Contents lists available at SciVerse ScienceDirect

Computational and Theoretical Chemistry

A new approach to construct the three-body correlation matrices for correlated excited states

D.R. Alcoba [a,*], C. Valdemoro [b], L.M. Tel [c]

[a] Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, and Instituto de Física de Buenos Aires,
Consejo Nacional de Investigaciones Científicas y Técnicas, Ciudad Universitaria, 1428 Buenos Aires, Argentina
[b] Instituto de Física Fundamental, Consejo Superior de Investigaciones Científicas, Serrano 123, 28006 Madrid, Spain
[c] Departamento de Química Física, Facultad de Ciencias Químicas, Universidad de Salamanca, 37008 Salamanca, Spain

ABSTRACT

The calculations carried out with the G-particle-hole hypervirial equation (GHV) method for a set of ground-states dominated by a single determinant of electronic systems have yielded highly-accurate results when compared to the equivalent full configuration interaction (FCI) quantities [26,28,30]. However, the results obtained when calculating states dominated by several determinants were not satisfactory. This problem is common to other contracted equations methodologies. The reason for this apparent shortcoming is that in these cases the existing algorithms yield inaccurate approximations for the 3-body correlation matrices involved in the contracted equations. Here, we propose a new set of algorithms for constructing the 3-order correlation matrix in terms of the 2-order one when a singlet zero-order wavefunction is formed by a single configuration state function (CSF) composed of two equally weighed Slater determinants. This type of correlated states are of great general interest but in particular in spectroscopy and quantum information. The results obtained are very satisfactory.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The concept of N-representability is at the core of the reduced density matrix (RDM) theory. Coleman introduced this concept in 1963 in his famous paper [1], where he stated that a matrix represented in a reduced space of 1, 2,... electrons can only be considered to be a 1-, 2-RDM,... when there exists a N-electron wave-function from which it can be derived by integration of the corresponding N-density over the variables of $N - 1, N - 2,...$ electrons. As a consequence of the need of this RDM property, when looking for a variational treatment for the 1-, 2-RDM,... one had to impose a set of N-representability constraints. This implies the search for the set of necessary and sufficient N-representability conditions for RDMs [2–8]. In the book by Coleman and Yukalov [9] a clear and detailed account of the necessary conditions for the ensemble N-representability condition of the 2-RDM is given. The different N-representability conditions implicitly define a set of matrices closely related to the 2-RDM; in what follows we are particularly concerned with two families of these matrices which describe the fermion correlation effects: the correlation [10–14] and the G-particle-hole matrices [6,11–13,15].

As Löwdin mentions in his article on the N-representability problem published in the 1987 book in honor of A. John Coleman [3], when a fundamental quantum mechanical equation expressed in terms of the N-electron density operator $\hat{\Gamma}$ is exactly solved no need for extra constraints exists; however when the solution is approximated the N-representability property of the matrices involved must be ascertained. This is the case of the two main methodologies which have been at the center of the work of our group: the solution of the contracted Schrödinger equation (CSE) [5,16–25] and the solution of the G-particle-hole hypervirial equation (GHV) [26–32]. Thus, it must be ensured that the 2-RDM resulting from an approximated iterative solution of these equations satisfies the main necessary N-representability conditions with sufficient accuracy. In the CSE case, a purification procedure is applied to the resulting 2-RDM after iteration [13,14]. This purification procedure is partially based on Coleman's unitarily invariant decomposition of a 2-RDM [33]. In the GHV case, the solving procedure used preserves to a great extent the N- and Spin-representability [34] of the initial trial matrix, which is one of the advantages of this approach.

All contracted equations are hierarchy equations. Thus, the analytical form of the CSE, whose solution is the 2-RDM corresponding to a given eigenstate, depends also on the 3- and 4-RDM; its antihermitian part, the antihermitian contracted Schrödinger equation (ACSE) [35], and the GHV equation depend respectively not only on the 2-RDM and the G-particle-hole matrix but also on the corresponding 3-order density and correlation matrices. This hierarchy character renders operationally indeterminate the contracted

* Corresponding author. Tel.: +54 11 4576 3353; fax: +54 11 4576 3357.
E-mail address: qfxaldad@lg.ehu.es (D.R. Alcoba).

equations. A way out of this difficulty was proposed by Colmenero et al. in 1993 by approximating the 3- and 4-RDM in terms of the 1- and 2-RDM [36]. The algorithm used was an extension of Valdemoro's proposal for approximating the 2-RDM in terms of the 1-RDM [37]. In 1996 Nakatsuji and Yasuda, by analogy with the many-body perturbation series, proposed a way to approximate the 3- and 4-body correlation terms [20] and 2 years later Mazziotti [22] identified these approximating algorithms with the statistical expression of the moment expansion of the 2-RDM. This author also proposed another procedure for approximating the 3- and 4-order cumulants, or equivalently, the 3- and 4-body correlation terms [38]. These, and other posterior related proposals [28,39] can be considered to give an answer to this question when the zeroth-order wave-function is a single determinant. However, when this is not the case, neither of these algorithms for approximating the 3- and 4-body correlation effects gives acceptable results [29]. As a preliminary step in the study of this open question we present here a set of algorithms for approximating the 3-body correlation matrix elements for the particular case in which the zeroth-order wave-function is formed by a single configuration state function (CSF) composed of two equally weighed Slater determinants in order to describe a singlet state. These 3-order matrices are of paramount importance in the GHV equation which is at the center of our present work.

The GHV equation is the most recent member of the family of 2-order contracted equations. When solving this equation one does not look for an *N*-electron function but for a 2-order matrix which is a 2-electron quantum average of the electronic correlation of the *N*-electron state considered which suffices to determine the energy of the corresponding state. The calculations carried out with the GHV method on the singlet, doublet and triplet ground states of a set of atoms and molecules have yielded results that are similar in accuracy to those obtained with a coupled cluster with single, double, and triple (CCSD(T)) treatment [26,28,30,32]. The common feature to all those ground states is that a single Slater determinant constitutes a reasonable zeroth-order trial function to start the iterative procedure leading to the approximate solution of the GHV equation. On the other hand, the multi-determinantal states which are highly correlated are still an open question [29]. The main cause of this problem is that the existing approximating algorithms for the 3-body correlation matrices involved in the GHV equation are not adequate when the occupation numbers of the natural spin–orbitals are significantly different from 1 or 0. As mentioned above, the aim of this work is to propose a new set of approximating algorithms for constructing the 3-order correlation matrix in terms of the lower-order matrices when the zero-order wave-function is formed by two equally weighed Slater determinants in order to describe a singlet state. This type of correlated states are of great general interest but in particular in spectroscopy and quantum information as well as in a more general context [40,41].

This paper is organized as follows. The basic definitions, an overview of the contracted equations properties, and a general theoretical background are given in the following section. In Section 3, it is shown how the number of apparent unknowns to be approximated can be reduced when dealing with singlet states. In Section 4 we propose a new set of approximating algorithms for the 3-body correlation matrices of this type of excited states. In Section 5 we report the results obtained when using these algorithms and give some final comments.

