Approximating q-order reduced density matrices in terms of the lower-order ones. II. Applications

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The general equation linking a q-order reduced density matrix (q-RDM) with the corresponding q-order hole reduced density matrix (q-HRDM) has been reported in the preceding paper [F. Colmenero, C. Perez del Valle, and C. Valdemoro, preceding paper, Phys. Rev. A **47**, 971 (1993)]. In this equation, neither Kronecker δ functions nor mixed products of elements of RDM's and HRDM's appear, and the part involving hole terms has the same structure as that involving particle terms. Recently [C. Valdemoro, Phys. Rev. A **45**, 4462 (1992)], a similar equation for $q=2$ has been used to approximate the 2-RDM from the knowledge of the 1-RDM. Here, the 3-RDM and the 4-RDM are approximated by using the 2-RDM as an initial datum. The ultimate aim of this research is to develop an iterative method for solving the contracted form of the Schrödinger equation [L. Cohen and C. Frishberg, Phys. Rev. A **13**, 927 (1976); H. Nakatsuji, *ibid.* **14**, 41 (1976)]. A matrix form in the orbital representation of this equation is reported here. Finally, the second-order hypervirial equation, also in its matrix form, has been derived so that the quality of the results can be judged.

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I. INTRODUCTION

By integrating the time-independent Schrödinger equation over $N-q$ variables, Cohen and Frishberg [1] and Nakatsuji [2] obtained an equation which gave the energy of an eigenstate of an N-electron system and the corresponding q-order reduced density matrix (q-RDM).

An equivalent equation [3], the contracted Schrödinger equation (CSchE), can be obtained by using a matrix contraction mapping [4]. This equation is indeterminate [5] because it contains terms which depend on the $(q+1)$-RDM and on the $(q+2)$-RDM. This indeterminacy could be removed if the $(q+1)$-RDM and the $(q+2)$-RDM could be calculated, or at least approximated, in terms of the q-RDM.

The aim of this paper is to show a way for approximating a RDM in terms of the lower-order ones as a step towards the iterative solution of the CSchE.

The main idea of a self-consistent iterative scheme for approximating the solution of this equation is described in Sec. II to show the purpose and importance of the present and preceding paper [6]. The details of the method for approximating the solution of the CSchE are still being investigated and results are not yet available. Nevertheless, the matrix representations of the q-CSchE for $q=2$ and $q=1$ are given in Sec. II.

In what follows, the model used for approximating the 2-RDM in terms of the 1-RDM [7] will be extended to approximate the 3- and 4-RDM's from the knowledge of the 2-RDM. Since the main theoretical developments needed have been already reported in paper I of this series [6], the notation, the graphs, and the acronyms used here are the same as in this preceding paper.

The test states chosen for this study are the three lowest singlet states of the beryllium atom and the two lowest singlet ones of the water molecule. In all the calculations, the initial data are low-order RDM's (2- and 3-RDM's) derived from a full configuration-interaction (FCI) wave function.

Since, for this test, the initial data entering into the approximating procedure are q-RDM's derived from an eigenstate of the system, they fulfill the hypervirial conditions exactly. An indication of the quality of the approximate $(q+1)$- and $(q+2)$-RDM's may be obtained by determining how well the first- [3] and the second-order hypervirial conditions are satisfied. The second-order hypervirial equation in the orbital representation, needed for this control, results from commuting a second-order replacement operator (2-RO) [8–11] with the Hamiltonian and is reported in Sec. III. The results obtained when approximating the 3-RDM and 4-RDM are analyzed in Sec. IV. Finally, a short discussion is given in Sec. V.

