$ is reported as well as the decomposition of the $^{(3;2,1)}C$ which gives rise to the $^{(3;1,1,1)}C$. It is therefore clear that the 3-RDM, when its decomposition is completed, is a functional of the 1-RDM, the Krönecker deltas, the 2-CM, and the $^{(3;1,1,1)}C$. It should be noted that here the anticommutation of the creator and annihilator operators gives rise to different matrices. For instance, anticommuting the operators appearing in the $^{(3;1,1,1)}G$, one has:

$$\begin{aligned} {}^{(3;1,1,1)}G_{ipj;rlq} &= \langle \Psi |\, {}^{1}\hat{\Gamma}_{i;p}\hat{\mathcal{Q}}\,{}^{1}\hat{\Gamma}_{j;q}\hat{\mathcal{Q}}\,{}^{1}\hat{\Gamma}_{l;r}|\Psi\rangle \\ &= \delta_{j,q}\left\langle \Psi \right| {}^{1}\hat{\Gamma}_{i;p}\hat{\mathcal{Q}}\,{}^{1}\hat{\Gamma}_{l;r}\left| \Psi \right\rangle \\ &\quad - \left\langle \Psi \right| {}^{1}\hat{\bar{\Gamma}}_{i;p}\hat{\mathcal{Q}}\,{}^{1}\hat{\bar{\Gamma}}_{j;q}\hat{\mathcal{Q}}\,{}^{1}\hat{\bar{\Gamma}}_{l;r}\left| \Psi \right\rangle \\ &\equiv \delta_{j,q}\,{}^{2}G_{ip;rl} - {}^{(3;\bar{1},\bar{1},\bar{1})}G_{piq;lrj} \end{aligned}$$

where the bar appearing above the different symbols indicate that the operators have a *hole* form, i.e., the annihilators are placed on the left of the creators. Hence, the family of the 3-CM is enlarged when the HRDMs are allowed to enter into their definition.

In the 4-CM case one has seven different but inter-related matrices corresponding to the possible respective orderings of the fermion and $\hat{\mathcal{Q}}$ operators. These matrices, whose density operators are of particle nature ($\hat{\Gamma}$) are: $^{(4;3,1)}C$, $^{(4;2,2)}C$, $^{(4;1,3)}C$, $^{(4;1,2,1)}C$, $^{(4;1,1,2)}C$, $^{(4;2,1,1)}C$, and $^{(4;1,1,1,1)}C$. The *hole*-CM (HCM) as well as the two mixed matrices related to $^{(4;2,2)}C$ which involve a $^{2}\hat{\Gamma}$ and a $^{2}\hat{\bar{\Gamma}}$ operator, although interesting in themselves, do not play a specific role in what is our object here.

The general CM properties which have been just described can be easily generalized in the 4-CM case. The scope of this article does not call for a more detailed description of these matrices. Nevertheless, it must be pointed out that the $^{(4;2,2)}C$, $^{(4;1,1,2)}C$, and $^{(4;2,1,1)}C$ play an important role in this theory since it has been proven [39] that

$$\langle \Psi | \hat{H}\hat{\mathcal{Q}}\,{}^{p}\hat{R} | \Psi \rangle = 0 \tag{27}$$

implies that the Ψ is an eigenstate of the system. In the above relation $\hat{H}$ is the Hamiltonian and $^{p}\hat{R}$ is an operator of an order p equal or larger than 2.

Using the same fermion algebra tools previously considered, the following *p*-CM general properties may be derived:

1. A *p*-CM is neither Hermitian nor a positive semi-definite matrix.
2. A *p*-CM is not necessarily antisymmetric with respect to the permutation of two-indices of its row/column labels.
3. The trace of a *p*-CM is null.

An important property which directly follows from property 3 and which is satisfied by all p-CMs is that no *p*-CM contributes to the trace of the *p*-RDM from which it derives.

2.4. NOTATION OF THE HAMILTONIAN OPERATOR AND EXPRESSION OF A SYSTEM ENERGY

In the form of the many-body Hamiltonian operator which we currently use, the one-electron terms are included into a unique 2-electron term [15–17, 55]. Thus,

$$\hat{H} = \frac{1}{2}\sum_{i,j,r,s} {}^{0}\mathrm{H}_{ij;rs}\, a_i^{\dagger}a_j^{\dagger}a_s a_r \equiv \frac{1}{2} tr({}^{0}\underline{\mathrm{H}}\,{}^{2}\hat{\Gamma}) \tag{28}$$

where

$${}^{0}\mathrm{H}_{ij;rs} = \frac{\delta_{i,r}\,\epsilon_{j;s} + \delta_{j,s}\,\epsilon_{i;r}}{N-1} + \langle ij|rs\rangle. \tag{29}$$

The symbol ϵ stands for the 1-electron integral matrix and the $\langle ij|rs\rangle$ is the 2-electron repulsion integral in the Condon and Shortley notation which is equivalent to (ir;js) in Mulliken's notation.

Because of relation (28) the energy of the Ψ state is

$$\mathcal{E} = \langle \Psi | \hat{H} | \Psi \rangle = tr({}^{0}\underline{\mathrm{H}}\,{}^{2}\underline{\mathrm{D}}). \tag{30}$$

Since, as has been shown previously, the 2-CM or, equivalently, the *G*-particle-hole are inter-related to

the 2-RDM, when knowing the 2-CM one also knows the electronic energy of the state considered.

It is interesting to note that an absolute and completely general measure of the correlation energy, which does not have as reference the Hartree–Fock energy, is given by

$$\mathcal{E}^{\text{corr}} = \frac{1}{2} tr({}^0\underline{\mathrm{H}}\,{}^2\underline{C}). \tag{31}$$

In fact, the decomposition of the 2-RDM given in (14) generates a partition of the energy in four terms which have a direct physical interpretation. In this connection, it must be mentioned that there is another related energy partition which is based on the moment expansion of the 2-RDM [59–62] and where the cumulant of this expansion may be interpreted as a statistical description of the correlation effects. The 2-order cumulant gathers the particle-hole polarization and the 2-CM terms [28]. We think that either of these partitions can be supported and, according to the type of problem in which one is interested, one may be more advantageous than the other.

3. The CCSE and the GHV Equations

The derivation of the CCSE and the GHV, as well as the method developed for solving the GHV, have been already described in detail [38, 39]. Therefore, only the main lines of this part of the theory will be described in this section.