2. Basic definitions and relations

The Hamiltonian operator of a pairwise interacting *N*-electron system may be written in the occupation number representation within the second quantization formalism as:

$$\widehat{H} = \frac{1}{2}\sum_{i,j,l,m} {}^{0}H_{ij;ml} a_i^{\dagger} a_j^{\dagger} a_l a_m \tag{1}$$

where

$$
{}^{0}H_{ij;ml} = \frac{(\epsilon_{i;m}\delta_{j,l} + \epsilon_{j;l}\delta_{i,m})}{(N-1)} + V_{ij;ml} \tag{2}
$$

and the matrix ϵ groups the one-electron integrals and V the 2-electron integrals. In (1) the fermion operators subscripts are the labels of the spin–orbitals. In what follows the orthonormal basis set considered is formed by $2K$ spin–orbitals.

The state under study is denoted by Ψ. This wave-function allows to define the two following projector operators:

$$\widehat{Q}^{\Psi} = \sum_{\Psi' \neq \Psi} |\Psi'\rangle\langle\Psi'| \quad \widehat{P} = |\Psi\rangle\langle\Psi|$$

as well as the set of relevant RDMs and related matrices.

2.1. Matrix definitions and their inter-relations

The RDMs and the correlation matrices are the matrices at the center of this work. Their respective structures are defined, in the occupation number representation of second quantization, as:

- The 1-RDM elements.

$$
{}^{1}D_{p;r} = \left\langle \Psi \left| a_p^{\dagger} a_r \right| \Psi \right\rangle \tag{3}
$$

- The hole 1-RDM (1-HRDM) elements.

$$
{}^{1}\overline{D}_{p;r} = \left\langle \Psi \left| a_r a_p^{\dagger} \right| \Psi \right\rangle \tag{4}
$$

- The 2-RDM elements.

$$
2!{}^{2}D_{pq;rs} = \left\langle \Psi \left| a_p^{\dagger} a_q^{\dagger} a_s a_r \right| \Psi \right\rangle \tag{5}
$$

- The 2-order correlation and the *G*-particle-hole matrix elements.

$$
C_{pq;rs} = \left\langle \Psi \left| a_p^{\dagger} a_r \widehat{Q} a_q^{\dagger} a_s \right| \Psi \right\rangle \equiv G_{pr;sq} \tag{6}
$$

Using the fermion relations, it can be shown that:

$$
2!{}^{2}D_{pq;rs} = {}^{1}D_{p;r}{}^{1}D_{q;s} - {}^{1}D_{q;r}{}^{1}D_{p;s} - {}^{1}\overline{D}_{q;r}{}^{1}D_{p;s} + C_{pq;rs} \tag{7}
$$

- The form of the 3-order correlation matrices used here are:

$$
{}^{(3;2,1)}C_{ipr;jqs} = \left\langle \Psi \left| a_i^{\dagger} a_p^{\dagger} a_q a_j \widehat{Q} a_r^{\dagger} a_s \right| \Psi \right\rangle \tag{8}
$$

$$
{}^{(3;1,1,1)}C_{ipr;jqs} = \left\langle \Psi \left| a_i^{\dagger} a_j \widehat{Q} a_p^{\dagger} a_q \widehat{Q} a_r^{\dagger} a_s \right| \Psi \right\rangle \tag{9}
$$

and the relation linking these two matrices is:

$$
{}^{(3;2,1)}C_{ipr;jqs} = -\delta_{p,j}C_{ir;qs} + {}^{1}D_{i;j}C_{pr;qs} + {}^{(3;1,1,1)}C_{ipr;jqs} \tag{10}
$$

2.2. Brief overview on the contracted equations

The different 2-order contracted equations result from the integration over the variables of $N-2$ electrons of the Schrödinger [16,17] and the Liouville equations, or equivalently from the application of a matrix contracting mapping to their matrix representations [18]. For the sake of brevity only a brief account of the main features of the different contracted equations will be given in the synopsis (Appendix A), where the information for each one of the contracted equations is collected in the following form:

$$
\text{Acronym} \begin{cases} \text{Name} \\ \text{Compact form of the equation} \\ \text{Matrices involved} \\ \text{Conditions implied by the equation} \\ \text{Solution and computational scaling} \end{cases}
$$

It is important to recall that there is a one-to-one correspondence between the solution of the Schrödinger equation and that of the CSE [16], of the correlation CSE (CCSE) [42], and of the 3-order

GHV equation [27], which depends also on the 4-order correlation matrix. While no proof of the sufficiency of the GHV equation has been found, no counter-example has been found either [29]. On the other hand, a counter-example has been reported for the ACSE [26,29]. It has also been proven that while the GHV solution implies the ACSE's one, the opposite is not true [26]. That is, the GHV implies a stronger condition than the ACSE. This is the reason why the former equation is at the center of our work. Let us also mention that, in a similar way to other 2-order contracted equations methods [5], evaluations in the GHV equation case have been also implemented using sum factorization and multiple-matrix-multiplication in order to reduce the computational costs to be proportional to K^6 in floating-point operations and K^4 in memory storage [27,32]. For the sake of comparison, MP2, CCSD, and CCSD(T) methods scale in floating point operations as K^5, K^6, and K^7, respectively. It is difficult to ascertain if the GHV method is faster or not than CCSD since present programs for the latter have been in use for a long time and are fully optimized.

2.3. The singlet states: particular properties

In singlet states the $G_{\alpha\beta;\alpha\beta}$ spin-block determines all the other spin-blocks of the G-particle-hole matrix [13]. As a consequence, it can be shown that [43]

$$E = Tr(h^1 D_{\alpha;\alpha}) - Tr(\mathcal{H} G_{\alpha\beta;\alpha\beta}) \tag{11}$$

where

$$\mathcal{H}_{im;lj} = (2^0 H_{ij;ml} - {}^0 H_{ij;lm}) \tag{12}$$

and

$$h_{i;m} = \sum_l \mathcal{H}_{il;ml} \tag{13}$$

Note that the term involving explicitly the 1-RDM in (11) is linear, while the well known expression of the energy involving the 2-RDM is quadratic in the 1-RDM elements (see Eq. (7)).

2.3.1. Symmetry properties of the $G_{\alpha\beta;\alpha\beta}$ spin-block
It can be established that for this spin-block

$$G_{ss;ss}, \quad G_{ss';ss'}, \quad G_{s's;ss'}, \quad G_{s's';ss} \tag{14}$$

are the only non-vanishing symmetry species, where s generically denotes the *orbital symmetry* of the point group of the studied molecular system.

It can also be shown that, for singlet states, in the natural spin–orbital basis set, the off-diagonal elements satisfy the following symmetry relations:

$$G_{p\bar{r};s\bar{q}} = G_{q\bar{s};r\bar{p}} = G_{r\bar{p};q\bar{s}} = G_{s\bar{q};p\bar{r}} \tag{15}$$

where the bar over an index denotes that the spin–orbital has a β spin. In practice, and in this representation, there are many elements which have a negligible value. Globally speaking, the $G_{\alpha\beta;\alpha\beta}$ matrix can be considered to be sparse which indicates the convenience, in large calculations, to carry out a preliminary selection of the elements to be evaluated.

