

Controlling the N - and S -representability of the second-order reduced density matrix: The doublet-state case

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A purification procedure that simultaneously corrects the N - and S -representability main defects of a second-order reduced density matrix (2RDM), second-order hole reduced density matrix (2HRDM), and second-order \mathcal{G} matrix is presented here. In this purifying procedure, the generalized unitarily invariant second-order matrix decomposition [D. R. Alcoba, *Int. J. Quantum Chem.* **97**, 776 (2004)] for the 2RDM and the 2HRDM as well as for the \mathcal{G} matrix is combined with the S -representability conditions. In particular, here we will focus our attention on the RDMs corresponding to doublet states. We will thus explicitly give the S -representability conditions that a two-body correlation matrix has to satisfy when an N -electron system is in a doublet spin-state in the spin-component of maximum projection. Furthermore, as a consequence of the \mathcal{G} -matrix spin properties (which directly affect the S -representability of the 2RDM), we show that a different contracting form for the 2RDM is possible. The numerical results presented in this work confirm the efficiency of our purifying procedure.

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I. INTRODUCTION

For an N -electron system with only pairwise interactions the second-order reduced density matrix (2RDM), corresponding to the N -electron state under study holds all the necessary information to evaluate the expectation values of the observables. The seminal works of Husimi [2], Löwdin [3], Mayer [4], McWeeny [5], and Coulson [6] are at the origin of the line of research that directly aimed at determining the 2RDM instead of looking for the wave function of the state considered [7–12]. In Ref. [13], the different aspects of the 2RDM theory are reviewed. An interested reader may find in this reference a rather complete account of the bibliography of the field up to 2006.

The great difficulty in directly looking for a 2RDM instead of deriving it from the knowledge of the N -electron wave function by integration over $N-2$ electron variables is that, even after more than 60 years of study, we cannot claim a complete knowledge of its mathematical-physical properties. This problem was first defined and studied by Coleman, who denoted it as the N -representability problem [14]. This author defined as N -representability conditions the sufficient set of properties that a matrix, represented in a p -electron space, must possess in order to ascertain that there exists an N -electron wave function from which this matrix can be derived by integration over the variables of $N-p$ electrons.

The requirement that a 2RDM be N -representable is analogous to the requirement that a well-behaved wave function should be continuous and single-valued, square-integrable, differentiable everywhere except where the potential becomes singular and antisymmetric under interchange of the coordinates of any two electrons. Therefore to impose N -representability conditions upon a two-electron matrix should be an obliged requirement in all the 2RDM oriented methods. There are two such methods that are currently investigated and applied. In the variational evalua-

tion of the energy, the N -representability conditions are imposed as constraints in the optimization process [12,13,15–22]. In the iterative solution of the second-order contracted Schrödinger equation (2CSE), or its variants [7,11–13,23–47], the N -representability conditions are imposed upon the outcome of the equation by subsequently applying a 2RDM purification procedure. One of the aims of this paper—the most applicative one—consists of establishing the conditions, as well as the strategy, for constructing a 2RDM purification procedure in the study of states of doublet symmetry.

Several of the approaches developed in order to purify the 2RDM [40,41,43,46] have a common feature: The 2RDM is decomposed into different matrix contributions, and the 1RDM remains fixed during the purification process while the two-body part is corrected. Another research line, where the developments reported here could well be proven useful, is quantum information [48]. Indeed, the correlation matrix that carries information about the spectrum of the system is probably related to the two-body quantum involvement.

Since, in general, one is interested in states having well-defined spin-quantum numbers, the spin- or S -representability concept has been defined [49]. In a similar way to the N -representability conditions, the S -representability conditions are those conditions that a 2RDM must satisfy in order to be certain that it derives from a pure spin state. In 1961, McWeeny and Mizuno [51] studied the 2RDM spin properties and in 2005 the general spin properties of the correlation matrix were reported [43]. These correlation matrix spin properties, which are very exacting and directly influence the 2RDM structure, should therefore be imposed as S -representability conditions in the 2RDM purification procedure for a given spin symmetry.

In the study carried out for the singlet Li_2 and BeH_2 [42,46] molecules using a combined 2CSE-purification method, the improvement brought about by the inclusion of

the purification procedure upon both the convergence of the method and its accuracy was dramatic. Indeed, the accuracy attained after including the purification procedure into the process was of 10^{-5} hartrees. It is therefore necessary to develop *ad hoc* purification procedures for higher spin multiplicities that play an important role in molecular physics. The aim of this paper is to develop such a purification procedure for doublet states.

One of the possible ways for decomposing the 2RDM in order to be able to keep the 1RDM fixed and to correct the two-body contribution is the unitarily invariant decomposition proposed by Coleman in 1974 [50]. This decomposition is at the base of Mazziotti's 2RDM purification procedure [40]. In order to devise a 2RDM purification procedure that would not only impose the main N -representability conditions but also the S -representability ones, Alcobra generalized Coleman's unitarily invariant decomposition [1] and proposed a purification procedure for 2RDMs corresponding to singlet states [46].

In order to attain our aim of building a 2RDM purification procedure for doublet states we start by reporting the explicit spin conditions that must be satisfied when the state considered is a component of a doublet with $M_s = 1/2$. Then, due to Alcobra's generalization of Coleman's matrix decomposition, the N - and S -representability conditions of the \mathcal{G} matrix can be included in the purification procedure.

The basic theoretical background is summarized in the following section. In Sec. III a set of S -representability conditions for the correlation matrix corresponding to a doublet state is explicitly given. The sequence of operations performed by the purification procedure is described in Sec. IV. The results obtained when purifying approximated 2RDMs, corresponding to the ground, first, and fourth excited states of the linear BeH_2^+ are reported in Sec. V. The initial non-negligible N - and S -representability defects of these three 2RDMs were smoothly and consistently corrected when the purification procedure was applied to these 2RDMs. Some general comments are finally given in Sec. VI.

II. BASIC THEORETICAL BACKGROUND

A. Definitions

1. Reduced density matrices

The well-known definitions of the 1RDM and 2RDM elements in second quantization in the occupation number representation are

$${}^1D_{i_\sigma j_\sigma} = \langle \Phi | a_{i_\sigma}^\dagger a_{j_\sigma} | \Phi \rangle \quad (1)$$

and

$$2! {}^2D_{i_\sigma j_\sigma; k_\sigma l_\sigma} = \langle \Phi | a_{i_\sigma}^\dagger a_{j_\sigma}^\dagger a_{l_\sigma} a_{k_\sigma} | \Phi \rangle, \quad (2)$$

respectively. The indices i, j, k , and l denote the elements of a finite basis set formed by K orthonormal orbitals. The spin functions α and β are generically denoted by σ, σ' , etc. The state being considered is represented by the symbol Φ . Note that the *bra* and *ket* states may be different. When this is the case, one has a transition reduced density matrix (TRDM).

The matrices defined in a similar way but with the creation operators to the right of the annihilators

$${}^1\bar{D}_{i_\sigma j_\sigma} = \langle \Phi | a_{j_\sigma} a_{i_\sigma}^\dagger | \Phi \rangle \quad (3)$$

and

$$2! {}^2\bar{D}_{i_\sigma j_\sigma; k_\sigma l_\sigma} = \langle \Phi | a_{l_\sigma} a_{k_\sigma} a_{i_\sigma}^\dagger a_{j_\sigma}^\dagger | \Phi \rangle \quad (4)$$

are hole reduced density matrices (HRDM), and will also play an important role in following paragraphs.

2. Two-body correlation and \mathcal{G} matrices

We define the elements of the second-order correlation matrix as

$$\begin{aligned} \mathcal{C}_{i_\sigma j_\sigma; k_\sigma l_\sigma} &= \sum_{\Phi' \neq \Phi} \langle \Phi | a_{i_\sigma}^\dagger a_{k_\sigma} | \Phi' \rangle \langle \Phi' | a_{j_\sigma}^\dagger a_{l_\sigma} | \Phi \rangle \\ &\equiv \langle \Phi | a_{i_\sigma}^\dagger a_{k_\sigma} \hat{P} a_{j_\sigma}^\dagger a_{l_\sigma} | \Phi \rangle, \end{aligned} \quad (5)$$

where \hat{P} is the operator that projects upon the space complementary to $|\Phi\rangle\langle\Phi|$. This definition arises from the following 2RDM decomposition [12,32–38,41,43,45–47]:

$$\begin{aligned} 2! {}^2D_{i_\sigma j_\sigma; k_\sigma l_\sigma} &= {}^1D_{i_\sigma; k_\sigma} {}^1D_{j_\sigma; l_\sigma} - \delta_{\sigma, \sigma'} \delta_{j, k} {}^1D_{i_\sigma; l_\sigma} \\ &\quad + {}^2\mathcal{C}_{i_\sigma j_\sigma; k_\sigma l_\sigma}. \end{aligned} \quad (6)$$

The well-known \mathcal{G} matrix [15,16] is formed by the same elements as the \mathcal{C} matrix but their ordering is different. Thus

$$\mathcal{C}_{i_\sigma j_\sigma; k_\sigma l_\sigma} \equiv \mathcal{G}_{i_\sigma k_\sigma; l_\sigma j_\sigma}. \quad (7)$$

In what follows we will center our attention on the \mathcal{G} matrix instead of on the \mathcal{C} matrix because \mathcal{G} is a Hermitian positive semidefinite matrix, while the \mathcal{C} matrix is not.

A very important property of either of these two matrices, which describe the correlation information carried by the 2RDM, is that they also appear when decomposing the 2HRDM [32]. Thus

$$\begin{aligned} 2! {}^2\bar{D}_{i_\sigma j_\sigma; k_\sigma l_\sigma} &= {}^1\bar{D}_{i_\sigma; k_\sigma} {}^1\bar{D}_{j_\sigma; l_\sigma} - \delta_{\sigma, \sigma'} \delta_{i, l} {}^1\bar{D}_{j_\sigma; k_\sigma} \\ &\quad + {}^2\bar{\mathcal{C}}_{i_\sigma j_\sigma; k_\sigma l_\sigma}. \end{aligned} \quad (8)$$

The fact that the \mathcal{G} matrix is a common part of both the 2RDM and the 2HRDM will be used later on.

