
Convergence and Computational Efficiency Enhancements in the Iterative Solution of the G -Particle-hole Hypervirial Equation

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ABSTRACT: The G -particle-hole hypervirial (GHV) equation has been recently reported (Valdemoro et al., Sixth International Congress of the International Society for Theoretical Chemical Physics Vancouver: Canada, 2008. Alcoba et al., *Int J Quantum Chem* 2009, 109, 3178; Valdemoro et al., *Int J Quantum Chem* 2009, 109, 2622). This equation is the newest member of the family of equations which can be obtained by applying a matrix-contracting mapping (Valdemoro, *An R Soc Esp Fís* 1983, 79, 106; Valdemoro, *Phys Rev A* 1985, 31, 2114; Valdemoro, in *Density Matrices and Density Functionals*, Reidel: Dordrecht, 1987; p 275.) to the matrix representation in the N -electron space of the Schrödinger, Liouville and hypervirial equations. The procedure that we have applied in order to solve the GHV equation exploits the stationary property of the hypervirials (Hirschfelder, *J Chem Phys* 1960, 33, 1462; Hirschfelder and Epstein, *Phys Rev* 1961, 123, 1495) and follows the general lines of Mazziotti's variational approach for solving the anti-Hermitian contracted Schrödinger equation (ACSE) (Mazziotti, *Phys Rev Lett* 2006, 97, 143002; Mazziotti, *Phys Rev A* 2007, 75, 022505; Mazziotti, *J Chem Phys* 2007, 126,

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184101). In this article, we report how the method's convergence has been significantly enhanced and how its computational scaling has been considerably reduced (in both floating-point operations and storage). The results for a variety of atomic and molecular calculations confirming these methodological improvements are reported here. © 2010 Wiley Periodicals, Inc. Int J Quantum Chem 00: 000–000, 2010

Key words: correlation matrix; G-matrix; reduced density matrix; electronic correlation effects; contracted Schrödinger equation; hypervirial of the G-particle-hole matrix

1. Introduction

The 2-order Correlation Contracted Schrödinger Equation (2-CCSE) [1] and its anti-Hermitian part, which is identical to the G-particle-hole hypervirial (GHV) equation [2–4], have recently been proposed for studying the electronic structure of an N-electron system. The development of the methodology based on these two equations continues a line of research which started long ago: to look for an accurate description of the electronic structure of the N-electron systems through the use of two-body physico-mathematical objects, the 2-order Reduced Density Matrices (2-RDM), which should be determined directly without recourse to the N-body wave-function. This search started more than fifty years ago with the remarkable papers by Husimi [5] and by Löwdin [6]. Since then, huge advances have been performed and many valuable works have contributed to enlightening the 2-RDM theory. Let us especially recall the outstanding 1963 paper by Coleman [7], as well as the 1964 one by Garrod and Percus [8], which set up a firm ground for the research which was to follow and which generated an extensive bibliography. The books by Davidson [9] and by Coleman and Yukalov [10], as well as the comprehensive reviews on the RDM theory [11–15] are a valuable record of the advances carried out in this line of research.

In 1976, the Schrödinger Equation (SE) was integrated over the variables of $(N - 2)$ electrons by Nakatsuji [16] and by Cohen and Frishberg [17]. In 1986, Valdemoro [18] applied to the matrix representation in the N-electron space of the SE a matrix-contracting mapping (MCM) [18–20], and obtained what this author denoted 2-order Contracted Schrödinger equation (2-CSE). These equations can be shown to be equivalent and are at the origin of the late developments in this line of research. The relevance of these equations was enhanced by a theorem of Nakatsuji (1976) [16], later verified by Mazziotti (1998) [21], who showed that the 2-RDM which solves the 2-CSE equation coincides with that

which would be obtained by integrating the N-electron density matrix, solution of the SE, over the variables of $(N - 2)$ electrons. Although the 2-CSE is represented in the 2-electron space and its solution is the 2-RDM, it also depends on the 3- and 4-RDMs in an averaged way, which renders it operationally indeterminate. This drawback was solved by approximating the 3- and 4-RDMs in terms of the 1- and 2-RDMs [22], which permitted the 2-CSE to be approximately solved iteratively by Colmenero and Valdemoro in 1994 [23]. This method has been significantly optimized later on (e.g., see Refs. [10, 14, 15], and references therein). When the MCM is applied to the matrix representation of the SE, and involves the 2-order correlation operator instead of the 2-order density one, the 2-CCSE is generated [3, 4]. A noteworthy result was reported by Alcobra, who demonstrated in 2002 [1] that a theorem similar to Nakatsuji's and Mazziotti's concerning the exactness of the 2-CSE, also holds in the 2-CCSE case.

Since the MCM is a general mapping, it has been applied in the past not only to the matrix representation in the N-electron space of the SE but also to the matrix representations of the Hamiltonian operator [18, 20], the Liouville, and hypervirial equations [18], and the spin-squared eigenequation [24]. A general property of the resulting family of p-order contracted equations is that they are hierarchy ones. That is, they involve contractions of matrices of a higher order than p. The type of contracted equations which involve less unknowns are the p-order contracted hypervirial ones. A large literature on the hypervirial conditions has been developed [25–33], thus establishing this name to refer to the expectation value of the commutator between the Hamiltonian and any linear operator, which vanishes when the state considered is a Hamiltonian eigenstate [25]. In 1994, Colmenero and Valdemoro [23] realized that the 2-order density hypervirial (2-HV) equation was the anti-Hermitian part of the 2-CSE and discussed in some detail its derivation as well as the attractive properties of this equation. These first studies have been subsequently extended by Valdemoro and coworkers, who investigated the hypervirial

properties and its possible applications and limitations as a tool for the direct calculation of reduced density matrices [34–37]. In 2006, Mazziotti [38–40] proposed an excellent iterative method for solving the 2-HV, which he denoted anti-Hermitian contracted Schrödinger equation (ACSE), and obtained excellent results [38–45]. Two important advantages of this approach were that the ACSE did not depend on the 4-RDM and that the N-representability properties [7] of the 2-RDM were practically preserved during the iterative process.

When the MCM which is applied to the N-electron density hypervirial equation involves the correlation operator or, equivalently, the G-particle-hole operator, one obtains the GHV equation, which can be identified with the anti-Hermitian part of the 2-CCSE [2–4]. It should be noted that since the 2-order density operator and the G-particle-hole operator are very different, the 2-order contracted hypervirial equations which they respectively generate, the ACSE and the GHV, are mathematically different. They present different basic properties which, when approximately solved, give rise to different convergence problems. Thus, we have shown [3] that while solving the GHV implies that the ACSE is also solved, the inverse is not true. In other words, the GHV is a different and more demanding equation. Moreover, in the p-order ACSE and p-order GHV case, with $N > p > 2$, it has been shown [4] that the p-GHV equation implies a sufficient condition to guarantee that there is a one-to-one correspondence between the p-GHV solutions and the SE ones, which is not true in the p-ACSE case. An iterative procedure leads to an accurate solution of the GHV equation. In view of the G-particle-hole operator structure, an evolution operator different to the one devised by Mazziotti in the ACSE case [38] had to be looked for [3, 4]. Our approach here, which is an alternative to that reported in [38–40], while following the general lines of Mazziotti's continuous variational formulation [38], is based on the stationary property of the Hamiltonian against a unitary transformation.

The preliminary results obtained with the GHV method were very accurate and satisfying [2, 3], and showed at least as efficient as the set of results obtained in the ACSE case. Nevertheless, the convergence, although very smooth, was very slow. Moreover, the time of each iteration was proportional to K^7 , where K is the number of orbitals in the basis set. On the other hand, the computational memory storage scaling was proportional to K^6 . The study reported here describes the new optimizing implementations introduced in order to enhance both the

convergence and the computational efficiency of this method.

