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# Some Theoretical Questions About the *G*-Particle-Hole Hypervirial Equation

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**ABSTRACT:** By applying a matrix contracting mapping, involving the *G*-particle-hole operator, to the matrix representation of the *N*-electron density hypervirial equation, one obtains the *G*-particle-hole hypervirial (GHV) equation (Alcoba, et al., *Int J Quant Chem* 2009, 109, 3178). This equation may be solved by exploiting the stationary property of the hypervirials (Hirschfelder, *J Chem Phys* 1960, 33, 1462; Fernández and Castro, *Hypervirial Theorems*, *Lecture Notes in Chemistry Series* 43, 1987) and by following the general lines of Mazziotti's approach for solving the anti-Hermitian contracted Schrödinger equation (Mazziotti, *Phys Rev Lett* 2006, 97, 143002), which can be identified with the second-order density hypervirial equation. The accuracy of the results obtained with this method when studying the ground-state of a set of atoms and molecules was excellent when compared with the equivalent full configuration interaction (FCI) quantities. Here, we analyze two open questions: under what conditions the solution of the GHV equation corresponds to a Hamiltonian eigenstate, and the possibility of extending the field of application of this

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methodology to the study of excited and multiconfigurational states. A brief account of the main difficulties that arise when studying this type of states is described. © 2010 Wiley Periodicals, Inc. Int J Quantum Chem 00: 000–000, 2010

**Key words:** correlation matrix;  $G$ -particle-hole matrix; reduced density matrix; electronic correlation effects; contracted Schrödinger equation

## 1. Introduction

The second-order reduced density matrix (2-RDM) contains all the required information to calculate the properties of an electronic system without resorting to the  $N$ -electron wave-function. An important basis for the RDM-theory was already set in the pioneering and outstanding works of Husimi [1], Mayer [2], and Löwdin [3], and since 1955, a large and valuable bibliography [4–10] has contributed to increase our understanding of the properties of these mathematical objects.

The search for a nonvariational approach to directly determine the 2-RDM with no previous knowledge of the wavefunction started in 1976 with the simultaneous papers of Nakatsuji [11] and Cohen and Frishberg [12]. These authors integrated the  $N$ -electron Schrödinger equation (SE) over the variables of  $(N-2)$  electrons and obtained what they respectively called the density equation and the hierarchy equation.

The application to the matrix representation of the Schrödinger equation of a general matrix contracting mapping (MCM) [13–15] yielded in 1983 the  $p$ -order contracted Schrödinger equation ( $p$ -CSE)—whose solution is equivalent to that obtained with Nakatsuji's density equation (P.O. Löwdin, 1985, Private Communication)—and also yielded the  $p$ -order contracted Liouville equation as well as the corresponding  $p$ -order density hypervirial equation [16]. The last one can be identified with the anti-Hermitian part of the  $p$ -CSE ( $p$ -order ACSE) [17–20].

There are two other families of contracted equations, which are generated by the correlation-MCM where the correlation, or equivalently, the  $G$ -particle-hole operators play a similar role as the density operator in the previously mentioned MCM, whose  $p$ -order members are the  $p$ -order correlation contracted Schrödinger equation ( $p$ -CCSE) [21–25] and the  $p$ -order  $G$ -particle-hole hypervirial equation ( $p$ -order GHV) [22–27].

When considering the relevance of the four second-order equations, the 2-CSE, the 2-CCSE, the second-order ACSE (or simply ACSE), and the second-order GHV one (or simply GHV), it is important to recall here that Nakatsuji proved in his 1976

paper that when all the matrices involved in the 2-CSE are  $N$ -representable [26, 27], there is a one to one correspondence between the 2-CSE solution and the SE one. This result was later on confirmed by Mazziotti [28]. A similar sufficiency theorem for the 2-CCSE has also been reported by Alcoba [21] but until now, no such sufficiency theorems have been proved for the ACSE and GHV cases. Note, however, that a sufficiency theorem has been proved by Valdemoro et al. for the third-order GHV equation [24].

When comparing the performance of the two hypervirial equations with that obtained in a full configuration interaction (FCI) calculation, both the ACSE and the GHV equations have been found to yield highly accurate results [19, 23, 25, 29–35]. On the other hand, it has been shown that while fulfilling the GHV equation implies that both the 1-CSE and the ACSE are also fulfilled [23–25], the reverse is not true. As no sufficiency theorem exists for the second-order GHV, it is pertinent to examine whether an ACSE solution, which has been shown to be spurious [23] (E. R. Davidson, 2008, Private Communication) also constitutes a counter-example for the GHV sufficiency. The study of this question is one of the aims of this work.

To extend the application of the GHV method to those states, whose electron density distribution is significantly spread out among most of the natural orbitals — such as some excited and multiconfigurational states — is the other question considered here. Thus, previous GHV results (Alcoba et al., unpublished results) obtained when studying this type of states, which are of high chemical physical interest, were not sufficiently accurate.

The plan of this article is the following. Next, the theoretical background of the GHV methodology is given. In section 3, we demonstrate that a state, which is not a Hamiltonian eigenstate but which nevertheless fulfills the ACSE, is not a counter-example for the GHV sufficiency, as it does not fulfill this equation. The results obtained for three different types of excited states are reported in section 4. These results show that the approximating algorithm for the construction of the third-order correlation matrix, which is used at present is inadequate when the state considered has a significant spread-out of

the density distribution among the natural orbitals. A discussion on the possible means to improve the performance and scope of the GHV method concludes this article.

## 2. Basic Definitions and General Background

In our approach,  $N$  is the number of electrons of the system under study and  $2K$  is the number of spin-orbitals spanning the one-electron orthonormal basis set. Throughout this article, unless otherwise stated,  $\Psi$  denotes the state under study.