B. Basic N -representability conditions

The ensemble N -representability problem for the 1RDM was solved by Coleman [14] by establishing that it must be a Hermitian, positive semidefinite matrix whose eigenvalues are less than one. This theorem applies also to the 1HRDM. This is seen by realizing that

$${}^1D_{i_\sigma j_\sigma} + {}^1\bar{D}_{i_\sigma j_\sigma} = \delta_{i, j} \quad (9)$$

The solution given by Coleman [52] for the N -representability of the 2RDM is unfortunately not feasible

[53]. However, in practice, there is a set of necessary conditions, which have been found to yield matrices, that are very close to N -representable ones. This set of conditions is as follows [7–12].

(1) The 2RDM, 2HRDM, and the \mathcal{G} matrix are Hermitian matrices.

(2) While the 2RDM and 2HRDM are antisymmetric under permutation of indices within a given row or column, the \mathcal{G} matrix is not antisymmetric. For instance, the permutation of two indices leads to the following relation:

$$\mathcal{G}_{i\sigma j\sigma';k\sigma j\sigma'} = {}^1D_{i\sigma;k\sigma} {}^1\bar{D}_{j\sigma';l\sigma'} + \delta_{\sigma,\sigma'} {}^1D_{i\sigma;l\sigma} {}^1\bar{D}_{j\sigma;k\sigma} - \mathcal{G}_{i\sigma k\sigma';l\sigma'j\sigma'}. \quad (10)$$

(3) The D N -representability condition states that the 2RDM is a positive semidefinite matrix.

(4) The 2HRDM can be expressed in terms of the 1- and 2-RDMs as

$$\begin{aligned} 2! {}^2\bar{D}_{i\sigma j\sigma';k\sigma j\sigma'} &= 2! {}^2D_{i\sigma j\sigma';k\sigma j\sigma'} + \delta_{i,k}\delta_{j,l} - \delta_{i,l}\delta_{j,k}\delta_{\sigma,\sigma'} \\ &\quad - {}^1D_{j\sigma';l\sigma'}\delta_{i,k} - {}^1D_{i\sigma;k\sigma}\delta_{j,l} + \delta_{\sigma,\sigma'}\delta_{i,l} {}^1D_{j\sigma;k\sigma} \\ &\quad + \delta_{\sigma,\sigma'}\delta_{j,k} {}^1D_{i\sigma;l\sigma}. \end{aligned} \quad (11)$$

The Q N -representability condition states that the 2HRDM is a positive semidefinite matrix.

(5) The G N -representability condition states that the \mathcal{G} matrix is a positive semidefinite matrix. This is a very important property, which is why in what follows we will center the attention upon this matrix, preferably instead of the C -matrix, in spite of the fact that the row and column labels of the 2RDM and the C matrix are the same.

(6) The 2RDM, 2HRDM, and \mathcal{G} matrix contract according to

$$\sum_j 2! {}^2D_{i\sigma j\sigma';k\sigma j\sigma'} = {}^1D_{i\sigma;l\sigma}(N_{\sigma'} - \delta_{\sigma,\sigma'}), \quad (12)$$

$$\sum_j 2! {}^2\bar{D}_{i\sigma j\sigma';k\sigma j\sigma'} = {}^1\bar{D}_{i\sigma;l\sigma}(K - N_{\sigma'} + \delta_{\sigma,\sigma'}), \quad (13)$$

$$\sum_k \mathcal{C}_{i\sigma k\sigma';j\sigma k\sigma'} = 0 = \sum_k \mathcal{G}_{i\sigma j\sigma';k\sigma k\sigma'}, \quad (14)$$

$$\sum_l \mathcal{G}_{i\sigma l\sigma';j\sigma l\sigma'} = (K - N_{\sigma'} + \delta_{\sigma,\sigma'}) {}^1D_{i\sigma;j\sigma} - ({}^1D^2)_{i\sigma;j\sigma} \delta_{\sigma,\sigma'}, \quad (15)$$

$$\sum_l \mathcal{G}_{l\sigma j\sigma';l\sigma j\sigma'} = N_{\sigma'} {}^1\bar{D}_{i\sigma';j\sigma'} + [{}^1D_{i\sigma';j\sigma'} - ({}^1D^2)_{i\sigma';j\sigma'}] \delta_{\sigma,\sigma'}. \quad (16)$$

These are standard contractions but, as will be seen later on, when the adequate spin conditions are taken into account, other types of important contractions arise.

C. General form of the unitarily invariant second-order matrix decomposition

In 1974 Coleman reported a unitarily invariant second-order matrix decomposition that could be applied to the 2RDM [50]. When one wishes to apply the same decomposition to the 2RDM, 2HRDM, and \mathcal{G} matrices, Coleman's decomposition cannot be applied, this is because the \mathcal{G} matrix is not antisymmetric with respect to permutation of the row or column indices. Alcoba [1] proposed a generalized unitarily invariant decomposition that may be applied to these three matrices. In this section we describe this generalized decomposition while paying special attention to the points more directly affected by the spin properties of the state considered.

Let us represent by \mathbf{M} the second-order matrix that is decomposed into three matrices ${}_0\mathbf{M}$, ${}_1\mathbf{M}$, and ${}_2\mathbf{M}$ that have a zero-, one-, and two-electron dependence, respectively

$$\mathbf{M} = {}_0\mathbf{M} + {}_1\mathbf{M} + {}_2\mathbf{M}. \quad (17)$$

Since the symmetry under permutation of indices of the \mathbf{M} matrix is arbitrary, the number of contractions that have to be taken into account is larger than in Coleman's decomposition. Thus the matrices ${}_0\mathbf{M}$, ${}_1\mathbf{M}$, and ${}_2\mathbf{M}$ are evaluated with the following auxiliary quantities defined by the contractions of \mathbf{M} :

(1) The contractions over one common index or single contractions:

$$\sum_m M_{im;jm} = B_{i;j}, \quad \sum_m M_{mi;mj} = B'_{i;j}, \quad (18)$$

$$\sum_m M_{im;mj} = R_{i;j}, \quad \sum_m M_{mi;jm} = R'_{i;j}. \quad (19)$$

(2) The double contractions:

$$\sum_{m,n} M_{mn;mn} = A, \quad \sum_{m,n} M_{mn;nm} = A'. \quad (20)$$

In terms of these magnitudes one has

$${}_0M_{ij;kl} = \frac{(KA - A')\delta_{i,k}\delta_{j,l} + (KA' - A)\delta_{i,l}\delta_{j,k}}{K(K^2 - 1)}, \quad (21)$$

$$\begin{aligned} {}_1M_{ij;kl} &= \frac{(4A' - 2KA)\delta_{i,k}\delta_{j,l} + (4A - 2KA')\delta_{i,l}\delta_{j,k}}{K(K^2 - 4)} \\ &\quad + \frac{2(B_{j;l}\delta_{i,k} + B'_{i;k}\delta_{j,l} + R_{j;k}\delta_{i,l} + R'_{i,l}\delta_{j,k})}{K(K^2 - 4)} \\ &\quad + \frac{(K^2 - 2)(B_{i;k}\delta_{j,l} + B'_{j;l}\delta_{i,k} + R_{i;l}\delta_{j,k} + R'_{j,k}\delta_{i,l})}{K(K^2 - 4)} \\ &\quad + \frac{B_{i;l}\delta_{j,k} + B_{j;k}\delta_{i,l} + B'_{i;k}\delta_{j,l} + B'_{j,l}\delta_{i,k}}{4 - K^2} \\ &\quad + \frac{R_{i,k}\delta_{j,l} + R_{j,l}\delta_{i,k} + R'_{i,l}\delta_{j,k} + R'_{j,k}\delta_{i,l}}{4 - K^2}, \end{aligned} \quad (22)$$

$${}_2M_{ij;kl} = M_{ij;kl} - {}_0M_{ij;kl} - {}_1M_{ij;kl}. \quad (23)$$

Note that in the 2RDM and 2HRDM cases the antisymmetry under permutation of the creation operators (or under permutations of the annihilators) forces all single and double contractions to be related; there is no more than one single and one double linearly independent contractions. Since there is no such antisymmetry in the \mathcal{G} -matrix case, four single contractions and two double contractions must be considered.

For our purpose, an important feature of this decomposition is that it allows one to *independently* modify the zero-, one- and two-body information of the \mathbf{M} matrix. Assuming that the 1RDM is ensemble N -representable, the N - and S -representability errors of the 2RDM, 2HRDM, and \mathcal{G} matrices will be caused by the ${}_2\mathbf{M}$ matrix. Consequently keeping the 1RDM fixed while correcting the two-body part of these three matrices lies at the base not only of the purification procedure that is reported here but of other previously published ones [40,41,43,46].

Rendering positive semidefinite the \mathbf{M} matrix

When diagonalizing a matrix \mathbf{M} that should be positive semidefinite one finds that some of its eigenvalues are negative, a purification has to be carried out in order to correct this positivity defect. In our procedure, we correct the positivity defects of our matrices by applying an extension of Mazzioti's algorithm [40] that may be summarized as follows.

Let us call $\{\mathbf{x}_p\}$ the eigenvectors corresponding to the negative eigenvalues λ_p of the \mathbf{M} matrix and let us consider the matrix

$$\mathbf{Y}^p = \mathbf{x}_p^\dagger \mathbf{x}_p. \quad (24)$$

The idea is to look for a matrix \mathbf{Z} when added to \mathbf{M} yields an updated matrix that keeps the same ${}_0\mathbf{M}$ and ${}_1\mathbf{M}$, thus preserving its traces. In general, if the updated matrix still has negative eigenvalues, those eigenvalues have smaller absolute values than the original ones.