3.1. THE CCSE EQUATION

Let us consider the set of the transition 2-CM matrices between two orthonormal states spanning the N-electron space, for instance the complete set of Slater determinants $\Omega, \Pi, \ldots$.

$${}^2C^{(\Lambda\Omega)}_{pl;qm} = \left\langle \Lambda \middle| a_p^\dagger a_q \hat{\mathcal{Q}} a_l^\dagger a_m \middle| \Omega \right\rangle \equiv \langle \Lambda | \, {}^2\hat{C}_{pl;qm} | \Omega \rangle \tag{32}$$

where $\hat{\mathcal{Q}}$ is, as in the previous section, the projector on the complementary space to the Ψ state under study. Let us now consider the matrix representation of the SE in this same space:

$$\sum_{\Omega} \mathcal{H}_{\Lambda\Omega} \langle \Omega | \Psi \rangle \langle \Psi | \Pi \rangle = \mathcal{E} \langle \Lambda | \Psi \rangle \langle \Psi | \Pi \rangle \tag{33}$$

where $\mathcal{H}_{\Lambda\Omega}$ is the $(\Lambda;\Omega)$ matrix element of the Hamiltonian operator representation in the N-electron space ($\underline{\mathcal{H}}$ is identical to the FCI matrix), and $\mathcal{E}$ is the energy of state Ψ. Let us now contract this matrix equation into the 2-body space by multiplying both sides of the equation by ${}^2C^{(\Lambda\Omega)}_{pq;ml}$ and taking the trace over the N-electron states:

$$\sum_{\Lambda,\Omega,\Pi} \mathcal{H}_{\Lambda;\Omega} \langle \Omega | \Psi \rangle \langle \Psi | \Pi \rangle \langle \Pi | \, {}^2\hat{C}_{pq;ml} | \Lambda \rangle = \mathcal{E} \sum_{\Lambda,\Pi} \langle \Lambda | \Psi \rangle \langle \Psi | \Pi \rangle \langle \Pi | \, {}^2\hat{C}_{pq;ml} | \Lambda \rangle.$$

After performing the sums indicated above, one obtains the compact form of the CCSE:

$$\langle \Psi | \hat{H} \, {}^2\hat{C}_{pq;ml} | \Psi \rangle = \mathcal{E} \langle \Psi | \, {}^2\hat{C}_{pq;ml} | \Psi \rangle \quad \forall p,q,m,l. \tag{34}$$

Note that the matrix representation of the SE may be contracted into any p-body space, by applying a similar contraction mapping, which yields the p-order CCSE.

In 2002, Alcoba showed [39] that there is a one-to-one correspondence between the CCSE solution and that of the SE. This theorem is similar to Nakatsuji's theorem for the 2-CSE [13]. Both Nakatsuji and Alcoba underlined that the unknown matrices appearing in the 2-CSE and CCSE had to be respectively RDMs and CMs. That is, when attempting to solve these equations, one had to make sure that these matrices were N-representable.

After replacing $\hat{H}$ and ${}^2\hat{C}$ by their expressions in terms of the fermion operators, one obtains two alternative and equivalent forms of this equation [39]:

- The first of these CCSE forms —whose approximate iterative solution method has been reported [63]— is obtained by rearranging the string of operators appearing on the left of $\hat{\mathcal{Q}}$ into a normal product form:

$$\mathcal{E}\,{}^2C_{pq;ml} = \frac{1}{2}{}^0\mathrm{H}_{ij;pr}{}^{(3;2,1)}C_{ijq;mrl} - \frac{1}{2}{}^0\mathrm{H}_{ij;rp}{}^{(3;2,1)}C_{ijq;mrl} + \frac{1}{2}{}^0\mathrm{H}_{ij;rs}{}^{(4;3,1)}C_{ijpq;mrsl} \equiv \mathcal{E}\,{}^2G_{pm;lq} \tag{35}$$

  where Einstein convention for summation over repeated indices has been, and will be, used in the rest of this article unless otherwise stated.

- The second alternative form of the CCSE is obtained by recalling relation (6), thus

$$\begin{aligned}\mathcal{E}\,{}^2C_{pq;ml} &= \langle\Psi|\hat{H}\hat{1}\,{}^2\hat{C}_{pq;ml}|\Psi\rangle \\ &= \mathcal{E}\,{}^2C_{pq;ml} + \langle\Psi|\hat{H}\hat{\mathcal{Q}}\,{}^2\hat{C}_{pq;ml}|\Psi\rangle \\ &= \mathcal{E}\,{}^2C_{pq;ml} + \frac{1}{2}{}^0\mathrm{H}_{ij;rs}\,{}^{(4;2,1,1)}C_{ijpq;rsml}.\end{aligned} \tag{36}$$

In 2002, Alcoba also showed [39] that the CCSE is satisfied *iff* $\langle\Psi|\hat{H}\hat{\mathcal{Q}}\,{}^2\hat{C}_{pq;ml}|\Psi\rangle = 0$. Because of Alcoba's theorems, solving the CCSE constitutes a relevant challenge. As shown in these relations, the CCSE depends on 2-, 3-, and 4-CMs. The method, devised to solve iteratively the CCSE, starts by choosing a 2-CM corresponding to an N-electron state which we suppose to have an energy close to that of the exact Hamiltonian eigenstate in which we are interested, for instance, a Hartree-Fock one. Then the 3- and 4-CMs are approximated in terms of the 2-CM. Replacing then these 3- and 4-CMs into (35) one may obtain a new 2-CM. To obtain an accurate and smooth convergence, a purification of the new approximate 2-CM must be carried out after each iteration. This is necessary because the 2-CM N-representability is not preserved during the iterative process.

3.2. THE GHV EQUATION

Let us consider the diagonal G-particle-hole hypervirial equation, GHV, which can be identified with the anti-Hermitian part of the CCSE [38]:

$$\langle\Psi|[{}^2\hat{C}_{pq;ml}, \hat{H}]|\Psi\rangle = 0 \quad \forall p,q,m,l. \tag{37}$$

This equation is satisfied by all CMs which correspond to a Hamiltonian eigenstate. Although it is not settled whether there are CMs which solve the GHV and yet they do not correspond to a Hamiltonian eigenstate, this equation offers many possibilities. Concerning this question, a related theorem is briefly stated below.

When developing the GHV equation, in the spin-orbital representation, and in the real field, the compact Eq. (37) becomes [38]:

$$\begin{aligned}&{}^0\mathrm{H}_{rs;ij}\,{}^{(3;2,1)}C_{ijq;rsl}\;{}^1\mathrm{D}_{p;m} - {}^0\mathrm{H}_{ij;rs}\,{}^{(3;2,1)}C_{rsm;ijp}\;{}^1\mathrm{D}_{l;q} \\ &\quad + 2\,{}^0\mathrm{H}_{rs;im}\,{}^{(3;2,1)}C_{piq;rsl} + 2\,{}^0\mathrm{H}_{ij;qr}\,{}^{(3;2,1)}C_{lrm;ijp} \\ &+ 2\,{}^0\mathrm{H}_{pr;ij}\,{}^{(3;2,1)}C_{ijq;mrl} + 2\,{}^0\mathrm{H}_{jl;rs}\,{}^{(3;2,1)}C_{rsm;qjp} = 0\end{aligned} \tag{38}$$

where, as mentioned above, the Einstein convention for the sums over repeated indices is used. This relation does not depend any longer on the 4-CM, which is a great advantage over the CCSE both from a computational and a theoretical point of view.