The article is organized as follows: In next section, the notation, definitions, and necessary background information are summarized. In section 3, the main features of the theory at the base of the GHV methodology are briefly recalled. The new techniques which we propose here in order to render the GHV method fully competitive are then reported in section 4. First, the procedure through which the iteration time and memory storage are rendered proportional to K^6 and K^4 , respectively, is described in some detail, and a set of comparative results are given. To accelerate the convergence of the iterative procedure and to simultaneously improve the precision of the solution, a new iterative methodology, based on applying Fehlberg's algorithm [46, 47] to the solution of a system of differential equations associated to the GHV equation, is reported and numerically tested in the second part of this section. A graph confirms that the convergence enhancement is noteworthy. Finally, section 5 is mainly devoted to assess the exactness and competitiveness of the new methodology. In the first part of this section, we study two different convergence stopping criteria and the dependence of the results thus obtained on the size and type of system studied, as well as on the kind and extension of the atomic orbitals basis used. In the second part of this section, the performance of the GHV is compared with that of other ab initio methods. A brief discussion on the possible ways which may permit to optimize and further extend the GHV method concludes this section.

2. Theoretical background

2.1. GENERAL NOTATION

The systems considered have a fixed number N of electrons and the finite number of orthonormal spin-orbitals spanning the one-electron space is $2K$.

The RDMs and the correlation matrices (CMs) are the matrices at the center of the reported theoretical approach. Their respective structures are defined, in the occupation number representation of second quantization, as:

- A p-RDM, ${}^p\mathbf{D}$, is a matrix whose elements have the form:

$$\begin{aligned} & {}^p D_{i_1 i_2 \dots i_p; m_1 m_2 \dots m_p} \\ &= \frac{1}{p!} \langle \Psi | a_{i_1}^\dagger a_{i_2}^\dagger \dots a_{i_p}^\dagger a_{m_p} \dots a_{m_2} a_{m_1} | \Psi \rangle \end{aligned}$$

$$\equiv \frac{1}{p!} \langle \Psi | {}^p \hat{\Gamma}_{i_1 i_2 \dots i_p; m_1 m_2 \dots m_p} | \Psi \rangle \quad (1)$$

where ${}^p \hat{\Gamma}$ is a p-electron density operator. That is, a p-RDM is the expectation value of ${}^p \hat{\Gamma}$ in the state Ψ considered.

- Similarly, an element of the p-order hole-RDM (p-HRDM), ${}^p \bar{D}$, is

$$\begin{aligned} & {}^p \bar{D}_{i_1 i_2 \dots i_p; m_1 m_2 \dots m_p} \\ &= \frac{1}{p!} \langle \Psi | a_{m_p} \dots a_{m_2} a_{m_1} a_{i_1}^\dagger a_{i_2}^\dagger \dots a_{i_p}^\dagger | \Psi \rangle \quad (2) \end{aligned}$$

- The 2-CCSE and the GHV equation depend on the 2-, 3-, and 4-order CMs which are respectively defined as [1, 48, 49]:
- The 2-CM and the G-particle-hole matrices [8], ${}^2 C$ and ${}^2 G$, respectively, have the form:

$${}^2 C_{ij;lm} = \sum_{\Psi' \neq \Psi} \langle \Psi | {}^1 \hat{\Gamma}_{i;l} | \Psi' \rangle \langle \Psi' | {}^1 \hat{\Gamma}_{j;m} | \Psi \rangle \equiv {}^2 G_{il;mj} \quad (3)$$

The 2-CM and the G-particle-hole operator definitions are therefore:

$${}^2 \hat{C}_{ij;lm} = {}^1 \hat{\Gamma}_{i;l} \hat{Q} {}^1 \hat{\Gamma}_{j;m} = {}^2 \hat{G}_{il;mj} \quad (4)$$

where

$$\hat{Q} \equiv \sum_{\Psi' \neq \Psi} |\Psi'\rangle \langle \Psi'| = \hat{I} - |\Psi\rangle \langle \Psi| \quad (5)$$

The ${}^2 \hat{C}$ and ${}^2 \hat{G}$ operators are very different to the 2-electron density operator, as they contain information, in an averaged way, on the whole spectrum of states, due to the role played by the \hat{Q} operator. This important feature reflects on the CMs. A complementary way of looking at these matrices is to realize that they are formed by sums of products of transition RDM's elements.

Note that Eq. (3) shows that the 2-CM matrix and the G-particle-hole matrix share the same elements, which are, however, identified by different (row; column) labels. Thus, while the 2-CM element's labels coincide with those of the 2-RDM, this is not the case for the G-particle-hole matrix. Both matrices have remarkable properties which will be considered below.

- There are three different types of 3-CMs whose structure can be defined as:

$${}^{(3;1,1,1)} C_{ijl;pqr} = \langle \Psi | {}^1 \hat{\Gamma}_{ip} \hat{Q} {}^1 \hat{\Gamma}_{jq} \hat{Q} {}^1 \hat{\Gamma}_{lr} | \Psi \rangle \quad (6a)$$

$${}^{(3;2,1)} C_{ijl;pqr} = \langle \Psi | {}^2 \hat{\Gamma}_{ijpq} \hat{Q} {}^1 \hat{\Gamma}_{lr} | \Psi \rangle \quad (6b)$$

$${}^{(3;1,2)} C_{ijl;pqr} = \langle \Psi | {}^1 \hat{\Gamma}_{ip} \hat{Q} {}^2 \hat{\Gamma}_{jl;qr} | \Psi \rangle \quad (6c)$$

- The seven different types of the 4-CMs are: ${}^{(4;1,1,1,1)} C$, ${}^{(4;1,1,2)} C$, ${}^{(4;1,2,1)} C$, ${}^{(4;2,1,1)} C$, ${}^{(4;2,2)} C$, ${}^{(4;3,1)} C$, and ${}^{(4;1,3)} C$. In a more general way, a p-CM is indicated by the notation ${}^{(p;p_1 p_2 \dots)} C$ with $p = p_1 + p_2 + \dots$. The structure of these matrices is easily deduced by applying the same notation rules as in the 3-CMs case [1, 48].

2.2. MAIN RDMS PROPERTIES AND INTER-RELATIONS LINKING THE RDMS AND THE CMS

The set of the 1-, 2-, 3-..., $(N - 1)$ -RDMs properties is not completely known. Indeed, the set of sufficient mathematical conditions that these matrices must satisfy in order to ascertain that there exists an N-electron wave-function from which they can be derived by integration over the variables of $(N - 1)$, $(N - 2)$, ... electrons is what Coleman [7] defined as N-representability conditions, which is the core of the research in RDM theory. However, those RDM properties which are at present known, coupled with the physical properties of the quantum mechanical operators, enable us to approximate fairly well the 1- and 2-RDMs corresponding to states whose zero-order function may be described by a single Slater determinant. The properties which may be considered essential are that all RDMs and the corresponding HRDMs are Hermitian positive semi-definite matrices (D- and Q-condition) and antisymmetric with regard to the permutation of the one-electron indices in the row/column labels [6, 7].

Another interesting and essential feature is that the p-RDMs, with $p > 1$, are interrelated with the p-CM matrices [1, 48, 49]. Let us just recall here how the 2-RDM is linked with the 2-CM. Thus, it can easily be shown that

$$\begin{aligned} 2! {}^2 D_{ij;ml} &= {}^1 D_{im} {}^1 D_{jl} - {}^1 D_{jm} {}^1 D_{il} - {}^1 D_{jm} {}^1 \bar{D}_{il} \\ &+ \langle \Psi | {}^1 \hat{\Gamma}_{im} \hat{Q} {}^1 \hat{\Gamma}_{jl} | \Psi \rangle \quad (7) \end{aligned}$$

where ${}^1 \bar{D}_{il} = \delta_{il} - {}^1 D_{il}$ is an element of the 1-HRDM.