Let us now apply the unitarily invariant decomposition to each of the \mathbf{Y}^p and let us call ${}_2\mathbf{Y}^p$ its two-body part. Then the \mathbf{Z} correction takes the form

$$\mathbf{Z} = \sum_p \gamma_p {}_2\mathbf{Y}^p, \quad (25)$$

where the coefficients γ_p are determined by solving the following linear system:

$$\lambda_p + \sum_{p'} \gamma_{p'} \text{tr}({}_2\mathbf{Y}^{p'} \mathbf{Y}^p) = 0 \quad (\forall p). \quad (26)$$

The relations linking different elements of the spin-blocks of the matrices involved in the 2RDM purification will be studied in the next section before describing in detail the strategy followed in the purification procedure itself, which will be described in Sec. V.

III. SPIN STRUCTURE OF THE \mathcal{G} MATRIX CORRESPONDING TO A DOUBLET STATE

Although the general spin properties of the correlation matrices [43] contain in an implicit way the information

about the particular and interlinked N - and S -representability conditions (NSG conditions) for doublets, it is important to obtain their explicit form. These new relations are those that permit one to obtain the elements of the \mathcal{G} -matrix spin components and, once these components have been purified, to reconstruct a new \mathcal{G} matrix. In this section, we report these relations as well as the form in which the 2RDM elements are affected. Also, some contraction relations of the set listed in this section can be considered different and relevant results.

The \mathcal{G} -matrix definition, Eq. (7), shows that all the spectrum states that are different from the state Φ being formally considered contribute to the value of this matrix element. However, due to the spin-symmetry rules, many of these contributions vanish. Thus the \mathcal{G} matrix can be decomposed into a sum of the spin components that, in principle, may have a non-null contribution. In order to refer to the spin-quantum numbers of the different states involved we denote:

$$\hat{P}_{(S',M'_s)} = \sum_{\Phi' \neq \Phi} |\Phi', S', M'_s\rangle \langle \Phi', S', M'_s|.$$

Here S' and M'_s represent the Φ' spin quantum numbers. A \mathcal{G} -matrix element corresponding to a doublet state Φ with ($M_s=1/2$) can be decomposed in terms of its spin components as

$$\begin{aligned} \mathcal{G}_{i_\sigma j_{\sigma'}; k_{\sigma''} l_{\sigma'''}} &= \langle \Phi | a_{i_\sigma}^\dagger a_{j_{\sigma'}} \hat{P}_{(1/2, M'_s)} a_{l_{\sigma''}}^\dagger a_{k_{\sigma'''}} | \Phi \rangle \\ &+ \langle \Phi | a_{i_\sigma}^\dagger a_{j_{\sigma'}} \hat{P}_{(3/2, M'_s)} a_{l_{\sigma''}}^\dagger a_{k_{\sigma'''}} | \Phi \rangle \\ &\equiv ({}_{1/2, M'_s}) \mathcal{G}_{i_\sigma j_{\sigma'}; k_{\sigma''} l_{\sigma'''}} + ({}_{3/2, M'_s}) \mathcal{G}_{i_\sigma j_{\sigma'}; k_{\sigma''} l_{\sigma'''}} \end{aligned} \quad (27)$$

where M'_s takes the appropriate value according to the element considered.

The spin properties of the \mathcal{G} components imply a new set of necessary N - and S -representability conditions including the positive-semidefiniteness of the \mathcal{G} components. It must be emphasized that imposing these latter conditions upon the \mathcal{G} components guarantees that the global condition $\mathcal{G} \geq 0$ is fulfilled. However, to have a positive semidefinite \mathcal{G} matrix does not imply that this new set of N - and S -representability conditions is satisfied.

In what follows, when the spin function considered is made explicit, the notation will be simplified by denoting the β function with a bar over the orbital symbol, i.e., \bar{k} .

The two relations linking the spin-block elements of the \mathcal{G} components among themselves are directly derived from general spin equations reported in [43]

$$\begin{aligned} ({}_{1/2, -1/2}) \mathcal{G}_{i, \bar{k}; l, \bar{j}}^- &= + ({}_{1/2, 1/2}) \mathcal{G}_{i, k; l, j} + ({}_{1/2, 1/2}) \mathcal{G}_{i, k; l, \bar{j}}^- - ({}_{1/2, 1/2}) \mathcal{G}_{i, k; l, \bar{j}}^- \\ &- ({}_{1/2, 1/2}) \mathcal{G}_{i, k; l, j}^- + ({}^1 D_{i, k} - {}^1 D_{i, \bar{k}}) ({}^1 D_{l, j} - {}^1 D_{l, \bar{j}}), \end{aligned} \quad (28)$$

$$\begin{aligned} \frac{1}{3}\mathcal{G}_{i,k;\bar{l},\bar{j}} &= \frac{1}{3}{}_{(3/2,3/2)}\mathcal{G}_{i,k;\bar{l},\bar{j}} = {}_{(3/2,-1/2)}\mathcal{G}_{i,k;\bar{l},\bar{j}} = {}_{(3/2,1/2)}\mathcal{G}_{i,k;\bar{l},\bar{j}} \\ &= {}_{(3/2,1/2)}\mathcal{G}_{i,k;\bar{l},\bar{j}}^- = -{}_{(3/2,1/2)}\mathcal{G}_{i,k;\bar{l},\bar{j}}^- = -{}_{(3/2,1/2)}\mathcal{G}_{i,k;\bar{l},\bar{j}}^- \end{aligned} \quad (29)$$

Essential S conditions for doublet states. The basic relations, just reported, permit one to establish the set of essential S conditions that will now be reported.

The $\mathcal{G}_{\beta\alpha;\beta\alpha}$ block is the matrix from which all the \mathcal{G} components' spin-blocks can be more easily derived. For instance, the relations linking the $\mathcal{G}_{\beta\alpha;\beta\alpha}$ block to other spin blocks of the same matrix are

$${}_{(1/2,1/2)}\mathcal{G}_{i,k;\bar{l},\bar{j}} = \mathcal{G}_{i,k;\bar{l},\bar{j}} + \frac{1}{3}\mathcal{G}_{i,k;\bar{l},\bar{j}}^-, \quad (30a)$$

$${}_{(1/2,1/2)}\mathcal{G}_{i,k;\bar{l},\bar{j}}^- = \mathcal{G}_{i,k;\bar{l},\bar{j}}^- + \frac{1}{3}\mathcal{G}_{i,k;\bar{l},\bar{j}}^-, \quad (30b)$$

$${}_{(1/2,1/2)}\mathcal{G}_{i,k;\bar{l},\bar{j}} = \mathcal{G}_{i,k;\bar{l},\bar{j}} - \frac{1}{3}\mathcal{G}_{i,k;\bar{l},\bar{j}}^-, \quad (30c)$$

$${}_{(1/2,1/2)}\mathcal{G}_{i,k;\bar{l},\bar{j}}^- = \mathcal{G}_{i,k;\bar{l},\bar{j}}^- - \frac{1}{3}\mathcal{G}_{i,k;\bar{l},\bar{j}}^-, \quad (30d)$$

$${}_{(1/2,-1/2)}\mathcal{G}_{i,\bar{l},m;\bar{j}} = \mathcal{G}_{i,\bar{l},m;\bar{j}} - \frac{1}{3}\mathcal{G}_{i,\bar{l},m;\bar{j}}^- - {}^1\bar{D}_{i,m} {}^1D_{\bar{j},\bar{l}} + {}^1D_{i,m} {}^1\bar{D}_{\bar{j},\bar{l}}. \quad (30e)$$

These relations allow us to calculate the elements of other spin blocks from the $\mathcal{G}_{\beta\alpha;\beta\alpha}$ block.

From a theoretical point of view, it is interesting to note that by imposing that Eq. (30e) is satisfied the fulfillment of the N -representability condition

$$\mathcal{G}_{i,\bar{l},m;\bar{j}} - \mathcal{G}_{\bar{j},m;\bar{l},i} = -{}^1\bar{D}_{i,m} {}^1D_{\bar{j},\bar{l}} + {}^1D_{i,m} {}^1\bar{D}_{\bar{j},\bar{l}} \quad (31)$$

is also guaranteed. Moreover, the basic relation

$${}^2D_{i,\bar{j};\bar{l},m} \equiv {}^2D_{\bar{j},i;\bar{l},m} \quad (32)$$

is simultaneously satisfied.

Contractions of the matrix diagonal spin blocks to be purified

1. Double contractions

The traces A and A' defined in Eqs. (20) corresponding to the 2RDM and 2HRDM take the following values:

$$A(\sigma\sigma; \sigma\sigma) = \begin{array}{cc} \text{2RDM} & \text{2HRDM} \\ + \binom{N_\sigma}{2} & + K - \binom{N_\sigma}{2} \end{array} \quad (33a)$$

$$A'(\sigma\sigma; \sigma\sigma) = \begin{array}{cc} - \binom{N_\sigma}{2} & - K + \binom{N_\sigma}{2} \end{array} \quad (33b)$$

$$A(\alpha\beta; \alpha\beta) = \begin{array}{cc} N_\alpha N_\beta & (K - N_\alpha)(K - N_\beta) \end{array} \quad (33c)$$

$$A'(\alpha\beta; \alpha\beta) = \begin{array}{cc} N_\beta & K - N_\alpha \end{array} \quad (33d)$$

Some of the results have been obtained by making use of the well-known fact that the result of the application of the \hat{S}_+ operator on a state with highest spin projection vanishes.

When considering the \mathcal{G} spin blocks only the A quantities have analytical expressions, since A' implies a sum over two creators and another over two annihilators that are not physically defined. However, since the A' appear in the unitarily invariant decomposition formula, these quantities are numerically calculated in each case.