### 2.1. THE OPERATORS AND MATRICES

#### 2.1.1. The Many-Body Hamiltonian Operator

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

$$\hat{H} = \frac{1}{2} \sum_{i,j,m,l} {}^0\mathbf{H}_{ij;ml} a_i^\dagger a_j^\dagger a_l a_m \quad (1)$$

where  $a_i^\dagger$  and  $a_j$  stand for the creator/annihilator operators, whose indices denote the spinorbitals, and where

$${}^0\mathbf{H}_{ij;ml} = \frac{\epsilon_{i,m}\delta_{j,l} + \epsilon_{j,l}\delta_{i,m}}{(N-1)} + \langle ij|ml \rangle \quad (2)$$

The matrix  $\epsilon$  is formed by the sum of the external potential and the kinetic one-electron integrals. The term  $\langle ij|ml \rangle$  is an element of the matrix formed by the two-electron repulsion integrals.

#### 2.1.2. The First- and Second-Order Reduced Density Matrices

In this formalism, the 1- and 2-RDM elements are

$${}^1\mathbf{D}_{p;s} = \langle \Psi | a_p^\dagger a_s | \Psi \rangle \equiv \langle \Psi | {}^1\hat{\Gamma}_{p;s} | \Psi \rangle \quad (3)$$

and

$${}^2\mathbf{D}_{pq;rs} = \langle \Psi | a_p^\dagger a_q^\dagger a_s a_r | \Psi \rangle \equiv \langle \Psi | {}^2\hat{\Gamma}_{pq;rs} | \Psi \rangle, \quad (4)$$

respectively, as expectation values of their corresponding density operators.

Both these matrices are Hermitian and positive semidefinite, as follows from their definition.

Because of the Fermion operator algebra, the 2-RDM are antisymmetric with respect to the permutation of two row/column indices. Although the  $N$ -representability problem is a basic one, we will here be only indirectly involved in it and will therefore recommend the interested reader to consult the specialized articles [4–6, 26, 27, 36–39], and in particular, the Coleman and Yukalov book [10].

In view of the definitions (1) and (4) the expression for the electronic energy is:

$$E = \langle \Psi | \hat{H} | \Psi \rangle \equiv \text{tr}({}^0\mathbf{H} {}^2\mathbf{D}) \quad (5)$$

#### 2.1.3. The 2-RDM Decomposition and the Energy Partition

When the 2-RDM is decomposed using the fermion operators anticommuting algebra one obtains:

$${}^2\mathbf{D}_{pq;rs} = {}^1\mathbf{D}_{p;r} {}^1\mathbf{D}_{q;s} - {}^1\mathbf{D}_{p;s} \delta_{q,r} + \langle \Psi | {}^1\hat{\Gamma}_{p;r} \hat{Q}^{\Psi 1} \hat{\Gamma}_{q;s} | \Psi \rangle \quad (6)$$

where

$$\hat{Q}^{\Psi} = \sum_{\Psi' \neq \Psi} |\Psi'\rangle \langle \Psi'| \quad (7)$$

is the complement projection operator of  $|\Psi\rangle \langle \Psi|$ .

When replacing this 2-RDM expression into Eq. (5), the first term on the RHS of Eq. (6) generates a repulsive Coulomb energy expression. The last term of Eq. (6) is a connected two-body term, which cannot be expressed as a product of one-body density probabilities. This term describes the correlation effects of two electrons, which are virtually excited into each of the states spanning the space complementary to  $\Psi$ . Therefore, we define the correlation matrix elements  ${}^2\mathbf{C}$  and the corresponding operators as

$${}^2\mathbf{C}_{pq;rs} = \langle \Psi | {}^1\hat{\Gamma}_{p;r} \hat{Q}^{\Psi 1} \hat{\Gamma}_{q;s} | \Psi \rangle \equiv \langle \Psi | {}^2\hat{\mathcal{C}}_{pq;rs} | \Psi \rangle. \quad (8)$$

Note that the correlation matrix does not contribute to the 2-RDM contractions into the 1- and 0-electron space. Also, whereas the 2-RDM is Hermitian, positive semidefinite and antisymmetric with respect to the permutation of two row/column indices, which are basic  $N$ -representability conditions, the  ${}^2\mathbf{C}$  matrix does not possess any of these  $N$ -representability properties. On the other hand, a Hermitian

positive semidefinite matrix, closely related to  ${}^2\mathcal{C}$ , the  $G$ -particle-hole matrix, is defined as:

$${}^2\mathbf{G}_{pr;sq} \equiv \langle \Psi | {}^2\hat{\mathbf{G}}_{pr;sq} | \Psi \rangle \equiv {}^2\mathcal{C}_{pq;rs}, \quad (9)$$

The definition as well as the basic properties of this matrix were reported by Garrod and Percus [27]. To interpret the meaning of the second term of Eq. (6) let us recall that the Krönecker delta may be expressed as

$$\delta_{q,r} = {}^1\mathbf{D}_{q,r} + {}^1\bar{\mathbf{D}}_{q,r} \quad (10)$$

where  ${}^1\bar{\mathbf{D}}_{q,r} \equiv \langle \Psi | a_r a_q^\dagger | \Psi \rangle$  is an element of the positive semidefinite first-order hole-RDM (1-HRDM). Note that this equation expresses the ensemble  $N$ -representability of the 1-RDM [26]. Therefore, replacing Eq. (10) into the second term of relation (6) one has:

$$-{}^1\mathbf{D}_{p;s} \delta_{q,r} = -{}^1\mathbf{D}_{p;s} {}^1\mathbf{D}_{q,r} - {}^1\mathbf{D}_{p;s} {}^1\bar{\mathbf{D}}_{q,r} \quad (11)$$

Clearly the first term on the RHS. of this equation describes an exchange effect, that is, it is an antisymmetric form of the Coulomb term. The second term describes a second type of correlation mechanism where the electron and hole probability densities polarize each other. Therefore, the matrix

$$\begin{aligned} {}^2\mathbf{\Delta}_{pq;rs} &= {}^2\mathcal{C}_{pq;rs} - {}^1\bar{\mathbf{D}}_{q,r} {}^1\mathbf{D}_{p;s} \\ &\equiv {}^2\mathbf{D}_{pq;rs} - {}^1\mathbf{D}_{p;r} {}^1\mathbf{D}_{q;s} - {}^1\mathbf{D}_{p;s} {}^1\mathbf{D}_{q,r} \end{aligned} \quad (12)$$

gathers the two types of electronic correlation included in the 2-RDM.