3. The GHV equation for singlet states

In this section we report an optimized form of the GHV equation for singlet states. We start by considering the compact form of the matrix-equation to be solved:

$$\langle \Psi | [\hat{H}, \hat{G}_{q\bar{p};m\bar{l}}] | \Psi \rangle = 0 \tag{16}$$

When developing this equation the resulting expression is a functional of the $^{(3;2,1)}C_{\sigma\sigma\bar{\sigma};\sigma\bar{\sigma}\sigma}$ and $^{(3;2,1)}C_{\sigma\sigma\bar{\sigma};\sigma\bar{\sigma}\sigma}$ types of elements, where σ denotes any of the two spin-functions α or β. In order to

reduce to the outmost the number of correlation matrix elements to be evaluated, we first convert all the $^{(3;2,1)}C$ types appearing in the GHV equation to the form $^{(3;2,1)}C_{\alpha\alpha\beta;\alpha\alpha\beta}$. The first consideration is to recall that for singlet states one may interchange the roles played by the two spin-functions α and β. Hence, one may just consider that the spin function σ is α. Moreover, it can be shown that:

$$^{(3;2,1)}C_{ip\bar{r};j\bar{q}s} = 2^2 D_{ip;js} {}^1\overline{D}_{\bar{r};\bar{q}} - {}^{(3;2,1)}C_{ip\bar{r};js\bar{q}} \tag{17}$$

$$^{(3;2,1)}C_{ip\bar{r};jq\bar{s}} = -2^2 D_{ip;q\bar{s}}\delta_{r,j} + 2^2 D_{ip;js}\delta_{r,q} - 2^2 D_{ir;jq}\delta_{\bar{p},\bar{s}} - {}^{(3;2,1)}C_{ir\bar{p};jq\bar{s}} \tag{18}$$

These two relations allow to express all the $^{(3;2,1)}C$-matrix elements appearing in the GHV equation in a unique form, which implies that for singlet states one has:

$$\left\langle \Psi | [\hat{H}, \hat{G}_{q\bar{p};m\bar{l}}] | \Psi \right\rangle = f \left({}^0H, \, {}^{(3;2,1)}C_{\alpha\alpha\beta;\alpha\alpha\beta} \right) \tag{19}$$

In our study of the weakly correlated ground-states Ref. [27], a set of approximating algorithms for the $^{(3;1,1)}C$ were reported. Therefore, in order to look for adequate algorithms to approximate the 3-order correlation matrix elements when the state is highly correlated we wish to take advantage of the experience gained in our previous study of weakly correlated states and look for $^{(3;1,1,1)}C_{\alpha\alpha\beta;\alpha\alpha\beta}$ instead of $^{(3;2,1)}C_{\alpha\alpha\beta;\alpha\alpha\beta}$ by using relation (10).

4. The approximating algorithms

As mentioned in Section 1, the so far proposed algorithms for the calculation of higher order correlation matrices in terms of the lower order ones, provide excellent results for singlet states dominated by a single Slater determinant, i.e. for states whose natural orbital occupation numbers are either close to 1 or to 0, close to fully occupied or empty. Those states can be considered as slightly correlated.

This paper is mainly devoted to the design of new approximating algorithms for states with stronger correlation effects. To solve this open question is not an easy task, since it implies to approximate the 3-body correlation matrix for those states where the perturbation theory does not give a sufficiently accurate answer. Our approach to this problem has been inductive. Thus, we have analyzed the numerical values of the correlation matrices obtained with the FCI method for a series of states, and in particular for the two states considered here. Our test system has been the BeH_2 in its linear symmetry, $D_{\infty h}$, which is the most stable conformation for the electronic ground state of this molecule. This system has repeatedly been our test molecule in the past because its structure – when calculated in a minimal basis set representation – is not trivial and yet, due to its high symmetry properties, the number of non-vanishing elements of its third order matrices is small, which significantly facilitates the analysis of the results. The two excited states selected for our study are: a member of the degenerate $^1\Pi_g$ level, and a $^1\Sigma_u^-$. These two states will be labelled in this paper as State A and State B. Both are dominated by a single CSF composed of two equally weighed Slater determinants to form a singlet state. As mentioned previously, these type of states are highly correlated and of great interest both in spectroscopic studies and in quantum information. Their natural orbital occupation numbers are, hence, close to fully occupied, close to half-occupied or empty. The active role played by the frontier orbitals in determining the values of the ground state cumulants, or equivalently, the correlation terms, has been already signaled [39]. Here the idea of frontier orbitals has been extended to those orbitals with intermediate occupancies, according to whether their

occupation numbers are above or below 0.5. The difference between the diagonal element in 1-RDM and in 1-HRDM classifies an orbital as occupied or empty.

$$T(i) = {}^1D_{i;i} - {}^1\overline{D}_{i;i} > 0 \quad i \text{ is occupied}$$
$$T(i) = {}^1D_{i;i} - {}^1\overline{D}_{i;i} < 0 \quad i \text{ is empty}$$

In addition to the orbital classification by its occupation number, in what follows use is made of their spatial symmetry properties, the irreducible representation to whom they belong.

When considering their contribution to correlation effects, not all the orbitals are similarly active. In fact, they can be classified as follows.

- The *active occupied orbitals* (o), which are the orbitals with occupation number larger than 0.5.
- The *frontier occupied orbital* (o_f), which is the o with the closest to 0.5 occupation number. This is given as input datum in the calculation.
- The *active empty orbitals* (e), which are the orbitals with occupation number lower than 0.5.
- The *frontier empty orbital* (e_f), which is the e with the closest to 0.5 occupation number. This is given as input datum in the calculation.
- The *independent occupied orbitals* (io), which do not contribute actively to correlation and which have an occupation number close to 1. These orbitals satisfy $1 - {}^1D_{i;i} < \epsilon_o$ where ϵ_o is an input datum in the code.
- The *independent empty orbitals* (ie), which do not contribute actively to correlation and which have an occupation number close to 0. These orbitals satisfy ${}^1D_{i;i} < \epsilon_e$ where ϵ_e is an input datum in the code.

The relative positions of the orbital labels in a given matrix element, the kind of orbitals involved, and whether one or various orbitals are repeated determine the element *type*. Our *first working hypothesis* is that its type determines the value of the correlation matrix element considered. In principle, the whole set of types of elements in the correlation matrix may be rather large but those types leading to non-negligible element values form, in practice, a small subset of them, the *active* types. This is an ideal situation since, in that case, only a small set of matrix elements need to be approximated.

In addition, subsets of active types for different stationary states of the molecule may have common elements. Our working hypothesis is, hence, that states with analogous zero-order wave-functions share many common active types of significant elements in their correlation matrices.

The results obtained when calculating the 3-body correlation matrix of the two singlet states A and B of the linear BeH$_2$ molecule with the FCI method and with other approximate methods have been carried out. In all these calculations a minimal basis set in the natural spin–orbital representation was used. The FCI values of the 1-RDM diagonal elements of these states in this representation are:

| State A | 0.99998 | 0.95545 | 0.04003 | 0.50037 | 0.00210 | 0.50000 | 0.00207 |
| State B | 0.99998 | 0.97949 | 0.49012 | 0.50168 | 0.00779 | 0.01047 | 0.01047 |

which implies that the orbitals in each of the two states considered can be classified as:

State	Orbital						
	1	2	3	4	5	6	7
A	io	o	e	o_f	e	e_f	e
B	io	o	e_f	o_f	e	e	e

This classification of the orbitals jointly with the exact value of the ${}^{(3;1,1,1)}C_{\alpha\alpha\beta;\alpha\alpha\beta}$, in each of the states, allows to establish which are the active types in these two excited singlet states. As expected, most of the active types were common to both states.