II. THE CONTRACTED SCHRÖDINGER EQUATION

By integrating the Schrödinger equation over $N-q$ variables, the following integral equation was obtained [1,2]:

$$E\rho_q = H_q\rho_q + (q+1)\int \left[\Omega_{q+1} + \sum_{i=1}^{q}\Omega_{i,q+1}\right]\rho_{q+1}dx_{q+1} + \tfrac{1}{2}(q+2)(q+1)\int \Omega_{q+1,q+2}\rho_{q+2}dx_{q+1}dx_{q+2} \ . \tag{1}$$

Here we have followed the notation given by Cohen and Frishberg [1]. Thus,

$$\rho_q = \begin{bmatrix} N \\ q \end{bmatrix} \int \rho_N(x_1,\ldots,x_q,x_{q+1},\ldots,x_N;x'_1,\ldots,x'_q,x_{q+1},\ldots,x_N)dx_{q+1},\ldots,dx_N \tag{2}$$

and the operators Ω represent the one- and two-electron operators which appear in the q-electron Hamiltonian H_q summed over the q-electron variables.

By using the mapping reported in Ref. [4] a discrete matrix representation of this equation was derived [3] for $q=1$ and $q=2$. In the orbital representation, the 1-CSchE takes the form

$$Ed_{pq}=2\sum_{j}({}^2\underline{D}\,{}^0\underline{H})_{pj,qj}+3\sum_{i,j,k,l}{}^0H_{ij,kl}\,{}^3D_{pij,qkl} \tag{3}$$

where the symbol ${}^0H_{ij,kl}$ represents a generalized two-electron integral [12]. The form of the 2-CSchE is

$$E^2D_{pq,rs}=R_{pq,rs}=({}^0\underline{H}\,{}^2\underline{D})_{pq,rs}+6\sum_{i,j,k,l}{}^0H_{ij,kl}\,{}^4D_{rsij,pqkl}+3\sum_{i,l,k}({}^0H_{iq,kl}\,{}^3D_{rsi,plk}+{}^0H_{ip,kl}\,{}^3D_{rsi,lqk}) . \tag{4}$$

As can be seen, both equations are easy to handle in this representation since only matrix operations are involved.

The idea, which is being developed in our laboratory, for solving the CSchE is the following: Let us take a reasonable initial 2-RDM (it can be one of the independent-particle type) and approximate from it the corresponding 3- and 4-RDM's. Having replaced these approximate 3- and 4-RDM's into the right-hand side (rhs) of Eq. (4) a new 2-RDM can be obtained. Since

$$E\,\mathrm{tr}\,{}^2\underline{D}=E\begin{bmatrix}N\\2\end{bmatrix}=\mathrm{tr}\underline{R} , \tag{5}$$

one can use either this value of the energy or that obtained in the previous iteration to calculate the new 2-RDM by means of

$${}^2D_{pq,rs}=\frac{R_{pq,rs}}{E} . \tag{6}$$

Then, this procedure can be repeated with the new RDM. Thus, an iterative self-consistent (SC) procedure for solving the 2-CSchE can be devised.

At first sight, the first-order equation is more appealing than the second-order one. However, the terms on the rhs of Eq. (3) are both average terms. Thus, the first term is averaged over an orbital index which appears twice, and the second term, involving the 3-RDM, is averaged over four orbital indices. Therefore, the information carried by the ${}^0\underline{H}$ matrix will influence the value of this side of the equation only in an averaged way. For this reason we suspect that convergence will probably be slow in the case of 1-CSchE. Thus, although the 1-CSchE may prove useful, our primary goal is to attempt a solution of the 2-CSchE.

Whether or not this equation can be solved iteratively depends on the possibility of obtaining good enough approximations to the higher-order RDM's from the knowledge of the lower-order ones.

III. THE SECOND-ORDER HYPERVIRIAL EQUATION

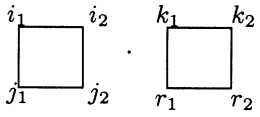
Since the initial data for the test samples considered here correspond to eigenstates of the system, it is convenient to verify how well the hypervirial theorem is fulfilled when the exact matrix is replaced by the new approximate one.