This matrix, which can be identified as the cumulant of the 2-RDM antisymmetrized moment expansion [40–42], yields the correlation energy of a given state [42], which is given as:

$$E_{\text{corr}} = \frac{1}{2} \text{tr}({}^0\mathbf{H}^2 \mathbf{\Delta}). \quad (13)$$

This expression of the correlation energy is self-consistent, as it does not refer to any particular approximate wavefunction (i.e., Hartree-Fock). Indeed, the antisymmetrized product involves two one-body density probabilities, which are obtained by contracting the 2-RDM that yields the total energy. Note that when evaluating either the 2-RDM, or alternatively, the cumulant, it is the  ${}^2\mathcal{C}$  matrix, which is the connected two-body part of the 2-RDM, what constitutes the problem.

## 2.1.4. The Higher Order RDMs and Correlation Matrices

Because of the hierarchy character of the family of contracted equations, the higher order RDMs and higher order correlation matrices play an important role in this theory. Further on, we will consider in some detail the constructing algorithms for some of these matrices. Here, we will just report the three types of correlation matrices, which are directly related with the GHV methodology. Thus,

$$\begin{aligned} {}^{(3;1,1,1)}\mathcal{C}_{ijm;pqr} &\equiv \langle \Psi | a_i^\dagger a_p \hat{\mathcal{Q}}^\Psi a_j^\dagger a_q \hat{\mathcal{Q}}^\Psi a_m^\dagger a_r | \Psi \rangle \\ &\equiv {}^{(3;1,1,1)}\mathbf{G}_{ijp;rmq} \end{aligned} \quad (14)$$

$$\begin{aligned} {}^{(4;2,2)}\mathcal{C}_{ijml;pqrs} &\equiv \langle \Psi | a_i^\dagger a_j^\dagger a_q a_p \hat{\mathcal{Q}}^\Psi a_m^\dagger a_l^\dagger a_s a_r | \Psi \rangle \\ &\equiv {}^{(4;2,2)}\mathbf{G}_{ijqp;rsem} \end{aligned} \quad (15)$$

and

$${}^{(4;2,1,1)}\mathcal{C}_{ijml;pqrs} \equiv \langle \Psi | a_i^\dagger a_j^\dagger a_q a_p \hat{\mathcal{Q}}^\Psi a_m^\dagger a_r \hat{\mathcal{Q}}^\Psi a_l^\dagger a_s | \Psi \rangle \quad (16)$$

Note that no Hermitian positive semidefinite  $G$ -particle-hole matrix exists in this last case, which shows that the correlation matrices family is much larger than the family of the Hermitian, positive semidefinite  $G$ -particle-hole family. The properties of this type of high-order correlation matrices, which are very relevant in the study of the many-body problem, have been widely studied [21, 22, 24, 43–52].

## 2.2. MCM AND CONTRACTED EQUATIONS

Let us consider a matrix represented in the  $N$ -electron space,  ${}^N\mathbf{M}(\phi, \hat{\mathcal{O}})$ , where  $\phi$  is an  $N$ -electron wavefunction and  $\hat{\mathcal{O}}$  is an operator (e.g., the Hamiltonian, the total spin-squared one,  $\hat{S}^2$ , etc.), which may be contracted into the  $p$ -electron space (with  $p < N$ ) by applying a linear MCM whose general expression is

$$\sum_{\Lambda, \Omega} {}^N\mathbf{M}_{\Lambda; \Omega} \langle \Lambda | {}^p\hat{\mathbf{B}}_{\lambda; \gamma} | \Omega \rangle = {}^p\mathbf{M}_{\lambda; \gamma}, \quad (17)$$

where  ${}^p\hat{\mathbf{B}}_{\lambda; \gamma}$  is a  $p$ -body operator and  $\{\Lambda, \Omega \dots\}$  and  $\{\lambda, \gamma \dots\}$  represent the elements of  $N$ -electron and  $p$ -electron basis sets, respectively.

When  ${}^p\hat{\mathbf{B}}_{\lambda; \gamma} = {}^p\hat{\Gamma}_{\lambda; \gamma}$  one has the density-MCM [13, 14, 16], which when applied to both sides of

the matrix representation of the SE in the  $N$ -electron space for  $p = 2$  leads to

$$\langle \Psi | \hat{\mathbf{H}}^2 \hat{\Gamma}_{\lambda,\gamma} | \Psi \rangle = E^2 \mathbf{D}_{\lambda,\gamma}, \quad (18)$$

which is the compact form of the 2-CSE.