3.2.1. The anti-Hermitian Part of the 3-order CCSE

A very recent theoretical result concerns the anti-Hermitian part of the p-order CCSE ($p > 2$). For simplicity's sake, let us consider the case $p = 3$. In this case, the anti-Hermitian part of the 3-order CCSE may be identified with the 3-order GHV. Its compact form is given by:

$$\begin{aligned}&\langle\Psi|[{}^{(3;1,1,1)}\hat{C}_{pqr;mln}, \hat{H}]|\Psi\rangle = 0 \quad \forall p,q,r,m,l,n \\ &= \langle\Psi|\,{}^{(3;1,1,1)}\hat{C}_{pqr;mln}\hat{\mathcal{Q}}\hat{H}|\Psi\rangle - \langle\Psi|\hat{H}\hat{\mathcal{Q}}\,{}^{(3;1,1,1)}\hat{C}_{pqr;mln}|\Psi\rangle\end{aligned} \tag{39}$$

It can be proved that satisfying this equation, or any other p-order GHV ($p > 2$), is a necessary and sufficient condition to guarantee a correspondence between its solution and that of the SE, as: (i) a p-order GHV is fulfilled by all CMs which correspond to a Hamiltonian eigenstate, and (ii) contraction of a p-order GHV into the 2-body space yields the CCSE/2-CSE, whose fulfillment implies that of the SE [13, 39]. This important property is counterbalanced by the fact that it depends on the 4-CM. On the other hand, it is far more convenient to solve this 3-order GHV equation than the CCSE/2-CSE since, as will be seen below, the iterative procedure for solving this hypervirial equation preserves the N-representability of the resulting solutions, which is not the case in the CCSE/2-CSE methods where an N-representability purification procedure must be combined with the iterative process [21, 27, 31, 33, 43, 48, 63–65].

As mentioned earlier, although a similar theorem has not yet been demonstrated for the (2-order) GHV equation, the results it yielded have proved to be highly accurate, which is why in what follows we will focus on this second-order equation.

3.2.2. A Sketch of the Iterative Method for Solving the GHV

As in the CCSE case, the main idea of the method for solving the GHV is to proceed iteratively by starting with an N-representable 2-CM corresponding to a state which we suppose to be sufficiently

close to the Hamiltonian eigenstate in which we are interested. In terms of this 2-CM the 3-CM is approximated, which permits to evaluate the different elements of the GHV matrix equation. Since the 2-CM does not correspond to a Hamiltonian eigenstate, Eq. (37) is not satisfied, i.e., initially its r.h.s. does not vanish. In this part of the theory, it is more convenient to use the *G*-matrix, instead of the 2-CM. Thus, the equation is:

$$\langle\Psi|[{}^2\hat{C}_{pq;ml},\hat{H}]|\Psi\rangle \equiv \langle\Psi|[{}^2\hat{G}_{pm;lq},\hat{H}]|\Psi\rangle = A_{pm;lq} \quad \forall p,q,m,l \quad (40)$$

where $\underline{A}$ is an anti-Hermitian matrix, which permits to develop a method based on applying to the *G*-matrix a sequence of unitary transformations. As a result, one obtains the following algorithm

$${}^2G^{(n)}_{pm;lq} = {}^2G^{(n-1)}_{pm;lq} + \langle\Psi|[\hat{A}^{(n-1)},{}^2\hat{G}_{pm;lq}]|\Psi\rangle \quad (41)$$

where

$$\hat{A} = A_{xy;vw}\,{}^2\hat{G}_{xy;vw} \quad (42)$$

and which permits to obtain at the nth iteration a *G*-particle-hole matrix expressed in terms of the *G*-particle-hole and the $\underline{A}$ matrices obtained in the previous iteration. As shown in [38], the results obtained when applying this algorithm to the study of several atomic and molecular systems of four and six electrons were very accurate. On the other hand, the convergence was rather slow.

4. Towards a Direct Evaluation of the 3-CM Spin-Blocks Needed in the GHV Methodology

In our previous studies [21, 27, 28, 31–34, 37, 38, 48, 49, 63], we have realized that, when solving the 2-CSE, the CCSE, the ACSE, and the GHV, it is essential to consider explicitly the electron spin-functions. In principle, it is a straightforward task to express Eq. (38) in terms of the α and β spin-functions.

In what follows, a short-hand notation for denoting the spin-functions is needed. Thus, a spin-orbital with α spin will be denoted by i, whereas that with a β spin will be denoted $\bar{i}$.

In practice, the number of the equation-terms, the number of sum-terms involved in each equation-term, and the number of 3-CM to be approximated must be reduced to the outmost. The strategy which has been chosen to decide upon these matters will now be described.

4.1. THE GHV SPIN-BLOCKS

In principle, according to Eq. (37), all the ${}^2\hat{C}_{pq;ml}$ should be considered. On the other-hand, the 2-CM elements do not appear explicitly in the GHV equation and we know that different 2-CM elements involving the same set of spin-orbitals may be interrelated [47–49]. These considerations will prove very helpful to reduce the size of the problem.

When considering explicitly the spin-functions for any set of orbital indices $(p,q;m,l)$, there will be six possible distributions of the α and β spin-functions among them. It would appear that we should have to solve six GHV spin-blocks to have a complete 2-CM (or *G*-particle-hole matrix). Nevertheless, as has been mentioned, because the interrelations among the 2-CM elements, only the following spin-blocks need to be considered: $\alpha\alpha;\alpha\alpha$, $\beta\beta;\beta\beta$, $\alpha\beta;\alpha\beta$.

Their relations with the elements of the other spin-blocks which are not considered are:

$${}^2C_{\bar{i}\bar{j};p\bar{q}} = {}^2C_{\bar{j}i;\bar{q}p} \quad (43)$$

$${}^2C_{\bar{i}\bar{j};\bar{q}p} = {}^1\mathrm{D}_{i;p}\,{}^1\bar{\mathrm{D}}_{\bar{j};\bar{q}} - {}^2C_{i\bar{j};p\bar{q}} \quad (44)$$

and

$${}^2C_{\bar{j}i;p\bar{q}} = {}^1\mathrm{D}_{\bar{j};\bar{q}}\,{}^1\bar{\mathrm{D}}_{i;p} - {}^2C_{i\bar{j},p\bar{q}}. \quad (45)$$

Some of these relations, which are frequently used, are given in graph form in the Appendix. We find the graphs very convenient because they provide a way of expressing the currently used relations in a form which is independent of the indices and labels.