In Eq. (7), the last term is the ${}^2C_{ij;ml}$ element, or, equivalently, the ${}^2G_{im;j}$ element. The G -particle-hole matrix has two important N -representability properties which are not shared by the 2-CM. Thus, 2G is a Hermitian positive semi-definite matrix [8]. This important matrix, and its counterpart the 2-CM, are at the center of the methodology reported here.

3. The GHV Equation Methodology

For a particular state of a system of N electrons with up to pairwise interactions, the 2-RDM or, equivalently, the 2-CM or the G -particle-hole matrix contain all the useful information to predict its properties without previous knowledge of the N -electron wave-function. For such a system, the Hamiltonian is written as

$$\hat{H} = \frac{1}{2} {}^0H_{pq;rs} a_p^\dagger a_q^\dagger a_s a_r \quad (8)$$

where the Einstein's convention of summation over common indices is and will be applied throughout this article except when otherwise stated. The 2-order matrix 0H collects the integrals over the $2K$ spin-orbitals and the total electronic energy is calculated as a contraction of this matrix with the 2-RDM.

$$\mathcal{E} = \text{tr}({}^0H^2D) \quad (9)$$

Similar expressions have been obtained for the 2-CM and the G -particle hole matrix [3, 4]. In this article the GHV methodology will be used to calculate any of these matrices.

3.1. THE 2-CCSE AND THE GHV EQUATION

The compact form of the 2-CCSE may be expressed as [1]:

$$\langle \Psi | \hat{H} {}^2\hat{C}_{ij;ml} | \Psi \rangle = \mathcal{E} \langle \Psi | {}^2\hat{C}_{ij;ml} | \Psi \rangle \quad \forall i, j, m, l \quad (10)$$

When developing this equation, it takes the form:

$$\mathcal{E} {}^2C_{ij;ml} = \frac{1}{2} {}^0H_{pq;ir} {}^{(3;2,1)}C_{pqj;mrl} - \frac{1}{2} {}^0H_{pq;ri} {}^{(3;2,1)}C_{pqj;mrl} + \frac{1}{2} {}^0H_{pq;rs} {}^{(4;3,1)}C_{pqij;mrl} \equiv \mathcal{E} {}^2G_{im;j} \quad (11)$$

which shows the dependence of the 2-CCSE on the 3- and 4-CMs.

As was mentioned in the introduction, Alcoba showed that there is a one-to-one correspondence between the solution of this equation and that of the SE [1].

The anti-Hermitian part of the 2-CCSE coincides with the GHV equation, whose compact form is [3, 4]:

$$\langle \Psi | [{}^2\hat{C}_{ij;ml}, \hat{H}] | \Psi \rangle \equiv \langle \Psi | [{}^2\hat{G}_{im;j}, \hat{H}] | \Psi \rangle = 0 \quad \forall i, j, m, l. \quad (12)$$

From a theoretical point of view, this equation may also be obtained from a direct contraction of the well-known hypervirial equation of the N -order density operator into the 2-body space by applying to it a linear general MCM [18–20]. To show this, let us consider the set of the transition 2-CM matrices between two orthonormal states spanning the N -electron space, for instance the complete set of Slater determinants Λ, Ω, \dots

$${}^2C_{ij;ml}^{(\Lambda\Omega)} = \langle \Lambda | a_i^\dagger a_m \hat{Q} a_j^\dagger a_l | \Omega \rangle \equiv \langle \Lambda | {}^2\hat{C}_{ij;ml} | \Omega \rangle \quad (13)$$

where \hat{Q} is, as in the previous section, the projector on the complementary space to the Ψ state under study. Let us now consider the matrix representation of the hypervirial equation of the N -order density operator in this same space:

$${}^N M_{\Lambda;\Omega} \equiv \langle \Psi | [{}^N \hat{\Gamma}_{\Lambda;\Omega}, \hat{H}] | \Psi \rangle = 0 \quad (14)$$

Let us now contract this matrix equation into the 2-body space by multiplying both sides of the equation by ${}^2C_{ij;ml}^{(\Lambda\Omega)}$ and taking the trace over the N -electron states:

$$\sum_{\Lambda,\Omega} {}^N M_{\Lambda;\Omega} \langle \Lambda | {}^2\hat{C}_{ij;ml} | \Omega \rangle = 0 \quad (15)$$

After performing some simple algebra, one obtains the compact form of the GHV equation given in Eq. (12).

When the GHV equation is represented in a real spin-orbital basis one has:

$${}^0H_{rs;pq} {}^{(3;2,1)}C_{pqj;rsl} {}^1D_{i;m} - {}^0H_{pq;rs} {}^{(3;2,1)}C_{rsm;pqi} {}^1D_{l;j} + 2 {}^0H_{rs;pm} {}^{(3;2,1)}C_{ipj;rsl} + 2 {}^0H_{pq;jr} {}^{(3;2,1)}C_{lrm;pqi} + 2 {}^0H_{ir;pq} {}^{(3;2,1)}C_{pqj;mrl} + 2 {}^0H_{ql;rs} {}^{(3;2,1)}C_{rsm;jqi} = 0 \quad (16)$$

When compared with the 2-CCSE given in Eq. (11), this equation is significantly simpler to solve

because in the GHV equation the dependence on the 4-CM cancels out.

It must be recalled here that Alcobra et al. recently reported [3, 4] a set of theorems proving that the 3-, 2-, and 1-order matrices satisfying the GHV also satisfy the ACSE, the 1-order CSE (1-CSE) [18] and the hypervirial of the 1-order density operator (1-HV) [18]; and that, in general, the converse is not true.

To take advantage of the RDMs' elements anti-symmetry with respect to permutation of their row/column labels, it is convenient to transform Eq. (16) into an equivalent one which depends on the 1-, 2-, and 3-RDMs instead of on the 3-CM. Because we do not know an exact algorithm for building the 3-order matrices, these matrices are approximated in terms of the lower-order ones. Then, the GHV equation is solved through an iterative process as follows [2–4]: the initial matrices entering the equation correspond to a 0-order approximation to the state one is interested in. In consequence, the r.h.s. of Eq. (12) does not initially vanish and what one obtains is:

$$\langle \Psi | [{}^2\hat{G}_{im;j}, \hat{H}] | \Psi \rangle = A_{im;j} \quad \forall i, j, m, l \quad (17)$$

where the error-matrix \mathbf{A} is necessarily anti-Hermitian, since, by construction, the GHV equation is anti-Hermitian. The operator \hat{A} representing this error-matrix may be expressed as:

$$\hat{A} = A_{pr;sq} {}^2\hat{G}_{pr;sq} \quad (18)$$

Having all these features in mind, and applying the criteria developed in [3], one may propose the following iterating algorithm:

$${}^2G_{im;j}^{(n)} = \frac{1}{\varepsilon} \langle \Psi | [\hat{A}^{(n-1)}, {}^2\hat{G}_{im;j}] | \Psi \rangle + {}^2G_{im;j}^{(n-1)} \quad (19)$$

This equation may be solved using all the information in the $(n - 1)$ iteration to build up a new G-particle-hole matrix for the next iteration until convergence.

3.2. AN ALTERNATIVE SOLUTION OF THE GHV EQUATION

An alternative to the previous straightforward solution of Eq. (12) is here reported. This approach, whose general lines follow, as mentioned above, the continuous formulation for solving the ACSE proposed by Mazziotti in [38–40], is based on the stationary condition of the eigenstates of the Hamiltonian

against any unitary transformation. These transformations, which preserve the norm, may be selected in a continuous way. Under this proposed alternative solution, the 2-RDM and the other matrices associated to the same state evolve in a continuous manner until they become stationary.