The second-order hypervirial condition may be written as

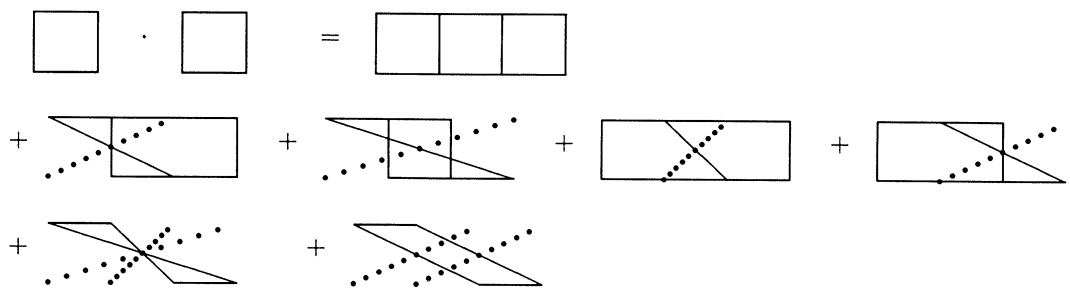
$$\langle\mathcal{L}|[{}^2E,\hat{H}]|\mathcal{L}\rangle=0 , \tag{7}$$

where ${}^2E$ and $\hat{H}$ are the 2-RO and the Hamiltonian operator, respectively.

Equation (7) involves operator products of the type ${}^2E^{i_1i_2}_{j_1j_2}\,{}^2E^{k_1k_2}_{r_1r_2}$. Such operator products can be performed easily by applying the graphical rules reported in Refs. [11,13]. The final result, in graphical form, is



or



(8)

The interpretation of these diagrams has been given in Table I of paper I (recall that the dotted lines represent Kronecker δ functions). The graphs in (8) have two, one, or no dotted lines and correspond to a 2-, a 3-, or a 4-RO, respectively. Using these diagrams it is easy to see that the second-order hypervirial condition can be written as

$$\mathcal{P}_{ij,kl}=0=2[{}^0\underline{H},{}^2\underline{D}]_{ij,kl}$$
$$+3\sum_{p,q,r}({}^0H_{pq,ir}{}^3D_{pqj,krl}+{}^0H_{pq,jr}{}^3D_{pqi,lrk}+{}^0H_{pq,ri}{}^3D_{pqj,rkl}+{}^0H_{pq,rj}{}^3D_{pqi,rlk}$$
$$-{}^0H_{kq,rp}{}^3D_{ijq,rlp}-{}^0H_{pk,rq}{}^3D_{ijp,qlr}-{}^0H_{lq,rp}{}^3D_{ijq,krp}-{}^0H_{pl,rq}{}^3D_{ijp,kqr}) . \quad (9)$$

When the 2-RDM and the 3-RDM appearing in relation (9) correspond to eigenstates of the Hamiltonian, the second-order hypervirial condition is fulfilled and $\underline{\mathcal{P}}$ is a null matrix. Hirschfelder showed [14] that if the expectation value of the commutator of the Hamiltonian with any operator was equal to zero, this was a sufficient condition for the state considered to be an eigenstate of the system. In the case of a q-RDM of an N-electron system, all the hypervirial equations involving p-RDM's of order $p \leq N$ should be fulfilled [15]. Moreover, when the q-RDM's are determined directly, i.e., not from a known antisymmetric function, the N-representability conditions may be fulfilled only approximately. Therefore, the satisfaction of the first- and second-order hypervirial conditions is a necessary but not a sufficient condition and has only indicative value. On the other hand, this test indicates the quality of the approximating procedure used here because if the method were exact, all the hypervirial conditions for $p \leq N$ would necessarily be fulfilled given that the initial q-RDM corresponds to an eigenstate.

IV. APPROXIMATIONS TO THE 3- RDM AND 4-RDM

In Eq. (21) of paper I each side is a sum of a part involving hole reduced density matrix (HRDM) terms and a part involving RDM terms. Since the structure of the part involving HRDM's is the same as that of the part involving RDM's, the approximating method proposed in Ref. [7] can be employed: identify the left-hand-side (lhs) holes part with the rhs holes part and identify the lhs electrons part with the rhs electrons part.

