Theor Chem Account (2007) 118:503–509
DOI 10.1007/s00214-007-0337-z

REGULAR ARTICLE

The contracted Schrödinger equation methodology: study of the third-order correlation effects

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Received: 9 January 2007 / Accepted: 1 February 2007 / Published online: 12 June 2007

Abstract In this paper we analyse the relevant role played by the third-order correlation terms in the contracted Schrödinger equation (CSE) methodology. The quality of the approximations used when evaluating these terms influence significantly both the convergence of the iterative procedure and the accuracy of the final energy value obtained. But where the performance of these approximating algorithms for the third-order terms becomes crucial is in the study of those states whose description, at first-order, needs more than one Slater determinant. This is still an unsolved problem, which is analysed here. Two possible ways for approximately solving this problem are outlined here.

Keywords Contracted Schrödinger equation · Reduced density matrix · Correlation matrix · Excited states

1 Introduction

It is both an honour and a personal obligation to render homage and affectionate souvenir to Professor Serafín Fraga by dedicating this paper to him. He was not only a highly stimulating teacher and scientific mentor but he also became a dear friend whose memory is unforgettable.

An ample review on the contracted Schrödinger equation (CSE) theory has recently been carried out [1]. This is a reduced density matrix (RDM) theory which can now be considered competitive in the study of the electronic structure of medium size systems. The aim of this paper is to consider how to improve the performance of the approximating algorithm for describing the three-body effects that play an important role in this theory. The second-order Anti-hermitian Contracted Schrödinger Equation (2-ACSE), which has just been reported by Mazziotti [2], has emphasized this point, since this equation does not depend—as the complete second-order CSE (2-CSE) does—on the fourth-order RDM (4-RDM). What is more, in the case of states whose description, at first order of accuracy involves more than one determinant, the approximating algorithm presently used for describing the three-body correlation effects is not adequate. This same problem has been very recently pointed out by Herbert [3]. That is, high-order cumulants do not vanish when the state is far from well described by a single electron configuration. We will therefore focus here our attention on these three-body correlation terms. In the following section, the notation and necessary theoretical background is described. Then, in Sect. 3, the 2-ACSE is tested by calculating the ground state of a set of four and six-electron systems. Each of these systems is calculated with three different types of algorithms for approximating the 3-RDM. The results obtained, which are very good, show to what extent the convergence of the equation is extremely sensitive to the kind of algorithm used for approximating the three-body correlation terms. Through the analysis of a simple example it will be shown why the 3-RDM approximation which works well for the ground state fails when two Slater determinants are equally dominant in the state considered. In the final section,we describe two

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Contribution to the Serafin Fraga Memorial Issue.

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possible approaches which are being investigated for approximating the 3-RDM. Both these approaches are based on the decomposition of the 3-RDM and on the structure and properties of the Correlation Matrices (CM).

2 Theoretical background

The 2-RDM is the matrix obtained when contracting the N-electron density matrix into the two-electron space. In second quantization the 2-RDM elements are defined as:

$$ {}^{2}\mathrm{D}_{ij;ml} = \frac{1}{2}\langle\Phi|a_i^{\dagger}a_j^{\dagger}a_l a_m|\Phi\rangle \tag{1}$$

where the ket $|\Phi\rangle$ is the state under study; the indices i, j, m, l denote the spin-orbitals which are elements of the one-electron finite basis set built from K orthonormal orbitals and the two spin-funtions α, β.

The electronic energy of a system can be written as

$$E = tr({}^{0}\mathrm{H}{}^{2}\mathrm{D}) \tag{2}$$

where ${}^{0}\mathrm{H}$ is a matrix formed by the one-electron integrals ε and by the two-electron integrals $\langle ij|kl\rangle$ (this latter in the Condon and Shortley notation: $\langle ij|kl\rangle = \langle\varphi_i(1)\varphi_j(2)|r_{12}^{-1}|\varphi_k(1)\varphi_l(2)\rangle$).

$$ {}^{0}\mathrm{H}_{ij;kl} = \left(\frac{\varepsilon_{ik}\delta_{jl} + \varepsilon_{jl}\delta_{ik}}{N-1} + \langle ij|kl\rangle\right) \tag{3}$$