The traces, the A parameter, for the different \mathcal{G} -spin blocks have the values:

$${}_{(3/2,3/2)}\mathcal{G}_{\beta\alpha;\beta\alpha}: (K - N_\alpha)N_\beta, \quad (34a)$$

$${}_{(1/2,1/2)}\mathcal{G}_{\alpha\alpha;\alpha\alpha}: (K - N_\alpha + 1)N_\alpha - \frac{1}{3}(K - N_\alpha)N_\beta - \text{tr}({}^1D_{\alpha,\alpha}^2), \quad (34b)$$

$${}_{(1/2,1/2)}\mathcal{G}_{\alpha\alpha;\beta\beta}: \left(\frac{K - N_\alpha}{3} + 1 \right) N_\beta - \text{tr}({}^1D_{\alpha,\alpha} {}^1D_{\beta,\beta}), \quad (34c)$$

$${}_{(1/2,1/2)}\mathcal{G}_{\beta\beta;\alpha\alpha}: \left(\frac{K - N_\alpha}{3} + 1 \right) N_\beta - \text{tr}({}^1D_{\alpha,\alpha} {}^1D_{\beta,\beta}), \quad (34d)$$

$${}_{(1/2,1/2)}\mathcal{G}_{\beta\beta;\beta\beta}: (K - N_\beta + 1)N_\beta - \frac{1}{3}(K - N_\alpha)N_\beta - \text{tr}({}^1D_{\beta,\beta}^2), \quad (34e)$$

$${}_{(1/2,-1/2)}\mathcal{G}_{\alpha\beta;\alpha\beta}: (K - N_\beta)N_\alpha - \frac{1}{3}(K - N_\alpha)N_\beta. \quad (34f)$$

2. Single contractions

The auxiliary quantities defined in Eqs. (18) and (19) have the following values for 2RDM and 2HRDM classified by the $(\sigma\sigma'; \sigma\sigma')$ elements of the parent matrix:

$$B_{i,k}(\sigma\sigma; \sigma\sigma) = \begin{array}{cc} \text{2RDM} & \text{2HRDM} \\ {}^1D_{i,\sigma;k,\sigma}(N_\sigma - 1) & {}^1\bar{D}_{i,\sigma;k,\sigma}(K - N_\sigma + 1) \end{array} \quad (35a)$$

$$B_{i,k}(\alpha\beta; \alpha\beta) = \begin{array}{cc} N_\beta {}^1D_{i,k} & (K - N_\beta + 1) {}^1\bar{D}_{i,k} \end{array} \quad (35b)$$

$$B'_{i,k}(\sigma\sigma; \sigma\sigma) = \begin{array}{cc} {}^1D_{i,\sigma;k,\sigma}(N_\sigma - 1) & {}^1\bar{D}_{i,\sigma;k,\sigma}(K - N_\sigma + 1) \end{array} \quad (35c)$$

$$B'_{i,k}(\alpha\beta; \alpha\beta) = \begin{array}{cc} N_\alpha {}^1D_{i,k}^- & (K - N_\alpha + 1) {}^1\bar{D}_{i,k}^- \end{array} \quad (35d)$$

$$R_{i,k}(\sigma\sigma; \sigma\sigma) = \begin{array}{cc} {}^1D_{i,\sigma;k,\sigma}(1 - N_\sigma) & {}^1\bar{D}_{i,\sigma;k,\sigma}(-K + N_\sigma - 1) \end{array} \quad (35e)$$

$$R_{i,k}(\alpha\beta; \alpha\beta) = \begin{array}{cc} {}^1D_{i,k}^- & {}^1\bar{D}_{i,k} \end{array} \quad (35f)$$

$$R'_{i,k}(\sigma\sigma; \sigma\sigma) = \begin{array}{cc} {}^1D_{i,\sigma;k,\sigma}(1 - N_\sigma) & {}^1\bar{D}_{i,\sigma;k,\sigma}(-K + N_\sigma - 1) \end{array} \quad (35g)$$

$$R'_{i,k}(\alpha\beta; \alpha\beta) = \begin{array}{cc} {}^1D_{i,k}^- & {}^1\bar{D}_{i,k} \end{array} \quad (35h)$$

When considering the \mathcal{G} -spin blocks, only the \mathbf{B} and \mathbf{B}' quantities have analytical expressions, since \mathbf{R} and \mathbf{R}' imply a sum over two creators or two annihilators that are not physically defined. However, since the \mathbf{R} and \mathbf{R}' appear in the unitarily invariant decomposition formula, these quantities are numerically calculated in each case.

The analytical expressions for \mathbf{B} and \mathbf{B}' quantities in the \mathcal{G} -spin components to be purified are as follows:

$$(1) \text{ For the } {}_{(3/2,3/2)}\mathcal{G}_{\beta\alpha;\beta\alpha} \quad B_{i,q} = (K - N_\alpha) {}^1D_{i,q}^-, \quad (36)$$

$$B'_{i;q} = N_\beta (\delta_{j;p} - {}^1D_{j;p}). \quad (37)$$

(2) For the ${}_{(1/2,-1/2)}\mathcal{G}_{\alpha\beta;\alpha\beta}$

$$B_{i;q} = (K - N_\beta) {}^1D_{i;q} - \frac{1}{3}(K - N_\alpha) {}^1D_{\bar{i};\bar{q}}, \quad (38)$$

$$B'_{i;q} = N_\alpha (\delta_{j;p} - {}^1D_{\bar{j};\bar{p}}) - \frac{1}{3}N_\beta (\delta_{j;p} - {}^1D_{j;p}). \quad (39)$$

(3) For the ${}_{(1/2,1/2)}\mathcal{G}_{\alpha\alpha;\alpha\alpha}$

$$B_{i;q} = (K - N_\alpha + 1) {}^1D_{i;q} - ({}^1D^2)_{i;q} - \frac{1}{3}(K - N_\alpha) {}^1D_{\bar{i};\bar{q}}, \quad (40)$$

$$B'_{i;q} = (N_\alpha - \frac{1}{3}N_\beta) (\delta_{j;p} - {}^1D_{j;p}) + {}^1D_{j;p} - ({}^1D^2)_{j;p}. \quad (41)$$

(4) For the ${}_{(1/2,1/2)}\mathcal{G}_{\beta\beta;\beta\beta}$

$$B_{i;q} = (K - N_\beta + 1) {}^1D_{\bar{i};\bar{q}} - \frac{1}{3}N_\beta (\delta_{j;p} - {}^1D_{j;p}) - ({}^1D^2)_{\bar{i};\bar{q}}, \quad (42)$$

$$B'_{i;q} = N_\beta \left(\frac{2}{3}\delta_{j;p} - {}^1D_{\bar{j};\bar{p}} + \frac{1}{3}{}^1D_{j;p} \right) + {}^1D_{\bar{j};\bar{p}} - ({}^1D^2)_{\bar{j};\bar{p}}. \quad (43)$$

Let us finish this section by noting that the set of A' traces and R and R' contractions of the 2RDM, 2HRDM, and the \mathcal{G} -matrix spin components form a stringent set of S -representability conditions that must be fulfilled by any 2RDM corresponding to a doublet state.

IV. DOUBLET PURIFICATION PROCEDURE

In our sequential procedure, each of the 2RDM and the 2HRDM spin-blocks $(\alpha\alpha; \alpha\alpha)$, $(\alpha\alpha; \beta\beta)$, and $(\beta\beta; \beta\beta)$ are separately purified. The positivity defects of the ${}_{(1/2,-1/2)}\mathcal{G}$, ${}_{(1/2,1/2)}\mathcal{G}$, and ${}_{(3/2,3/2)}\mathcal{G}$ spin components will also be independently corrected. The main aim here will be to render positive each of these matrices.

As will be described below, the correct \mathbf{B} , \mathbf{B}' , \mathbf{R} , and \mathbf{R}' contractions for the 2RDM will be imposed at the beginning of each iteration. As a consequence, the 2HRDM will correctly contract, as well as the initial \mathcal{G} matrix. It must be noted that the only \mathcal{G} contractions that are imposed are \mathbf{B} and \mathbf{B}' . Having these ideas in mind, let us now consider the sequence of operations that are carried out.

The initial data for the procedure are a 2RDM and an ensemble N -representable 1RDM. The 1RDM will be kept fixed during all the purification operations. Usually, the selected 1RDM is obtained by contracting the initial 2RDM and, if necessary, it is rendered ensemble N -representable by following the method described in detail in [41].

A. Initial tests and corrections of the 2RDM

The unitarily invariant decomposition is applied to each of the 2RDM spin blocks. That is, using the traces and the contractions of this spin-block, its ${}_0\mathbf{M}$ and ${}_1\mathbf{M}$ parts are evaluated; then, using Eq. (23), one obtains the two-body part, ${}_2\mathbf{M}$. Once this part is obtained, an updated 2RDM is calculated by using the matrices ${}_0\mathbf{M}^{(f)}$ and ${}_1\mathbf{M}^{(f)}$, which are

considered fixed; hence the superscript f . Thus one has

$${}_0\mathbf{M}^{(f)} + {}_1\mathbf{M}^{(f)} + {}_2\mathbf{M} \rightarrow {}^2\mathbf{D}. \quad (44)$$

This updated 2RDM and its associated 2HRDM have N -representable contractions into the zero- and one-body space.