It should be stressed that the holes and the particles are interrelated through the fermion anticommutation relation and therefore this is not an exact operation. As a consequence, this procedure is only an approximate one. However, it works well, as will be shown in the following subsections, particularly when additional properties that the RDM's must fulfill are imposed.

Let us now consider the form of the approximate 3-RDM,

$${}^3D_{ijk,lmn}\approx{}^3M_{ijk,lmn}=-\tfrac{1}{3}d_{il}d_{jm}d_{kn}+\tfrac{1}{6}(d_{im}d_{jl}d_{kn}+d_{in}d_{jm}d_{kl}+d_{il}d_{jn}d_{km})$$
$$-\tfrac{1}{12}(d_{in}d_{jl}d_{km}+d_{im}d_{jn}d_{kl})+\tfrac{1}{3}(d_{il}{}^2D_{jk,mn}+d_{jm}{}^2D_{ik,ln}+d_{kn}{}^2D_{ij,lm})$$
$$-\tfrac{1}{6}(d_{jl}{}^2D_{ik,mn}+d_{im}{}^2D_{jk,ln}+d_{kl}{}^2D_{ij,nm}+d_{in}{}^2D_{jk,ml}+d_{km}{}^2D_{ij,ln}+d_{jn}{}^2D_{ik,lm}) . \quad (10)$$

The elements of the 4-RDM will be approximated in a similar way from Eq. (21) in paper I with $q=4$. The matrices obtained using this approximate method will be denoted by ${}^qM$ while keeping ${}^qD$ for the exact RDM's.

In this section a series of results concerning the three lowest singlet states of the beryllium atom and the two lowest singlet ones of the water molecule will be reported. The rest of this section is divided into two paragraphs in which the results concerning the approximate 3-RDM's and 4-RDM's are discussed, respectively.

A. The 3-RDM

In these calculations, the 3-RDM's were approximated by using the 2-RDM's as initial data. To obtain the initial 2-RDM's, FCI calculations were performed with a CI program based in the unitary-group approach [10,16,17] (UGA) code written in our laboratory. The following basis sets were used: Double ζ [18] for the beryllium atom and minimal STO-3G [19] for the water molecule. These basis sets were orthonormalized by the canonical transformation [20] and subsequently transformed into the Hartree-Fock (HF) basis [21]. The molecular geometry used for the water molecule was O-H bond lengths of 1.814 a.u. and a HOH angle of 104.5°.

1. Normalization

In Ref. [7] it was shown that the 2-RDM, when approximated from the 1-RDM, had a trace error by excess, which was corrected by using a special *normalization algorithm* (NA). This NA was devised in order to concentrate the normalization modifications on the elements of the approximate 2-RDM which did not correspond to the geminal configurations dominant in the state considered, that is, corresponding to high value 2-HRDM elements. It did now, however, fulfill all the requirements. Thus, the resulting 2-RDM was only approximately spin pure. In addition, the two diagonal elements of the ground-state matrix corresponding to the frontier geminal configurations (i.e., the highest-energy geminal with a high occupation number and the lowest-energy geminal with a large hole occupation number in the ground state) which were responsible for most of the error, but whose errors compensate each other to a great extent, were not modified by this NA.

In order to analyze the situation in the third-order case, let us start by considering the value of $\mathrm{tr}({}^3\underline{M})$. From the result previously reported [Eq. (6) in paper I] and by using the contraction of the 2-RDM to the one-electron space, it can be shown that

$$\mathrm{tr}({}^3\underline{M})=\frac{N^3}{6}-\frac{N^2}{2}+\frac{\mathrm{tr}[({}^1\underline{D})^2]}{2}-\frac{\mathrm{tr}[({}^1\underline{D})^3]}{6} . \quad (11)$$

Hence, the trace error in the approximate 3-RDM is

$$\mathrm{tr}({}^3\underline{M})-\mathrm{tr}({}^3\underline{D})=-\frac{\mathrm{tr}({}^1\underline{D})}{3}+\frac{\mathrm{tr}[({}^1\underline{D})^2]}{2}-\frac{\mathrm{tr}[({}^1\underline{D})^3]}{6} . \quad (12)$$