Once this task was completed we based our research in our second and main working hypothesis: *the value of any given* ${}^{(3;1,1,1)}C_{\alpha\alpha\beta;\alpha\alpha\beta}$ *element is a functional of the* $C_{\alpha\beta;\alpha\beta}$.

Having in mind all these considerations we have constructed a set of algorithms which have been subsequently codified in the computational program used in the calculation of the 3-order correlation matrices of the two states under study in order to compare the results with the corresponding FCI ones.

4.1. The algorithms for the diagonal elements

The different active types for the generic diagonal element ${}^{(3;1,1,1)}C_{ijl;ijl}$ and their approximating algorithms are reported in Table 1. In this table the generic i, j, l subscripts are replaced when necessary by the symbols indicating the possible o, e, o_f, e_f character of the orbitals involved (the io and ie orbitals are not generally involved in the active types).

4.2. The algorithms for the off-diagonal elements

In Table 2 we report the approximating algorithms for the off-diagonal elements whose generic element is ${}^{(3;1,1,1)}C_{ijl;pqr}$.

Table 1
Main contributions to the third-order correlation matrix: diagonal elements.

${}^{(3;1,1,1)}C$ type	Algorithm
${}^{(3,1,1,1)}C_{o_f e_f \bar{e}_f ; o_f e_f \bar{e}_f}$	$C_{o_f e_f ; o_f e_f} \cdot {}^1\overline{D}_{e_f,e_f}$
${}^{(3,1,1,1)}C_{o_f \bar{o}_f e_f ; o_f e_f \bar{o}_f}$	$C_{o_f \bar{o}_f ; o_f \bar{o}_f} \cdot {}^1\overline{D}_{e_f,e_f}$
${}^{(3,1,1,1)}C_{e_f o_f \bar{e}_f ; e_f o_f \bar{e}_f}$	$C_{e_f e_f ; e_f e_f} \cdot {}^1\overline{D}_{o_f,o_f}$
${}^{(3,1,1,1)}C_{e_f \bar{o}_f \bar{o}_f ; e_f o_f \bar{o}_f}$	$C_{e_f \bar{o}_f ; e_f \bar{o}_f} \cdot {}^1 D_{o_f;o_f}$
${}^{(3,1,1,1)}C_{e_f o_f \bar{o} ; e_f o_f \bar{o}}$	$C_{o_f \bar{o} ; o_f \bar{o}}$
${}^{(3,1,1,1)}C_{oe_f \bar{e}_f ; oe_f \bar{e}_f}$ $(s(o) \neq s(e))$	$C_{oe_f ; oe_f} \cdot {}^1\overline{D}_{e_f,e_f}$
${}^{(3,1,1,1)}C_{oe_f \bar{e}_f ; oe_f \bar{e}_f}$ $(s(o) = s(e))$	$-C_{oe_f ; oe_f} \cdot {}^1\overline{D}_{e_f,e_f}$
${}^{(3,1,1,1)}C_{ie_f \bar{e}_f ; ie_f \bar{e}_f}$	$C_{ie_f ; ie_f} \cdot {}^1\overline{D}_{e_f,e_f}$
${}^{(3,1,1,1)}C_{io_f \bar{o}_f ; io_f \bar{o}_f}$	$C_{io_f ; io_f} \cdot {}^1 D_{o_f;o_f}$
${}^{(3,1,1,1)}C_{io_f \bar{e}_f ; io_f \bar{e}_f}$	$C_{ie_f ; ie_f}$
${}^{(3,1,1,1)}C_{eo_f \bar{e}_f ; eo_f \bar{e}_f}$	$-C_{ee_f ; ee_f} \cdot {}^1 D_{o_f;o_f}$
${}^{(3,1,1,1)}C_{o_f e_f \bar{l} ; o_f e_f \bar{l}}$	$-C_{o_f l ; o_f l} \cdot {}^1\overline{D}_{e_f,e_f}$
${}^{(3,1,1,1)}C_{ee\bar{l} ; ee\bar{l}}$	$C_{e\bar{l} ; e\bar{l}}$
${}^{(3,1,1,1)}C_{oe\bar{o}_f ; oe\bar{o}_f}$	$C_{o\bar{o}_f ; o\bar{o}_f}$
${}^{(3,1,1,1)}C_{ee_f \bar{o}_f ; ee_f \bar{o}_f}$	$-C_{e\bar{o}_f ; e\bar{o}_f} \cdot {}^1\overline{D}_{e_f;e_f}$
${}^{(3,1,1,1)}C_{e_f ee_f ; e_f ee_f}$	$-C_{e_f e_f ; e_f e_f} \cdot {}^1\overline{D}_{e;e}$
${}^{(3,1,1,1)}C_{o_f e\bar{o}_f ; o_f e\bar{o}_f}$	$C_{o_f \bar{o}_f ; o_f \bar{o}_f} \cdot {}^1 D_{e;e}$
${}^{(3,1,1,1)}C_{le_f l ; le_f l}$	$C_{ll;ll} \cdot {}^1\overline{D}_{e_f,e_f}$
${}^{(3,1,1,1)}C_{lo_f l ; lo_f l}$	$C_{ll;ll} \cdot {}^1 D_{o_f,o_f}$
${}^{(3,1,1,1)}C_{e_f e_f \bar{e}_f ; e_f e_f \bar{e}_f}$	$C_{e_f e_f ; e_f e_f} \cdot {}^1\overline{D}_{e_f,e_f}$
${}^{(3,1,1,1)}C_{oo_f l ; oo_f l}$	$C_{ol;ol}$
${}^{(3,1,1,1)}C_{oe_f l ; oe_f l}$	$C_{ol;ol}$
${}^{(3,1,1,1)}C_{e_f ee ; e_f ee}$	$C_{e_f e ; e_f e}$
${}^{(3,1,1,1)}C_{eo\bar{o} ; eo_f \bar{o}}$	$-C_{o_f \bar{o} ; o_f \bar{o}} \cdot {}^1 D_{e;e}$
${}^{(3,1,1,1)}C_{ee\bar{l} ; ee_f \bar{l}}$	$-C_{e\bar{l} ; e\bar{l}} \cdot {}^1\overline{D}_{e_f;e_f}$
${}^{(3,1,1,1)}C_{iee;iee}$ $(s(i) = s(e))$	$-C_{ee;ee}$
${}^{(3,1,1,1)}C_{iee;iee}$ $(s(i) \neq s(e))$	$C_{ie;ie}$
${}^{(3,1,1,1)}C_{iei;iei}$ $(s(i) \neq s(e))$	$-C_{ei;ei}$
${}^{(3,1,1,1)}C_{ie\bar{i};ie\bar{i}}$ $(s(i) = s(e))$	$C_{ii;ii}$

The numerous types which determine elements with non-negligible value can be classified according to one characteristic. Thus, the elements can be classified according to the following conditions:

- $j = p \in e$
- $j = p \in o$
- $j = q \in e$
- $j = q \in o$
- $j = r \in e$
- $j = r \in o$

Besides these main conditions, other inter-relations have, in some cases, to be taken into account. As was the case for the diagonal elements we will mark in the $^{(3;1,1,1)}C$ the general subscripts by using the symbols o, o_f, e and e_f.