In Eq. (17) the inaccuracy of the description of the state implies that the error matrix \mathbf{A} does not vanish. The problem is, therefore, to modify the state under study until the GHV equation is fulfilled.

Because the elements of the 2-RDM, the 2-CM, and the G-particle-hole matrices are, respectively, the expectation values of the density, the correlation and the G-particle-hole operators, their modifications may be interpreted as caused by the modification of the operators.

A unitary transformation may be represented by an exponential operator $e^{\lambda\hat{B}}$, provided that the \hat{B} operator is anti-Hermitian. The real parameter λ is used to indicate the extent of the transformation. The transformation is close to an identity whenever the \hat{B} operator gets closer to the null-operator. The unitary modification of the density, the correlation and the G-particle-hole operators by this unitary transformation is given by,

$${}^2\hat{\Gamma}'_{ij;ml} = e^{\lambda\hat{B}} {}^2\hat{\Gamma}_{ij;ml} e^{-\lambda\hat{B}} \quad (20)$$

$${}^2\hat{C}'_{ij;ml} = e^{\lambda\hat{B}} {}^2\hat{C}_{ij;ml} e^{-\lambda\hat{B}} = e^{\lambda\hat{B}} {}^2\hat{G}_{im;j} e^{-\lambda\hat{B}} = {}^2\hat{G}'_{im;j} \quad (21)$$

The first-order variation in their expectation values is then

$$\frac{d {}^2D_{ij;ml}}{d\lambda} = \langle \Psi | [\hat{B}, {}^2\hat{\Gamma}_{ij;ml}] | \Psi \rangle_{\lambda} \quad (22)$$

$$\begin{aligned} \frac{d {}^2C_{ij;ml}}{d\lambda} &= \langle \Psi | [\hat{B}, {}^2\hat{C}_{ij;ml}] | \Psi \rangle_{\lambda} \\ &= \langle \Psi | [\hat{B}, {}^2\hat{G}_{im;j}] | \Psi \rangle_{\lambda} = \frac{d {}^2G_{im;j}}{d\lambda} \end{aligned} \quad (23)$$

Then, the problem is to select an operator \hat{B} that becomes the null-operator as the state approaches an eigenstate of the Hamiltonian and guarantees that the associated 2-RDM, 2-CM, and the G-particle-hole matrix fulfill the N-representability conditions.

Out of the many possible choices for the \hat{B} operator, a linear combination of all the G-particle-hole operators, similar to the one given in Eq. (18), has been shown to be adequate for the solution of the GHV equation.

$$\hat{B} = B_{pr;sq} \hat{\Gamma}_{p;r} \hat{Q} \hat{\Gamma}_{q;s} = B_{pr;sq} {}^2\hat{G}_{pr;sq} \quad (24)$$

where the sum over the common indices is implicit. The numerical coefficients must form an anti-Hermitian matrix

$$B_{sq;pr} = -B_{pr;sq}$$

for the \hat{B} operator to be anti-Hermitian. They must vanish as the state approaches an eigenstate of the Hamiltonian, that is, the state reaches the stationary condition and the modification becomes an identity.

The construction of the B-matrix by the algorithm

$$\begin{aligned} B_{pr;sq} &= \langle \Psi | [{}^1\hat{\Gamma}_{p;r} \hat{Q} {}^1\hat{\Gamma}_{q;s}, \hat{H}] | \Psi \rangle_{\lambda} \\ &= \langle \Psi | [{}^2\hat{G}_{pr;sq}, \hat{H}] | \Psi \rangle_{\lambda} \end{aligned} \quad (25)$$

guarantees that, on convergence, it will vanish; for it is an expression of the GHV equation. In addition, the fulfillment of the GHV equation enforces those of the 1-CSE, of the ACSE and of the 1-HV. At this point, it must be noted that Mazziotti's continuous formulation proposed in [38–40] differs from the one proposed here, as it uses a different algorithm than the one given by Eqs. (24)–(25), thus enforcing a weaker stationarity condition, the ACSE one [3, 39].

To render the GHV method competitive with other ab initio approaches, two very effective methodological implementations, which are explained in some detail in the following section, have been introduced into the GHV general scheme just described.

4. Convergence and Computational Enhancements of the GHV Method

To increase the efficiency of the computations, two optimizing implementations are proposed here. They have been applied to the study of a series of electron systems that include the Be isoelectronic atomic series (Be through O^{4+}) in a Clementi's Double-Zeta basis and the LiH, Li_2 , BeH_2 , BH, CH_4 , NH_3 , H_2O , and HF molecules in their singlet ground states, at their experimental geometries and with both the STO-3G and the 6-31G orbital basis. The PSI3 program [50] has been used to calculate the integrals matrix ${}^0\mathbf{H}$, the orthonormal MOs and the initial values, at the HF level of approximation, of all the matrices required for the iterative GHV process.

4.1. RENDERING THE ITERATION TIME PROPORTIONAL TO K^6 AND THE MEMORY STORAGE TO K^4

As previously mentioned, the present version of our computational code implements Eq. (16) in the form which explicitly depends on the RDMs. To render the construction time of the r.h.s. of this equation proportional to K^6 we have followed a well-known approach termed as sum factorization, which consists in subdividing a nest of x loops into several nests of y loops with $y < x$ (e.g., see Refs. [40, 51–53]). The most time-consuming part of the process is to calculate the terms of the type

$${}^0H_{rs;pm} {}^3D_{ipj;rst} \quad (26)$$

where a triple sum, over the $\{r, s, p\}$ indices has to be performed for every $\{i, j, m, l\}$. Hence, the time of each iteration is proportional to K^7 , and the memory storage computational scaling is proportional to K^6 corresponding to the six indices of the largest matrix to be stored.

To explain how the time for calculating this type of terms may be rendered proportional to K^6 , let us first consider how a 3-RDM element is approximated in our approach:

$$\begin{aligned} 3! {}^3D_{ijk;pqr} &= -2\hat{A}' ({}^1D_{i;p} {}^1D_{j;q} {}^1D_{k;r}) \\ &\quad + 2!\hat{A}'' ({}^1D_{i;p} {}^2D_{jk;qr} + {}^1D_{j;q} {}^2D_{ik;pr} + {}^1D_{k;r} {}^2D_{ij;pq}) \\ &\quad + 3! {}^3\Delta_{ijk;pqr} \end{aligned} \quad (27)$$

where \hat{A}' antisymmetrizes the column indices of the three 1-RDM involved and \hat{A}'' antisymmetrizes the column index of the 1-RDM with the column indices of the 2-RDM. The 3-order cumulant matrix ${}^3\Delta$, which in principle is unknown, appears in a moment expansion of the 3-RDM and accounts for the statistically irreducible three-body correlation effects [54–56].

For the study here reported, the 3-order cumulant matrix has been approximated with a modified version of Nakatsuji-Yasuda's algorithm [57] which may be written as:

$$\begin{aligned} {}^3\Delta_{ijk;pq\bar{r}} &\approx \hat{A}''' {}^2\Delta_{i\bar{k};p\bar{t}} ({}^1D_{t;\bar{t}}^{(*)} - {}^1\bar{D}_{t;\bar{t}}^{(*)}) {}^2\Delta_{\bar{j};q\bar{r}} \\ {}^3\Delta_{i\bar{j};k;pq\bar{r}} &\approx \hat{A}''' {}^2\Delta_{i\bar{j};t\bar{q}} ({}^1D_{t;t}^{(*)} - {}^1\bar{D}_{t;t}^{(*)}) {}^2\Delta_{t\bar{k};p\bar{r}} \end{aligned} \quad (28)$$

where \hat{A}''' is the antisymmetrizer operator, ${}^1D^{(*)}$ and ${}^1\bar{D}^{(*)}$ are the 1-RDM and the 1-HRDM corresponding to a Hartree-Fock reference calculation,

the indices label spin-orbitals and the bar over an index indicates that the spin-orbital has a β spin. The matrix ${}^2\mathbf{\Delta}$ is the 2-order cumulant of a moment expansion of the 2-RDM related to the 2-CM as follows:

$${}^2\Delta_{ij;ml} = -{}^1D_{j;m} {}^1\bar{D}_{i;l} + \langle \Psi | {}^1\hat{\Gamma}_{i;m} \hat{Q} {}^1\hat{\Gamma}_{j;l} | \Psi \rangle \quad (29)$$

The remaining elements of ${}^3\mathbf{\Delta}$ are set to zero. We apply a simplified version of Nakatsuji's formula because we have noticed that the only antisymmetrization which must be performed is that involving $\alpha\beta$ spin-orbitals pairs. Note that this ${}^3\mathbf{\Delta}$ approximation only performs well when a single Slater determinant is a good zero-order approximation to the state considered [48].