The dependence of energy on the 2-RDM is at the origin of the great interest in this matrix which began with Husimi [4], Mayer [5] and Löwdin [6]. After these seminal works, the search to obtain directly the 2-RDM, without a previous knowledge of the wave function has constituted an ample field of research [7–13]. It was soon realized that, in the variational determination of the Energy of the ground-state of an electronic system, an unknown set of constraints should be imposed upon the 2-RDM; otherwise unrealistic results were obtained. These variational constraints constitute what Coleman [14] defined as the N-representability conditions whose determination has centered the efforts during several decades and which cannot yet be considered a closed question [15]. In 1976 Cohen and Frishberg [16] and Nakatsuji [17] reported an integro-differential hierarchy equation for the 2-RDM. Moreover, Nakatsuji [17] showed that, when the RDMs solving this equation are N-representable, the solution of this equation coincides with that of the Schrödinger Equation. That is, there is a one-to-one correspondence between the solutions of these two equations. However, this integro-differential equation is indeterminate since it depends not only on the 2-RDM but also on the 3- and 4-RDMs. In view of this indeterminacy, the research along this line was interrupted for nearly ten years. In 1983 Valdemoro reported a matrix contracting mapping [18] which was later applied to the matrix representation of the Schrödinger equation [19–21]. The generic form of the resulting equation, which was termed as p-order Contracted Schrödinger Equation (p-CSE), is given by:

$$\begin{aligned}&\langle\Phi|\hat{H}a_{i_1}^{\dagger}a_{i_2}^{\dagger}\cdots a_{i_p}^{\dagger}a_{j_p}\cdots a_{j_2}a_{j_1}|\Phi\rangle\\ &\quad = Ep!\,{}^{p}\mathrm{D}_{i_1 i_2\ldots i_p;j_1 j_2\ldots.j_p}\end{aligned} \tag{4}$$

where $\hat{H}$ is the N-body Hamiltonian operator, E is the energy and Φ its corresponding eigen-state.

When replacing in (4), for $p = 2$, the Hamiltonian by its second quantized expression

$$\hat{H} = \frac{1}{2}\sum_{i,j,k,l} {}^{0}\mathrm{H}_{ij;kl}a_i^{\dagger}a_j^{\dagger}a_l a_k \tag{5}$$

one obtains:

$$\frac{1}{2}\sum_{i,j;k,l} {}^{0}\mathrm{H}_{ij;kl}\langle\Phi|a_i^{\dagger}a_j^{\dagger}a_l a_k a_r^{\dagger}a_s^{\dagger}a_q a_p|\Phi\rangle = E2!\,{}^{2}\mathrm{D}_{rs;pq} \tag{6}$$

Once the string of fermion operators is transformed into its normal form the equation becomes

$$\begin{aligned}2!\,E\,{}^{2}\mathrm{D}_{rs;pq} &= 2!\left({}^{0}\mathrm{H}{}^{2}\mathrm{D}\right)_{rs;pq}\\ &\quad +3!\sum_{i,j,k}\left({}^{0}\mathrm{H}_{ij;kr}{}^{3}\mathrm{D}_{ijs;pqk} + {}^{0}\mathrm{H}_{ij;sk}{}^{3}\mathrm{D}_{ijr;pqk}\right)\\ &\quad +\frac{1}{2}4!\sum_{i,j,k,l} {}^{0}\mathrm{H}_{ij;kl}{}^{4}\mathrm{D}_{ijrs;klpq}\end{aligned} \tag{7}$$