As was also the case in the diagonal elements, most of the off-diagonal algorithms are rather simple. There are, however, some special off-diagonal types whose approximation requires more complex algorithms; these special cases are collected in Table 3.

5. Results

In this section we report the results obtained with the algorithms previously reported for those elements of the $^{(3;1,1,1)}C_{\alpha\alpha\beta,\alpha\alpha\beta}$ corresponding to the two singlet states denoted state A and state B above described. In Tables 4–7 (provided as electronic Supplementary material, Appendix B) our results are compared with the exact FCI values thus showing the quality of the presently proposed approximations. In order to show the improvement in accuracy achieved when compared with previous approximations we also report the value obtained when using the modified Nakatsuji–Yasuda (m-NY) algorithm [28,30] which was used in the successful calculations of the ground states of a series of compounds with the GHV [28,30–32] mentioned above.

5.1. Diagonal elements of state A

The values of the diagonal elements having an absolute value larger than 0.002 are shown in Table 4. Only in seven cases the m-NY algorithm yields a slightly better approximation to the correct value of the element considered; in all the remaining cases the algorithm proposed here shows an unquestionable improvement. The good performance of our algorithm is particularly striking when evaluating the two elements with larger absolute value $^{(3;1,1,1)}C_{464;464}$ and $^{(3;1,1,1)}C_{466;466}$ which are both approximated with a high accuracy. These elements are respectively of the following types: $^{(3;1,1,1)}C_{o_f e_f \bar{o}_f; o_f e_f \bar{o}_f}$ and $^{(3;1,1,1)}C_{o_f e_f \bar{o}_f; o_f o_f \bar{o}_f}$. This shows that all the orbitals involved in the type of the higher valued $^{(3;1,1,1)}C_{\alpha\alpha\beta,\alpha\alpha\beta}$ elements of this state are *frontier orbitals*. The remaining elements with a significant value involve one or two frontier orbitals.

5.2. Off-diagonal elements of state A

The values of the off-diagonal elements having an absolute value larger than 0.008 are shown in Table 5.

The values of the off-diagonal elements are significantly larger than those of the diagonal ones. Thus, the largest element, which is well approximated, is $^{(3;1,1,1)}C_{456;564}$ whose value is 0.45863. As was the case in the diagonal elements all the orbitals involved in this element are frontier ones. In fact, the trends shown by the diagonal elements (Table 4) are enhanced here, thus the larger values correspond to the elements involving more frontier orbitals.

The performance of the new algorithms is excellent and strikingly better than the m-NY algorithm.

Table 2
Main contributions to the third-order correlation matrix: off-diagonal elements.

$^{(3;1,1,1)}C$ type	Algorithm
$^{(3;1,1,1)}C_{ie_f\bar{i};e_f q\bar{q}}$	$C_{\bar{i}\bar{i};q\bar{q}} \cdot {}^1\overline{D}_{e_f;e_f}$
$^{(3;1,1,1)}C_{ie_f\bar{o}_f;e_f o_f\bar{i}}$	$C_{i\bar{o}_f;o_f\bar{i}}$
$^{(3;1,1,1)}C_{ie\bar{e}_f;ee_f\bar{i}}$	$C_{i\bar{e}_f;e_f\bar{i}} \cdot {}^1\overline{D}_{e,e}$
$(|T(e)| < \epsilon)$	
$^{(3;1,1,1)}C_{ie\bar{l};eq\bar{r}}$	$C_{\bar{i}\bar{l};q\bar{r}}$
$^{(3;1,1,1)}C_{io_f\bar{i};o_f q\bar{r}}$	$C_{\bar{i}\bar{i};q\bar{r}} \cdot {}^1\overline{D}_{o_f,o_f}$
$^{(3;1,1,1)}C_{io_f\bar{o}_f;o_f q\bar{r}}$	$C_{i\bar{o}_f;q\bar{r}}$
$^{(3;1,1,1)}C_{ij e_f;j e_f\bar{i}}$	$C_{i\bar{e}_f;e_f\bar{i}} \cdot {}^1\overline{D}_{e,e}$
$^{(3;1,1,1)}C_{ij\bar{o}_f;j o_f\bar{i}}$	$C_{i\bar{o}_f;o_f\bar{i}} \cdot {}^1\overline{D}_{o_f;o_f}$
$(|T(j)| < \epsilon)$	
$^{(3;1,1,1)}C_{io_f\bar{l};p o_f\bar{r}}$	$C_{\bar{i}\bar{l};p\bar{r}} \cdot {}^1D_{o_f,o_f}$
$^{(3;1,1,1)}C_{io\bar{l};p o\bar{r}}$	$C_{\bar{i}\bar{l};p\bar{r}}$
$^{(3;1,1,1)}C_{ie_f\bar{l};p e_f\bar{p}}$	$C_{\bar{i}\bar{l};p\bar{p}} \cdot {}^1\overline{D}_{e_f;e_f}$
$^{(3;1,1,1)}C_{ie_f\bar{o}_f;p e_f\bar{o}_f}$	$C_{io_f;p\bar{o}_f} \cdot {}^1\overline{D}_{e_f;e_f}$
$^{(3;1,1,1)}C_{ie_f\bar{e}_f;p e_f\bar{e}_f}$	$C_{i\bar{e}_f;p\bar{e}_f} \cdot {}^1\overline{D}_{e_f;e_f}$
$^{(3;1,1,1)}C_{ie_f\bar{l};l e_f\bar{i}}$	$C_{\bar{i}\bar{l};l\bar{i}} \cdot {}^1\overline{D}_{e_f;e_f}$
$^{(3;1,1,1)}C_{o_f e_f\bar{l};o_f e_f\bar{r}}$	$C_{o_f\bar{l};o_f\bar{r}} \cdot {}^1\overline{D}_{e_f;e_f}$
$^{(3;1,1,1)}C_{ie_f\bar{o}_f;o_f e_f\bar{i}}$	$C_{io_f;o_f\bar{i}} \cdot {}^1\overline{D}_{e_f;e_f}$
$^{(3;1,1,1)}C_{ie\bar{l};p e\bar{r}}$	$C_{\bar{i}\bar{l};p\bar{r}}$
$^{(3;1,1,1)}C_{io e;ie\bar{o}}$	$-C_{io;io}$
$^{(3;1,1,1)}C_{io o';p o'\bar{o}}$	$C_{io';p\bar{o}'} \cdot {}^1D_{o,o}$
$^{(3;1,1,1)}C_{io\bar{l};pq\bar{o}}$	$C_{\bar{i}\bar{l};pq}$
$^{(3;1,1,1)}C_{ie\bar{o}_f;p o_f\bar{e}}$	$-C_{i\bar{o}_f;p\bar{o}_f}$
$^{(3;1,1,1)}C_{ie e_f;p e_f\bar{e}}$	$-C_{i\bar{e}_f;p\bar{e}_f}$
$^{(3;1,1,1)}C_{o_f e\bar{e};o o_f\bar{e}_f}$	$C_{o_f\bar{e};o\bar{o}_f}$
$^{(3;1,1,1)}C_{ie_f\bar{e};pe\bar{e}_f}$	$-C_{i\bar{e}_f;i\bar{e}_f}$
$^{(3;1,1,1)}C_{ee_f\bar{e};pe\bar{e}_f}$	$-C_{ee_f;p\bar{e}_f}$
$^{(3;1,1,1)}C_{ie\bar{l};pq\bar{e}}$	$-C_{\bar{i}\bar{l};pq}$
$^{(3;1,1,1)}C_{e_f j e_f;pq\bar{e}_f}$	$-C_{j e_f;p\bar{q}} \cdot {}^1D_{e_f;e_f}$
$^{(3;1,1,1)}C_{oj\bar{l};p o\bar{r}}$	$-C_{j\bar{l};p\bar{r}}$
$^{(3;1,1,1)}C_{oj\bar{e}_f;e_f o\bar{r}}$	$-C_{j\bar{e}_f;e_f\bar{r}} \cdot {}^1D_{o;o}$
$^{(3;1,1,1)}C_{ol\bar{l};p o\bar{p}}$	$-C_{\bar{l}\bar{l};p\bar{p}} \cdot {}^1D_{o;o}$
$^{(3;1,1,1)}C_{oj\bar{l};l o\bar{j}}$	$-C_{j\bar{l};l\bar{j}} \cdot {}^1D_{o;o}$
$^{(3;1,1,1)}C_{o_f j\bar{l};p o_f\bar{p}}$	$-C_{j\bar{l};p\bar{p}}$
$^{(3;1,1,1)}C_{ij\bar{o}_f;o_f e\bar{e}}$	$-C_{ij;e\bar{e}}$
$^{(3;1,1,1)}C_{io o_f;o_f q\bar{r}}$	$-C_{io_f;q\bar{r}} \cdot {}^1\overline{D}_{o_f;o_f}$
$^{(3;1,1,1)}C_{ij\bar{e}_f;e_f q\bar{e}_f}$	$-C_{ij;q\bar{e}_f} \cdot {}^1\overline{D}_{e_f;e_f}$
$^{(3;1,1,1)}C_{e_f j\bar{e}_f;e_f q\bar{e}_f}$	$C_{j\bar{e}_f;e_f\bar{q}} \cdot {}^1D_{e_f;e_f}$
$^{(3;1,1,1)}C_{e_f j\bar{e}_f;p e_f\bar{r}}$	$-C_{j\bar{e}_f;p\bar{r}}$
$^{(3;1,1,1)}C_{e_f e\bar{e};p e_f\bar{p}}$	$C_{e\bar{e};p\bar{p}} \cdot {}^1D_{e_f;e_f}$
$(s(e) = s(e_f))$	
$^{(3;1,1,1)}C_{e_f e\bar{e};p e_f\bar{p}}$	$-C_{e\bar{e};p\bar{p}} \cdot {}^1D_{e_f;e_f}$
$(s(e) \neq s(e_f))$	
$^{(3;1,1,1)}C_{e_f o_f\bar{l};p e_f\bar{p}}$	$-C_{o_f\bar{l};p\bar{p}}$
$^{(3;1,1,1)}C_{ij\bar{e}_f;p e_f\bar{p}}$	$C_{ij;p\bar{p}}$
$^{(3;1,1,1)}C_{ij\bar{e}_f;p e_f\bar{r}}$	$C_{ij;p\bar{r}}$
$^{(3;1,1,1)}C_{o_f j\bar{j};pq\bar{o}_f}$	$-C_{j\bar{j};p\bar{q}}$