4.2. THE RELEVANT TYPES OF 3-CM

It is easy to show that

$${}^{(3;2,1)}C_{vtx;wyz} \equiv -{}^2C_{vx;yz}\delta_{w,t} + {}^1\mathrm{D}_{v;w}\,{}^2C_{tx;yz} + {}^{(3;1,1,1)}C_{vtx;wyz} \quad (46)$$

In the Appendix, the graph form of this equation is also given. Since we aim at constructing the 3-CM in terms of the 2-CM, one starts by approximating the value of ${}^{(3;1,1,1)}C_{vtx;wyz}$ and then, using this equation, the corresponding ${}^{(3,2,1)}C_{vtx;wyz}$ is evaluated and entered into the equation.

When considering which are the ${}^{(3;1,1,1)}C$ spin-blocks needed, it is easy to see that the only two

distributions of spin which have to be considered are ${}^{(3;1,1,1)}C_{\sigma\sigma\sigma;\sigma\sigma\sigma}$ and ${}^{(3;1,1,1)}C_{\sigma\sigma\bar{\sigma};\sigma\sigma\bar{\sigma}}$ where σ may be α or β. An example of this equivalence of treatment for different 3-CM spin-blocks will be described later on.

4.3. THE 3-CM APPROXIMATING ALGORITHMS

Our working hypothesis for this study is that the information contained in the 2-CM and in the 1-RDM (hence also in the 1-HRDM) must be sufficient to approximate at least those 3-CM elements describing one and two electron transitions. In all the cases studied, the relevant transitions appeared to be those involving a largely occupied spin-orbital and a largely empty spin-orbital in the state Ψ under study. The amount of occupied and empty character of the spin-orbitals can easily be determined by considering the values of the diagonal elements of the 1-RDM and 1-HRDM, respectively. Thus, a large positive or negative value of ${}^{1}D_{i,i} - {}^{1}\bar{D}_{i,i}$ tells us whether the spin-orbital i can be considered as mostly occupied or empty, respectively. This concept is also relevant when looking for the 2- and 3-order cumulant elements having relevant values, and caused us to extend the concept of frontier-orbitals [28].

It may be argued that the information contained in the 2-CM does not seem sufficient to approximate those 3-CM elements, which have non-negligible values and which involve triple electron transitions. There are, however, two theoretical arguments which permit to assume that the overall effect of the 3-CM elements describing triple electron transitions may be neglected [28, 37]. Thus, the energy expression (30) only involves the 2-CM. Moreover, as mentioned previously, the second term of the r.h.s. of Eq. (36), which describes the 4-body correlation effects, where the 3-body effects are included, has to vanish for the equation to be satisfied [39]. In fact this equation shows that, for Hamiltonian eigenstates, all correlation effects of higher-order than two cancel out [30, 32, 39, 46, 47, 66].

As has been mentioned, this study is limited to looking for the algorithms which permit to approximate the ${}^{(3;1,1,1)}C_{\sigma\sigma\sigma;\sigma\sigma\sigma}$ elements. Until now [38], the third-order correlation effects of the ${}^{(3;1,1,1)}C_{\sigma\sigma\sigma;\sigma\sigma\sigma}$ type were neglected because the great majority of the elements of these spin-blocks, which played an active role, were rather small. The other spin blocks were constructed in two steps. In the first step, the 3-order cumulant spin-blocks ${}^{3}\Delta_{\sigma\sigma\bar{\sigma};\sigma\sigma\bar{\sigma}}$ were evaluated with a set of approximating algorithms devised in the framework of the 2-CSE and ACSE theory [28, 31, 33, 34, 37]. Then, the corresponding 3-CM was derived from this cumulant. One of the lines of work which we are now pursuing is to look for the set of algorithms which would directly yield accurate approximations of the 3-CM elements. The present status of this problem will be analyzed here.

4.3.1. Value of Some Special ${}^{(3;2,1)}C$ Elements

Let us recall that when in a string of fermion operators a repetition of two creators/annihilators occurs, the term is null. However, when a $\hat{\mathcal{Q}}$ operator separates these repeated operators, this term does not necessarily vanish.

Here we consider those ${}^{(3;1,1,1)}C_{\sigma\sigma\sigma;\sigma\sigma\sigma}$ elements which, because they involve repeated creator/annihilator indices, can be exactly evaluated in terms of the 2-CM and 1-RDM elements.

- Since ${}^{(3;2,1)}C_{pii;qrs} = -{}^{(3;2,1)}C_{ipi;qrs}$ only the first element needs to be considered. Recalling that ${}^{3}D_{pii;qrs} = 0$ one has:

$${}^{(3;2,1)}C_{pii;qrs} = 2!(-{}^{2}D_{pi;qr}\,{}^{1}D_{i;s} + \delta_{i,q}\,{}^{2}D_{pi;rs} + \delta_{i,r}\,{}^{2}D_{pi;qs}) \tag{47}$$

- The other non-null element will be:

$${}^{(3;2,1)}C_{pqr;sii} = 2!\,{}^{2}D_{pq;si}\,{}^{1}\bar{D}_{r;i} \tag{48}$$

4.3.2. The Different Alternative Approaches for Approximating the 3-CM

Previously, when working on the 2-CSE it proved extremely useful to use a basis set for representing the 2-, 3-, and 4-RDMs where a unique ordering of the creators/annihilators spin-orbital indices was considered, i.e., in ${}^{3}D_{ijl;pqr}$, the only element considered would be that which corresponded to $i < j < l$ and $p < q < r$. In this way, a given element was only considered once instead of 3!.3! = 36 times if no ordering of the indices was imposed.

When considering the 3-CM case, one may also impose a similar ordering of the indices and approximate only the corresponding 3-CM elements. Then, when the terms appearing in the GHV equations refer to a different ordering, one may apply the interrelations linking different 3-CM elements, to obtain the appropriate value for the particular case being considered. In this approach, the number of algorithms needed in order to approximate the different types of 3-CM elements is optimized. On the other

hand, the number of inter-relations linking 3-CM elements involving the same creators/annihilators although in different orderings is rather large, which renders more complex the evaluation of the different GHV terms.

The alternative approach is to look for suitable algorithms for approximating directly the 3-CM elements, irrespective of the indices ordering. That is, if a different algorithm is needed for each ordering of the creator/annihilator indices, the number of algorithms needed is multiplied by 36. In what follows, we will consider the first alternative and then a preliminary analysis of the second one will be given.