As can be seen, this matrix equation, which is equivalent to the integro-differential one reported by Cohen and Frishberg and by Nakatsuji, depends not only on the 2-RDM but also on the 3- and 4-RDMs and is therefore indeterminate [22]. The way to lift the indeterminacy of this equation was to approximate the 3- and 4-RDMs as functions of the 1- and 2-RDMs replacing these matrices in the 2-CSE, and then solve the equation iteratively. This was first carried out in 1994 by Colmenero and Valdemoro [23,24]. The iterative solution of the 2-CSE, when combined with a purification algorithm for the second-order Reduced Dentsity Matrix (2-RDM) and with a convergence enhancement device, has recently yielded extremely accurate results. For instance, the accuracy of the calculation of the linear BeH_2 and of the Li_2 ground state was of 10^{-5} Hartrees [15,25]. Very recently, Mazziotti [2] reported an important advance in the 2-CSE methodology, in which the 2-RDM is directly calculated from the anti-hermitian part of the 2-CSE. The second-order anti-hermitian CSE (2-ACSE)

$$\langle\Phi|[a_r^{\dagger}a_s^{\dagger}a_q a_p, \hat{H}]_{-}|\Phi\rangle = 0 \tag{8}$$

which is *equivalent* to the second-order hypervirial relation [19,24], only involves the 2- and 3-RDM. It has been solved by means of a system of differential equations resulting from examination of infinitesimal unitary transformations applied to a trial wavefunction, which produces a sequence of 2-RDMs that minimize the energy until the 2-ACSE is satisfied. This last development stresses the relevance of the role played by the 3-RDM.

3 The 3-RDM approximating algorithms

In the first part of this section the different 3-RDM approximations used by two of the groups working in the field will be schematically described. The attention will be centered on the term of the algorithm describing the three-body correlation effects, which can be identified with the third-order cumulant in a moment expansion of the 3-RDM. Then, a set of results obtained by solving the 2-ACSE with the different approximations will be reported.

3.1 Approximations currently used

The algorithm used until now for approximating the 3-RDM [1] is:

$$\begin{aligned} 3!\,{}^3\mathrm{D}_{ijk;pqr} &= -2\mathcal{A}_1({}^1\mathrm{D}^1_{i;p}\mathrm{D}^1_{j;q}\mathrm{D}_{k;r}) \\ &\quad +\mathcal{A}_2 2!\left({}^1\mathrm{D}_{i;p}{}^2\mathrm{D}_{jk;qr} + {}^1\mathrm{D}_{j;q}{}^2\mathrm{D}_{ik;pr} \right. \\ &\quad \left. + {}^1\mathrm{D}_{k;r}{}^2\mathrm{D}_{ij;pq}\right) + 3!\,{}^3\Delta_{ijk;pqr} \end{aligned} \tag{9}$$

where $\mathcal{A}_1$ antisymmetrizes the column indices of the three 1-RDM involved and $\mathcal{A}_2$ antisymmetrizes the column index of the 1-RDM with the column indices of the 2-RDM. The last term ${}^3\Delta$ represents the approximation error. This algorithm, in a spin-free basis of representation, was initally proposed by Colmenero et al. [26], and several works have been since then dedicated to its study [27–43]. Mazziotti [30,31,35,36] has identified the ${}^3\Delta$ as Kubo's [44] third-order cumulant in a moment expansion of the 3-RDM; and Nakatsuji and Yasuda [27,29] base their approximation in the three-body approximation of the Green-function perturbative treatment. This ${}^3\Delta$ term, which is antisymmetric with respect to the permutation of the row and of the column indices, accounts for the three-body correlation effects; and, since at each iteration one obtains a 2-RDM and the corresponding 1-RDM, this is the term which must be approximated. Mazziotti [35] solves the problem by working with natural orbitals, which decouples the algorithm obtained when contracting the 4-RDM algorithm; and he then solves an homogenous system of equations to obtain the 3-RDM. This latter method involves at each iteration a basis set transformation of all the matrices which is followed by the resolution of an equation system. Since this is a rather expensive approach, it is not being considered here. Nakatsuji and Yasuda [27,29] approximate this term as:

$${}^3\Delta_{ijr;pqk} \approx \mathcal{A}\sum_{l,t} {}^2\Delta_{ij;ql}({}^1\mathrm{D}^{(HF)}_{l;t} - {}^1\bar{\mathrm{D}}^{(HF)}_{l;t})^2\; {}^2\Delta_{tr;qk} \tag{10}$$

where $\mathcal{A}$ is an antisymmetrizer, ${}^2\Delta$ is the second-order cumulant and ${}^1\mathrm{D}^{(HF)}$ and ${}^1\bar{\mathrm{D}}^{(HF)}$ are the 1-RDM and the hole 1-RDM corresponding to a Hartree-Fock reference calculation. This approximation will be called NY in what follows.