B. Rendering the 2RDM and the 2HRDM simultaneously positive

In order to impose the D and Q N -representability conditions upon the 2RDM (i.e., that ${}^2\mathbf{D}$ and ${}^2\bar{\mathbf{D}}$ be simultaneously positive semidefinite) one diagonalizes each of these matrices. Let us call $\mathbf{x}_p/\bar{\mathbf{x}}_q$ the 2RDM/2HRDM eigenvectors corresponding to the negative eigenvalues $\lambda_p/\bar{\lambda}_q$. Let us also call $\mathbf{Y}^p/\bar{\mathbf{Y}}^q$ the matrices formed, respectively, by the eigenvectors $\mathbf{x}_p/\bar{\mathbf{x}}_q$ as described in Sec. II C. In this case, the linear equations to be simultaneously solved are

$$\lambda_p + \sum_{p'} \gamma_{p'} \text{tr}({}_2\mathbf{Y}^{p'} \mathbf{Y}^p) + \sum_{q'} \bar{\epsilon}_{q'} \text{tr}({}_2\bar{\mathbf{Y}}^{q'} \mathbf{Y}^p) = 0 \quad (\forall p), \quad (45)$$

$$\bar{\lambda}_q + \sum_{p'} \gamma_{p'} \text{tr}({}_2\mathbf{Y}^{p'} \bar{\mathbf{Y}}^q) + \sum_{q'} \bar{\epsilon}_{q'} \text{tr}({}_2\bar{\mathbf{Y}}^{q'} \bar{\mathbf{Y}}^q) = 0 \quad (\forall q). \quad (46)$$

By solving this set of equations one obtains the set of coefficients γ_p and ϵ_q . The correction matrix \mathbf{Z} for the 2RDM (and hence for the 2HRDM) is given by

$$\mathbf{Z} = \sum_p \gamma_p {}_2\mathbf{Y}^p + \sum_q \epsilon_q {}_2\bar{\mathbf{Y}}^q. \quad (47)$$

The updated 2RDM is therefore

$${}^2\mathbf{D} + \mathbf{Z} \rightarrow {}^2\mathbf{D}. \quad (48)$$

C. Incorporating the \mathcal{G} S -representability conditions into the $(\alpha\beta; \alpha\beta)$ 2RDM spin block

1. Correcting the ${}_{(3/2,3/2)}\mathcal{G}$ component spin block

Due to the relations reported in the previous section, this \mathcal{G} spin component is the pivot in the purification of the $(\alpha\beta; \alpha\beta)$ 2RDM spin block. Therefore this part of the calculating program starts by correcting the positivity defect of this spin block. This is done by applying the method described in Sec. II C. When recalculating the $(\alpha\beta; \alpha\beta)$ 2RDM spin block by applying relations (6), (7), and (10) one finds that, as a consequence of the correcting operations carried out upon the ${}_{(3/2,3/2)}\mathcal{G}$ the \mathbf{R} and \mathbf{R}' contractions of the $(\alpha\beta; \alpha\beta)$ 2RDM have been modified. Therefore the $(\alpha\beta; \alpha\beta)$ 2RDM spin block is recalculated by imposing the correct values to the \mathbf{R} and \mathbf{R}' .

2. Correcting the ${}_{(1/2,-1/2)}\mathcal{G}$ component spin block

The positivity error of the ${}_{(1/2,-1/2)}\mathcal{G}$ is corrected by applying the method described in Sec. II C. Here again, the \mathbf{R} and

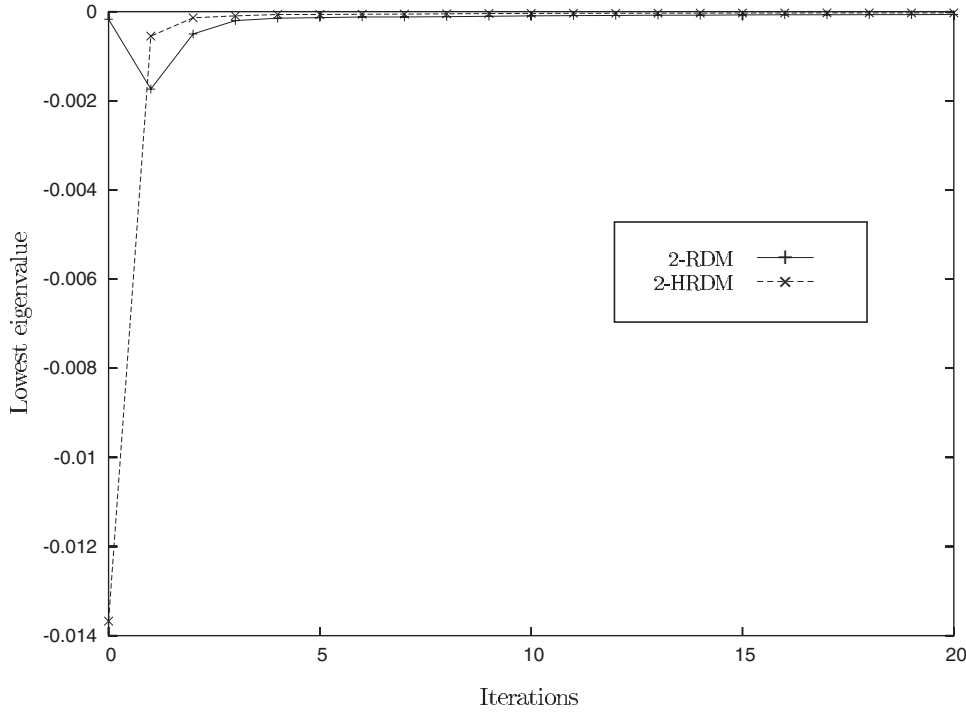


FIG. 1. Lowest eigenvalue of the 2RDM and 2HRDM at each iteration of the doublet purification procedure for the ground state of the BeH_2^+ .

\mathbf{R}' corresponding to the $(\alpha\beta; \alpha\beta)$ blocks of the 2RDM and the 2HRDM have been modified. In order to get the new $\alpha\beta; \alpha\beta$ block of the 2RDM we use the following equation:

$$\begin{aligned} {}_{(1/2,-1/2)}\mathcal{G}_{i,\bar{l};m,\bar{j}} + \frac{1}{3}{}_{(1/2,-1/2)}\mathcal{G}_{j,\bar{m};l,\bar{i}} = \frac{8}{9}\mathcal{G}_{j\bar{m};l\bar{i}} + ({}^1\bar{D}_{\bar{j};l}^{-1}D_{i,m} \\ - {}^1\bar{D}_{i,m}^{-1}D_{\bar{j};l}) + \frac{1}{3}({}^1\bar{D}_{i,\bar{m}}^{-1}D_{j,l} - {}^1\bar{D}_{j,l}^{-1}D_{i,\bar{m}}), \end{aligned} \quad (49)$$

which is the inverse of Eq. (30e).

D. Incorporating the $\mathcal{G}S$ representability conditions into the $(\sigma\sigma; \sigma\sigma)$ 2RDM spin blocks

Since according to Eq. (29)

$${}_{(3/2,1/2)}\mathcal{G}_{\sigma\sigma;\sigma\sigma} = \frac{1}{3}{}_{(3/2,3/2)}\mathcal{G}_{\beta\alpha;\beta\alpha} \quad (50)$$

the ${}_{(3/2,1/2)}\mathcal{G}_{\sigma\sigma;\sigma\sigma}$ is approximately positive semidefinite. Therefore we center our attention on correcting the negativity error of the other component, ${}_{(1/2,1/2)}\mathcal{G}_{\sigma\sigma;\sigma\sigma}$. Thus its negativity is approximately corrected by applying the method described in Sec. II C. The next operation is to evaluate the corresponding 2RDM blocks by applying Eqs. (6), (7), (30c), and (30d) and assuming that ${}_{(3/2,3/2)}\mathcal{G}_{\beta\alpha;\beta\alpha}$ remains fixed.

E. Final tests on the 2RDM

The purification of the three matrices 2RDM, 2HRDM, and \mathcal{G} matrix is considered to be completed when the initial tests including positivity checks satisfy the established tolerance limit (in general 10^{-4} to 10^{-5}). If the tolerance limits have not been reached, a new iterative cycle of the whole set of operations restarts.

V. PERFORMANCE OF THE DOUBLET PURIFICATION PROCEDURE

The purification procedure described above has been applied to correct the N - and S -representability defects of the approximated 2RDM corresponding to the ground state and to the first and fourth excited states of the linear BeH_2^+ cation ($\text{Be}-\text{H}$ bond length is $2.54a_0$). An orthonormalized basis set of seven Hartree-Fock orbitals optimized for the neutral molecule and, hence, adapted to the symmetry of the problem were used.

In order to prepare a suitable 2RDM to be purified (i.e., a matrix that cannot be considered neither N nor S representable while nevertheless being a sensible one) a constructing algorithm [33] for evaluating a 3RDM in terms of the 1- and 2RDMs has been used. This 3RDM was then contracted in order to obtain the corresponding 2RDM. It could have been done via a random process but in this way other properties, such as the spatial symmetry, are preserved.

The initial 1- and 2RDMs used were obtained from a full-configuration-interaction (FCI) calculation; and therefore these initial data for approximating the 3RDM are exact. Since the 3RDM is an approximated matrix so is the 2RDM derived from it. Indeed, the 2RDM thus obtained, as will be shown below, does not completely satisfy the N - and S -representability conditions described in Secs. II and IV. The results reported below correspond to the 2RDM purification, which in its turn corresponds to the three selected states of the molecular cation.

In the purifications of all the matrices that have been carried out, the number of iterative cycles has been 20. The significant results are reported in six self-explanatory figures and in three tables.