4.3.3. Approximating Algorithms for Evaluating ${}^{(3;1,1,1)}C_{\sigma\sigma\sigma;\sigma\sigma\sigma}$ Elements

In what follows, we focus on approximating the ${}^{(3;1,1,1)}C_{\sigma\sigma\sigma;\sigma\sigma\sigma}$ elements needed for the calculation of the structure of the singlet ground-state of the BeH_2 linear molecule, using a minimal basis set of 7 orbitals. The 1, 2, and 3 orbitals are of the σ_g symmetry, 4 and 5 are σ_u and 6 and 7 are of the degenerate π symmetry type. A reference FCI calculation was carried out to obtain the 2-CM and the 1-RDM which are the initial data, as well as, the 3-CM elements whose value should be reproduced by our algorithms. As previously mentioned, the occupation number of the different orbitals is given by de diagonal elements of the 1-RDM. Also, the extent of the relative occupancy or emptiness of an i orbital may be measured by $T(i) = {}^1\mathrm{D}_{i,i} - {}^1\bar{\mathrm{D}}_{i,i}$. Thus, when $T(i) > 0$ the orbital is occupied, otherwise it may be considered an empty orbital. According to the diagonal 1-RDM values, the 1, 2, and 4 orbitals are mostly occupied and the rest of the basis orbitals are mostly empty.

In our first alternative approach, a unique ordering of the creators/annihilators indices is assumed. It is interesting to note that, in this ordered indices basis, only a very small number of elements have non negligible values in the ${}^2C_{\sigma\sigma;\sigma\sigma}$ as well as in the ${}^{(3;1,1,1)}C_{\sigma\sigma\sigma;\sigma\sigma\sigma}$. This is the reason why, in previous calculations [38], this type of 3-CM elements were considered negligible. However, if one is aiming at a higher degree of accuracy, even these few non-negligible elements should be evaluated and, as will be seen, a set of very simple operations yield excellent results.

Let us now describe the three algorithms which approximate the elements of the ${}^{(3;1,1,1)}C_{\sigma\sigma\sigma;\sigma\sigma\sigma}$ which are relevant when the 3-CM are represented in the ordered basis. In what follows, the element considered will be denoted ${}^{(3;1,1,1)}C_{ijl;mpq}$.

- When

$$i = p; \quad T(i) > 0; \quad {}^2C_{jl;mq} \neq 0$$

then

$${}^{(3;1,1,1)}C_{ijl;mpq} \approx -{}^2C_{jl;mq}\,{}^1\mathrm{D}_{p,p}$$

- When

$$i = m; \quad T(i) > 0; \quad {}^2C_{jl;pq} \neq 0$$

then

$${}^{(3;1,1,1)}C_{ijl;mpq} \approx -{}^2C_{jl;pq}\,{}^1\mathrm{D}_{i,i}$$

- When

$$j = p; \quad T(j) > 0; \quad {}^2C_{il;mq} \neq 0$$

then

$${}^{(3;1,1,1)}C_{ijl;mpq} \approx {}^2C_{il;mq}T(j)$$

Guided by the assumptions which constituted our working hypothesis, these algorithms were established empirically having the exact value of the 3-CM element as reference. Before analyzing the results obtained when applying these algorithms, let us remark that, when two or three of the previous conditions occur, the algorithm to be applied is that involving the larger ${}^1\mathrm{D}_{t;t}$ value.

4.3.4. Analysis of the Results in a Basis of Ordered Indices

In Tables I and II, respectively, we report the values of the diagonal elements of the ${}^1\mathrm{D}_{\sigma;\sigma}$ and the values of ${}^2C_{\sigma\sigma;\sigma\sigma}$ having absolute values larger than

TABLE I

Full configuration interaction (FCI) diagonal elements of the 1-RDM.

Orbital label	${}^1\mathrm{D}_{i,i}$ value
1	0.9999868
2	0.9854037
3	0.0143341
4	0.9874572
5	0.0062057
6	0.0033063
7	0.0033063

TABLE II

Full configuration interaction (FCI) elements of the ${}^2C_{\sigma\sigma;\sigma\sigma}$ spin-block with absolute value larger than 10^{-4}.

(row;column)-Labels	FCI value	(row;column)-Labels	FCI value
2 3; 1 2	−0.0001786	4 6; 3 4	−0.0046055
2 6; 1 6	−0.0001143	1 4; 3 5	−0.0002983
3 5; 1 4	−0.0002983	1 7; 2 7	−0.0001143
2 3; 2 3	−0.0055602	2 4; 3 4	0.0001498
2 4; 2 4	0.0001303	2 4; 3 5	−0.0046206
2 4; 2 5	0.0003864	2 5; 3 4	0.0043343
2 5; 2 4	0.0003864	2 7; 2 7	−0.0032005
2 5; 2 5	−0.0025526	3 4; 3 4	−0.0086579
2 6; 2 6	−0.0032005	2 3; 4 5	−0.0046055
2 7; 1 7	−0.0001143	4 5; 4 5	−0.0036221
3 4; 2 4	0.0001498	4 6; 4 6	−0.0001180
3 4; 2 5	0.0043343	4 6; 5 6	−0.0002065
3 5; 2 4	−0.0046206	4 7; 4 7	−0.0001180

10^{-4}, which constitute the building blocks for constructing the ${}^{(3;1,1,1)}C_{\sigma\sigma\sigma;\sigma\sigma\sigma}$. As can be seen, the 1, 2, and 4 orbitals may be considered to be double-occupied while the 3, 5, 6, and 7 are mostly empty orbitals. It must be signaled that the orbital symmetry determines also to a great extent the value of a 3-CM element. As we mentioned previously, in our example, the 1, 2, and 3 orbitals have a σ_g symmetry, the 4 and 5 have σ_u symmetry, and 6 and 7 have π degenerate symmetry, respectively. It is easy to appreciate the role played by the electron-transitions involving frontier electrons corresponding to each symmetry. It is also worth commenting the very sparse character of this 2-CM spin-block in this ordered basis. This underlines the fact that the leading terms in the corresponding 2-RDM elements are the Coulomb, the exchange, and the particle-hole polarization terms.

TABLE III

Exact full configuration interaction (FCI) and estimated values of the elements of the ${}^{(3;1,1,1)}C_{\sigma\sigma\sigma;\sigma\sigma\sigma}$ spin-block with absolute value larger than 10^{-4}.

(row;column) Labels	Approximated value	FCI value
1 4 6; 2 4 6	−0.0001114	−0.0001108
2 3 5; 1 2 4	0.0002939	0.0002987
2 4 5; 2 4 5	−0.0024886	−0.0024679
2 4 6; 1 4 6	−0.0001128	−0.0001108
2 4 6; 2 4 6	−0.0031603	−0.0030968
2 4 6; 2 5 6	0.0002035	0.0002199
2 5 6; 2 4 6	0.0002035	0.0002199

A summary of the results concerning the ${}^{(3;1,1,1)}C_{\sigma\sigma\sigma;\sigma\sigma,\sigma}$ is given in Table III which collects the exact and the estimated values of the elements having absolute value larger than 10^{-4}.