Initially, Valdemoro and co-workers considered ${}^3\Delta$ as an error which was approximately corrected by imposing the positivity N-representability condition on the 4-RDM, normalising this matrix and then contracting it into the three electron space [24,28]. This approximation will be denoted here as V. Later on, Valdemoro, Tel and Pérez-Romero analysed the performance of the NY approximation in the singlet ground-state of several systems and realised that the ${}^3\Delta$'s elements which had a not negligible value were those of the ${}^3\Delta^{\alpha\alpha\beta}$ and ${}^3\Delta^{\alpha\beta\beta}$ spin-blocks which involved frontier orbitals. As a result of this analysis an approximation based on the role played by the frontier electrons was proposed [38].

In order to define the frontier orbitals in this context we consider the configuration which is expected to dominate in the state under study. Thus the set of frontier spin-orbitals is formed by the highest-occupied spin-orbital (**o**) and lowest-empty spin-orbital (**e**) for each molecular symmetry. In the singlet ground states which have been studied until now, it was clear (by comparison with FCI results) that only the two following types of ${}^3\Delta^{\alpha\alpha\beta}$ elements had non negligible values and should be estimated: ${}^3\Delta_{oe\bar{o};eo\bar{o}}$ and ${}^3\Delta_{eo\bar{e};oe\bar{e}}$, where the bar over the index indicates that the spin-orbital has a beta spin (for the corresponding ${}^3\Delta^{\alpha\beta\beta}$ elements the α spin plays the role played by β). The approximations used for this type of elements are:

$$3!\,{}^3\Delta_{o_1e_1\bar{o}_2;e_2o_3\bar{o}_4} = -2!2!\,{}^2\Delta_{o_1\bar{o}_2;e_2\bar{x}}\;{}^2\Delta_{e_1\bar{x};o_3\bar{o}_4} \tag{11}$$

$$3!\,{}^3\Delta_{e_1o_1\bar{e}_2;o_2e_3\bar{e}_4} = +2!2!\,{}^2\Delta_{e_1\bar{e}_2;o_2\bar{y}}\;{}^2\Delta_{o_1\bar{y};e_3\bar{e}_4} \tag{12}$$

where $\bar{x}$ and $\bar{y}$ are the lowest empty and highest occupied orbitals respectively. Since the ${}^3\Delta$ is antisymmetric with respect to the permutation of the indices, an antisymmetrizer should be, strictly speaking, inserted into these two formulae; but, in practice, when comparing the results with the corresponding full configuration interaction values, this extra care does not seem to be necessary. This approximation will be denoted in what follows as VTP.

Table 1 Energy of the isoelectronic series of the Beryllium atom

Approx	Iteration	Energy	Iteration	Energy
Be	E(HF) = −14.5723689		E(FCI) = −14.5871556	
V	1	−14.5726074	8,000	−14.5871708
VTP	1	−14.5726074	8,000	−14.5871526
NY	1	−14.5726074	8,000	−14.5871181
B^+	E(HF) = −24.2338257		E(FCI) = −24.2484047	
V	1	−24.2342607	3,000	−24.2484605
VTP	1	−24.2342607	3,000	−24.2484467
NY	1	−24.2342607	3,000	−24.2484181
C^{+2}	E(HF) = −36.4007173		E(FCI) = −36.4148907	
V	1	−36.4013687	2,500	−36.4150750
VTP	1	−36.4013687	2,500	−36.4150626
NY	1	−36.4013687	2,500	−36.4150376
N^{+3}	E(HF) = −51.0698086		E(FCI) = −51.0837830	
V	1	−51.0707216	1,500	−51.0840206
VTP	1	−51.0707216	1,500	−51.0840126
NY	1	−51.0707216	1,500	−51.0839956
O^{+4}	E(HF) = −68.2381775		E(FCI) = −68.2519572	
V	1	−68.2394022	1,000	−68.2522676
VTP	1	−68.2394022	1,000	−68.2522620
NY	1	−68.2394022	1,000	−68.2522497

3.1.1 Some examples of the performance of these $^3\Delta$ approximations

As has been mentioned the 2-ACSE is the anti-hermitian 2-CSE very recently reported by Mazziotti, which only requires the knowledge of the 1-, 2- and 3-RDMs. Here, Maziotti's method will be used in order to calculate the isoelectronic series of the Beryllium atom and the BeH_2 and Li_2 molecules.