Alternatively,  ${}^p \hat{\mathbf{B}}_{\lambda,\gamma} = {}^p \hat{\mathbf{C}}_{\lambda,\gamma}$  in the correlation-MCM. When applying this latter mapping to the SE one obtains the  $p$ -CCSE, whose compact form for  $p = 2$  is:

$$\langle \Psi | \hat{\mathbf{H}}^2 \hat{\mathbf{C}}_{\lambda,\gamma} | \Psi \rangle = E^2 \mathbf{C}_{\lambda,\gamma} \quad (19)$$

Let us now apply these two mapping relations to the  $N$ -order density hypervirial equation

$$\langle \Psi | [\hat{\mathbf{H}}, {}^N \hat{\Gamma}_{\Lambda;\Omega}] | \Psi \rangle = 0 \quad (20)$$

It can be shown [23–25] that the density-MCM yields the compact form of the ACSE

$$\langle \Psi | [\hat{\mathbf{H}}, {}^2 \hat{\Gamma}_{\lambda,\gamma}] | \Psi \rangle = 0, \quad (21)$$

whereas the correlation-MCM generates the second-order correlation hypervirial equation, which can equivalently be expressed as the GHV equation

$$\langle \Psi | [\hat{\mathbf{H}}, {}^2 \hat{\mathbf{G}}_{\lambda,\gamma}] | \Psi \rangle = 0. \quad (22)$$

It is important to realize that all these Eqs. (18), (19), (21), and (22) are different. Therefore, they are not equivalent, as each of them imposes different conditions on the 2-RDM, which is the unknown. On the other hand, the 2-RDM, the G-particle-hole matrix, the  ${}^2 \mathbf{C}$ , and the  ${}^2 \mathbf{A}$  matrices are all interrelated second-order matrices. Therefore, when planning the computation code one may choose as variable the most convenient one. As the developed forms of the ACSE and of the GHV equation [18, 23, 29] are not needed here, their explicit structure is omitted in what follows. It is only important to remember that these equations depend not only on the second-order matrices but also on the third-order ones, which constitutes one of the problems studied in section 4.

### 3. Some Considerations on the Exactness of the Solutions of the Hypervirial Equations

When  $\Psi$  is not a Hamiltonian eigenstate, the RHS of the second-order hypervirial Eqs. (21) and (22) does not generally vanish. Thus,

$$\langle \Psi | [\hat{\mathbf{H}}, {}^2 \hat{\Omega}_{\lambda,\gamma}] | \Psi \rangle \neq 0 \quad (23)$$

where  ${}^2 \hat{\Omega}$  represents either of the  ${}^2 \hat{\mathbf{C}}$ ,  ${}^2 \hat{\mathbf{G}}$  or  ${}^2 \hat{\Gamma}$  operators. Instead of looking for the wavefunction that solves the second-order hypervirial equation, in the ACSE and the GHV methods one looks directly for the 2-RDM (or, alternatively, for the G-particle-hole matrix). At present, we approximate the third-order RDM (or third-order G-particle-hole matrix) in terms of the second-order matrix  ${}^2 \mathbf{A}$  (or the G-particle-hole matrix) by applying a modified version of Nakatsuji–Yasuda’s algorithm [25, 53]. To solve the corresponding hypervirial equation, the problem is transformed into solving a system of differential equations as described in [19] for the ACSE and in [25] for the GHV, respectively. Then, after starting with an initial trial matrix, one proceeds iteratively.

The question of whether the second-order hypervirial equations vanishes **iff** the wavefunction  $\Psi$  is a Hamiltonian eigenstate, is what concerns us here. It has been shown [20, 22, 23] that in the real case,

$$\langle \Psi | [\hat{\mathbf{H}}, {}^2 \hat{\Omega}_{\lambda,\gamma}] | \Psi \rangle = \Theta_{\lambda,\gamma}^{\Omega} - (\Theta_{\lambda,\gamma}^{\Omega})^{\text{T}} \quad (24)$$

where

$$\Theta_{\lambda,\gamma}^{\Omega} = \langle \Psi | \hat{\mathbf{H}} \hat{\mathbf{Q}}^{\Psi} {}^2 \hat{\Omega}_{\lambda,\gamma} | \Psi \rangle \quad (25)$$

is a two-body matrix resulting from a contraction over two-electron indices of the product of the two-electron  ${}^0 \mathbf{H}$  matrix and the fourth-order correlation matrix  $\langle \Psi | {}^2 \hat{\Gamma}_{\omega;\tau} \hat{\mathbf{Q}}^{\Psi} {}^2 \hat{\Omega}_{\lambda,\gamma} | \Psi \rangle$ . Therefore, when the second-order hypervirial Eq. (24) vanishes, two alternatives exist:

- First possibility:  $\Theta^{\Omega} = 0$

Let us recall that the theorems of Nakatsuji and Alcoba proved that when the Hamiltonian has only pair-wise interactions, and the matrices involved are  $N$ -representable, there is a one to one correspondence between the SE solution and those of the 2-CSE and 2-CCSE, respectively. Alcoba also proved [21] that when the Hamiltonian has only pair-wise interactions, and the matrix involved is  $N$ -representable, the equation

$$\Theta^{\Omega} = 0 \quad (26)$$

is satisfied **iff** the contracted equation from, which it derives is also satisfied. In view of these theorems, it follows that when Eq. (26) is fulfilled, the 2-RDM or the G-particle-hole

matrix, which solve the respective hypervirial equations correspond to a Hamiltonian eigenstate.