Correcting the positivity defects of the 2RDM and the 2HRDM in the three states considered. The curves shown in

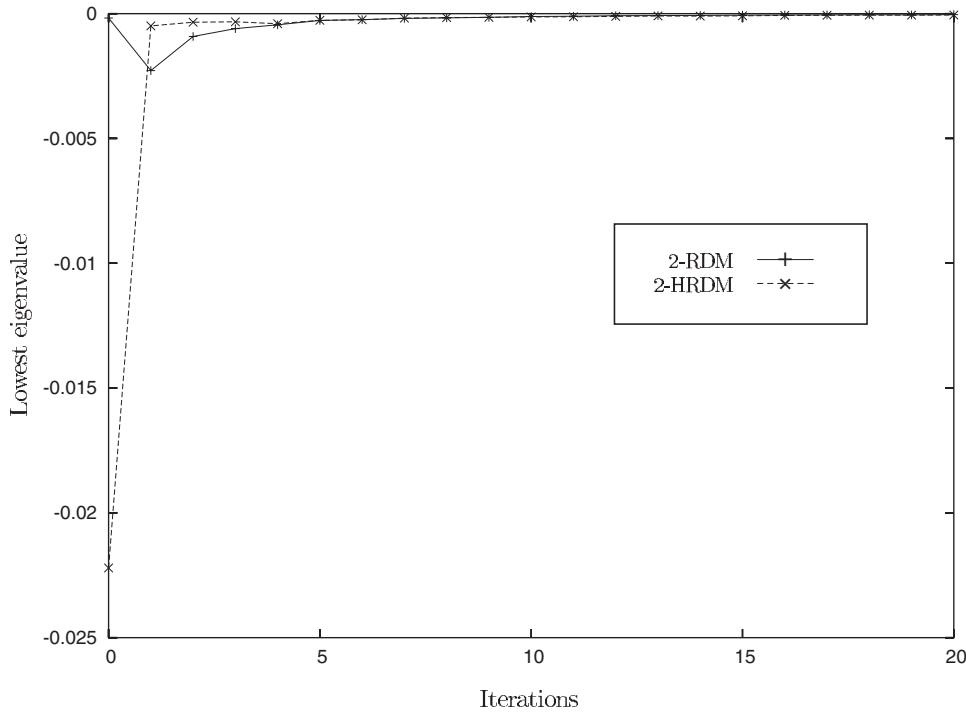


FIG. 2. Lowest eigenvalue of the 2RDM and 2HRDM at each iteration of the doublet purification procedure for the first excited state of the BeH_2^+ .

Figs. 1–3 describe the correction of the positivity defects of the 2RDM and 2HRDM by showing the lowest negative eigenvalue of these matrices for the ground, first, and fourth excited states, respectively. Also, the initial and final values of these eigenvalues are reported in the second and third columns of Table I. As can be seen, after 20 purification iterations these matrices can be considered to be positive semidefinite in both the ground and the excited states considered. An interesting feature that is common to all the curves is that in the first three iterations the negativity of both matrices rapidly tend to zero and is already of the order of 10^{-4} .

Correcting the positivity defects of the \mathcal{G} spin blocks in the three states considered. The curves shown in Figs. 4–6, together with the numerical data reported in the fourth, fifth, and sixth columns of Table II, show that the $_{(1/2,-1/2)}\mathcal{G}$, $_{(3/2,3/2)}\mathcal{G}$, and $_{(1/2,1/2)}\mathcal{G}$ matrices are rendered smoothly positive in the three states being studied. Here also, the error rapidly diminishes and, in fact, in most of these calculations the error decays in two orders of magnitude in the first three iterations. It must be underlined that, although only the diagonal spin blocks of the $_{(1/2,1/2)}\mathcal{G}$ spin component are purified within our procedure, the whole $_{(1/2,1/2)}\mathcal{G}$ spin component has been considered for testing its positivity defect.

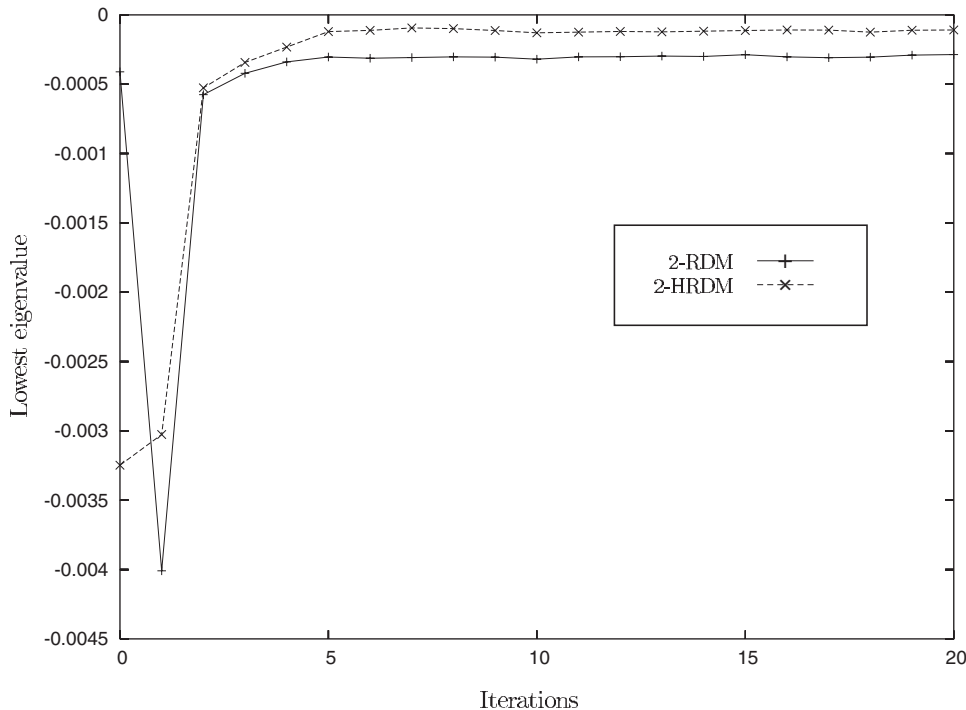


FIG. 3. Lowest eigenvalue of the 2RDM and 2HRDM at each iteration of the doublet purification procedure for the fourth excited state of the BeH_2^+ .

TABLE I. Performance of the doublet purification procedure when applied to approximated 2RDMs corresponding to the ground, first, and fourth state of the cation BeH_2^+ : Positivity defects of the 2RDM, 2HRDM, and $_{(1/2,-1/2)}\mathcal{G}$, $_{(3/2,3/2)}\mathcal{G}$, and $_{(1/2,-1/2)}\mathcal{G}$ spin components.

Iterations	Lowest eigenvalue				
	2RDM	2HRDM	$_{(1/2,-1/2)}\mathcal{G}$	$_{(3/2,3/2)}\mathcal{G}$	$_{(1/2,-1/2)}\mathcal{G}$
Ground state					
0	-1.705×10^{-4}	-1.367×10^{-2}	-1.170×10^{-2}	-1.316×10^{-2}	-1.136×10^{-2}
20	-6.312×10^{-5}	-2.597×10^{-5}	-4.839×10^{-7}	-1.882×10^{-5}	-1.400×10^{-4}
First excited state					
0	-1.749×10^{-4}	-2.221×10^{-2}	-2.151×10^{-2}	-2.029×10^{-2}	-2.069×10^{-2}
20	-3.886×10^{-5}	-5.410×10^{-5}	-5.309×10^{-7}	-2.253×10^{-5}	-1.799×10^{-4}
Fourth excited state					
0	-4.106×10^{-4}	-3.248×10^{-3}	-1.658×10^{-2}	-2.495×10^{-2}	-8.344×10^{-3}
20	-2.862×10^{-4}	-1.092×10^{-4}	-1.161×10^{-5}	-1.746×10^{-5}	-6.039×10^{-4}

Analysis of the convergence of the 2RDM contractions. The root-mean-square deviation (RMSD) of the \mathbf{B} , \mathbf{B}' , \mathbf{R} , and \mathbf{R}' contractions of the 2RDM toward the initial first-order matrices, which are considered fixed during the purification process, is shown in Table II. Although the RMSD of the different contractions in the three states considered is initially rather small, these defects have important consequences upon the S -representability of the 2RDM. It is remarkable that already in the second iteration there is a decrease of two or three orders of magnitude in their RMSD, except in the fourth excited state where for the convergence of the \mathbf{R} and \mathbf{R}' contractions the decrease of the RMSD is only of one order, as can be seen in Table II.

Correcting the error on the expectation value of the \hat{S}^2 operator. In Table III we report the results concerning the S representability of the 2RDM. As can be appreciated in the

table, for the ground, first, and fourth excited states, the initial expectation value of \hat{S}^2 has an error of 10^{-3} , 10^{-2} , and 10^{-3} , respectively; and after the purification has been carried out the errors are reduced to 10^{-6} for the ground and first excited state and to 10^{-5} for the fourth excited state. That is, after 20 iterations, the expectation value of \hat{S}^2 becomes practically equal to 0.75 in all the states considered. This clearly shows that the S representability has been attained.