5.3. Diagonal elements of state B

The values of the diagonal elements having an absolute value larger than 0.002 are shown in Table 6. Only very few diagonal elements have significant values. However, as was the case in state A, the two really large values correspond to elements involving only frontier orbitals. An interesting feature is that, while in state A the element with negative sign involved twice the frontier occupied orbital, the negative element in the B state, with a much higher energy value, involves twice the frontier empty orbital.

Table 3
Main contributions to the third-order correlation matrix: some special cases.

$^{(3;1,1,1)}C$ type	Algorithm
$^{(3;1,1,1)}C_{e o_f \bar{e}_f ; p e_f \bar{o}_f}$	$C_{e \bar{e}_f ; p \bar{e}_f} - \frac{1}{2}\left(C_{e e \bar{e}_f ; e \bar{e}_f} + C_{p \bar{e}_f ; p \bar{e}_f} \right)$
$^{(3;1,1,1)}C_{o o_f \bar{e}_f ; p e_f \bar{o}_f}$	$-C_{o \bar{e}_f ; p \bar{e}_f} + \frac{1}{2}\left(C_{o \bar{e}_f ; o \bar{e}_f} + C_{p \bar{e}_f ; p \bar{e}_f} \right)$
$^{(3;1,1,1)}C_{o \bar{e}_f \bar{o}_f ; p o_f \bar{e}_f}$	$C_{o \bar{e}_f ; p \bar{e}_f} - \frac{1}{2}\left(C_{o \bar{o}_f ; o \bar{o}_f} + C_{p \bar{o}_f ; p \bar{o}_f} \right)$
$^{(3;1,1,1)}C_{e e_f \bar{o}_f ; p o_f \bar{e}_f}$	$-C_{i \bar{e}_f ; p \bar{e}_f} + \frac{1}{2}\left(C_{e \bar{o}_f ; e \bar{o}_f} + C_{p \bar{o}_f ; p \bar{o}_f} \right)$
$^{(3;1,1,1)}C_{o o_f \bar{e}_f ; o e_f \bar{o}_f} = -{}^{(3;1,1,1)}C_{o e_f \bar{o}_f ; o o_f \bar{e}_f}$	$C_{o \bar{o}_f ; o \bar{o}_f} + C_{o \bar{e}_f ; o \bar{e}_f}$
$^{(3;1,1,1)}C_{e o_f \bar{e}_f ; e e_f \bar{o}_f} \approx -{}^{(3;1,1,1)}C_{e e_f \bar{o}_f ; e o_f \bar{e}_f}$	$-\left(C_{e \bar{o}_f ; e \bar{o}_f} + C_{e \bar{e}_f ; e \bar{e}_f} \right)$
$^{(3;1,1,1)}C_{e o_f \bar{e} ; p e \bar{o}_f}$	$\frac{1}{2}\left(C_{e \bar{o}_f ; e \bar{o}_f} + C_{p \bar{o}_f ; p \bar{o}_f} \right)$
$^{(3;1,1,1)}C_{o_f e_f \bar{l} ; l o_f \bar{r}}$	$-\frac{1}{2}\left(C_{l \bar{o}_f ; l o_f} + C_{l \bar{r} ; l \bar{r}} \right)$
$^{(3;1,1,1)}C_{e e_f \bar{o}_f ; o_f e_f \bar{o}} = {}^{(3;1,1,1)}C_{o_f e_f \bar{o} ; e o_f \bar{e}_f}$	$-\frac{1}{4}\left(C_{o \bar{o}_f ; o \bar{o}_f} + C_{o \bar{e}_f ; o \bar{e}_f} + C_{o_f \bar{e} ; o_f \bar{e}} + C_{e_f \bar{e} ; e_f \bar{e}} \right)$
$\approx {}^{(3;1,1,1)}C_{o_f e_f \bar{o} ; e e_f \bar{o}_f} \approx -{}^{(3;1,1,1)}C_{o o_f \bar{e}_f ; o_f e_f \bar{e}}$	

5.4. Off-diagonal elements of state B

The values of the off-diagonal elements having an absolute value larger than 0.008 are shown in Table 7. The first noticeable characteristic of this table is that there are fewer elements with a significant value and, in general, all elements have much lower values than in state A. Apart from this characteristic, the performance of the new algorithms is similar as in state A. Thus, the elements involving more frontier orbitals have also here the larger value. Also, as was the case in state A, the new algorithm performs well and clearly much better than the m-NY.