- Second possibility:  $\Theta^\Omega \neq 0$  and  $\Theta^\Omega = (\Theta^\Omega)^\top$

It has been shown [20, 22] that the  $\Theta^\Omega$  structure corresponds to that of a second-order transition reduced density/correlation matrix. Initially, we expected that a transition reduced density/correlation matrix could not be Hermitian; in which case, when the ACSE/GHV was satisfied, it was safe to assume that its solution should correspond to an eigenstate. Nevertheless, Davidson (private communication) proposed the following enlightening counter-example for the ACSE, that is, when  ${}^2\hat{\Omega}_{\lambda,\gamma} = {}^2\hat{\Gamma}_{\lambda,\gamma}$ : suppose two nondegenerate Hamiltonian eigenstates  $A$  and  $B$  with spin quantum numbers  $|S^A - S^B| > 2$ . Then

$$\langle A | {}^2\hat{\Gamma}_{\lambda,\gamma} | B \rangle = 0 \quad (27)$$

and consider

$$|\Phi\rangle = \frac{1}{\sqrt{2}}(|A\rangle + |B\rangle) \quad (28)$$

Then

$$\hat{H}|\Phi\rangle \neq E|\Phi\rangle \quad (29)$$

and yet

$$\langle \Phi | [\hat{H}, {}^2\hat{\Gamma}_{\lambda,\gamma}] | \Phi \rangle = 0. \quad (30)$$

Davidson also demonstrated that in this case

$$\Theta^\Gamma = (\Theta^\Gamma)^\top = (E_A - E_B)({}^2\mathbf{D}^A - {}^2\mathbf{D}^B), \quad (31)$$

which implies that  $\Theta^\Gamma$  is a non-null symmetric matrix. These results demonstrate that the ACSE is not a sufficient condition to ensure that its 2-RDM solution corresponds to a Hamiltonian eigenstate. Moreover, our initial assumption that a second-order transition RDM cannot be Hermitian is also invalidated.

Let us now examine whether the  $\Phi$  wavefunction proposed by Davidson, Eq. (28), constitutes a counter-example for the possible sufficiency of the GHV equation, that is, when  ${}^2\hat{\Omega}_{\lambda,\gamma} = {}^2\hat{\Gamma}_{\lambda,\gamma}$ . To this aim, let us start by evaluating the four matrix elements appearing

when developing this second-order hypervirial equation:

$$\langle A | {}^2\hat{G}_{ij;qp}^\Phi | B \rangle = -{}^1\mathbf{D}_{ij}^A {}^1\mathbf{D}_{p;q}^B \quad (32)$$

$$\langle B | {}^2\hat{G}_{ij;qp}^\Phi | A \rangle = -{}^1\mathbf{D}_{ij}^B {}^1\mathbf{D}_{p;q}^A \quad (33)$$

$$\langle A | {}^2\hat{G}_{ij;qp}^\Phi | A \rangle \equiv \langle A | {}^2\hat{G}_{ij;qp}^A | A \rangle = {}^2\mathbf{G}_{ij;qp}^A \quad (34)$$

$$\langle B | {}^2\hat{G}_{ij;qp}^\Phi | B \rangle \equiv \langle B | {}^2\hat{G}_{ij;qp}^B | B \rangle = {}^2\mathbf{G}_{ij;qp}^B \quad (35)$$

Therefore,

$$\begin{aligned} \langle \Phi | [\hat{H}, {}^2\hat{G}_{ij;qp}] | \Phi \rangle &= (E_A - E_B) \\ &\times ({}^1\mathbf{D}_{ij}^A {}^1\mathbf{D}_{p;q}^B - {}^1\mathbf{D}_{ij}^B {}^1\mathbf{D}_{p;q}^A) \end{aligned} \quad (36)$$

and in this case an element of the  $\Theta^G$  matrix takes the value:

$$\begin{aligned} \Theta_{ij;qp}^G &= -(E_A - E_B)({}^1\mathbf{D}_{ij}^B {}^1\mathbf{D}_{p;q}^A - {}^1\mathbf{D}_{ij}^A {}^1\mathbf{D}_{p;q}^B) \\ &+ (E_A - E_B)({}^2\mathbf{G}_{ij;qp}^A - {}^2\mathbf{G}_{ij;qp}^B) \end{aligned} \quad (37)$$

Therefore, the GHV equation does not vanish and  $\Theta^G \neq (\Theta^G)^\top$ , which means that Davidson's  $\Phi$  is not a counter-example for the GHV equation. Indeed, the GHV equation corresponding to such a  $\Phi$  could only vanish iff  ${}^1\mathbf{D}^A = {}^1\mathbf{D}^B$ , which would imply that

1. The two nondegenerate Hamiltonian eigenstates could have the same density- and spin-distributions
2. The difference between the two nondegenerate eigenstates 2-RDMs,  ${}^2\mathbf{D}^A$  and  ${}^2\mathbf{D}^B$ , would only be due to their correlation terms  ${}^2\mathbf{C}^A$  and  ${}^2\mathbf{C}^B$ , Eq. (6). In this case the energy difference between these states would be:

$$E_A - E_B = \text{tr}({}^0\mathbf{H}({}^2\mathbf{C}^A - {}^2\mathbf{C}^B)) \quad (38)$$

Although perhaps this could be theoretically possible, there is no evidence, to our knowledge, of any quantum-chemical system having among its spectrum two such eigenstates. Therefore, except for some possible exceptional systems, Davidson's  $\Phi$  is not a counter-example for the GHV equation. Nevertheless, the question whether other types of counter-examples different from Davidson's could exist cannot still be considered closed. Therefore, in order to ensure the GHV equation reliability, when choosing the initial trial

G-particle-hole matrix—and to avoid falling into any exceptional case—it is necessary to make sure that the initial trial matrix be  $N$ -, Spin-, and  $\Sigma$ -representable, where  $\Sigma$  stands for each of the other possible invariances of the system. Because of the unitary invariant transformations used during the iterative solving procedure, these properties are not essentially altered and it should therefore be sufficient to purify only the initial trial-matrix.

Let us finish this section by remarking that it has been proved [24] that there is a one to one equivalence between the SE solution and that of the 3-GHV, whereas no similar theorem exists in the 3-ACSE case. This is a further indication of the highly demanding character of this family of hypervirial equations.