When replacing in (26) the construction algorithm for the 3-RDM elements, the structure of this simple term is transformed into a sum of terms which are themselves formed by a triple or quadruple product of matrix elements. Thus,

$$\begin{aligned} {}^0H_{rs;pm} {}^3D_{ipj;rst} &= {}^0H_{rs;pm} (-2\hat{A}' {}^1D_{i;r} {}^1D_{p;s} {}^1D_{j;l} \\ &+ 2!\hat{A}'' ({}^1D_{i;r} {}^2D_{pj;sl} + {}^1D_{p;s} {}^2D_{ij;rl} + {}^1D_{j;l} {}^2D_{ip;rs}) \\ &+ 3!\hat{A}''' {}^2\Delta_{ik;pt} ({}^1D_{t;t}^{(*)} - {}^1\bar{D}_{t;t}^{(*)}) {}^2\Delta_{jt;qr} \end{aligned} \quad (30)$$

As an example, let us just consider three of the elementary products occurring in this expression:

- The first elementary product is given by:

$${}^2T_{ij;ml} = \sum_{r,s,p} {}^0H_{rs;pm} {}^1D_{i;l} {}^1D_{p;r} {}^1D_{j;s} \quad (31)$$

We will decompose this sum as

$$\begin{aligned} {}^2T_{ij;ml} &= \left[\sum_s \left[\sum_{r,p} {}^0H_{rs;pm} {}^1D_{p;r} \right] {}^1D_{j;s} \right] {}^1D_{i;l} \\ &\equiv \left[\sum_s {}^1X_{s;m} {}^1D_{j;s} \right] {}^1D_{i;l} \equiv {}^1Y_{j;m} {}^1D_{i;l} \end{aligned} \quad (32)$$

where the common summation indices have been highlighted. The calculations have been performed starting from the inner brackets outwards, and the auxiliary matrices perform the following types of operations:

$$\begin{aligned} {}^0H_{rs;pm} {}^1D_{p;r} &= {}^1X_{s;m} \\ {}^1X_{s;m} {}^1D_{j;s} &= {}^1Y_{j;m} \\ {}^1Y_{j;m} {}^1D_{i;l} &= {}^2T_{ij;ml} \end{aligned}$$

where 1X and 1Y represent auxiliary first-order matrices.

- The second elementary product is given by:

$${}^2R_{ij;ml} = \sum_{r,s,p} {}^0H_{rs;pm} {}^2D_{ip;sl} {}^1D_{j;r} \quad (33)$$

It can be calculated as follows

$$\begin{aligned} {}^2R_{ij;ml} &= \sum_r \left[\sum_{s,p} {}^0H_{rs;pm} {}^2D_{ip;sl} \right] {}^1D_{j;r} \\ &\equiv \sum_r {}^2X_{ri;ml} {}^1D_{j;r} \end{aligned} \quad (34)$$

where the auxiliary matrix needed is deduced in a similar way as in the previous example.

- The third elementary product is given by:

$${}^2P_{ij;ml} = \sum_{r,s,p} {}^0H_{rs;pm} {}^2\Delta_{ij;st} ({}^1D_{t;t}^{(*)} - {}^1\bar{D}_{t;t}^{(*)}) {}^2\Delta_{pt;rl} \quad (35)$$

It can be calculated as follows

$$\begin{aligned} {}^2P_{ij;ml} &= \sum_{s,u} \left[\sum_t {}^2\Delta_{ij;st} {}^1J_{t;u} \right] \\ &\times \left[\sum_{r,p} {}^0H_{rs;pm} {}^2\Delta_{pu;rl} \right] \equiv \sum_{s,u} {}^2Y_{ij;su} {}^2Z_{su;ml} \end{aligned} \quad (36)$$

where the auxiliary matrix 1J is given by

$${}^1J_{t;u} = \delta_{t;u} ({}^1D_{t;t}^{(*)} - {}^1\bar{D}_{t;t}^{(*)}) \quad (37)$$

When analyzing these three examples, it is clear that many different topologies or patterns can occur. Consequently, a high number of different auxiliary matrices are needed in order to partition the multiple sums of products involved in the process. Nevertheless, this classification and partitioning permit a significant improvement in the code computational rate, as may be appreciated in Table I. Instead of giving absolute values of computer time, which may be strongly dependent on hardware facilities, the table presents the quotient $(t(K^7)/t(K^6))$ of computer

TABLE I
Comparison of K^7 and K^6 GHV computational algorithms: time relations.

System	Basis set (K)	$t(K^7)/t(K^6)$
Be	DZ-CLEMENTI (4)	0.53
LiH	STO-3G (6)	0.59
H ₂ O	STO-3G (7)	0.61
CH ₄	STO-3G (9)	0.84
Li ₂	STO-3G (10)	1.61
HF	6-31G (11)	2.22
H ₂ O	6-31G (13)	3.28
NH ₃	6-31G (15)	5.33
CH ₄	6-31G (17)	6.95

time spent per iteration. Note that the improvement increases with the size of the basis set. It should also be remarked that the 3-order matrices do not explicitly appear. The largest matrices to be stored are all of the 2-order type. Because their elements are labeled by four spin-orbital indices, the storage requirements grow as the fourth power of the basis set size, K^4 .

4.2. ACCELERATING THE CONVERGENCE: THE FEHLBERG'S ALGORITHM

To obtain an optimized 2-RDM, the differential Eq. (22) must be integrated. It provides the information on how the elements of the 2-RDM evolve with λ . It is a matrix-functional named \mathbf{g} for the sake of brevity, of the λ parameter and of the 2-RDM elements.

For the numerical integration, the single configuration HF calculation has been used as the starting point. A new 2-RDM element is obtained for a finite, although small, variation of the λ parameter. The increase of the parameter represents a step. The process continues until the energy, which is the result of the contraction of the 2-RDM with the integrals matrix ${}^0\mathbf{H}$, reaches a minimum. In this study, instead of the simple Euler's method or any of its modifications based on dividing the integration interval in a number of steps with fixed lengths, a variable step method has been used. This type of methods compare two different approaches for a given step. If the difference is less than a given threshold, the function behaves smoothly for that value of the variable and the step can be safely enlarged, thus reducing the total number of steps. On the contrary, if the difference is larger than the threshold, it means that it is safer to reduce the step-length.

