# Four New Forms of the Contracted Schrödinger Equation and Their Connection With the Second-Order Hypervirial Condition 

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Received 18 September 2007; accepted 30 October 2007
Published online 10 January 2008 in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/qua. 21576


#### Abstract

Through the use of an important property of a fourth-order correlation matrix previously reported (Valdemoro, C.; Tel, L. M.; Alcoba, D. R.; PerezRomero, E.; Casquero, F. J. Int J Quantum Chem 2002, 90, 1555; Alcoba, D. R.; Valdemoro, C. Phys Rev A 2001, 64, 062105) four new equivalent forms of the secondorder contracted Schrödinger equation (2-CSE) are obtained. The role played by the energy terms involving these correlation matrices is crucial in the solution of these equations. The relations linking the Hermitian (Yasuda, K. Phys Rev A 1999, 59, 4133) and antiHermitian parts (Mazziotti, D. A. Phys Rev Lett 2006, 97, 142002) of the 2-CSE with these correlation energy terms are analyzed in detail. A discussion of the secondorder hypervirial condition is also given here. © 2008 Wiley Periodicals, Inc. Int J Quantum Chem 108: 1090-1096, 2008


Key words: contracted Schrödinger equation; antiHermitian contracted Schrödinger equation; reduced density matrix; correlation matrix; electronic correlation effects

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## 1. Introduction

The second-order reduced density matrix (2RDM) is the matrix obtained by contracting the $N$-electron density matrix ( $N$-DM) into the twoelectron space. In first quantization it is obtained by integrating the $N$-DM over $N-2$ electron variables. The interest in the RDMs starts with Dirac [1], Husimi [2], Mayer [3], Löwdin [4] and McWeeny [5]. These authors realized that knowledge of the 2-RDM should be sufficient in the study of electronic systems. In 1963, Coleman pointed out the need for what he denominated the $N$-representability conditions, which should be imposed upon the 2 -RDM in any variational calculation [6]. The paper by Garrod and Percus [7] in 1964 also constituted an important milestone in the determination of the properties of an N -representable 2-RDM. After these seminal works, the search to obtain directly the $2-\mathrm{RDM}$, without a previous knowledge of the wave function, has constituted an ample field of research [8-12].

In 1976, Cohen and Frishberg [13, 14] and Nakatsuji [15] reported an integro-differential hierarchy equation for the 2-RDM that depends not only on the 2 -RDM but also on the 3 - and 4 -RDMs. In his paper, Nakatsuji demonstrated that when the 2-CSE is satisfied, and the RDMs involved in this equation are $N$-representable, there is a one-to-one correspondence between the solution of the Schrödinger equation and that of this density equation. In 1983, Valdemoro reported a matrix contracting mapping [16] which, when applied to the matrix representation of the Schrödinger equation, leads to the compact form of the 2-CSE [17], which is equivalent to the integro-differential density equation. To remove the indeterminacy of the 2-CSE, the highorder RDMs were approximated in terms of the lower-order ones $[18,19]$ by extending a method proposed in 1992 by Valdemoro [20]. This approach permitted Colmenero and Valdemoro [21] to solve iteratively the 2-CSE in 1994. Since then, this methodology has been significantly improved by the groups of Nakatsuji [22-25], Mazziotti [26-30], Herbert and Harriman [31, 32], Yasuda [33], and Valdemoro [34-42]. A recent revision of the achievements on the contracted Schrödinger equation (CSE) theory has been carried out [43, 44].

In this article, a new analysis of the 2-CSE structure and the conditions determining its solution are reported. This analysis, based on an important correlation matrix property, reported in 2001 by our
group [34, 35, 41, 42, 45], sheds light upon the determinant role played by the pure fourth-order correlation energy effects in the solution of the 2-CSE. Also, four new equivalent forms of the 2-CSE are derived. Although two of these forms depend on the $2-, 3-\mathrm{RDMs}$ and on a term involving the fourth-order correlation matrix (4-CM),[37] the two other forms, directly related to the Hermitian part of the Contracted Schrödinger Equation (HCSE),[33, 46] only depend on a fourth-order correlation energy term, which vanishes when the 2-CSE is satisfied [45]. When this term vanishes, not only the HCSE but also the antiHermitian part of the 2-CSE (ACSE) is satisfied.