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#### 4. Performance of the GHV Method in the Study of Excited States

As has been previously mentioned, the results obtained with the GHV method, when the state being studied is the ground-state of an atom or a molecular system whose interatomic distances are close to the equilibrium ones, have been extremely accurate. Moreover, the time and storage cost of these calculations was proportional to  $K^6$  and  $K^4$ , respectively, which shows the high efficiency of the GHV method.

The aim of this section is to give an outlook on the performance of the GHV method in the study of excited and multiconfigurational states where there are still some open, or still partially-open questions.

When considering the application of the GHV to the study of excited states two different types of difficulties arise. We first describe the general feature of the iterative solution of the GHV equation in those cases where the process, although not yet optimized, may easily be improved. The other type of difficulty, which is considered here arises when studying states whose density distribution is significantly spread out among the different spin-orbitals. This difficulty is an open question not only for the GHV but also for other ab-initio methods, including the ACSE, the 2-CSE, and the 2-CCSE. Our analysis shows that in the GHV case a different and new algorithm is needed for expressing the third-order cumulant in terms of the second-order one.

#### 4.1. GENERAL FEATURE OF THE EXCITED STATES CALCULATION WITH THE GHV METHOD

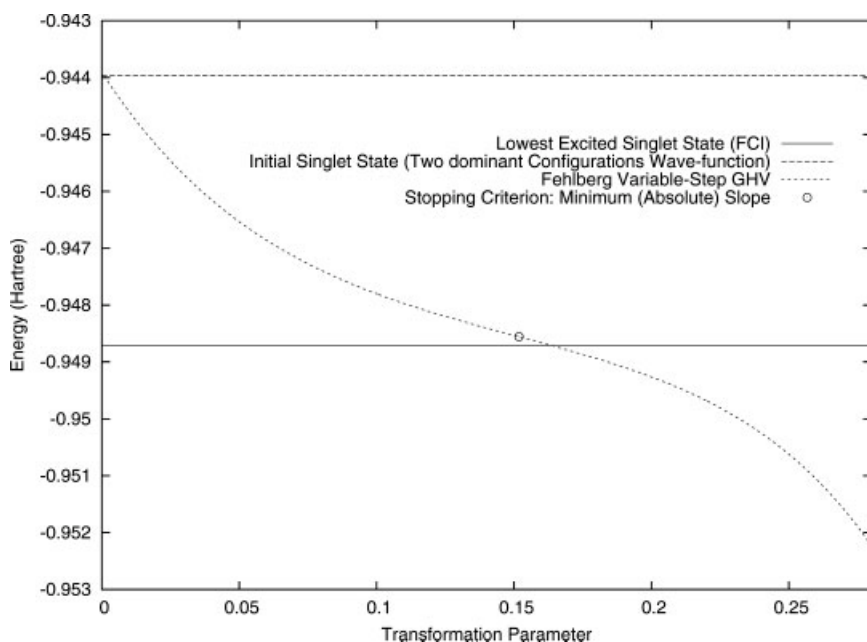
Let us first describe a feature of the iterative process, which always occurs when studying excited states, and which in some cases may result in a loss of accuracy. Thus, the graph of an excited state energy obtained when solving iteratively any of the four contracted Schrödinger equations (2-CSE, ACSE, 2-CCSE, and GHV) has a similar shape to that obtained with the GHV method for the Helium atom, for which the solution is exact, as it is a two-electron system. This is shown in Figure 1, which describes the GHV iterative process for Helium atom in a 6-31G basis set. The process first converges towards the correct energy and then falls towards a lower Hamiltonian eigenstate.

A similar result is obtained whenever the excited state considered has a reasonable zero-order approximation  $\Psi^0$ , which is a spin eigenstate involving one or two Slater determinants. In these cases, the corresponding energy produced by the GHV method constitutes a reasonable estimation. This is the case, for instance, of the Beryllium lowest singlet excited state calculated with a Clementi's Double-Zeta basis set [54], which is given in Figure 2.

The only delicate feature when applying the GHV method to study this type of excited states is to determine which point of the iterative procedure corresponds to the excited state energy. Until now, the Fehlberg's variable-step iterative method [25, 55, 56] has been used to integrate the system of differential equations for solving the GHV and has been coupled with an absolute minimum slope stopping criterion. Other alternatives are now being studied to further optimize how to determine the inflection point of the iterative process.

#### 4.2. STATES WITH SPREAD-OUT NATURAL ORBITAL OCCUPATION NUMBERS

In common with other ab-initio methods, when the zero-order function  $\Psi^0$  of a state is a multiconfigurational state the results are much less satisfactory. Some states, including the excited ones, multiconfigurational states and far from equilibrium ground-states, have spread out natural orbital occupation numbers and cannot, at present, be satisfactorily studied with the GHV method. As an example, let us consider the lowest excited singlet state of the linear  $\text{BeH}_2$  molecule. This test calculation has been carried