As can be appreciated, our algorithms, although involving very simple operations, do reproduce with good accuracy the value of the relevant 3-CM elements. Obviously this is due to the information carried by the 2-CM element about the electron transitions which are present in the 3-CM element considered.

Let us finish by remarking that when a more extended basis set having more than one empty orbital of each symmetry is used, the set of algorithms just given will probably have to be extended, even when the basis used imposes a unique ordering of the creators/annihilators indices. Indeed, with an extended basis set, different 3-CM topologies, mixing mostly-empty (e) with mostly-occupied (o) orbitals such as ${}^{(3;1,1,1)}C_{oeo;eoo}$ may occur. This question is discussed in the next paragraph.

4.3.5. Some Accurate and Semi-Accurate Results in a Nonordered Indices Basis

In the previous paragraph, the 3-CM elements, derived from the FCI 3-RDM, correspond to the elements where the fermion row and column indices are in an increasing order: $i < j < l; m < p < q$. In this ordered basis, not all the possible relative positions of the indices in the 3-CM, Eq. (26), are taken into account, which is a great advantage but which complicates the evaluation of the different GHV terms. On the other hand, when all possible indices orderings are considered, the number of different topologies and, hence, of different algorithms

to be investigated is very large. In our opinion, a partial ordering of the indices should be kept. Thus, if the ordering of the indices is considered in the Hamiltonian operator, and only those $^2\hat{C}$ elements with ordered indices are commuted with it, the disorder of the indices in the $^{(3;2,1)}C_{ijl;mpq}$ labels thus generated will only be partial. Moreover, the indices i and j as well as the m and p can be easily permuted at convenience. In this way, those 3-CM topologies which are more difficult to approximate may be avoided and simultaneously the number of algorithms to be determined is reduced. As a first step towards this methodological development, we are analyzing the values of the BeH_2 FCI 3-CM when represented in a nonordered basis. In this way, once this analysis is completed, the choice of those 3-CM topologies which is convenient to avoid can be optimized. Moreover, this study, which generates all types of topologies, yields a large set of algorithms which should cover all the possibilities ocurring when the basis set is an extended one. This last point is particularly convenient, since a FCI reference calculation would hardly be possible with an extended basis set.

In this base of representation, there are three main types of 3-CM elements:

1. Elements in which none of the creators' indices matches any of the annihilators ones.

   These elements may have non negligible values, but we do not yet know how to approximate them. Fortunately, when contracting the 3-CM, these terms do not contribute to the 2-CM and, as we mentioned previously, they do not directly contribute to the energy.
2. A creator and an annihilator have the same index.

   The cases given in the previous paragraph, when an ordered basis was used, are three of the possible ones. In the nonordered basis, one may also have

$$\langle\Psi|a_i^\dagger a_m \hat{\mathcal{Q}} a_j^\dagger a_p \hat{\mathcal{Q}} a_l^\dagger a_i|\Psi\rangle \approx \langle\Psi|a_j^\dagger a_m \hat{\mathcal{Q}} a_l^\dagger a_p|\Psi\rangle {}^1\mathrm{D}_{i;i}$$

$$\langle\Psi|a_i^\dagger a_m \hat{\mathcal{Q}} a_j^\dagger a_q \hat{\mathcal{Q}} a_l^\dagger a_j|\Psi\rangle \approx -\langle\Psi|a_i^\dagger a_m \hat{\mathcal{Q}} a_l^\dagger a_q|\Psi\rangle {}^1\mathrm{D}_{j;j}$$

$$\langle\Psi|a_i^\dagger a_m \hat{\mathcal{Q}} a_m^\dagger a_q \hat{\mathcal{Q}} a_l^\dagger a_r|\Psi\rangle \approx \langle\Psi|a_i^\dagger a_q \hat{\mathcal{Q}} a_l^\dagger a_r|\Psi\rangle {}^1\bar{\mathrm{D}}_{m;m}$$

$$\langle\Psi|a_i^\dagger a_m \hat{\mathcal{Q}} a_j^\dagger a_q \hat{\mathcal{Q}} a_m^\dagger a_r|\Psi\rangle \approx -\langle\Psi|a_i^\dagger a_q \hat{\mathcal{Q}} a_j^\dagger a_r|\Psi\rangle {}^1\bar{\mathrm{D}}_{m;m}$$

$$\langle\Psi|a_i^\dagger a_m \hat{\mathcal{Q}} a_j^\dagger a_q \hat{\mathcal{Q}} a_q^\dagger a_r|\Psi\rangle \approx \langle\Psi|a_i^\dagger a_m \hat{\mathcal{Q}} a_j^\dagger a_r|\Psi\rangle {}^1\bar{\mathrm{D}}_{q;q}$$

   That is, the fermion operators with the same indices disappear as well as a $\hat{\mathcal{Q}}$ operator. Note that when the operators ordering is $a_i \ldots a_i^\dagger$, the multiplying matrix element is the 1-HRDM while the structure $a_i^\dagger \ldots a_i$ involves the 1-RDM element. Clearly, when the multiplying element is the 1-HRDM, the spin-orbital should be mostly empty and vice versa when the matrix involved is the 1-RDM. On the l.h.s. of these equations, the three sets of creator/annihilator are separated by the $\hat{\mathcal{Q}}$ operators. When the indices that match are either in adjacent sets or in more distant sets, the signs of the approximation for the holes and for the particles are opposite to each other.
3. Two or three matchings occur between creators and annihilators.

   These matchings may involve empty as well as occupied orbitals. Within this 3-CM type some topologies are somewhat more complex. As an example of the type of difficulties which may arise, let us consider some examples:

   - Approximating $^{(3;1,1,1)}C_{534;354}$ whose FCI value is -0.0035208:

     This case is comparatively simple since the operators involved, the $a_4^\dagger a_4$ and $a_3 \hat{\mathcal{Q}} a_3^\dagger$, correspond to different sets (their inter-linking is not important), and since $^1\mathrm{D}_{4;4} = 0.9874572$ and $^1\bar{\mathrm{D}}_{3;3} = 0.993794$, the appropriate approximation is similar to the third one in the previous account. The value thus obtained is -0.0035995.
   - Approximating $^{(3;1,1,1)}C_{126;612}$ whose FCI value is 0.985374:

     There are three possible approximations. The approximation involving the product of $^1\bar{\mathrm{D}}_{6;6} = 0.9966937$ and $^2C_{12;12}$ will be nearly null since this 2-CM element does not describe any transition. The other two possibilities involve only occupied orbitals and, as in the cases appearing in the ordered basis, the higher 1-RDM element value determines the approximation to be applied. Thus the approximation is $^2C_{26;62}{}^1\mathrm{D}_{1;1} = -0.9853265$.
   - Approximating $^{(3;1,1,1)}C_{126;261}$ whose FCI value is 0.0113472:

     This is an interesting topology. Here the values of the 1-RDM and 1-HRDM elements are very similar, the 2-CM elements involved in each of the possible approximations describe electron transitions, both approximations are interlinked and both have the same sign. In this case the algorithm combines both possibilities. Thus, $^2C_{26;62}{}^1\mathrm{D}_{1;1} + {}^2C_{12;21}{}^1\bar{\mathrm{D}}_{6;6} = 0.0113473$.