The Beryllium isoelectronic series In Table 1 we report the energy values obtained for the Beryllium isoelectronic series by solving iteratively the 2-ACSE as described in [2]. The initial and final iterations are reported in each case. The Hartree-Fock (HF) and full configuration interaction (FCI) results for these systems are also shown in Table 1. The basis set used is a double-zeta one. All the energy values obtained are good, particularly the NY and VTP ones. The root-mean-square deviation for the 2-RDM was 1.17×10^{-4} in the lighter ions and 3.40×10^{-5} in the Oxigen cation. The error in positivity of the 2-RDM and of the hole 2-RDM was of the order of 10^{-6}. These results confirm the good performance both of the 2-ACSE and of the NY and VTP three-body error estimations.

The ground state of the Li_2 *and* BeH_2 *molecules* A minimal basis set formed by eight spin-orbitals was used in the calculation of the Li_2 molecule and the bond length was of 5.50 a_0.

For the linear BeH_2 molecule, the basis set was formed by the Hartree-Fock orbitals built out of the Slater orbitals $1s$, $2s$, and $2p$, centered at the Beryllium atom; and by a $1s$ orbital of exponent 1.1, centered at each Hydrogen atom. The Be–H bond length was of 2.54 a_0.

The results obtained for BeH_2 and Li_2 are given in Table 2. As can be seen, although both the NY and VTP approximations of $^3\Delta$ yield accurate values of the energy for these molecules, the VTP shows a slight improvement upon the NY approximation. When analysing the values of the $^3\Delta$ elements for the ground-state of the Li_2 molecule, a very striking feature appears: Nearly all the elements are equal to zero, both in the FCI and in the approximated calculations. In Table 3 we report the values of those elements having an absolute value larger than 10^{-4} in the different calculations. Note that the values corresponding to elements involving the frontier-orbitals 3 and 4 are rather large (since the basis set in the Li_2 calculation is very small these two orbitals are the only frontier ones).

As can be seen, in Li_2, the VTP approximates the $^3\Delta$ in a significantly better way than the NY algorithm. It should be stressed that a good estimate of the $^3\Delta$ elements is crucial for the convergence of the iterative procedure of the ACSE—

Table 2 Energy of the BeH_2 and Li_2 molecules

Approx	Iteration	Energy	Iteration	Energy
Li_2	E(HF) = −14.8323167		E(FCI) = −14.8470867	
V	1	−14.8324460	444	−14.8495368
VTP	1	−14.8324460	1,100	−14.8469393
NY	1	−14.8324460	890	−14.8476953
BeH_2	E(HF) = −15.7345453		E(FCI) = −15.7640945	
V	1	−15.7363481	150	−15.7651872
VTP	1	−15.7363481	150	−15.7642117
NY	1	−15.7363481	150	−15.7643454

Table 3 Most significant values of the $^3\Delta$ for the ground state of the Li_2 molecule

Element	FCI	NY	VTP
$14\bar{1};34\bar{3}$	2.675	2.232	2.676
$14\bar{3};34\bar{3}$	−1.838	−1.199	−2.203
$14\bar{4};34\bar{4}$	1.846	1.206	1.846
$24\bar{2};34\bar{3}$	2.689	2.244	2.689
$34\bar{1};34\bar{3}$	−1.838	−1.199	−2.203
$34\bar{3};34\bar{3}$	632.584	413.234	757.769
$34\bar{4};34\bar{4}$	−632.586	−413.233	−757.769

The values appear multiplied by 10^4. The bar over a number orbital implies that the spin function is β