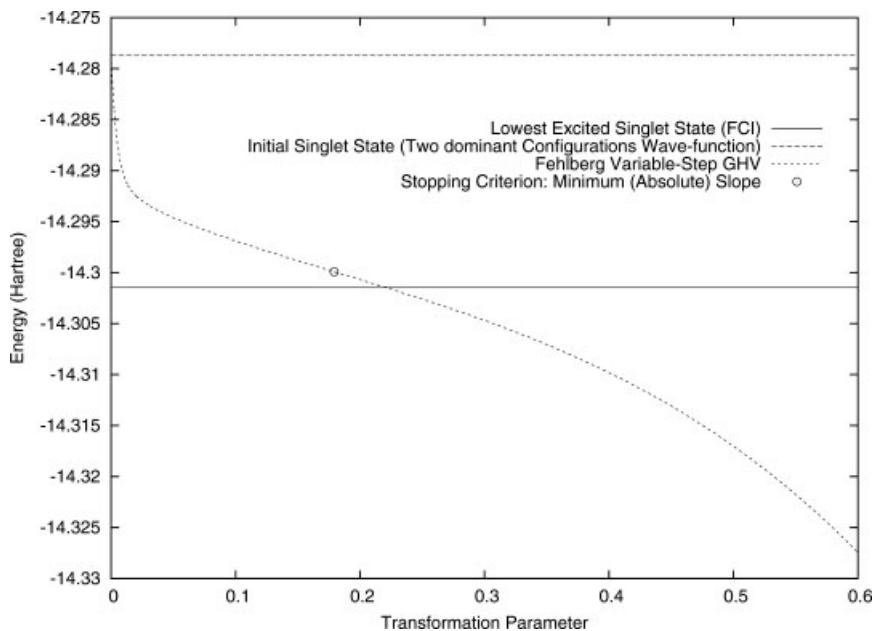


**FIGURE 1.** Convergence of the GHV iterative process for Helium lowest excited Singlet state (6-31G basis set).

out with a basis set formed by the seven Hartree-Fock orbitals built out of Slater orbitals 1s, 2s, and 2p centered at the Beryllium atom and by a 1s orbital centered at each hydrogen atom. The Be–H bond length was of  $2.54a_0$ , close to the equilibrium distance for the ground state. The corresponding FCI

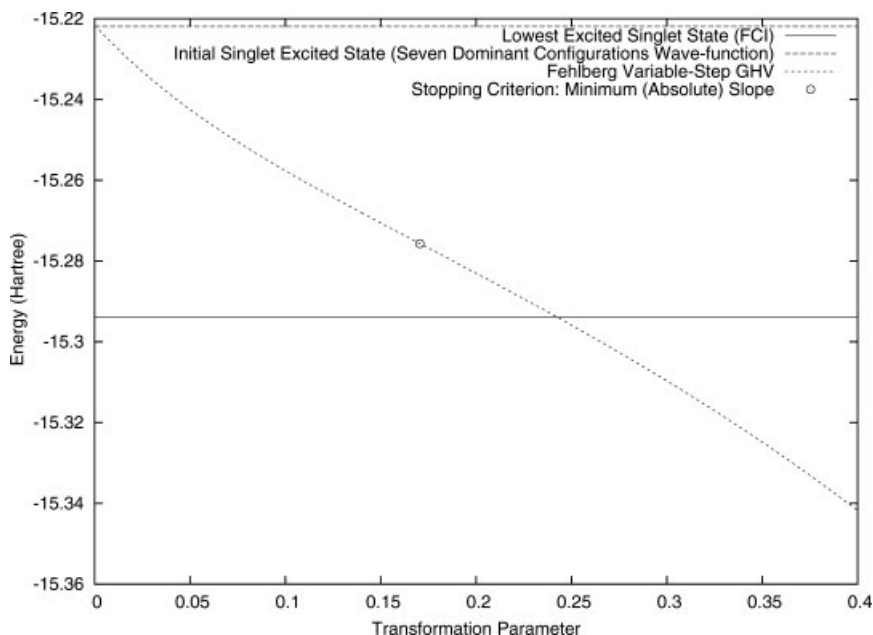
calculation for this state yielded the following occupation numbers for each of the natural spin-orbitals ( $\alpha$  or  $\beta$ ):

$$\begin{array}{llll} n_1 = 0.9999 & n_2 = 0.5122 & n_3 = 0.3038 & n_4 = 0.6464 \\ n_5 = 0.0144 & n_6 = 0.2616 & n_7 = 0.2616 & \end{array}$$



**FIGURE 2.** Convergence of the GHV iterative process for Beryllium lowest excited Singlet state (Clementi's Double-Zeta basis set).





**FIGURE 3.** Convergence of the GHV iterative process for BeH<sub>2</sub> lowest excited Singlet state (minimal basis set).

That is, the electron density is rather spread out among the different spin-orbitals. Indeed, only orbital 1 and orbital 5 are clearly occupied and empty, respectively.

When studying this state with the GHV method, we chose an initial trial matrix corresponding to a  $\Psi^0$ , which was rather close to this FCI state:

$$|\Psi^0\rangle = \frac{1}{\sqrt{7}}(|\bar{1}\bar{1}\bar{2}\bar{2}\bar{3}\bar{3}\rangle - |\bar{1}\bar{1}\bar{2}\bar{3}\bar{4}\bar{4}\rangle - |\bar{1}\bar{1}\bar{3}\bar{2}\bar{4}\bar{4}\rangle - |\bar{1}\bar{1}\bar{2}\bar{2}\bar{6}\bar{6}\rangle - |\bar{1}\bar{1}\bar{2}\bar{2}\bar{7}\bar{7}\rangle + |\bar{1}\bar{1}\bar{4}\bar{4}\bar{6}\bar{6}\rangle + |\bar{1}\bar{1}\bar{4}\bar{4}\bar{7}\bar{7}\rangle).$$

A bar over the orbital label indicates a  $\beta$  spin. The resulting GHV iteration curve is shown in Figure 3. As it is apparent, the curve does not have a clear absolute minimum slope point. As a result, the calculation yields a far from negligible error for the energy of this state.

The reason for this apparent shortcoming of the GHV approach is due to the failure, in this type of states, of the only approximation used in the GHV method: the construction of the three-body matrix elements in terms of the two-body ones. The unknowns of the problem are the correlation [43, 45–48] or equivalently, the  ${}^3\Delta$  [40–42] cumulant matrices. We have prospected several alternative algorithms for constructing these third-order matrices [23–25, 31, 45, 57]. The two types of algorithms, which have been used in practice until now are modified versions of the approximation proposed

by Nakatsuji and Yasuda [53]. We will first describe the simplest and nevertheless very effective algorithm when the zero-order function involves one, or at the most, two Slater determinants. This algorithm, denoted as VTP, was proposed by Valdemoro et al. [45] and is based on the relevant role played by the frontier orbitals within each of the orbital symmetries. To define the Frontier-orbitals in an unambiguous way, the state  $\Psi$  considered must have a clearly dominant configuration. When this is the case, the highest occupied spin-orbital (HOMO) and lowest empty spin-orbital (LUMO) of each symmetry are, within this framework, the Frontier orbitals.