In Fehlberg's method [46, 47], three calculations for every matrix element are involved at the n -th step, that is, for the value λ_n of the integration variable which is modified by the step-length δ .

$$X_{ij;lm} = \mathbf{g}_{ij;lm}(\lambda_n, {}^2\mathbf{D}^{(n)})$$

$$Y_{ij;lm} = \mathbf{g}_{ij;lm}(\lambda_n + \delta, {}^2\mathbf{D}^{(n)} + \delta \mathbf{X})$$

$$Z_{ij;lm} = \mathbf{g}_{ij;lm}\left(\lambda_n + \frac{\delta}{2}, {}^2\mathbf{D}^{(n)} + \frac{\delta}{4}(\mathbf{X} + \mathbf{Y})\right)$$

Two new approximated values of the 2-RDM element are then calculated.

$$({}^2\mathbf{D}_{ij;lm}^{(n)})' = {}^2\mathbf{D}_{ij;lm}^{(n)} + \frac{\delta}{2}(\mathbf{X}_{ij;lm} + \mathbf{Y}_{ij;lm})$$

$$({}^2\mathbf{D}_{ij;lm}^{(n)})'' = {}^2\mathbf{D}_{ij;lm}^{(n)} + \frac{\delta}{6}(\mathbf{X}_{ij;lm} + \mathbf{Y}_{ij;lm} + 4\mathbf{Z}_{ij;lm})$$

The largest value of those differences for all the elements of the matrix is used to select the length of the next step in the numerical integration process.

$$r = \max_{i,j,l,m} \frac{1}{\delta} |({}^2\mathbf{D}_{ij;lm}^{(n)})'' - ({}^2\mathbf{D}_{ij;lm}^{(n)})'|$$

If $r > \varepsilon$, where ε is a preselected threshold, the step should be recalculated with a shorter step-length

$$\delta' = 0.9 \sqrt{\frac{\varepsilon}{r}} \delta$$

The factor 0.9 is included for safety reasons to avoid divergencies. If $r < \varepsilon$ the procedure goes to the next step taking the pair $(\lambda_n + \delta, ({}^2\mathbf{D}_{ij;lm}^{(n)})'')$ as the starting point and a step-length of $\delta' = 0.9 \sqrt{\frac{\varepsilon}{r}} \delta$. The process continues until a stopping criterion has been reached.

The use of the Fehlberg's variable-step integration method drastically reduces the required number of steps and the computer time. As an example, in Figure 1 we report the resulting energies of the iterative process as a function of the transformation parameter λ for the Be-atom ground state calculation in Clementi's Double Zeta basis set. Both HF and FCI results are also included for reference. To avoid overcrowding of circles, only one in every forty steps has been depicted. The filled circles indicate the progress of the integration under Fehlberg's variable-step method. The Euler's fixed-step method of integration is equivalent to the iterative solution of Eq. (19). As can be seen, the GHV method recovers 100.00% of the correlation energy by converging to

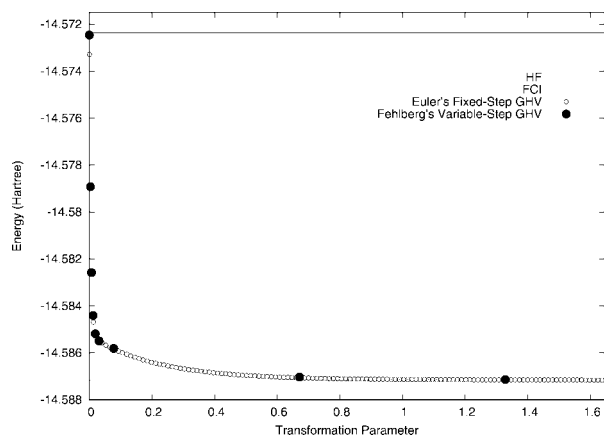


FIGURE 1. Convergence acceleration with variable-step integration method: Be-atom ground state.

$0.6 \mu E_h$ from the FCI energy. The introduction of the continuous parameter λ has allowed us to use the more efficient variable-step methods.

5. Assessing the Exactness and Competitiveness of the Method

5.1. ASSESSING THE EXACTNESS OF THE RESULTS OBTAINED IN A SET OF CALCULATIONS

Because the GHV equation which is solved is an approximated one,—the constructing algorithm given in Eq. (28) for the 3-RDM is not an exact one—different stopping criteria for the iterative process lead to slightly different results. Two possibilities have been analyzed: extending the numerical integration of the system of differential equations in λ until either (i) the error of the 1-CSE or (ii) the error of the GHV ceases to decrease. The results obtained with both criteria are presented in Table II for a series of molecules in the minimal STO-3G basis. These results show that, similarly to the ACSE case [38–40], the use of the convergence of the 1-CSE leads almost in every case, to the recovery of the 100% of the correlation energy; whereas the criterion of the convergence in the GHV equation slightly overruns the FCI results. In this respect, it may be worth mentioning that the most significant difference was found in the calculation of the Li_2 molecule in a STO-3G basis. In this GHV calculation, when the 1-CSE stopping criterion is applied, a 97.7% of the correlation energy is recovered while, when convergence of the GHV equation is used as stopping criterion, the recovered correlation energy is 100.8%. Similar results have

been obtained for the Be isoelectronic atomic series in a Clementi's Double-Zeta. Thus, the recovered correlation energy by this method has been in every case close to 100%, equating in quality the FCI calculation by converging to at most $2.13 \mu E_h$ from the FCI energy when the 1-CSE stopping criterion is applied. Hence, from now on only the results obtained with the convergence of the 1-CSE will be reported.

As an additional control on the exactness of the results obtained, the r. m. s. deviations from FCI results have been calculated for a few relevant matrices: the 1- and 2-HV matrices, which must vanish for an exact solution, and the 1-CSE and GHV errors, which should decrease as the iterative process approaches the exact solution. This analysis has been carried out on the studied molecules in the minimal STO-3G and also in a larger 6-31G basis on those molecular systems with the largest energy deviations from FCI. As can be appreciated from Table III the deviations in all those matrices are negligible. The largest deviation is of the order of 10^{-3} . Moreover, it must be noted that there is no significant effect due to the basis set.

The deviations of the resulting 2-order matrices from N- and S-representability [58, 59] have also been calculated. The D- and Q-conditions indicate that the 2-RDM and the 2-HRDM must be Hermitian and positive semi-definite. Their lowest eigenvalues provide a measure of the fulfillment of those conditions. The relevant eigenvalues for selected molecular systems are collected in Table IV. In the 2-RDM and the 2-HRDM case, which should be positive semi-definite matrices, their respective lowest eigenvalues are slightly negative. The N- and S-representability of the G -particle-hole matrix

TABLE II Percentage of the correlation energy recovered by the solution of the GHV equation.

System	GHV	1-CSE
LiH	100.2	100.0
Li_2	100.8	97.7
BeH_2	100.5	99.3
BH	100.7	99.9
CH_4	100.1	100.0
NH_3	100.1	100.1
H_2O	100.7	100.3
HF	100.1	100.1

Convergence of GHV and 1-CSE as stopping criterion. Basis set: STO-3G.

TABLE III
Root mean square deviations on various quantities from their exact (FCI) counterparts.