As traces are invariant with respect to linear transformations, let us suppose that ${}^1\underline{D}$ is diagonal. Then, Eq. (12) may be written as

$$\mathrm{tr}({}^3\underline{M})-\mathrm{tr}({}^3\underline{D})=-\tfrac{1}{6}\sum_i^K \lambda_i(2-\lambda_i)(1-\lambda_i) , \quad (13)$$

where λ_i denotes an eigenvalue of ${}^1\underline{D}$. Because $(1-\lambda_i)$ may be positive or negative the trace error may be by excess or by defect. When the state has a clear dominant configuration of the closed-shell type, some λ_i will have values close to 2 while the rest will have values close to zero. Consequently, the trace error, independently of its sign, will be very small in this case.

In all the calculations performed, the trace error found was extremely small (see Table I) and consequently *no normalization* procedure was applied.

The direct application of the approximating algorithm (see Tables II-IV) showed a strong cancellation of errors between certain pairs of diagonal elements corresponding to configuration of the "*iij*" and "*jji*" types. This effect is observed when the i and j indices denote orbitals with a high particle and a high hole occupation number, respectively, and it is greater when these configurations are the frontier ones. Thus, when one of these elements is overestimated, the other one is underestimated, the errors having practically the same absolute value. As a result of this almost exact cancellation, the trace value of ${}^3\underline{M}$ is good.

2. Correction of negative diagonal elements

The cancellation of errors just mentioned occurring between certain pairs of diagonal elements was the reason why the 3-RDM did not show noticeable trace errors. On the other hand, when this error was large, the underestimated element had a slightly negative value. In order to correct this kind of error, whenever a negative diagonal matrix element ${}^3\underline{M}_{iij,iij}$ appeared the following corrections were applied:

$$\begin{aligned}
&\delta \leftarrow {}^3\underline{M}_{iij,iij} ,\\
&{}^3\underline{M}_{iij,iij} \leftarrow {}^3\underline{M}_{iij,iij}-\delta=0 ,\\
&{}^3\underline{M}_{jji,jji} \leftarrow {}^3\underline{M}_{jji,jji}+\delta ,\\
&{}^3\underline{M}_{iij,jji} \text{ and } {}^3\underline{M}_{jji,iij} \leftarrow 0 ,
\end{aligned} \quad (14)$$

where the symbol "$\leftarrow$" denotes the computational replacement operations. Obviously, these operations do not modify the values of the trace.

These corrections must be also applied to the equivalent matrix elements resulting from the symmetry property,

$${}^q D_{i_1 i_2 \cdots i_q, j_1 j_2 \cdots j_q} = {}^q D_{\hat{P}(i_1 i_2 \cdots i_q),\hat{P}(j_1 j_2 \cdots j_q)} , \quad (15)$$

where $\hat{P}$ is an arbitrary permutation of the indices.

It can also be shown (see the Appendix for a proof) that

$${}^3 D_{iij,iji} = -\tfrac{1}{2}\,{}^3 D_{iij,iij} , \quad (16)$$

$${}^3 D_{iij,ijj} = -\tfrac{1}{2}\,{}^3 D_{iij,jji} . \quad (17)$$

The approximate RDM's fulfill the relations (15) and (16) as well as the most general one given in the Appendix. As a consequence, when applying the corrections given in (14) one must make sure that these equalities continue to hold. Therefore, one must introduce the additional corrections

$$\begin{aligned}
&{}^3\underline{M}_{iij,iji} \leftarrow {}^3\underline{M}_{iij,iji}+\delta/2=0 ,\\
&{}^3\underline{M}_{jji,jij} \leftarrow {}^3\underline{M}_{jji,jij}-\delta/2 ,\\
&{}^3\underline{M}_{iij,ijj} \text{ and } {}^3\underline{M}_{ijj,iij} \leftarrow -{}^3\underline{M}_{iij,jji}/2=0 .
\end{aligned} \quad (18)$$

3. Results

The accuracy of the approximate 3-RDM's may be appreciated by looking at the row denoted by 2→3 in the "Calculation" column of Table V. The notation 2→3 indicates that the 3-RDM has been approximated from the 2-RDM. Then, by contraction, a new 2-RDM was obtained and used for calculating the energy and the standard deviations with respect to the initial 1-RDM (σ_{1_D}), the initial 2-RDM (σ_{2_D}), the first- [3,22] and the second-order hypervirial matrices (σ_{hv} and σ_{hv_2}, respectively).