It should be stressed that all these calculations have been carried out with a unique code, thus showing that, as we expected, a similar wave-function structure implies that the active types coincide in both cases to a great extent.

5.5. Final comments and future work

The study presented in the previous sections can be considered a strong inductive argument since it confirms our working hypothesis that:

- The three-body correlation effects are somehow implicit and can be estimated, or at least fairly well approximated, from the two-body correlation effects.
- The type of a $^{(3;1,1,1)}C_{\alpha\alpha\beta,\alpha\alpha\beta}$ element fixed by the o, e, o_f, e_f character, the relative positions, and, in some cases, by the symmetry of the natural orbitals involved in the element determines its value.
- The value of a $^{(3;1,1,1)}C_{\alpha\alpha\beta,\alpha\alpha\beta}$ element can be accurately determined by a simple functional of two-body correlation matrix elements.

On the other hand we are aware that, while keeping the size of the problem compatible with the possibility of a FCI treatment, it is convenient to extend the sample for our enumerative inductive argument to a system with a non-linear geometry so as to analyze the influence of a different point-group symmetry of the orbitals.

The next aspect of the problem which will be studied concerns the N-representability of the approximated matrix. However, no particular N-representability condition is known for the $^{(3;1,1,1)}C_{\alpha\alpha\beta,\alpha\alpha\beta}$ spin-block. On the other hand, this spin-block is directly related with the $^{(3;1,1,1)}C_{\alpha\beta\alpha,\alpha\beta\alpha}$ spin-block whose elements, in different matrix positions, form the $^{(3;1,1,1)}G_{\alpha\alpha\beta,\alpha\alpha\beta}$ spin-block which is both symmetric and positive semi-definite [11]. Therefore, the spin-block formed by the elements

$$^{(3;1,1,1)}C_{ijl;p\bar{q}r} = {}^{(3;1,1,1)}G_{ip\bar{j};rl\bar{q}}$$

must also be both symmetric and positive semi-definite.

Although these future studies may introduce some optimization on the algorithms reported here, we do not expect that they will be much modified. Therefore, we anticipate that the study of a large class of correlated states using the GHV method will now be possible. At this respect it should be noted that the simplicity of the algorithms is a very attractive feature since it largely compensates the need to specify which are the active types. Another important trait which, in future, will also greatly contribute to reduce the cost of the GHV calculations is the fact that the $C_{\alpha\beta;\alpha\beta}$ matrix is rather sparse and that its non-negligible types are easily foretold when the 1-RDM is known. Consequently, for singlet states, only a small number of the $G_{\alpha\beta;\alpha\beta}$ elements play an active role when solving the GHV equations.

Another very interesting general property of the $^{(3;2,1)}C_{\alpha\alpha\beta,\alpha\alpha\beta}$ spin-block is the fact that only very few elements have large values. It suggests the possibility of designing a semi-empirical or parametrized type method which could work for larger systems.

Excited states which require more than two Slater determinants to reasonably describe their zero-order wavefunction will constitute the next goal. In those cases the algorithms will be plagued by the fact that many orbitals play the role of "frontier orbitals".

Acknowledgements

Appendix A. Synopsis of the 2-order contracted equations

CSE
- { 2-order contracted Schrödinger equation
- { Density equation, Hierarchy equation
- $\left\langle \Psi \left| \hat{H} a_i^\dagger a_j^\dagger a_q a_p \right| \Psi \right\rangle = E 2!^2 D_{ij;pq}$
- Depends on the 2-, 3-, 4-RDM
- Necessary and sufficient
- Iterative solution (N-representability partially lost), K^6 scaling

ACSE
- { Anti-Hermitian contracted Schrödinger equation
- { 2-order contracted Liouville equation
- $\left\langle \Psi \left| [\hat{H}, a_i^\dagger a_j^\dagger a_q a_p] \right| \Psi \right\rangle = 0$
- Depends on the 2-, 3-RDM
- Necessary
- Iterative solution (N-representability almost preserved), K^6 scaling

CCSE
- 2-order correlation contracted Schrödinger equation
- $\left\langle \Psi \left| \hat{H} a_i^\dagger a_p \hat{Q} a_j^\dagger a_q \right| \Psi \right\rangle = E\, C_{ij;pq}$
- Depends on the 2-, 3-, and 4-order correlation matrices
- Necessary and sufficient
- Iterative solution (N-representability partially lost), K^6 scaling

GHV
- { 2-order G-particle-hole hypervirial equation
- { 2-order correlation contracted Liouville equation
- $\left\langle \Psi \left| [\hat{H}, a_i^\dagger a_p \hat{Q} a_j^\dagger a_q] \right| \Psi \right\rangle = 0$
- Depends on the 2- and 3-order correlation matrices
- Necessary, stronger than ACSE
- Iterative solution (N-representability almost preserved), K^6 scaling

Appendix B. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.comptc.2012.09.021.

References

[1] A.J. Coleman, Structure of fermion density matrices, Rev. Mod. Phys. 35 (1963) 668–689.

[2] E.R. Davidson, Reduced Density Matrices in Quantum Chemistry, Academic Press, New York, 1976.

[3] Density matrices and density functionals, in: R.M. Erdahl, V. Smith (Eds.), Proceedings of the A.J. Coleman Symposium, Kingston, Ontario, 1985, Reidel, Dordrecht, 1987.

[4] J. Cioslowski, Many-electron Densities and Reduced Density Matrices, Kluwer, Dordrecht, The Netherlands, 2000.

[5] D.A. Mazziotti (Ed.), Reduced-density-matrix mechanics with applications to many-electron atoms and molecules, Adv. Chem. Phys. (2007) 134.

[6] C. Garrod, J.K. Percus, Reduction of N-particle variational problem, J. Math. Phys. 5 (1964) 1756–1776.

[7] H. Kummer, N-representability problem for reduced density matrices, J. Math. Phys. 8 (1967) 2063–2081.

[8] R.M. Erdahl, Representability, Int. J. Quantum Chem. 13 (1978) 697–718.

[9] A.J. Coleman, V.I. Yukalov, Reduced Density Matrices: Coulson's Challenge, Springer Verlag, New York, 2000.

[10] C. Valdemoro, M.P. de Lara-Castells, E. Pérez-Romero, L.M. Tel, The first order contracted density equations: correlation effects, Adv. Quantum Chem. 31 (1999) 37–52.

[11] C. Valdemoro, L.M. Tel, E. Pérez-Romero, N-representability problem within the framework of the contracted Schrödinger equation, Phys. Rev. A 61 (2000) 032507.

[12] C. Valdemoro, L.M. Tel, D.R. Alcoba, E. Pérez-Romero, F.J. Casquero, Some basic properties of the correlation matrices, Int. J. Quantum Chem. 90 (2002) 1555–1561.