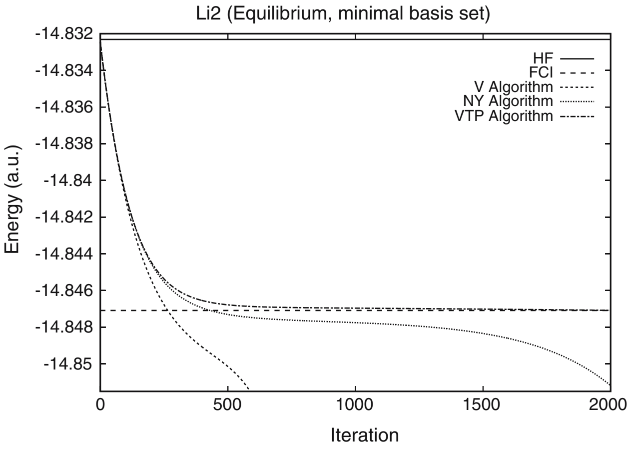

Fig. 1 Li_2: 2-ACSE results for different aproximations of the 3-RDM

as can be seen in Fig. 1, which clearly shows that the NY approximation is not good enough.

4 The problem of the states whose first-order description involves more than one Slater determinant

Since the solution of the 2-CSE must be the 2-RDM and the energy of an eigen-state of the Hamiltonian, irrespective of the structure of its wave-function, the reason for the treatment of those states whose first-order description involves more than one determinant not being successful must be due to the approximating algorithms used. When considering the algorithms for constructing the 3-RDM in terms of the 1- and 2-RDM one realizes, in view of our knowledge of the role played by the frontier orbitals, why these algorithms are not suitable approximations in the study of this type of states. Indeed, let us consider the singlet excited state whose first-order spin-adapted description is $\frac{1}{\sqrt{2}}\left(|1\bar{1}2\bar{2}3\bar{4}\rangle + |1\bar{1}2\bar{2}4\bar{3}\rangle\right)$. Clearly, the frontier spin-orbitals (without considering the different symmetry shells) are 3, $\bar{3}$, 4 and $\bar{4}$. But there is not a clear criterion to decide which are the *o*-frontier orbitals and which are the *e*-frontier orbitals since, according to the Slater determinant that is being considered, the role played by the orbital switches between **o-** and **e-**. This is the reason why neither the NY nor the VTP approximations work. This is particularly obvious in the NY algorithm, since the 1-RDM and hole 1-RDM elements corresponding to these orbitals are identical and therefore cancel each other. It implies that the above mentioned $^3\Delta$ elements, which have probably a non-negligible value, will nevertheless have a zero value when approximated with this algorithm.

4.1 An alternative approach

The correlation matrices (CM) have very interesting properties [1,15,32,33,37–40,43,45–50], which suggests looking for an alternative approach to derive an approximation for the 3-RDM in algorithms which use these matrices instead of the cumulant ones. Therefore, in what follows the attention is focused on the functional dependence of the RDM upon the corresponding CM. Let us therefore begin by recalling the structure of the 2- and 3-CMs, respectively.

$$^{(2)}\mathcal{C}_{ij;ml} = \langle\Phi|a_i^\dagger a_m \hat{P} a_j^\dagger a_l|\Phi\rangle \equiv \sum_{\Phi'\neq\Phi} {}^1\mathrm{D}_{i;m}^{\Phi\Phi'}\ {}^1\mathrm{D}_{j;l}^{\Phi'\Phi} \tag{13}$$

and

$$^{(3;1,1,1)}\mathcal{C}_{ikm;jln} = \langle\Phi|a_i^\dagger a_j \hat{P} a_k^\dagger a_l \hat{P} a_m^\dagger a_n|\Phi\rangle \tag{14}$$

where $\hat{P}$ is a projector defined as:

$$\hat{P} \ = \hat{1} - |\Phi\rangle\langle\Phi| \tag{15}$$

and the 1, 1, 1 labels on the upper left side of C indicate that the operators appearing between two succesive $\hat{P}$'s are one-electron substitution operators.