The ground state of the beryllium atom has a dominant closed-shell configuration involving orbitals 1 and 2 while the first excited state has a dominant configuration in which orbital 1 is doubly occupied and orbitals 2 and 3 share two electrons. Therefore, the *frontier* orbitals are the 2 and 3 ones in both cases. As has been mentioned, the higher errors occur in the diagonal elements (223) and (233) and in the off-diagonal ones (223,232) and (332,323).

TABLE I. Traces of the approximate 3-RDM for the three lowest singlet states of the beryllium atom and the two lowest ones of the water molecule.

System	State	$\mathrm{Tr}({}^3\underline{D})$	$\mathrm{Tr}({}^3\underline{M})$
Be	Ground	4.0	4.000 00
	First excited	4.0	4.000 00
	Second excited	4.0	4.000 00
H_2O	Ground	120.0	120.000 08
	First excited	120.0	120.000 03

TABLE II. Comparison of the exact (second column) and the approximate (third column) ${}^3\underline{D}_{ijk,ijk}$ of the ground state of the Be atom. Only the elements involving an error greater than 10^{-6} are given. The fourth column shows the applied corrections (larger than 10^{-5}). The modified off-diagonal elements are reported.

Element	Exact (FCI)	Approximation	Correction	Error
113	0.002 20	0.002 18		−0.000 02
114	0.000 00	−0.000 26	+0.000 26	0.000 00
114,141	0.000 00	0.000 13	−0.000 13	0.000 00
134	0.000 00	0.000 02		0.000 02
144	0.000 01	0.000 27	−0.000 26	0.000 00
144,414	0.000 00	−0.000 14	+0.000 13	0.000 00
223	0.000 02	−0.002 12	+0.002 12	−0.000 02
223,232	−0.000 01	0.001 06	−0.001 06	0.000 01
223,332	0.000 00	0.000 03	−0.000 03	0.000 00
223,233	0.000 00	−0.000 02	+0.000 02	0.000 00
233	0.000 00	0.002 14	−0.002 12	0.000 02
233,323	0.000 00	−0.001 07	+0.001 06	−0.000 01
244	0.000 26	0.000 27		0.000 01

TABLE III. Comparison of the exact (second column) and the approximate (third column) ${}^3\underline{D}_{ijk,ijk}$ of the first singlet excited state of the Be atom. Only the elements involving an error greater than 10^{-6} are given. The fourth column shows the applied corrections (larger than 10^{-5}). The modified off-diagonal elements are reported.

Element	Exact (FCI)	Approximation	Correction	Error
112	0.323 16	0.323 15		−0.000 01
114	0.000 00	−0.000 26	+0.000 26	0.000 00
114,141	0.000 00	0.000 13	−0.000 13	0.000 00
122	0.000 29	0.000 31		+0.000 02
144	0.000 02	0.000 28	−0.000 26	0.000 00
144,414	−0.000 01	−0.000 14	+0.000 13	0.000 00
223	0.000 01	0.004 65	−0.004 62	+0.000 01
223,232	0.000 00	−0.002 32	+0.002 31	0.000 00
223,332	0.000 00	−0.041 99	+0.041 99	0.000 00
223,233	0.000 00	0.021 00	−0.021 00	0.000 00
224	0.000 01	0.000 00		−0.000 01
233	0.000 01	−0.004 62	+0.004 62	0.000 00
233,323	0.000 00	0.002 31	−0.002 31	0.000 00

TABLE IV. Comparison of the exact (second column) and the approximate (third column) ${}^3\underline{D}_{ijk,ijk}$ of the ground state of H_2O. Only the elements involving an absolute value error greater than 10^{-6} and having a value larger than 0.005 are reported. (The modified elements are smaller than this threshold.)