[13] D.R. Alcoba, C. Valdemoro, Spin structure and properties of the correlation matrices corresponding to pure spin states: controlling the S-representability of these matrices, Int. J. Quantum Chem. 102 (2005) 629–644;
D.R. Alcoba, C. Valdemoro, Spin structure and properties of the correlation matrices corresponding to pure spin states: controlling the S-representability of these matrices, Int. J. Quantum Chem. 106 (2006) 2999.

[14] D.R. Alcoba, C. Valdemoro, L.M. Tel, E. Pérez-Romero, Controlling the N- and S-representability of the second-order reduced density matrix: the doublet-state case, Phys. Rev. A 77 (2008) 042508.

[15] C. Garrod, M. Rosina, Particle-hole matrix – its connection with symmetries and collective features of ground state, J. Math. Phys 10 (1975) 1855–1861.

[16] H. Nakatsuji, Equation for direct determination of density matrix, Phys. Rev. A. 14 (1976) 41–50.

[17] L. Cohen, C. Frishberg, Hierarchy equations for reduced density matrices, Phys. Rev. A. 13 (1976) 927–930.

[18] C. Valdemoro, Density matrices and density functionals, in: R.M. Erdahl, V. Smith (Eds.), Proceedings of the A.J. Coleman Symposium, Kingston, Ontario, 1985, Reidel, Dordrecht, 1987.

[19] F. Colmenero, C. Valdemoro, Self-consistent approximate solution of the second-order contracted Schrödinger equation, Int. J. Quantum Chem. 51 (1994) 369–388.

[20] H. Nakatsuji, K. Yasuda, Direct determination of the quantum-mechanical density matrix using the density equation, Phys. Rev. Lett. 76 (1996) 1039.

[21] C. Valdemoro, L.M. Tel, E. Pérez-Romero, The contracted Schrödinger equation: some results, Adv. Quantum Chem. 28 (1997) 33–46.

[22] D.A. Mazziotti, Contracted Schrödinger equation: determining quantum energies and two-particle density matrices without wave functions, Phys. Rev. A 57 (1998) 4219–4234.

[23] C. Valdemoro, L.M. Tel, E. Pérez-Romero, A. Torre, The iterative solution of the contracted Schrödinger equation: a new quantum chemical method, J. Mol. Struct. (Theochem.) 537 (2001) 1–8;
C. Valdemoro, L.M. Tel, E. Pérez-Romero, A. Torre, The iterative solution of the contracted Schrödinger equation: a new quantum chemical method, J. Mol. Struct. (Theochem.) 574 (2001) 255–256.

[24] D.R. Alcoba, C. Valdemoro, Family of modified-contracted Schrödinger equations, Phys. Rev. A 64 (2001) 062105.

[25] D.R. Alcoba, F.J. Casquero, L.M. Tel, E. Pérez-Romero, C. Valdemoro, Convergence enhancement in the iterative solution of the second-order contracted Schrödinger equation, Int. J. Quantum Chem. 102 (2005) 620–628.

[26] D.R. Alcoba, C. Valdemoro, L.M. Tel, E. Pérez-Romero, The correlation contracted Schrödinger equation: an accurate solution of the G-particle-hole hypervirial, Int. J. Quantum Chem. 109 (2009) 3178–3190.

[27] C. Valdemoro, D.R. Alcoba, L.M. Tel, E. Pérez-Romero, Theoretical and applicative properties of the correlation and G-particle-hole matrices, Int. J. Quantum Chem. 109 (2009) 2622–2638.

[28] D.R. Alcoba, L.M. Tel, E. Pérez-Romero, C. Valdemoro, Convergence and computational efficiency enhancements in the iterative solution of the G-particle-hole hypervirial equation, Int. J. Quantum Chem. 111 (2011) 937–949.

[29] C. Valdemoro, D.R. Alcoba, L.M. Tel, E. Pérez-Romero, Some theoretical questions about the G-particle-hole hypervirial equation, Int. J. Quantum Chem. 111 (2011) 245–255.

[30] D.R. Alcoba, C. Valdemoro, L.M. Tel, E. Pérez-Romero, O. Oña, Optimized solution procedure of the G-particle-hole hypervirial equation for multiplets: application to doublet and triplet states, J. Phys. Chem. A 115 (2011) 2599–2605.

[31] C. Valdemoro, D.R. Alcoba, O.B. Oña, L.M. Tel, E. Pérez-Romero, Combining the G-particle-hole hypervirial equation and the hermitian operator method to study electronic excitations and de-excitations, J. Math. Chem. 50 (2012) 492–509.

[32] G.E. Massaccesi, D.R. Alcoba, O.B. Oña, Symmetry-adapted formulation of the G-particle-hole hypervirial equation method, J. Math. Chem. 50 (2012) 2155–2167.

[33] A.J. Coleman, in: R.M. Erdahl (Ed.), Reduced Density Matrices with Applications to Physical and Chemical Systems II, Queen's Papers on Pure and Applied Mathematics—No. 40, Queen's University, Kingston, Ontario, 1974.

[34] E. Pérez-Romero, L.M. Tel, C. Valdemoro, Traces of spin-adapted reduced density matrices, Int. J. Quantum Chem. 61 (1997) 55–61.

[35] D.A. Mazziotti, Anti-Hermitian contracted Schrödinger equation: direct determination of the two-electron reduced density matrices of many-electron molecules, Phys. Rev. Lett. 97 (2006) 143002.

[36] F. Colmenero, C. Pérez del Valle, C. Valdemoro, Approximating q-order reduced density-matrices in terms of the lower-order ones. 1. General relations, Phys. Rev. A 47 (1993) 971–978.

[37] C. Valdemoro, Approximating the 2nd-order reduced density-matrix in terms of the 1st-order one, Phys. Rev. A 45 (1992) 4462–4467.

[38] D.A. Mazziotti, Approximate solution for electron correlation through the use of Schwinger probes, Chem. Phys. Lett. 289 (1998) 419–427.

[39] C. Valdemoro, L.M. Tel, E. Pérez-Romero, in: J. Cioslowski (Ed.), Many-electron Densities and Reduced Density Matrices, Kluwer, Dordrecht, The Netherlands, 2000.

[40] H. Van Aggelen, P. Bultinck, B. Verstichel, D. Van Neck, P.W. Ayers, Incorrect diatomic dissociation in variational reduced density matrix theory arises from the flawed description of fractionally charged atoms, Phys. Chem. Chem. Phys. 11 (2009) 5558–5560.

[41] B. Verstichel, H. Van Aggelen, D. Van Neck, P.W. Ayers, P. Bultinck, Subsystem constraints in variational second order density matrix optimization: curing the dissociative behavior, J. Chem. Phys. 132 (2010) 114113.

[42] D.R. Alcoba, Equivalence theorems between the solutions of the fourth-order modified contracted Schrödinger equation and those of the Schrödinger equation, Phys. Rev. A 65 (2002) 032519.

[43] C. Valdemoro, L.M. Tel, E. Pérez-Romero, in: C. King, M. Bylicki, J. Karwowski Symmetry (Eds.), Spectroscopy and SCHUR, Nicolaus Copernicus University Press, 2006.