Recently, Mazziotti [46-48] has proposed a new variational method for solving the ACSE whose application to the ground state of several molecules has yielded excellent results. This method has also been successfully applied by our group in the calculation of the ground state of the isoelectronic series of the Beryllium atom and the linear form of the $\mathrm{BeH}_{2}$ and $\mathrm{Li}_{2}$ molecules [49].

It should be stressed that the ACSE is a particular case of the hypervirial condition first deduced by Hirschfelder [50] in the early 1960s. The sufficiency of this condition in variational procedures for deducing optimized wave functions has largely been discussed among others by Epstein [51], Aslangul et al.[52], Harriman [53], Kutzelnigg [54], and Fernández and Castro [55]. It is here shown that, while satisfying the second order hypervirial condition implies that the two types of pure fourth-order correlation energy terms involved must be equal, this condition seems not to be sufficient to guarantee their individual vanishment.

## 2. Theoretical Background

### 2.1. THE REDUCED DENSITY MATRICES AND THEIR DECOMPOSITIONS

The $p$-order reduced density matrix ( $p$-RDM) is the matrix obtained when contracting the $N$-electron density matrix into the $p$-electron space. In second quantization, the $p$-RDM elements are defined as:

$$
\begin{equation*}
\langle\Phi| a_{i 1}^{\dagger} a_{i,}^{\dagger} \ldots a_{i p}^{\dagger} a_{j_{p}} \ldots a_{j 2} a_{j 1}|\Phi\rangle=p!{ }^{p} \mathrm{D}_{i i_{1}, \ldots i_{p}, \mathrm{j}, j_{2} \ldots j_{p}} \tag{1}
\end{equation*}
$$

The operators $a_{i p}^{\dagger}$ and $a_{j p}$ are the creators/annihilators of electrons on the spin-orbitals $i_{p} / j_{p}$, respectively. These spin-orbitals are elements of the one-

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electron finite basis set built from $K$ orthogonal orbitals and the two spin-functions $\alpha, \beta$. The matrix ${ }^{p} \mathbf{D}$ is normalized as $\operatorname{tr}\left({ }^{p} \mathbf{D}\right)=\binom{N}{p}$.

The expression (1) can be transformed by using the fermion algebra to decompose the high-order matrix into a sum of products of lower-order RDM elements and some CM elements [37]. This type of RDM decomposition involves, besides the usual fermion algebra operations, a partition of the unit operator into a projector on the state from which the RDM being decomposed derives and another projector upon its complementary space. Thus:

$$
\begin{equation*}
\hat{I}=|\Phi\rangle\langle\Phi|+\sum_{\Phi^{\prime} \neq \Phi}\left|\Phi^{\prime}\right\rangle\left\langle\Phi^{\prime}\right| \tag{2}
\end{equation*}
$$

As a result of these operations, the 4-RDM, which plays an important role in the CSE theory, can be expressed as follows:

$$
\begin{array}{r}
4!{ }^{4} \mathrm{D}_{p q i j ; r s k l}=+2!{ }^{2} \mathrm{D}_{p q ; k l}\left(\delta_{i s} \delta_{j r}-\delta_{i r} \delta_{j s}\right)+3!{ }^{3} \mathrm{D}_{p q i ; r k l} \delta_{j s} \\
-3!{ }^{3} \mathrm{D}_{p q j ; r k l} \delta_{i s}-3!{ }^{3} \mathrm{D}_{p q i ; s k l} \delta_{j r}+3!{ }^{3} \mathrm{D}_{p q j ; s k l} \delta_{i r} \\
+2!{ }^{2} \mathrm{D}_{i j ; k l} 2!^{2} \mathrm{D}_{p q ; r s}+{ }^{(4 ; 2,2)} \mathrm{C}_{p q i j ; r k l} \tag{3}
\end{array}
$$

where ${ }^{(4 ; 2,2)} \mathrm{C}$ is one of the four different but interrelated 4-CMs [39], which can be expressed as:

$$
\begin{equation*}
{ }^{(4 ; 2,2)} C_{p q i j ; r s k l}=\sum_{\Phi^{\prime} \neq \Phi}\langle\Phi| a_{p}^{\dagger} a_{q}^{\dagger} a_{s} a_{r}\left|\Phi^{\prime}\right\rangle\left\langle\Phi^{\prime}\right| a_{i}^{\dagger} a_{j}^{\dagger} a_{l} a_{k}|\Phi\rangle \tag{4}
\end{equation*}
$$

This expression of the ${ }^{(4 ; 2,2)} \mathrm{C}$ describes how the virtual excitations of the electrons described by a given state $\boldsymbol{\Phi}$ accounts for the correlation effects within the RDM theory. This type of correlation matrices, which carry information about the system spectrum, is at the basis of the analysis, which is presented in the following section.