Element	Exact (FCI)	Approximation	Error
226	0.005 70	0.005 04	−0.000 65
227	0.007 63	0.007 44	−0.000 19
236	0.008 35	0.007 87	−0.000 48
237	0.005 33	0.004 84	−0.000 49
246	0.007 73	0.007 01	−0.000 72
247	0.011 51	0.011 50	−0.000 01
277	0.005 29	0.005 48	0.000 19
346	0.006 07	0.004 90	−0.001 17
447	0.005 26	0.004 12	−0.001 14
456	0.009 88	0.009 90	0.000 01
556	0.008 41	0.007 93	−0.000 48
557	0.008 82	0.008 75	−0.000 07
577	0.005 45	0.005 51	0.000 06

TABLE V. Results obtained for the three lowest singlet states of the beryllium atom and the two lowest ones of the water molecule.

System	State	Calculation	Properties				
			E (a.u.)	σ_{1_D}	σ_{2_D}	σ_{hv}	σ_{hv_2}
Be	Ground	FCI (reference)	−14.5872	0.0	0.0	0.0	0.0
		2→3	−14.5867	0.000 015	0.000 002	0.000 070	0.000 042
		3→4	−14.5870	0.000 018	0.000 045	0.000 198	0.000 102
		2→3→4	−14.5864	0.000 019	0.000 074	0.000 311	0.000 120
	First excited	FCI (reference)	−14.3014	0.0	0.0	0.0	0.0
		2→3	−14.3013	0.000 012	0.000 012	0.000 097	0.000 435
		3→4	−14.3029	0.000 396	0.000 030	0.000 335	0.003 019
		2→3→4	−14.3021	0.000 397	0.000 036	0.000 288	0.003 103
	Second excited	FCI (reference)	−13.9850	0.0	0.0	0.0	0.0
		2→3	−13.9845	0.000 009	0.000 001	0.000 049	0.000 033
		3→4	−13.9848	0.000 009	0.000 020	0.000 134	0.000 082
		2→3→4	−13.9837	0.000 009	0.000 045	0.000 173	0.000 068
H_2O	Ground	FCI (reference)	−75.0130	0.0	0.0	0.0	0.0
		2→3	−75.0122	0.000 024	0.000 002	0.000 030	0.000 020
	First excited	FCI (reference)	−74.5580	0.0	0.0	0.0	0.0
		2→3	−74.5575	0.000 017	0.000 004	0.000 013	0.000 043

The values of these elements reported in Tables II and III show that, after applying the corrections described in Sec. IV A 2, the final errors are negligible.

B. The 4-RDM

The results concerning the 4-RDM are reported in this paragraph. The test samples are the three lowest singlet states of the beryllium atom. It should be emphasized that the 4-RDM coincides with the density matrix of the corresponding state in this case.

Two different kinds of calculations were performed. A calculation where the 4-RDM was calculated by using the 3-RDM as initial datum and a calculation where the initial datum was the 2-RDM. As before, the initial matrices were obtained from FCI calculations. These two paths are represented in Table V by 3→4 and 2→3→4, respectively. In the last case the approximation of the 3-RDM is just an intermediate step to calculate the final approximate 4-RDM.

A few negative diagonal elements appeared. Setting these elements to zero the trace errors were very small for the ground and for the second excited states. In the first excited state the trace error was small but not negligible which is why a simple vector normalization was used in this case.

The results obtained are reported in Table V and as can be seen they are quite satisfactory. In the first excited state of the beryllium atom the results are slightly worse than those obtained with the path 2→3.

V. CONCLUDING REMARKS

The numerical results reported here concern two very different systems in their ground and excited states. We think that these results have shown that a high-order RDM can be approximated with a high degree of accuracy when at least one lower-order RDM is known. Therefore, the idea described of solving the CSchE by applying a self-consistent iterative procedure (see Sec. II) appears to be a realistic one and is now being explored.