Convergence of the approximated 2RDM toward the FCI 2RDM. The quantities given in the third column of Table III are the expectation values of the energy obtained with the final RDMs. These expectation values are close to the eigenvalues of the Hamiltonian. Since the initial non N - nor S -representable 2RDMs to be purified were approximations to the FCI RDMs, these results show that when rendering N and S representable the initial 2RDMs, the purification pro-

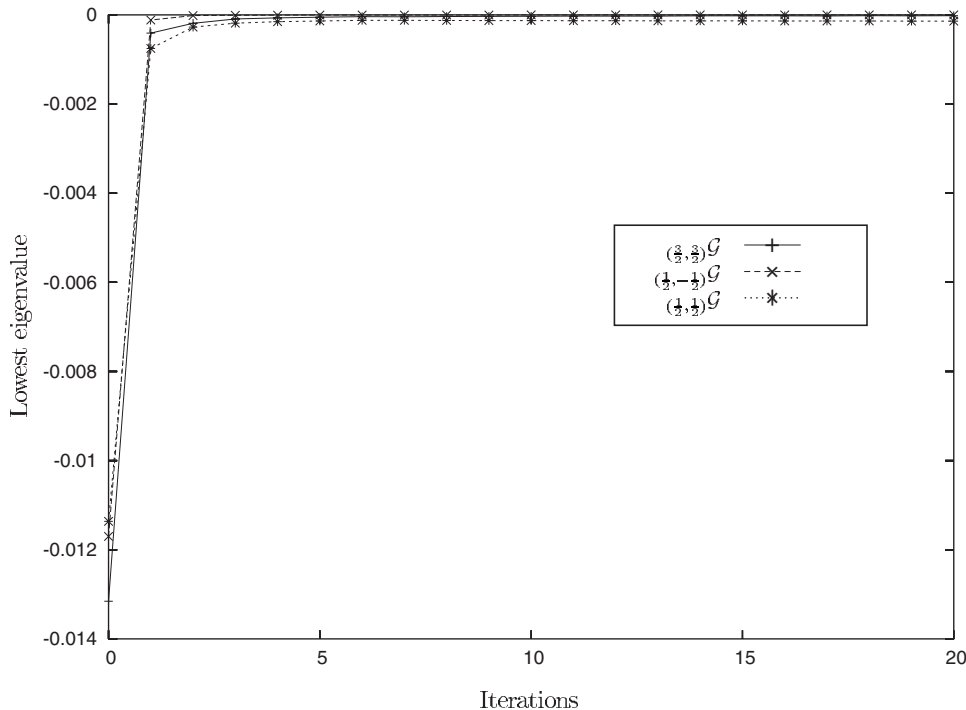


FIG. 4. Lowest eigenvalue of the $_{(1/2,-1/2)}\mathcal{G}$, $_{(3/2,3/2)}\mathcal{G}$, and $_{(1/2,-1/2)}\mathcal{G}$ spin components at each iteration of the doublet purification procedure for the ground state of the BeH_2^+ .

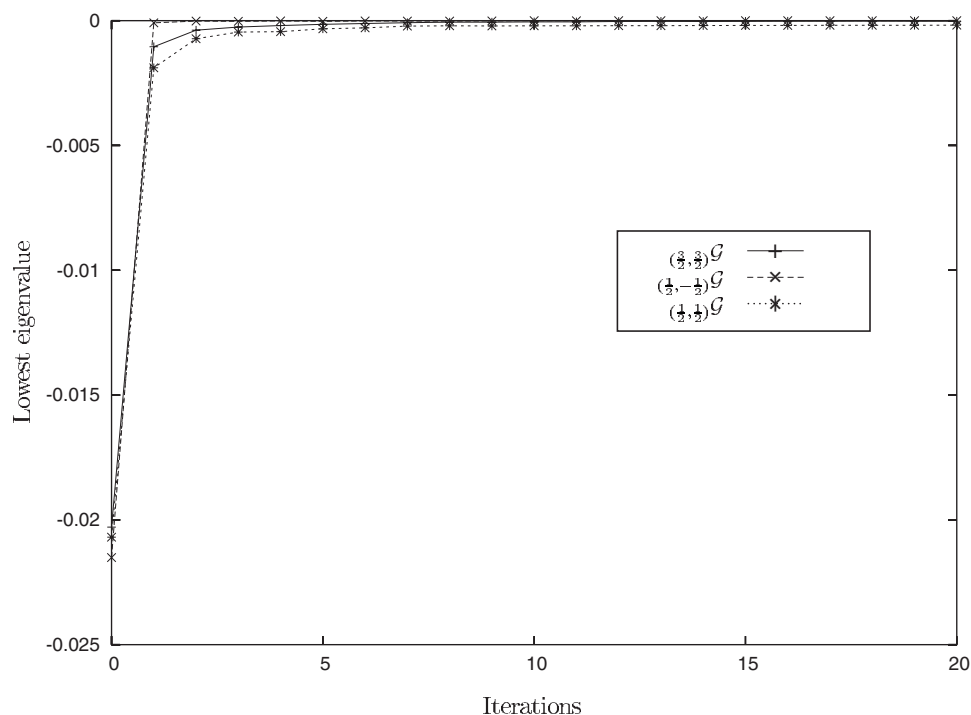


FIG. 5. Lowest eigenvalue of the $(1/2, -1/2)\mathcal{G}$, $(3/2, 3/2)\mathcal{G}$, and $(1/2, -1/2)\mathcal{G}$ spin components at each iteration of the doublet purification procedure for the first excited state of the BeH_2^+ .

cedure does not essentially modify the structure of the matrix. This is an important feature since otherwise the utility of the purification procedure would be impaired. Indeed, the purification procedure is to be applied to the 2RDM output of the iterative solution of the 2CSE; and no convergence of the combined process would occur if the purification procedure deeply perturbed the RDM structure. That is, the purification procedure of the matrix should render it closely N and S representable while modifying it as little as possible. Let us, however, remark that, since the purification procedure is just aimed at the correction of the N - and

S -representability defects, the final RDMs are in no way constrained to correspond to an eigenstate of the Hamiltonian.

Also concerning the quantities given in the third column of Table III, it is interesting to note that, for the ground-state, the expectation value of the energy lies above the FCI one—which is a necessary N -representability condition—indicating that it is a mixture of the ground and some other states.

Last but not least, the RMSD values given in the fourth column of Table III show that the purification procedure clearly diminishes the differences between the purified

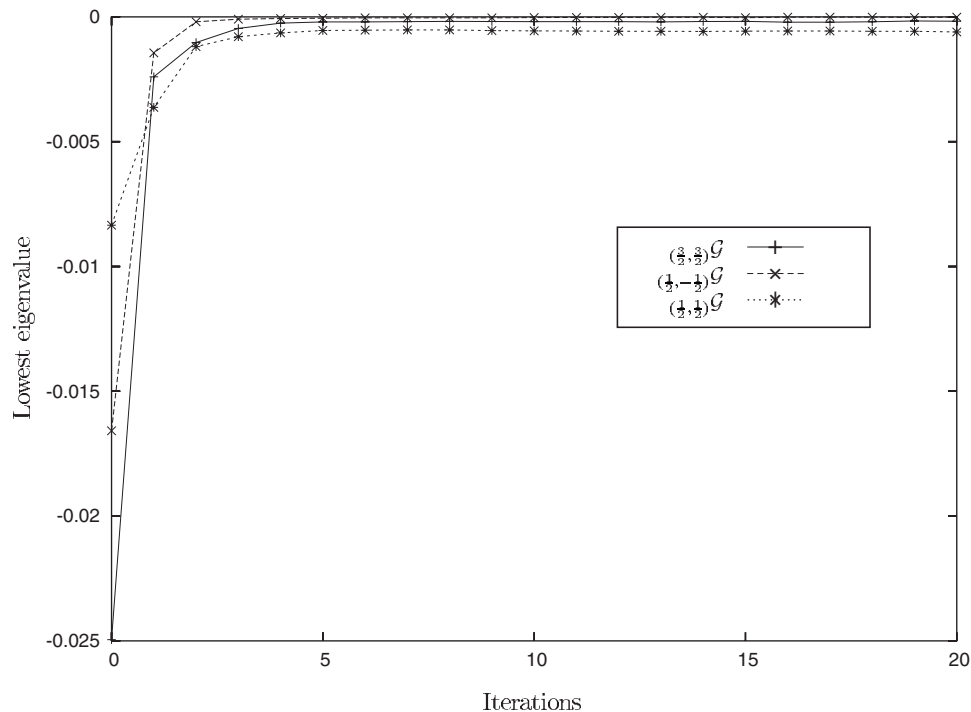


FIG. 6. Lowest eigenvalue of the $(1/2, -1/2)\mathcal{G}$, $(3/2, 3/2)\mathcal{G}$, and $(1/2, -1/2)\mathcal{G}$ spin components at each iteration of the doublet purification procedure for the fourth excited state of the BeH_2^+ .

TABLE II. Performance of the doublet purification procedure when applied to approximated 2RDMs corresponding to the ground, first, and fourth state of the cation BeH_2^+ : Contraction defects of the 2RDM.

Iterations	RMSD from fixed (FCI) matrices			
	B	B'	R	R'
Ground state				
0	8.500×10^{-4}	1.012×10^{-3}	1.461×10^{-3}	1.461×10^{-3}
2	1.996×10^{-6}	1.678×10^{-6}	2.575×10^{-5}	2.575×10^{-5}
20	8.785×10^{-7}	2.007×10^{-8}	3.056×10^{-7}	3.056×10^{-7}
First excited state				
0	1.268×10^{-3}	1.410×10^{-3}	3.789×10^{-3}	3.789×10^{-3}
2	3.612×10^{-6}	1.706×10^{-6}	3.023×10^{-5}	3.023×10^{-5}
20	2.353×10^{-7}	1.165×10^{-7}	5.409×10^{-7}	5.409×10^{-7}
Fourth excited state				
0	1.194×10^{-3}	1.262×10^{-3}	5.037×10^{-3}	5.037×10^{-3}
2	3.742×10^{-6}	4.247×10^{-6}	1.383×10^{-4}	1.383×10^{-4}
20	1.129×10^{-6}	4.584×10^{-7}	5.778×10^{-6}	5.778×10^{-6}

2RDM and the exact FCI 2RDM. The improvement is rather marked in the ground state, less so in the other states but in all cases it is noticeable. This shows that the changes undergone by the approximated 2RDM in order to become N and S representable have brought this matrix closer to the FCI 2RDM. Although, due to the consistency of all the tests carried out these results were to be expected, we nevertheless consider them to be a confirmation of the effectiveness of the purification procedure.