System	Basis set	1-HV	1-CSE	2-HV	GHV
LiH	STO-3G	$8.637 \cdot 10^{-6}$	$2.587 \cdot 10^{-5}$	$1.664 \cdot 10^{-4}$	$1.666 \cdot 10^{-5}$
Li ₂	STO-3G	$8.088 \cdot 10^{-5}$	$5.394 \cdot 10^{-4}$	$1.300 \cdot 10^{-4}$	$1.526 \cdot 10^{-4}$
BeH ₂	STO-3G	$4.296 \cdot 10^{-5}$	$3.987 \cdot 10^{-5}$	$2.347 \cdot 10^{-4}$	$7.359 \cdot 10^{-5}$
BH	STO-3G	$1.725 \cdot 10^{-4}$	$9.191 \cdot 10^{-4}$	$5.722 \cdot 10^{-4}$	$3.058 \cdot 10^{-4}$
CH ₄	STO-3G	$3.552 \cdot 10^{-5}$	$6.185 \cdot 10^{-5}$	$9.721 \cdot 10^{-5}$	$3.507 \cdot 10^{-5}$
	6-31G	$4.645 \cdot 10^{-4}$	$3.393 \cdot 10^{-4}$	$3.141 \cdot 10^{-5}$	$4.869 \cdot 10^{-5}$
NH ₃	STO-3G	$2.497 \cdot 10^{-5}$	$1.269 \cdot 10^{-4}$	$1.393 \cdot 10^{-4}$	$4.996 \cdot 10^{-5}$
	6-31G	$4.999 \cdot 10^{-5}$	$5.856 \cdot 10^{-4}$	$4.750 \cdot 10^{-5}$	$7.969 \cdot 10^{-5}$
H ₂ O	STO-3G	$4.477 \cdot 10^{-5}$	$1.762 \cdot 10^{-4}$	$2.283 \cdot 10^{-4}$	$6.943 \cdot 10^{-5}$
	6-31G	$6.890 \cdot 10^{-5}$	$8.805 \cdot 10^{-4}$	$7.431 \cdot 10^{-5}$	$1.286 \cdot 10^{-4}$
HF	STO-3G	$8.132 \cdot 10^{-6}$	$3.547 \cdot 10^{-5}$	$1.042 \cdot 10^{-4}$	$1.532 \cdot 10^{-5}$
	6-31G	$1.874 \cdot 10^{-4}$	$1.101 \cdot 10^{-3}$	$1.288 \cdot 10^{-4}$	$1.965 \cdot 10^{-4}$

is assessed by inspecting the order of the positive/negative error of the lowest/highest eigenvalue of the ${}_{(0,0)}\mathbf{G}/{}_{(1,0)}\mathbf{G}$ matrices. These two matrices respectively collect the contributions of the singlet/triplet Ψ' states shown in formula (5). As can be appreciated, in the *G*-particle-hole case these *N*- and *S*-representability errors are also negligible. Although we do not report it here, the consistency of the contraction into the 1-body space of the 2-RDM, the 2-HRDM and the *G*-particle-hole matrix has also been verified.

5.2. COMPARING THE PERFORMANCE OF SEVERAL AB INITIO METHODS

The results reported in the previous paragraph are mainly focused on verifying the intrinsic goodness and consistency of the method. Let us now compare the effectiveness of the GHV method with that of other standard ab initio ones.

As has been previously mentioned, the ${}^3\Delta$ approximations — available at present — are very accurate when the zero-order function describing the state considered is a single Slater determinant. Therefore,

the methods whose performance is compared here with the GHV one are MP2, SDCI, and CCSD, which consider the same zero-order function. All the energy values obtained with these methods are given in Table V together with those obtained with FCI. Both the STO-3G and the 6-31G basis set have been used. The percentage of correlation energy recovered with the GHV method is in every case very close to 100%.

These results clearly show that the accuracy of the GHV method is as good as the CCSD one and performs better than the MP2 and SDCI. This is a highly satisfactory situation since the GHV method has had less than two years to be developed; while the other ab initio methods considered here have benefited from many decades of experience. On the other hand, similarly to the (single-reference) ACSE algorithm [40], the present GHV implementation is not as efficient as the CCSD one, as the latter scales in floating-point operations as $K_o^2 K_e^4 + K_e^2 K_o^4$, where K_o and K_e are the number of occupied and empty orbitals in the Hartree–Fock reference wavefunction respectively. However, it can be expected that the GHV can still be developed and optimized much further.

TABLE IV
***N*- and *S*-representability deviations of 2-order matrices.**

System	2-RDM	2-HRDM	${}_{(0,0)}\mathbf{G}$	${}_{(1,0)}\mathbf{G}$
CH ₄	$-8.062 \cdot 10^{-5}$	$-8.413 \cdot 10^{-7}$	$-5.216 \cdot 10^{-4}$	$8.722 \cdot 10^{-6}$
NH ₃	$-6.831 \cdot 10^{-5}$	$-2.387 \cdot 10^{-6}$	$-6.291 \cdot 10^{-4}$	$1.070 \cdot 10^{-5}$
H ₂ O	$-5.197 \cdot 10^{-5}$	$-1.931 \cdot 10^{-5}$	$-5.638 \cdot 10^{-4}$	$1.223 \cdot 10^{-5}$
HF	$-3.111 \cdot 10^{-5}$	$-2.030 \cdot 10^{-5}$	$-4.273 \cdot 10^{-4}$	$1.455 \cdot 10^{-5}$

Basis set: 6-31G.

TABLE V

Comparison of the effectiveness of the GHV method with that of other standard ab initio ones: calculated energies in E_h units.

System	Basis set	HF	MP2	SDCI	CCSD	FCI	GHV
LiH	STO-3G	-7.862002	-7.874872	-7.882378	-7.882381	-7.882392	-7.882393
Li ₂	STO-3G	-14.638725	-14.655475	-14.667231	-14.667260	-14.667340	-14.666670
BeH ₂	STO-3G	-15.559405	-15.582893	-15.594081	-15.594456	-15.594861	-15.594607
BH	STO-3G	-24.752780	-24.782280	-24.808145	-24.809787	-24.809945	-24.809907
CH ₄	STO-3G	-39.726464	-39.783441	-39.803681	-39.806177	-39.806417	-39.806406
	6-31G	-40.180175	-40.294875	-40.280393	-40.299529	-40.301469	-40.301298
NH ₃	STO-3G	-55.454087	-55.501307	-55.517613	-55.519005	-55.519219	-55.519284
	6-31G	-56.161021	-56.285483	-56.277981	-56.290705	-56.292571	-56.293085
H ₂ O	STO-3G	-74.963023	-74.998569	-75.011873	-75.012462	-75.012578	-75.012734
	6-31G	-75.983974	-76.114086	-76.112825	-76.119354	-76.120874	-76.122028
HF	STO-3G	-98.570758	-98.588093	-98.596587	-98.596587	-98.596587	-98.596614
	6-31G	-99.983407	-100.110393	-100.112091	-100.114644	-100.115685	-100.116885

From a theoretical point of view, it should be emphasized that the results reported here confirm that a study of the electronic structure of a many-electron system may be competitively carried out by directly determining a 2-body correlation matrix, or, equivalently, the G-particle-hole matrix, without a previous determination of the state wave function.

5.3. FURTHER POSSIBLE OPTIMIZATION AND EXTENSION OF THE GHV METHODOLOGY

Besides a still possible optimization of the code, we expect that significant progress can still be achieved in the theoretical and applicative aspects related to this methodology. In this paragraph, we will briefly consider those aspects of the GHV method which are at present under study.

- Some small N- and S-representability deviations of the 2-RDM and G-particle-hole matrices occur during the iterative process. This could be avoided by inserting N- and S-purification procedures [58, 59] aimed at correcting these deviations at every iteration.
- Another relevant question is whether the accuracy of the present approximating ${}^3\Delta$, or, equivalently, the 3-CM algorithms may be improved. Thus, when the zero-order state considered is a multiconfigurational one, the accuracy of the approximated ${}^3\Delta$ elements, when compared with the FCI corresponding values, is rather poor. In spite of this, it should be mentioned that, in some multi-configurational cases, the

results obtained with these “poor” algorithms were reasonable, which is probably due to error cancelations. At any rate it is clear that further research is needed on this question.

Let us conclude by saying that, in our opinion, the GHV is an excellent and competitive ab initio method whose range of application may, however, still be enlarged. We are at present investigating how to extend the GHV method usefulness to the study of larger systems by incorporating the simplifications which these systems’ symmetry properties afford. The use of core potentials and model Hamiltonians are also being considered.