Obviously, a series of unknown difficulties may arise. However, given the quality of results, it is reasonable to expect that convergence may be achieved provided that the initial matrices are chosen reasonably. We expect that any 2-RDM obtained with a standard method such as the Hartree-Fock will be satisfactory initial datum for solving the CSchE.

There is a side result of this study: since an ensemble N-representable 1-RDM may easily be built, the N-representability problem for higher-order RDM's can be given an approximate solution.

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APPENDIX: THE DERIVATION OF RELATIONS (16) AND (17)

Let us consider the definition of the 3-RDM element:

$$ {}^3D_{ijj,rll} = \frac{1}{3!}\left\langle \mathcal{L} \left| \sum_{\sigma_1,\sigma_2,\sigma_3} b^\dagger_{i\sigma_1} b^\dagger_{j\sigma_2} b^\dagger_{j\sigma_3} b_{l\sigma_3} b_{l\sigma_2} b_{r\sigma_1} \right| \mathcal{L} \right\rangle . \tag{A1} $$

Due to the Pauli principle two electrons with the same spin cannot occupy the same orbital and consequently this matrix element can be rewritten as

$$ {}^3D_{ijj,rll} = \frac{1}{3!}\left\langle \mathcal{L} \left| \sum_{\sigma_1} (b^\dagger_{i\sigma_1} b^\dagger_{j\alpha} b^\dagger_{j\beta} b_{l\beta} b_{l\alpha} b_{r\sigma_1} + b^\dagger_{i\sigma_1} b^\dagger_{j\beta} b^\dagger_{j\alpha} b_{l\alpha} b_{l\beta} b_{r\sigma_1}) \right| \mathcal{L} \right\rangle . \tag{A2} $$

Now, using the anticommutation property of fermion operators and developing the sum over the remaining spin variable,

$$ {}^3D_{ijj,rll} = \frac{2}{3!}\left\langle \mathcal{L} \left| \sum_{\sigma_1} b^\dagger_{i\sigma_1} b^\dagger_{j\alpha} b^\dagger_{j\beta} b_{l\beta} b_{l\alpha} b_{r\sigma_1} \right| \mathcal{L} \right\rangle $$

$$ = -\frac{2}{3!}\left\langle \mathcal{L} \left| b^\dagger_{i\alpha} b^\dagger_{j\alpha} b^\dagger_{j\beta} b_{l\beta} b_{r\alpha} b_{l\alpha} + b^\dagger_{i\beta} b^\dagger_{j\alpha} b^\dagger_{j\beta} b_{l\beta} b_{r\beta} b_{r\alpha} \right| \mathcal{L} \right\rangle . \tag{A3} $$

Now, let us consider the 3-RDM element,

$$ {}^3D_{ijj,lrl} = \frac{1}{3!}\left\langle \mathcal{L} \left| \sum_{\sigma_1\sigma_2\sigma_3} b^\dagger_{i\sigma_1} b^\dagger_{j\sigma_2} b^\dagger_{j\sigma_3} b_{l\sigma_3} b_{r\sigma_2} b_{l\sigma_1} \right| \mathcal{L} \right\rangle \tag{A4} $$

which can be developed in a similar way

$$ {}^3D_{ijj,lrl} = \frac{1}{3!}\langle \mathcal{L} | b^\dagger_{i\alpha} b^\dagger_{j\alpha} b^\dagger_{j\beta} b_{l\beta} b_{r\alpha} b_{l\alpha} + b^\dagger_{i\beta} b^\dagger_{j\alpha} b^\dagger_{j\beta} b_{l\beta} b_{r\beta} b_{r\alpha} | \mathcal{L} \rangle . \tag{A5} $$

Taking into account (A3) and (A5) one finds that

$$ {}^3D_{ijj,rll} = -2\,{}^3D_{ijj,lrl} . \tag{A6} $$

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