- Approximating ${}^{(3;1,1,1)}C_{132;231}$ whose FCI values is -0.0228953:

  This is a rather complex case. In the graph form given in the Appendix, the lines joining creators and annihilators with equal labels would present a triple crossing. Also the central set o operators correspond to an empty orbital. Until now, we have not figured out how to approximate the elements having this type of topology. Therefore, one must either avoid their appearance through a reordering of the indices or obtain them through the use of the interrelations between another topology involving the same orbitals such as that appearing in the previous example.

In the tests that we have carried out, the accuracy has been higher than 10^{-4} which renders us confident that, provided that the exceptional elements such as the last described, are either indirectly evaluated or its appearance in the calculation is avoided, a high accuracy can be attained when solving the GHV equation.

Let us conclude by saying that when the occupancy of the orbitals is close to 0.5, the role played by the 1-RDM and 1-HRDM diagonal elements becomes ambiguous. This is another question which is now being studied.

Appendix

The criterium for constructing the graphs which are reported here is similar to that used previously [27, 41]. Thus, the creator indices are on the top of the graph and those corresponding to annihilators are at the bottom of the graph.

I. BASIC GRAPHS

$\delta_{i;j}$ graph $\longrightarrow$

$\langle\Psi|a_i^\dagger a_j|\Psi'\rangle$ graph$\longrightarrow$

$\langle\Psi|a_i^\dagger a_j^\dagger a_l a_k|\Psi'\rangle$ graph$\longrightarrow 2!$  $\longrightarrow 2!$ 

$\langle\Psi|a_i^\dagger a_j^\dagger a_k^\dagger a_r a_q a_p|\Psi\rangle$ graph$\longrightarrow 3!$ 

$\langle\Psi|a_i^\dagger a_k \hat{\mathcal{Q}} a_j^\dagger a_l|\Psi\rangle$ graph$\longrightarrow$ 

$\langle\Psi|a_i^\dagger a_j^\dagger a_r a_q \hat{\mathcal{Q}} a_l^\dagger a_p|\Psi\rangle$ graph$\longrightarrow 2!$ 

$\langle\Psi|a_i^\dagger a_q \hat{\mathcal{Q}} a_j^\dagger a_r \hat{\mathcal{Q}} a_l^\dagger a_p|\Psi\rangle$ graph$\longrightarrow$ 

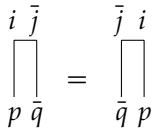
II. BASIC RELATIONS

The graph relations given here are very general since they do not depend on the indices.

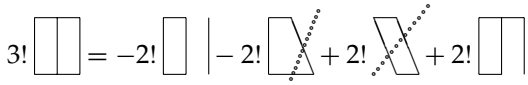
Decomposition of the 2-RDM, Eq. (14)

$2!$ 

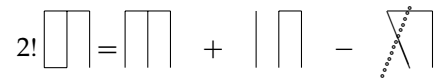
Equation (43)



Decomposition of the 3-RDM

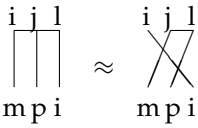


Inter-relation of ${}^{(3;2,1)}C$ and ${}^{(3;1,1,1)}C$

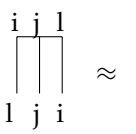


III. TWO EXAMPLES OF 3-CM TOPOLOGIES AND APPROXIMATIONS

An approximation example in graph form:



Type of topology where i and l are occupied orbitals and j is empty which should be avoided.



ACKNOWLEDGMENT

We feel very honored and have great pleasure in contributing an article in this volume dedicated to Professor Istvan Mayer. Our common interest in the approaches to the study of the atomic and molecular structure, based on concepts such as the localization of orbitals and bond functions, the role of nonorthonormal orbitals in molecular calculations and, in general, in the methodological aspects of Quantum Chemistry, has enhanced the friendly relations established during the visits of one of the authors (C.V.) to Budapest. We therefore highly appreciate this occasion to show our admiration for his work.