References

1. Alcoba, D. R. *Phys Rev A* 2002, 65, 032519.
2. Valdemoro, C.; Alcoba, D. R.; Tel, L. M.; Pérez-Romero, E. Sixth International Congress of the International Society for Theoretical Chemical Physics; Vancouver: Canada, 2008.
3. Alcoba, D. R.; Valdemoro, C.; Tel, L. M.; Pérez-Romero, E. *Int J Quantum Chem* 2009, 109, 3178.
4. Valdemoro, C.; Alcoba, D.M.R.; Tel, L. M.; Pérez-Romero, E. *Int J Quantum Chem* 2009, 109, 2622.
5. Husimi, K. *Proc Soc Japan* 1940, 22, 264.
6. Löwdin, P. O. *Phys Rev* 1955, 97, 1474.
7. Coleman, A. J. *Rev Mod Phys* 1963, 35, 668.
8. Garrod, C.; Percus, J. K. *J Math Phys* 1964, 5, 1756.
9. Davidson, E. R. *Reduced Density Matrices in Quantum Chemistry*, Academic Press: New York, 1976.
10. Coleman, A. J.; Yukalov, V. I. *Reduced Density Matrices: Coulson’s Challenge*. Springer Verlag: New York, 2000.

11. Coleman, A. J.; Erdahl, R. M., Eds. *Reduced Density Matrices with Applications to Physical and Chemical Systems*. Queen's Papers on Pure and Applied Mathematics, N.11; Queen's University; Kingston, Ontario, 1968.
12. Erdahl, R. M., Ed. *Reduced Density Matrices with Applications to Physical and Chemical Systems II*. Queen's Papers on Pure and Applied Mathematics, N.40; Queen's University; Kingston, Ontario, 1974.
13. Erdahl, R.; Smith, V., Eds. *Density Matrices and Density Functionals*, Proceedings of the A. J. Coleman Symposium; Kingston, Ontario, 1985, Reidel: Dordrecht, 1987.
14. Cioslowsky, J., Ed. *Many electron Densities and Reduced Density Matrices*; Kluwer: Boston, 2000.
15. Mazziotti, D. A., Ed. *Reduced Density Matrix Mechanics with Applications to Many-Electron Atoms and Molecules*; Wiley: New York, 2007; *Adv Chem Phys* 134.
16. Nakatsuji, H. *Phys Rev A* 1976, 14, 41.
17. Cohen, L.; Frishberg, C. *Phys Rev A* 1976, 13, 927.
18. Valdemoro, C. In *Density Matrices and Density Functionals*, Erdahl, R.; Smith, V., Eds. Reidel: Dordrecht, 1987, Proceedings of the A. J. Coleman Symposium; Kingston, Ontario, 1985, p 275.
19. Valdemoro, C. *An R Soc Esp Fís* 1983, 79, 106.
20. Valdemoro, C. *Phys Rev A* 1985, 31, 2114.
21. Mazziotti, D. A. *Phys Rev A* 1998, 57, 4219.
22. Colmenero, F.; Pérez del Valle, C.; Valdemoro, C. *Phys Rev A* 1994, 47, 971.
23. Colmenero, F.; Valdemoro, C. *Int J Quantum Chem* 1994, 51, 369.
24. Valdemoro, C.; Tel, L. M.; Pérez-Romero, E. *Adv Quantum Chem* 1997 28, 33.
25. Hirschfelder, J. O. *J Chem Phys* 1960, 33, 1462.
26. Hirschfelder, J. O.; Epstein, S. T. *Phys Rev* 1961, 123, 1495.
27. Hirschfelder, J. O.; Coulson, C. A. *J Chem Phys* 1962, 36, 941.
28. Rosina, M.; Percus, J. K.; Kijewski, L. J.; Garrod, C. *J Math Phys* 1969, 10, 1761.
29. Kijewski, L. J.; Percus, J. K. *Phys Rev* 1969, 179, 45.
30. Erdahl, R. M. *Int J Quantum Chem* 1978, 13, 697.
31. Harriman, J. E. *Phys Rev A* 1979, 19, 1893.
32. Harriman, J. E. *Phys Rev A* 1984, 30, 19.
33. Fernández, F. M.; Castro, E. A. *Hypervirial Theorems.*, Lecture Notes in Chemistry Series 43: Berthier, G.; Dewar, M. J. S.; Fischer, H.; Fukui, K.; Hall, G. G.; Hinze, J.; Jaffé, H. H.; Jortner, J.; Kutzelnigg, W.; Ruedenberg, K.; Tomasi, J., Eds.; Springer Verlag: Heidelberg, 1987; and references therein.
34. Valdemoro, C.; de Lara-Castells, M. P.; Pérez-Romero, E.; Tel, L. M. *Adv Quantum Chem* 1999, 31, 37.
35. Tel, L. M.; Pérez-Romero, E.; Valdemoro, C.; Casquero, F. J. *Int J Quantum Chem* 2001, 82, 131.
36. Alcoba, D. R.; Casquero, F. J.; Tel, L. M.; Pérez-Romero, E.; Valdemoro, C. *Int J Quantum Chem* 2005, 102, 620.
37. Valdemoro, C.; Tel, L. M.; Pérez-Romero, E.; Alcoba, D. R. *Int J Quantum Chem* 2008, 108, 1090.
38. Mazziotti, D. A. *Phys Rev Lett* 2006, 97, 143002.
39. Mazziotti, D. A. *Phys Rev A* 2007, 75, 022505.
40. Mazziotti, D. A. *J Chem Phys* 2007, 126, 184101.
41. Valdemoro, C.; Tel, L. M.; Alcoba, D. R.; Pérez-Romero, E. *Theor Chem Acc* 2007, 118, 503.
42. Mazziotti, D. A. *Phys Rev A* 2007, 76, 052502.
43. Mazziotti, D. A. *J Phys Chem A* 2008, 112, 13684.
44. Valdemoro, C.; Alcoba, D. R.; Tel, L. M.; Pérez-Romero, E. *Progr Theor Chem Phys* 2008, 18, 175.
45. Foley, J. J. IV; Rothman, A. E.; Mazziotti, D. A. *J Chem Phys* 2009, 130, 184112.
46. Fehlbberg, E. NASA Technical Report 1968, R287.
47. Fehlbberg, E. NASA Technical Report 1969, R315.
48. Valdemoro, C.; Tel, L. M.; Pérez-Romero, E. In *Many-Electron Densities and Reduced Density Matrices*; Cioslowski, J., Ed.; Kluwer: Dordrecht, 2000; p 17.
49. Valdemoro, C.; Tel, L. M.; Alcoba, D. R.; Pérez-Romero, E.; Casquero, F. J. *Int J Quantum Chem* 2002, 90, 1555.
50. Crawford, T. D.; Sherrill, C. D.; Valeev, E. F.; Fermann, J. T.; King, R. A.; Leininger, M. L.; Brown, S. T.; Janssen, C. L.; Seidl, E. T.; Kenny, J. P.; Allen, W. D. *J Com Chem* 2007, 28, 1610.
51. McLean, A. D. In *Proceedings of the Conference on Potential Energy Surfaces in Chemistry*: Lester, W. A., Jr., Ed.; IBM San Jose, 1971; p 87.
52. Shavitt, I. In *Methods of Electronic Structure Theory*; Schaefer, H. F. III, Ed.; Plenum: New York, 1977; p 189.
53. Mazziotti, D. A. *J Chem Phys* 2002, 116, 1239.
54. Kubo, R. *J Phys Soc Jpn* 1962, 17, 1100.
55. Mazziotti, D. A. *Chem Phys Lett* 1998, 289, 419.
56. Mazziotti, D. A. *Int J Quantum Chem* 1998, 70, 557.
57. Nakatsuji, H.; Yasuda, K. *Phys Rev Letts* 1996, 76, 1039.
58. Alcoba, D. R.; Valdemoro, C. *Int J Quantum Chem* 2005, 102, 629. *ibid* 2006, 106, 2999.
59. Alcoba, D. R.; Valdemoro, C.; Tel, L. M.; Pérez-Romero, E. *Phys Rev A* 2008, 77, 042508.