A different type of correlation effects is hidden in the Krönecker $\delta$ s present in Eq. (3). This other type of correlation effects can be factorized in terms of elements of particle and hole lower-order RDMs corresponding to the state being considered [37].

It should be stressed that the decomposition just reported, although not unique, is exact, provided the 4 -RDM is $N$-representable; i.e. there exists an $N$-electron wave-function from which the 4-RDM can be derived by integration over $N-4$ electron variables [6].

It is evident that the notion of $N$-representability can be extended to the $4-\mathrm{CM}$ in the sense that these matrices must derive from the decomposition of an
$N$-representable 4-RDM. Moreover, one may also decompose the 4-CM matrix into a Hermitian and an antiHermitian matrix, which would respectively have the following elements:

$$
\begin{equation*}
{ }_{\text {Herm }}^{(4 ; 2,2)} \mathrm{C}_{p q i j ; r s k l}=\frac{1}{2}\left({ }^{(4 ; 2,2)} \mathrm{C}_{p q i j ; r s k l}+{ }^{(4 ; 2,2)} \mathrm{C}_{i j p q ; k l r s}\right) \tag{5}
\end{equation*}
$$

and

$$
\begin{equation*}
{ }_{\text {antiHerm }}^{(4,2)} C_{p q i j ; r s k l}=\frac{1}{2}\left({ }^{(4 ; 2,2)} \mathrm{C}_{p q i j ; r s k l}-{ }^{(4 ; 2,2)} \mathrm{C}_{i j p q ; k l r s}\right) \tag{6}
\end{equation*}
$$

And again the concept of $N$-representability can be extended to these matrices.

### 2.2. THE SECOND-ORDER CONTRACTED SCHRÖDINGER EQUATION

The generic form of the $p$-CSE can be expressed as:

$$
\begin{align*}
& \langle\Phi| \hat{H} a_{i_{1}}^{\dagger} a_{i_{2}}^{\dagger} \ldots a_{i_{p}}^{\dagger} a_{j_{p}} \ldots a_{j_{2}} a_{j_{1}}|\Phi\rangle \\
& \quad=p!E^{p} \mathrm{D}_{i_{11} i_{2} \ldots i_{p ; i j} j_{2} \ldots j_{p}} \tag{7}
\end{align*}
$$

where $\hat{H}$ is the $N$-body Hamiltonian operator, $E$ is the energy, and $\boldsymbol{\Phi}$ the corresponding Hamiltonian eigenstate. The general form of this equation for $p=$ 2 , the $2-\mathrm{CSE}$, can be expressed in matrix form as

$$
\begin{equation*}
\langle\Phi| \hat{H}^{2} \hat{\Gamma}|\Phi\rangle=2!E^{2} \mathrm{D} \tag{8}
\end{equation*}
$$

or, equivalently

$$
\begin{equation*}
\langle\Phi|{ }^{2} \Gamma \hat{H}|\Phi\rangle=2!E^{2} \mathrm{D} \tag{9}
\end{equation*}
$$

where ${ }^{2} \widehat{\Gamma}$ denotes an arbitrary second-order density operator. In what follows, the quantities derived from the action of the Hamiltonian operator on the left/right of the second-order density operator will be labeled by the letters $l / r$ respectively.

Let us now replace in Eq. (8) the Hamiltonian by its second quantization expression

$$
\begin{equation*}
\hat{H}=\frac{1}{2} \sum_{i, j, k, l}{ }^{0} \mathrm{H}_{i j ; k l} a_{i}^{\dagger} a_{j}^{\dagger} a_{l} a_{k} \tag{10}
\end{equation*}
$$

where

$$
\begin{equation*}
{ }^{0} \mathrm{H}_{i j ; k l}=\left(\frac{\varepsilon_{i k} \delta_{j l}+\varepsilon_{j l} \delta_{i k}}{N-1}+\langle i j \mid k l\rangle\right) \tag{11}
\end{equation*}
$$