References

1. Husimi, K. Proc Soc Jpn 1940, 22, 264.
2. Löwdin, P. O. Phys Rev 1955, 97, 1474.
3. Ayres, R. U. Phys Rev 1958, 111, 1453.
4. McWeeny, R. Rev Mod Phys 1960, 32, 335.
5. Coleman, A. J. Rev Mod Phys 1963, 35, 668.
6. Garrod, C.; Percus, J. K. J Math Phys 1964, 5, 1756.
7. Davidson, E. R. Reduced Density Matrices in Quantum Chemistry; Academic Press: New York, 1976.
8. Coleman, A. J.; Yukalov, V. I. Reduced Density Matrices: Coulson's Challenge; Springer Verlag: New York, 2000.
9. Coleman, A. J.; Erdahl, R. M., Eds. Reduced Density Matrices with Applications to Physical and Chemical Systems. Queen's Papers on Pure and Applied Mathematics, N.11; Queen's University: Kingston, ON, 1968.
10. Erdahl, R.; Smith, V., Eds. Density Matrices and Density Functionals (Proceedings of the A. J. Coleman Symposium, Kingston, Ontario). Reidel: Dordrecht, 1987.
11. Cioslowsky, J., Ed. Many-Electron Densities and Reduced Density Matrices; Kluwer: Boston, 2000.
12. Mazziotti, D. A., Ed. Reduced-Density-matrix Mechanics with Applications to Many-electron Atoms and Molecules. Advances in Chemical Physies Vol. 134; Wiley: New York, 2007.
13. Nakatsuji, H. Phys Rev A 1976, 14, 41.
14. Cohen, L.; Frishberg, C. Phys Rev A 1976, 13, 927.
15. Valdemoro, C. In Density Matrices and Density Functionals (Proceedings of the A. J. Coleman Symposium, Kingston, Ontario, 1985). Erdahl, R.; Smith, V., Ed.; Reidel: Dordrecht, 1987; p 275.
16. Valdemoro, C. An R Soc Esp Fís 1983, 79, 106.
17. Valdemoro, C. Phys Rev A 1985, 31, 2114.
18. Mazziotti, D. A. Phys Rev A 1998, 57, 4219.
19. Valdemoro, C. Phys Rev A 45, 4462, (1992).
20. Colmenero, F.; Pérez del Valle, C.; Valdemoro, C. Phys Rev A 1994, 47, 971.
21. Colmenero, F.; Valdemoro, C. Int J Quantum Chem 1994, 51, 369.
22. Nakatsuji, H.; Yasuda, K. Phys Rev Letts 1996, 76, 1039.
23. Yasuda, K.; Nakatsuji, H. Phys Rev A 1997, 56, 2648.
24. Nakata, M.; Ehara, M.; Yasuda, K.; Nakatsuji, H. J Chem Phys 2000, 112, 8772.
25. Mazziotti, D. A. Phys Rev A 1999, 60, 3618.
26. Mazziotti, D. A. J Chem Phys 2002, 116, 1239.
27. Valdemoro, C.; Tel, L. M.; Pérez-Romero, E. Adv Quantum Chem 1997, 28, 33.
28. Valdemoro, C.; Tel, L. M.; Pérez-Romero, E. In Many-Electron Densities and Reduced Density Matrices, Cioslowski, J. Ed.; Kluwer: Dordrecht 2000; p 117.
29. Valdemoro, C.; Tel, L. M.; Pérez-Romero, E.; Torre, A. J Mol Struct (Theochem) 2001, 537, 1.
30. Alcoba, D. R.; Valdemoro, C. Phys Rev A 2001, 64, 062105.
31. Alcoba, D. R.; Casquero, F. J.; Tel, L. M.; Pérez-Romero, E.; Valdemoro, C. Int J Quantum Chem 2005, 102, 620.
32. Valdemoro, C. In Reduced-Density-Matrix Mechanics with Applications to Many-electron Atoms and Molecules. Advance Chemical Physies, vol. 134, Mazziotti, D. A. Ed.; Wiley: New York, 2007; p 121.
33. Alcoba, D. R. In Reduced-Density-Matrix Mechanics with Applications to Many-electron Atoms and Molecules. Advances in Chemical Physies, vol. 134, Mazziotti, D. A. Ed.; Wiley: New York, 2007; p 205.
34. Valdemoro, C.; Alcoba, D. R.; Tel, L. M.; Pérez-Romero, E. Prog Theor Chem Phys 2008, 18, 175.
35. Mazziotti, D. A. Phys Rev Lett 2006, 97, 143002.
36. Mazziotti, D. A. Phys Rev A 2007, 75, 022505.
37. Valdemoro, C.; Tel, L. M.; Alcoba, D. R.; Pérez-Romero, E. Theor Chem Acc 2007, 118, 503.
38. Alcoba, D. R.; Valdemoro, C.; Tel, L. M.; Pérez-Romero, E. Int J Quantum Chem 2008.
39. Alcoba, D. R. Phys Rev A 2002, 65, 032519.
40. Valdemoro, C.; Alcoba, D. R.; Tel, L. M.; Pérez-Romero, E. Sixth International Congress of the International Society for Theoretical Chemical Physics, Vancouver, Canada, 2008.
41. Valdemoro, C.; de Lara-Castells, M. P.; Pérez-Romero, E.; Tel, L. M. Adv Quantum Chem 1999, 31, 37.
42. Valdemoro, C. In Topics in Current Chemistry: Correlation and Localization; Surjan, P. R. Ed.; Springer-Verlag: Berlin, 1999; p 187.
43. Valdemoro, C.; Tel, L. M.; Pérez-Romero, E. Phys Rev A 2000, 61, 032507.
44. Valdemoro, C.; Tel, L. M.; Pérez-Romero, E. In Quantum Systems in Chemistry and Physics I; Hernández-Laguna, A.; Maruani, J.; McWeeny, R.; Wilson, S., Eds.; Kluwer: Dordrecht, 2000; p 3.
45. Valdemoro, C.; Alcoba, D. R.; Tel, L. M.; Pérez-Romero, E. Int J Quantum Chem 2001, 85, 214.
46. Tel, L. M.; Pérez-Romero, E.; Valdemoro, C.; Casquero, F. J. Int J Quantum Chem 2001, 82, 131.
47. Valdemoro, C.; Tel, L. M.; Alcoba, D. R.; Pérez-Romero, E.; Casquero, F. J. Int J Quantum Chem 2002, 90, 1555.
48. Valdemoro, C.; Alcoba, D. R.; Tel, L. M. Int J Quantum Chem 2003, 93, 212.
49. (a) Alcoba, D. R.; Valdemoro, C. Int J Quantum Chem 2005, 102, 629; (b) Alcoba, D. R.; Valdemoro, C. Int J Quantum Chem 2006, 106, 2999.

50. Avery, J. Creation and Annihilation Operators; McGraw-Hill: London, 1976.
51. Surjan, P. R. Second Quantized Approach to Quantum Chemistry: An Elementary Introduction; Springer-Verlag: Berlin, Heidelberg, 1989.
52. Jørgensen, P.; Simons, J. Second Quantization-Based Methods in Quantum Chemistry; Academic Press: New York, 1981.
53. Coleman, A. J. J Math Phys 1972, 13, 214.
54. Erdahl, R. M. Int J Quantum Chem 1978, 13, 697.
55. Coleman, A. J.; Absar, I. Int J Quantum Chem 1980, 18, 1279.
56. Garrod, C.; Rosina, M. J Math Phys 1969, 10, 1855.
57. Mihailovic, M. V.; Rosina, M. Nucl Phys A 1969, 130, 386.
58. Mazziotti, D. A.; Erdahl, R. M. Phys Rev A 2001, 63, 042113.
59. Kubo, R. J Phys Soc Jpn 1962, 17, 1100.
60. Kladko, K.; Fulde, P. Int J Quantum Chem 1998, 66, 377.
61. Mazziotti, D. A. Chem Phys Lett 1998, 289, 419.
62. Kutzelnigg, W.; Mukherjee, D. J Chem Phys 1999, 110, 2800.
63. Alcoba, D. R. Estudio de las Cuestiones Cruciales en la Solución Iterativa de la Ecuación de Schrödinger Contraída, PhD Thesis; Universidad Autónoma de Madrid: Madird, 2004.
64. Alcoba, D. R.; Valdemoro, C.; Tel, L. M.; Pérez-Romero, E. Phys Rev A 2008, 77, 042508.
65. Alcoba, D. R. Int J Quantum Chem 2004, 97, 776.
66. Valdemoro, C.; Tel, L. M.; Pérez-Romero, E.; Alcoba, D. R. Int J Quantum Chem 2008, 108, 1090.