When one decomposes the 3-RDM and the projector $\hat{P}$ is applied one obtains:

$$\begin{aligned}3!\,{}^{3}\mathrm{D}_{ikm;jln} = {} & -2!\,{}^{2}\mathrm{D}_{ik;jn}\delta_{ml} + 2!\,{}^{2}\mathrm{D}_{ik;ln}\delta_{jm} \\ & + 2!\,{}^{2}\mathrm{D}_{ik;jl}{}^{1}\mathrm{D}_{m;n} - \delta_{kj}{}^{(2)}\mathcal{C}_{im;ln} \\ & + {}^{1}\mathrm{D}_{i;j}{}^{(2)}\mathcal{C}_{km;ln} + {}^{(3;1,1,1)}\mathcal{C}_{ikm;jln} \qquad (16)\end{aligned}$$

It should be stressed that this formula is analytically exact, that is, it is not an approximation of the 3-RDM. In fact, the expressions relating the 2- and 3-CM to the second- and third-order errors ${}^{2}\Delta$ and ${}^{3}\Delta$, respectively are easily derived by comparing Eq. (9) with Eq. (16).

Since the 2-RDM is given at each iteration by the 2-CSE (or by the 2-ACSE), the unknown is of course the ${}^{(3;1,1,1)}\mathcal{C}$. The question is, therefore, whether the 3-CM can be approximated with sufficient accuracy. Thus, an alternative approach is to evaluate the 3-RDM according to Eq. (16) and approximate the 3-CM by exploiting the properties of these matrices. This line of research is being initiated at present. There are several strategies that may lead to an adequate approximation of the relevant 3-CM elements but here we will just discuss two of the working hypotheses:

1. *The main role of the 3-CM is to couple two 2-body effets while the description of 3-electron virtual excitations would play a secondary role*
   It seems that the first question that should be investigated is why the VTP approximation works well. Since ${}^{2}\Delta^{\alpha\beta} = {}^{(2)}\mathcal{C}^{\alpha\beta}$, the product of two such 2-CM elements, which is at the basis of the VTP algorithm, was transformed by using Eq. (15) in order to see whether this product was equivalent to an expression which would involve a 3-CM element. This, however, is not the case. Thus, all the 3- and 4-CM's elements appearing during the transformation cancelled out at the end of the development. This seems to indicate that the VTP (and the NY one too) approximate the correlation effects by only involving two-electron excitations. In fact, this was also apparent in a previous calculation of the BeH$_2$ [37] where, while the ${}^{3}\Delta$ elements corresponding to two excitations were rather well approximated with the VTP and NY algorithms, it was not so for those elements which corresponded to three-electron excitations. This suggests that the role played by the 3-CM may be indirectly taken into account. Now, the 3-CM terms, which do not contribute under contraction of relation (16) to the 2-RDM, do influence an important N-representability condition: the antisymmetry of the 3-RDM with respect to a permutation of the row or column indices. In view of this, an indirect way of taking into account the contribution of the 3-CM terms to the 3-RDM may be to omit the 3-CM term when constructing the 3-RDM according to Eq. (16) and subsequently antisymmetrize this matrix. If this approximation were adequate it should be so, irrespective of the structure of the state considered. The code for testing this approximation is now being programmed.
2. *Decomposing a 4-CM*
   Another idea which is being prospected consists in decomposing a 4-CM in terms of lower-order terms. The basic hypothesis is to suppose that a 4-CM element should have a smaller value (and therefore might be neglected) than the third-order term obtained by decomposing it.
   Let us assume that the element one wishes to evaluate is ${}^{(3;1,1,1)}\mathcal{C}_{ipr;jqs}$, then we start with

$$\begin{aligned}& {}^{(4;1,1,1,1)}\mathcal{C}_{lipr;ljqs} \\ & \quad \equiv \langle\Phi|a_l^{\dagger}a_l\hat{P}a_i^{\dagger}a_j\hat{P}a_p^{\dagger}a_q\hat{P}a_r^{\dagger}a_s|\Phi\rangle \qquad (17)\end{aligned}$$

and shift the pair of operators $a_l^{\dagger}a_l$ towards the end of the string. This, although slightly laborious can be done in a straightforward manner by using Eq. (15) and the anticommuting fermion algebra.