and $\varepsilon$ and $\langle i k \mid p q\rangle$ are the usual one- and two-electron integrals, respectively (this latter in the Condon and Shortley notation). The generic form Eq. (8) of the 2-CSE becomes:

$$
\begin{equation*}
\frac{1}{2} \sum_{i, j, j, l}{ }^{0} \mathrm{H}_{i j, k l}\langle\Phi| a_{i}^{+} a_{j}^{\dagger} a_{l} a_{k} a_{k} a_{p}^{\dagger} a_{q}^{\dagger} a_{s} a_{r}|\Phi\rangle=E 2!^{2} \mathrm{D}_{p q ; 7 s} \tag{12}
\end{equation*}
$$

When transforming the string of fermion operators into its normal form one obtains:

$$
\begin{align*}
& 2!E^{2} \mathrm{D}_{p q, r s}=2!\left({ }^{0} \mathrm{H}^{2} \mathrm{D}\right)_{p q, r s}-3!\sum_{i, j, k}\left({ }^{0} \mathrm{H}_{i j, j k k} \mathrm{D}_{i j q, r s k}\right. \\
& \left.+{ }^{0} \mathrm{H}_{i j, k \neq q}{ }^{3} \mathrm{D}_{i j p, r s k}\right)+\frac{1}{2} 4!\sum_{i, j, k, l}{ }^{0} \mathrm{H}_{i j ; k l}{ }^{4} \mathrm{D}_{i j p q ;, s k l} \tag{13}
\end{align*}
$$

which may be expressed schematically as

$$
\begin{equation*}
2!E^{2} \mathrm{D}_{p q ; r s}=\mathcal{F}_{p q ; i s}+\frac{1}{2} 4!\sum_{i, j, k, l}{ }^{0} \mathrm{H}_{i, j k l}{ }^{4} \mathrm{D}_{i j p q ; 7 s k l} \tag{14}
\end{equation*}
$$

When the Hamiltonian operator appears to the right of the 2-density operator in Eq. (9) instead of to its left, one has:

$$
\begin{equation*}
2!E^{2} \mathrm{D}_{p q ; i s}={ }_{r} \mathcal{F}_{p q ; r s}+\frac{1}{2} 4!\sum_{i, j, k, l}{ }^{0} \mathrm{H}_{i j, k l}{ }^{4} \mathrm{D}_{p q i j ; k l s} \tag{15}
\end{equation*}
$$

When subtracting Eqs. (14) and (15) one obtains

$$
\begin{equation*}
0=, \mathcal{F}-, \mathcal{F}=\langle\Phi|\left[\hat{H},{ }^{2} \stackrel{\Gamma}{\Gamma}\right]-|\Phi\rangle \tag{16}
\end{equation*}
$$

which is the second-order Hypervirial (2-HV) condition [50] or, equivalently, Mazziotti's ACSE. That is, the fourth-order term appearing in the 2-CSE cancels out, as well as the l.h.s. of the 2-CSE.

The remaining part of the 2-CSE is given by the HCSE, whose operatorial form in Mazziotti's notation is:

$$
\begin{equation*}
\frac{1}{2}\langle\Phi|\left\{\hat{H},{ }^{2} \Gamma\right\}_{+}|\Phi\rangle=2!E^{2} \mathrm{D} \tag{17}
\end{equation*}
$$

The structure of this equation will be analyzed in detail in the following section.

## 3. Four New 2-CSE Forms: The Role Played by the Vanishing Correlation Energy Terms

### 3.1 FOUR NEW 2-CSE FORMS

Let us now reconsider the fourth-order term of Eq. (13), which, due to the fermion-operators' anticommuting properties, can be written in the two following equivalent forms:

$$
\begin{equation*}
4!\sum_{i, j, k, l}{ }^{0} \mathrm{H}_{i j ; k l}{ }^{4} \mathrm{D}_{i j p q ; k l r s} \equiv 4!\sum_{i, j, k, l}{ }^{0} \mathrm{H}_{i j, k l}{ }^{4} \mathrm{D}_{p q i j ; s k l} \tag{18}
\end{equation*}
$$

and let us decompose both forms of this fourthorder term. The resulting expressions can be schematically written as:

$$
\begin{array}{r}
\frac{1}{2} 4!\sum_{i, j, k, l}{ }^{0} H_{i j ; k l}{ }^{4} \mathrm{D}_{p q j i ; r k l}=-{ }_{r} \mathcal{F}_{p q ; r s}+\left({ }^{(4,2,2)}{ }_{r} \Theta_{p q ; r s}\right. \\
 \tag{19}\\
+2! \\
\operatorname{tr}\left({ }^{0} \mathrm{H}^{2} \mathrm{D}\right) \mathrm{D}_{p q ; r s}
\end{array}
$$

and

$$
\begin{align*}
\frac{1}{2} 4!\sum_{i, j, k, l}{ }^{0} \mathrm{H}_{i j, k l} \mathrm{D}_{i j p q ; k l \mathrm{ls}}=- & \mathcal{F}_{p q ; 7 s}+{ }^{\left.(4,2,2,)_{l}\right) \Theta_{p q ; i s s}} \\
& +2!  \tag{20}\\
& \operatorname{tr}\left({ }^{0} \mathrm{H}^{2} \mathrm{D}\right) \mathrm{D}_{p q ; r s}
\end{align*}
$$

respectively. In these equations the ${ }^{(4 ; 2,2)} \Theta$ terms have the following structures:

$$
\begin{align*}
{ }_{(4 ; 2,2)}^{r} \Theta_{p q, r s} & \equiv \sum_{\Phi^{\prime} \neq \Phi}\langle\Phi| a_{p}^{+} a_{q}^{+} a_{s} a_{r}\left|\Phi^{\prime}\right\rangle\left\langle\Phi \Phi^{\prime}\right| \hat{H}|\Phi\rangle \\
& =\frac{1}{2} \sum_{i, j, k, l}{ }^{(4 ; 2,2)} C_{p q j i j, s k l}{ }^{0} \mathrm{H}_{i j, k l} \tag{21}
\end{align*}
$$

and

$$
\begin{align*}
&\left.{ }^{(4 ; 2,2)}\right)_{l} \Theta_{p q ; r s} \equiv \sum_{\Phi^{\prime} \neq \Phi}\langle\Phi| \hat{H}\left|\Phi^{\prime}\right\rangle\left\langle\Phi^{\prime}\right| a_{p}^{\dagger} a_{q}^{\dagger} a_{s} a_{r}|\Phi\rangle \\
&=\frac{1}{2} \sum_{i, j, k, l}{ }^{0} \mathrm{H}_{i j ; k l}{ }^{(4+2,2)} \mathrm{C}_{i j p ; k k l \mathrm{~s}} \tag{22}
\end{align*}
$$

These ${ }^{(4 ; 2,2)} \Theta$ terms are elements of an important family studied in 2001 by Tel et al. [42]. When the state considered $|\Phi\rangle$ is an eigenstate of the Hamiltonian, then either form of ${ }^{(4 ; 2,2)} \Theta_{r s ; p q}$ vanishes for any values of $p, q, r$, s. Alcoba [45] demonstrated

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that when the $4-C M$ derives from an $N$-representable $4-R D M$ then ${ }^{(4 ; 2,2)} \Theta=0$ iff the density matrix, preimage of the 4-RDM, satisfies the Schrödinger equation.

As has been shown, there are two different forms of the 2-CSE given by Eqs. (14) and (15) and also two different forms of expanding the fourth-order energy term. This implies that there are four ways to combine them.

1. Replacing Eq. (19) into Eq. (14), the following new form of the 2-CSE is obtained:

$$
\begin{align*}
2!E^{2} \mathrm{D}_{p q ; r s}=2!\operatorname{tr}\left({ }^{0} \mathrm{H}^{2} \mathrm{D}\right)^{2} \mathrm{D}_{p q ; r s} & +{ }_{l} \mathcal{F}_{p q ; r \mathrm{rs}}-{ }_{r} \mathcal{F}_{p q ; r s} \\
& +{ }_{r}^{(4 ; 2,2)} \Theta_{p q ; r s s} \tag{23}
\end{align*}
$$

Because of Alcoba's theorem, when the 2-CSE is satisfied, $\left.{ }^{(4 ; 2,2)}\right)_{r s ; p q}=0$, and then the ACSE-and equivalently the hypervirial condition-according to Eq. (16), is also satisfied.
2. Following a parallel reasoning, by replacing Eq. (20) in Eq. (15), one obtains

$$
\begin{align*}
& 2!E{ }^{2} \mathrm{D}_{p q ; r s}=2!\operatorname{tr}\left({ }^{0} \mathrm{H}^{2} \mathrm{D}\right)^{2} \mathrm{D}_{p q ; r s}+ \mathcal{F}_{p q ; r s}-{ }_{l} \mathcal{F}_{p q ; r s} \\
&+\left({ }^{(4 ; 2,2)} \Theta_{p q q ; r s}\right. \tag{24}
\end{align*}
$$