VI. FINAL REMARKS

As has been commented in the previous section, the iterative purification process of the three approximated 2RDMs considered was rapidly and smoothly convergent. Moreover, its consistency was remarkable. Indeed, since rendering positive semidefinite the \mathcal{G} spin blocks is a process that is only indirectly influenced by the process by which the 2RDM and 2HRDM are rendered positive semidefinite, oscillations could easily have occurred in the convergence of the \mathbf{R} and \mathbf{R}' contractions of the inter-related spin blocks. For instance, while the purification procedure based on the 2RDM Coleman's decomposition yielded smooth and rapidly convergent results when applied to the singlet ground state of BeH_2 [46], it did not yield consistent convergent results for the \mathbf{R} and \mathbf{R}' contractions. It seems therefore that Alcoba's generalization of Coleman's decomposition [1] is more generally efficient. The satisfying consistency with which all the S -representability conditions are fulfilled by all the \mathcal{G} spin blocks clearly indicates that the S representability is attained at the end of the purification process. With respect to the N representability, although the set of necessary conditions that

TABLE III. Performance of the doublet purification procedure when applied to approximated 2RDMs corresponding to the ground, first, and fourth state of the cation BeH_2^+ : Expectation value of the Hamiltonian^a, of the \hat{S}^2 ^b operator, and root-mean-square deviations of the 2RDM from the FCI matrix.

Iterations	$\langle \hat{S}^2 \rangle$	$\langle \hat{H} \rangle$	RMSD of 2RDM from FCI matrix
Ground state (FCI energy: -15.304537)			
0	0.7496958	-15.298811	4.196×10^{-4}
2	0.7503577	-15.304673	3.893×10^{-5}
20	0.7500023	-15.304541	3.437×10^{-5}
First excited state (FCI Energy: -15.260690)			
0	0.7674983	-15.255676	6.209×10^{-4}
2	0.7503905	-15.259706	1.185×10^{-4}
20	0.7500003	-15.259711	1.092×10^{-4}
Fourth excited state (FCI Energy: -15.084550)			
0	0.7484445	-15.084047	6.402×10^{-4}
2	0.7515535	-15.082821	2.472×10^{-4}
20	0.7500512	-15.082707	2.396×10^{-4}

^aQuoted values of the energy are given in hartrees.

^b $\langle \hat{S}^2 \rangle$ values in units of \hbar^2 .

we have imposed may still not be complete, there is no doubt that after purification the 2RDM N -representability defects are much smaller and such a matrix may be considered a quasi- N -representable 2RDM. Let us finally mention that the theoretical study of molecular compounds, both neutral and charged, having an odd number of electrons is not easy. On the other hand, these compounds are among the most reactive systems in nature. Therefore to have a reliable and efficient method for calculating with high accuracy the electronic structure of this type of compounds is extremely convenient.

At present, the version of the 2CSE code is being optimized also having in view the study of systems with doublet symmetry. We expect that this code, in combination with the purification procedure reported here, will constitute a suitable method for studying this type of compound. Indeed, we expect to obtain results as accurate in the calculation of doublets as this approach yielded in the study of singlets [27,29,33,42,45,46].

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- [1] D. R. Alcoba, *Int. J. Quantum Chem.* **97**, 776 (2004).
- [2] K. Husimi, *Proc. Phys. Math. Soc. Jpn.* **22**, 264 (1940).
- [3] P. O. Löwdin, *Phys. Rev.* **97**, 1474 (1955).
- [4] J. E. Mayer, *Phys. Rev.* **100**, 1579 (1955).
- [5] R. McWeeny, *Proc. R. Soc. London, Ser. A* **235**, 496 (1956).
- [6] C. A. Coulson, *Rev. Mod. Phys.* **32**, 170 (1960).
- [7] A. J. Coleman and V. I. Yukalov, *Reduced Density Matrices: Coulson's Challenge* (Springer-Verlag, New York, 2000).
- [8] E. R. Davidson, *Reduced Density Matrices in Quantum Chemistry* (Academic Press, New York, 1976).
- [9] *Reduced Density Matrices with Applications to Physical and Chemical Systems*, Queen's Papers on Pure and Applied Mathematics - No. 1, edited by A. J. Coleman and R. M. Erdahl (Queen's University, Kingston, Ontario, 1968).
- [10] *Reduced Density Matrices with Applications to Physical and Chemical Systems II*, Queen's Papers on Pure and Applied Mathematics - No. 40, edited by R. M. Erdahl (Queen's University, Kingston, Ontario, 1974).
- [11] *Proceedings of the A. J. Coleman Symposium, Kingston, Ontario, 1985*, edited by R. M. Erdahl and V. Smith (Reidel, Dordrecht, 1987).
- [12] *Many-Electron Densities and Reduced Density Matrices*, edited by J. Cioslowski (Kluwer, Dordrecht, The Netherlands, 2000).
- [13] *Reduced-Density-Matrix Mechanics with Applications to Many-Electron Atoms and Molecules*, *Advances in Chemical Physics*, Vol. 134, edited by D. A. Mazziotti (John Wiley and Sons, New York, 2007).
- [14] A. J. Coleman, *Rev. Mod. Phys.* **35**, 668 (1963).
- [15] C. Garrod and J. K. Percus, *J. Math. Phys.* **5**, 1756 (1964).
- [16] F. Weinhold and E. B. Wilson, *J. Chem. Phys.* **47**, 2298 (1967).
- [17] L. J. Kijewski and J. K. Percus, *Phys. Rev. A* **2**, 1659 (1970).
- [18] C. Garrod, M. V. Mihailovic, and M. Rosina, *J. Math. Phys.* **16**, 868 (1975).
- [19] R. M. Erdahl and B. Jin, *J. Mol. Struct.: THEOCHEM* **527**, 207 (2000).
- [20] M. Nakata, H. Nakatsuji, M. Ehara, M. Fukuda, K. Nakata, and K. Fujisawa, *J. Chem. Phys.* **114**, 8282 (2001).
- [21] Z. Zhao, B. J. Braams, H. Fukuda, M. L. Overton, and J. K. Percus, *J. Chem. Phys.* **120**, 2095 (2004).
- [22] D. A. Mazziotti, *Phys. Rev. Lett.* **93**, 213001 (2004).
- [23] S. Cho, *Sci. Rep. Gumma Univ.* **11**, 1 (1962).
- [24] H. Nakatsuji, *Phys. Rev. A* **14**, 41 (1976).
- [25] L. Cohen and C. Frishberg, *Phys. Rev. A* **13**, 927 (1976).
- [26] C. Valdemoro, in *Proceedings of the A. J. Coleman Symposium, Kingston, Ontario, 1985*, edited by R. M. Erdahl and V. Smith (Reidel, Dordrecht, 1987).
- [27] F. Colmenero and C. Valdemoro, *Int. J. Quantum Chem.* **51**, 369 (1994).
- [28] H. Nakatsuji and K. Yasuda, *Phys. Rev. Lett.* **76**, 1039 (1996).
- [29] C. Valdemoro, L. M. Tel, and E. Pérez-Romero, *Adv. Quantum Chem.* **28**, 33 (1997).
- [30] D. A. Mazziotti, *Phys. Rev. A* **57**, 4219 (1998).
- [31] M. Nakata, M. Ehara, K. Yasuda, and H. Nakatsuji, *J. Chem. Phys.* **112**, 8772 (2000).
- [32] C. Valdemoro, M. P. de Lara-Castells, E. Pérez-Romero, and L. M. Tel, *Adv. Quantum Chem.* **31**, 37 (1999).
- [33] C. Valdemoro, L. M. Tel, and E. Pérez-Romero, in *Many-Electron Densities and Reduced Density Matrices*, edited by J. Cioslowski (Kluwer, Dordrecht, The Netherlands, 2000).
- [34] C. Valdemoro, L. M. Tel, and E. Pérez-Romero, *Phys. Rev. A* **61**, 032507 (2000).
- [35] L. M. Tel, E. Pérez-Romero, C. Valdemoro, and F. J. Casquero, *Int. J. Quantum Chem.* **82**, 131 (2001).
- [36] C. Valdemoro, D. R. Alcoba, L. M. Tel, and E. Pérez-Romero, *Int. J. Quantum Chem.* **85**, 214 (2001).
- [37] D. R. Alcoba and C. Valdemoro, *Phys. Rev. A* **64**, 062105 (2001).
- [38] D. R. Alcoba, *Phys. Rev. A* **65**, 032519 (2002).
- [39] J. M. Herbert and J. E. Harriman, *Phys. Rev. A* **65**, 022511 (2002).
- [40] D. A. Mazziotti, *Phys. Rev. E* **65**, 026704 (2002).
- [41] C. Valdemoro, D. R. Alcoba, and L. M. Tel, *Int. J. Quantum Chem.* **93**, 212 (2003).
- [42] D. R. Alcoba, F. J. Casquero, L. M. Tel, E. Pérez-Romero, and C. Valdemoro, *Int. J. Quantum Chem.* **102**, 620 (2005).
- [43] D. R. Alcoba and C. Valdemoro, *Int. J. Quantum Chem.* **102**, 629 (2005).
- [44] D. A. Mazziotti, *Phys. Rev. Lett.* **97**, 143002 (2006).
- [45] C. Valdemoro in *Reduced-Density-Matrix Mechanics with Applications to Many-Electron Atoms and Molecules* (Ref. [13]) p. 121.
- [46] D. R. Alcoba in *Reduced-Density-Matrix Mechanics with Applications to Many-Electron Atoms and Molecules* (Ref. [13]) p. 205.
- [47] C. Valdemoro, L. M. Tel, D. R. Alcoba, and E. Pérez-Romero, *Theor. Chem. Acc.* **118**, 503 (2007).
- [48] M. A. Nielsen and I. L. Chuang, *Quantum Computation and Quantum Information* (Cambridge University Press, Cambridge, England, 2000).
- [49] E. Pérez-Romero, L. M. Tel, and C. Valdemoro, *Int. J. Quantum Chem.* **61**, 55 (1997).
- [50] A. J. Coleman, in *Reduced Density Matrices with Applications to Physical and Chemical Systems II* (Ref. [10]).
- [51] R. McWeeny and Y. Mizuno, *Proc. R. Soc. London, Ser. A* **259**, 554 (1961).
- [52] A. J. Coleman, *J. Math. Phys.* **13**, 214 (1972).
- [53] A. Beste, K. Runge, and R. Barlett, *Chem. Phys. Lett.* **355**, 263 (2002).