As a result one obtains:

$$\begin{aligned}& {}^{(4;1,1,1,1)}\mathcal{C}_{lipr;ljqs} - {}^{(4;1,1,1,1)}\mathcal{C}_{iprl;jqsl} \\ & \quad \equiv \left(\delta_{li} - \delta_{lj} + \delta_{lp} - \delta_{lq} + \delta_{lr} - \delta_{ls}\right){}^{(3;1,1,1)}\mathcal{C}_{ipr;jqs} \\ & \qquad + \left(\delta_{lp} - \delta_{lq} + \delta_{lr} - \delta_{ls}\right){}^{(2)}\mathcal{C}_{pr;qs}{}^{1}\mathrm{D}_{i;j} \\ & \qquad + {}^{(2)}\mathcal{C}_{lr;ls}{}^{1}\mathrm{D}_{i;j}{}^{1}\mathrm{D}_{p;q} - {}^{1}\mathrm{D}_{i;j}{}^{1}\mathrm{D}_{r;s}{}^{(2)}\mathcal{C}_{pl;ql} \\ & \qquad - {}^{(2)}\mathcal{C}_{il;jl}{}^{(2)}\mathcal{C}_{pr;qs} + {}^{(2)}\mathcal{C}_{ip;jq}{}^{(2)}\mathcal{C}_{lr;ls} + A \qquad (18)\end{aligned}$$

where

$$A = {}^{(3;1,1,1)}\mathcal{C}^{1}_{prl;qsl}\mathrm{D}_{i;j} - {}^{(3;1,1,1)}\mathcal{C}^{1}_{ipl;jql}\mathrm{D}_{r;s} \qquad (19)$$

is a third-order term which will now be approximated. In order to approximate it we will proceed in a similar way by decomposing

$${}^{(4;1,1,1,1)}\mathcal{C}_{lnml;ltvl} \equiv \langle\Phi|a_l^{\dagger}a_l\hat{P}a_n^{\dagger}a_t\hat{P}a_m^{\dagger}a_v\hat{P}a_l^{\dagger}a_l|\Phi\rangle \qquad (20)$$

Here again, the pair of operators $a_l^{\dagger}a_l$ are pushed towards the end of the operators string. As a result, one obtains:

$$\begin{aligned}& {}^{(4;1,1,1,1)}\mathcal{C}_{lnml;ltvl} \\ & \quad \equiv (-2n_l + 1 + \delta_{ln} - \delta_{lt} + \delta_{lm} - \delta_{lv}){}^{(3;1,1,1)}\mathcal{C}_{mnl;tvl} \\ & \qquad + {}^{1}\mathrm{D}^{(2)}_{n;t}\mathcal{C}_{ml;vl}\,(-2n_l + 1 + \delta_{lm} - \delta_{lv}) \\ & \qquad + \left({}^{1}\mathrm{D}^{1}_{n;t}\mathrm{D}_{m;v} + {}^{(2)}\mathcal{C}_{nm;tv}\right)(n_l - n_l^2) \\ & \qquad - {}^{(2)}\mathcal{C}_{nl;tl}{}^{(2)}\mathcal{C}_{ml;vl} \qquad (21)\end{aligned}$$

where n_l is the occupation number of spin-orbital l. If the spin-orbital l could be chosen independently of the element one wishes to study, this approximation would yield good results since, by chosing the occupation number n_l to be either close to one or to zero, the corresponding 4-CM element could be expected to be small. However, because of the δ terms which multiply the 3-CM elements, the l orbital is not arbitrary and, therefore, the crucial open question is whether the 4-CM elements involving frontier electrons are small enough and can thus be neglected.

These two approaches for approximating the 3-CM effects in the excited and transition states which cannot be studied with the currently used algorithms are now being codified and hopefully may extend the field of application of the 2-ACSE.

Acknowledgments This report has been financially supported by the spanish Ministerio de Educación y Ciencia under project BFM2003-05133. D. R. Alcoba acknowledges the financial support obtained from the *Universidad de Buenos Aires* under Project X-024 and *Consejo Nacional de Investigaciones Científicas y Ténicas, República Argentina* under Project PIP No 5098/05.

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