Both the two 2-CSE forms, Eqs. (23) and (24), include the antiHermitian contribution.
3. On the other hand, by combining Eqs. (20) and (14) one obtains

$$
\begin{equation*}
2!E^{2} \mathrm{D}_{p q ; r s}=2!\operatorname{tr}\left({ }^{0} \mathrm{H}^{2} \mathrm{D}\right)^{2} \mathrm{D}_{p q ; r s}+{ }_{(4 ; 2,2)} \Theta_{p} \Theta_{p q ; r s} \tag{25}
\end{equation*}
$$

4. And, replacing Eq. (19) in Eq. (15) yields

$$
\begin{equation*}
2!E^{2} \mathrm{D}_{p q ; r s}=2!\operatorname{tr}\left({ }^{0} \mathrm{H}^{2} \mathrm{D}\right)^{2} \mathrm{D}_{p q ; r s}+{ }^{(4 ; 2,2)} \Theta_{p q ; r s} \tag{26}
\end{equation*}
$$

The antiHermitian part has disappeared from both these two 2-CSE forms, Eqs. (25) and (26).

Note that, Eqs. (25) and (26) become identities when the ${ }^{(4 ; 2,2)} \Theta$ term vanishes, i.e. when all the correlation effects of an order higher than two cancel out, the 2-CSE is satisfied.

### 3.2. THE ROLE PLAYED BY THE VANISHING CORRELATION ENERGY TERMS

The structure of the four 2-CSE forms just reported sheds light upon the conditions governing the solution of the 2-CSE. Thus, as will be shown here, several consequences and theorems can be drawn from the relationships that can be estab-
lished among these equations and the HCSE and the ACSE.

### 3.2.1. The Structure of the HCSE

When taking the average of Eqs. (23) and (24), or equivalently of Eqs. (25) and (26), one obtains the HCSE as a function of the vanishing correlation energy terms:

$$
\begin{align*}
2!E^{2} \mathrm{D}_{p q ; r s}=2! & \operatorname{tr}\left({ }^{0} \mathrm{H}^{2} \mathrm{D}\right){ }^{2} \mathrm{D}_{p q ; r s} \\
& +\frac{1}{2}\left({ }^{(4 ; 2,2)} \Theta_{p q ; r s}+{ }^{(4 ; 2,2)} \Theta_{p q ; ; s}\right) \tag{27}
\end{align*}
$$

The last term represents the Hermitian part of the vanishing ${ }^{(4 ; 2,2)} \Theta$ matrix, which derives from the Hermitian part of the $4-\mathrm{CM}$, Eq. (5).

Obviously, this equation is satisfied when the sum of the two ${ }^{(4 ; 2,2)} \Theta$ terms deriving from the decomposition of $N$-representable 4-RDM vanishes, because then the 2-RDM corresponds to an eigenstate of the Hamiltonian. Moreover, each of the Eqs. (25) and (26), which are equivalent to the 2-CSE, can also be identified with the Hermitian part of the 2-CSE as described by Eqs. (23) and (24), because the ACSE is given by Eq. (16). Therefore:

$$
\begin{aligned}
& 2!E^{2} \mathrm{D}_{p q ; r s}=2!\operatorname{tr}\left({ }^{0} \mathrm{H}^{2} \mathrm{D}\right)^{2} \mathrm{D}_{p q ; r s}+\frac{1}{2}\left({ }^{(4 ; 2,2)} \Theta_{r q q ; r s}\right. \\
& \left.+{ }^{(4 ; 2,2)} \Theta_{p q ; r s}\right)=2!\operatorname{tr}\left({ }^{0} \mathrm{H}^{2} \mathrm{D}\right)^{2} \mathrm{D}_{p q ; r s}+{ }^{(4 ; 2,2)}{ }_{r} \Theta_{p q ; r s} \\
& \quad=2!\operatorname{tr}\left({ }^{0} \mathrm{H}^{2} \mathrm{D}\right)^{2} \mathrm{D}_{p q ; r s}+{ }^{(4 ; 2,2)} \Theta_{p q ; r r s}
\end{aligned}
$$