The VTP approximation proposes two different algorithms according to whether they involve sums over HOMO or LUMO orbitals. Thus, denoting by  $o$  and  $e$  the occupied and empty orbitals respectively, these two algorithms are:

$${}^3\Delta_{o_1 e_1 \bar{e}_2; e_3 e_4 \bar{e}_2} = \frac{1}{6} ({}^2\Delta_{o_1 \bar{l}; e_3 \bar{e}_2} {}^2\Delta_{e_1 \bar{e}_2; e_4 \bar{l}}) \quad (l = \text{HOMO}) \quad (39)$$

and

$${}^3\Delta_{e_1 o_1 \bar{e}_2; o_3 o_4 \bar{e}_2} = -\frac{1}{6} ({}^2\Delta_{e_1 \bar{e}_2; o_3 \bar{l}} {}^2\Delta_{o_1 \bar{l}; o_4 \bar{e}_2}) \quad (l = \text{LUMO}) \quad (40)$$

where the  ${}^2\Delta$  expression is the second-order cumulant, Eq. (12). All the other  ${}^3\Delta$  elements are set to

zero. When examining the occupation numbers of the different orbitals in  $\Phi$ , only orbital 4, which is a  $\sigma_u$ , has a very slight HOMO character. On the other hand, there are four orbitals with different symmetries within the LUMO set: orbital 5, which is  $\sigma_u$ , orbital 3, which is  $\sigma_g$ , and orbitals 6 and 7, which are degenerate orthogonal  $\pi$  orbitals. As the correlation effects involve virtual excitations, it is not easy, in view of the orbital symmetry, to guess which will be the virtual excitations involved.

The other algorithm, which has been used for approximating the third-order cumulant in the study of excited states is still closer to Nakatsuji–Yasuda's algorithm. It has the form [25]:

$$\begin{aligned} {}^3\Delta_{ijk;pq\bar{r}} &\approx \hat{A} \sum_{\bar{i}} {}^2\Delta_{ik;p\bar{i}} \left( {}^1\mathbf{D}_{\bar{i},\bar{i}}^{(*)} - {}^1\bar{\mathbf{D}}_{\bar{i},\bar{i}}^{(*)} \right) {}^2\Delta_{\bar{j}\bar{i};q\bar{r}} \\ {}^3\Delta_{ijk;pq\bar{r}} &\approx \hat{A} \sum_t {}^2\Delta_{ij;t\bar{q}} \left( {}^1\mathbf{D}_{t,t}^{(*)} - {}^1\bar{\mathbf{D}}_{t,t}^{(*)} \right) {}^2\Delta_{ik;p\bar{r}} \quad (41) \end{aligned}$$

where  $\hat{A}$  is the antisymmetrizer of the indices labels corresponding to the two different  ${}^2\Delta$  cumulant matrices. Note that in this algorithm no explicit mention of the Frontier orbitals appears. However, the algorithm takes them indirectly into account. Thus, the sum runs over all orbital indices but each of the sum terms involves the product of the two  ${}^2\Delta$  cumulant matrix elements and the diagonal element  $({}^1\mathbf{D}_{t,t}^{(*)} - {}^1\bar{\mathbf{D}}_{t,t}^{(*)})$  where  ${}^1\mathbf{D}_{t,t}^{(*)}$  and  ${}^1\bar{\mathbf{D}}_{t,t}^{(*)}$  are the 1-RDM and 1-HRDM corresponding to the Slater determinant, which dominates in the state considered. This last term acts as a selective device assigning a positive or negative sign to the sum terms, according to whether the orbital considered is occupied or empty. For calculating purposes, the use of this device is very convenient. As happened with the VTP algorithm, when a single determinant is not a good zero-order description of the state under study, this device cannot perform well.

Another difficulty appears in the study of this multiconfigurational type of states. Thus, an appropriate initial trial 2-RDM entering the GHV iterative process is not easy to guess, which implies that previous to the GHV application, one must carry out a multireference SCF-CI calculation, which cancels the simplifying advantages of the GHV method.

In view of the difficulties just described it seems necessary to investigate how to solve the two following problems:

- To devise an appropriate procedure for determining directly an initial  $N$ -, Spin-, and  $\Sigma$ -representable 2-RDM without a prior knowledge of the  $\Phi^0$  zero-order state.

- To investigate how to approximate the  ${}^3\Delta$  cumulant matrix when the  $\Phi^0$  zero-order of the state under study is multiconfigurational.

Finding a satisfactory approximate answer to these two far from trivial questions constitutes a long-term project in which much of our present research effort is focused. In the next paragraph we describe the short-term questions, which are also in progress.

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## 5. Final Comment

Let us conclude this article by briefly commenting on other possible means to improve the performance and scope of the GHV method.

To apply the GHV method to the study of systems of chemical-physical interest, the simplifying features of the system symmetry properties have to be taken into account. To this aim, a thorough group-theoretical study of the GHV structure is being carried out by Massaccesi and Alcoba (in preparation). This study will be at the base of a new computational code, which would be much faster and which would take explicitly into account all the invariants of the system under study. This new code should permit to extend the application of the GHV method to larger and periodic systems, as well as systems in states with other spin multiplicities. Moreover, this basic symmetry study ensures the handling of matrices corresponding to any multiplet spin-states, pure momentum- states, ..., and any other invariants.

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