Because we know that there is a one-to-one correspondence between the 2-CSE solution and the vanishing value of the ${ }^{(4 ; 2,2)} \Theta$ terms, one has:

- The HCSE is satisfied iff either ${ }^{(4 ; 2,2)} \Theta=0$ or $\left.{ }^{(4 ; 2,2)}\right)_{r} \Theta=0$.
- As Yasuda showed in 1999 [33], the solution of the HCSE is equivalent to the solution of the 2-CSE.
- The Hermitian part of ${ }^{(4 ; 2,2)} \Theta$, deriving from $N$-representable Hermitian 4-CM, vanishes iff the HCSE is satisfied.

These theoretical results emphasize the importance of the fourth-order vanishing correlation energy terms and stress the importance of looking directly for accurate approximations of the $4-\mathrm{CM}$ in terms of the lower order CMs. Because the approx-
imation of the fourth-order cumulant proposed by Nakatsuji and by Mazziotti has given satisfactory results, this can be a possible way to approach this practical problem; which, at present, is being considered.

### 3.2.2. The Structure of the ACSE

We will now focus our attention upon the ACSE. By construction, the ACSE can be identified with the contraction of the matrix representation of the $N$-order Liouville equation, as reported by Valdemoro in Ref. [17], when both the bra and ket wavefunctions are the same. Now, Esnault and coworkers $[52,56]$ showed that, when the density matrix corresponds to a pure state, the solution of the Liouville equation is equivalent to the solution of the Schrödinger equation. We also know that an $N$-representable RDM has as pre-image the idempotent $N$-electron density matrix corresponding to a pure state. In view of this, it would seem reasonable to expect that when the ACSE is satisfied by a set of $N$-representable RDMs, these matrices would correspond to an eigenstate of the Hamiltonian. However, Mazziotti [47] reported that he had found RDMs which, although satisfying the ACSE, they did not correspond to eigenstates of the Hamiltonian. It seemed therefore appropriate to try to clarify this question by considering the relations reported above. Let us therefore compare Eq. (20) and Eq. (19); it follows that for $N$-representable RDMs one has

$$
\begin{equation*}
\left.{ }_{l} \mathcal{F}-{ }_{r} \mathcal{F}={ }^{(4 ; 2,2)} \Theta\right)-{ }_{r}^{(4,2,2)} \Theta \tag{28}
\end{equation*}
$$

where the r.h.s. represents the antiHermitian part of the vanishing ${ }^{(4 ; 2,2)} \Theta$ matrix, which derives from the antiHermitian part of the fourth-order correlation matrix, Eq. (6). As a consequence, when the ACSE is satisfied

$$
\begin{equation*}
{ }_{r}^{(4 ; 2,2)} \Theta=(4 ; 2,2) \Theta \tag{29}
\end{equation*}
$$

This condition does not imply that the correlation energy terms vanish; and therefore, unless it could be demonstrated that ${ }^{(4 ; 2,2)} \Theta={ }_{r}^{(4 ; 2,2)} \Theta$ iff

$$
\begin{aligned}
& { }_{r}^{(4 ; 2,2)} \Theta_{p q ; r s}=0 \\
& { }_{(4 ; 2,2)}^{l} \Theta_{p q ; r s}=0,
\end{aligned}
$$

the solution of the ACSE does not imply that the 2-CSE is also satisfied. Indeed, accidental vanishings of the expectation value of the commutator might therefore happen.

In Mazziotti's method for solving the ACSE, the lack of sufficiency in the second-order hypervirial condition could be compensated by combining the solution of the equation with a minimization procedure. This variational approach, although excluding the possibility of applying the method to the study of excited states, brings in the extra condition needed for getting solutions of the ACSE comparable in accuracy to those obtained with an FCI treatment for the lowest state of a given spin-symmetry.

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    Contract grant sponsor: Spanish Ministerio de Educación y
    Ciencia.
    Contract grant number: BFM2003-05133.
    Contract grant sponsor: Universidad de Buenos Aires.
    Contract grant number: X-024.
    Contract grant sponsor: Consejo Nacional de Investigaciones
    Científicas y Técnicas, República Argentina.
    Contract grant number: 5098/05.

