Optimized Solution Procedure of the *G*-Particle−Hole Hypervirial Equation for Multiplets: Application to Doublet and Triplet States

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ABSTRACT: Highly accurate descriptions of the correlated electronic structure of atoms and molecules in singlet states have recently been directly obtained within the framework of the *G*-particle−hole hypervirial (GHV) equation method, without any reference to the wave function. Here, the GHV method is optimized and applied to the direct study of doublet and triplet atomic and molecular states. A new set of spin-representability conditions for triplet states has been derived and is also reported here. The results obtained with this optimized version of the GHV method are compared with those yielded by several standard wave function methods. This analysis shows that the GHV energies are more accurate than those obtained with a single−double excitation configuration interaction as well as with a coupled-cluster singles and doubles treatment. Moreover, the resulting 2-body matrices closely satisfy a set of stringent *N*- and spin-representability conditions.

$$\langle\Phi|\,[\,{}^2\hat{G}_{im;lj},\ \hat{H}\,]\,|\Phi\rangle\ =\ 0 \qquad \forall,i,j,l,m$$

$${}^2\hat{G}_{im;lj}:\ \text{elements of the }G\text{-particle-hole operator}$$

I. INTRODUCTION

Since all the fundamental electronic properties including the energy can be expressed as expectation values of one- and two-electron operators, they can be determined from a mathematical object which only depends on the variables of two electrons, the second-order reduced density matrix (2-RDM).[5−9] The quest for a method of studying the structure of electronic systems by directly determining the 2-RDM without any use of the wave function dates from the fifties.[10−13] A difficulty in this approach is that the *N*-representability condition,[14,15] which collects the conditions imposed by the *N*-fermion antisymmetry properties upon the RDMs, is still not completely known.[5−9,16] This problem has greatly hindered the progress on the field. However, in the search for a method of solving the second-order contracted Schrödinger equation (2-CSE),[6−9] a set of approximated construction algorithms for the RDMs were recently devised.[2,3,17−28] These algorithms jointly with the conditions imposed by the system Hamiltonian and those *N*-representability conditions which are known, lead to a direct determination of the 2-RDM without a previous computation of the wave function.[6−9]

The 2-CSE was initially derived in 1976 in first quantization by Cho,[29] Cohen and Frishberg,[30] and Nakatsuji[31] and deduced later on in second quantization by Valdemoro[32] through the contraction of the matrix representation of the Schrödinger equation into the two-electron space. This equation was shown to be equivalent to the Schrödinger equation (by the necessary and sufficient condition) within the *N*-representable space of

RDMs.[31] The drawback of this very attractive equation is that it is operationally indeterminate.[33] This is due to the fact that the 2-CSE depends not only upon the 2-RDM but also upon the 3- and 4-RDMs. In 1992 Valdemoro proposed a method to approximate the 2-RDM in terms of the 1-RDM,[22] which was extended in order to approximate the 3- and 4-RDM in terms of the lower-order matrices.[23] In 1994 Colmenero and Valdemoro[17] applied these approximate constructing algorithms to avoid the indeterminacy problem and solved iteratively the 2-CSE. These authors reported also in this same paper[17] the compact as well as the explicit form of the hypervirial of the 2-electron density operator (2-HV)[17,23,32−36] which they identified with the antihermitian part of the 2-CSE and used as a mean to assess the accuracy of the results obtained with the 2-CSE. This started a successful line of work which has been mainly developed by the groups led by Valdemoro, Nakatsuji, and Mazziotti.[7,8,18−21,24−28,37−53]

A significant step forward was recently made by Mazziotti.[54,55] This author proposed an iterative method[54,55] for solving only the antihermitian part of the 2-CSE, the 2-HV, which he called the antihermitian contracted Schrödinger equation (ACSE).[54] He applied his methodology to several electronic systems obtaining excellent results.[1,27,28,53−61] The main advantages of this approach are that the ACSE does not depend on the 4-RDM and that the *N*-representability properties of the 2-RDM are practically

preserved during the iterative process. Motivated by this author's work, some of the authors of this manuscript have recently studied the properties of the hypervirial of the two-body correlation operator or, equivalently, the G-particle—hole hypervirial (GHV) equation.[1-4] The particular interest of this approach lies in that satisfying the GHV equation implies that the ACSE is also fulfilled while solving the ACSE does not guarantee that the GHV equation is also satisfied; that is, the GHV equation is a more demanding condition than the ACSE.[1,2,4]

Following the ideas reported by Kutzelnigg for the solution of the hypervirials of density operators[34,62,63] and by Mazziotti for the solution of the ACSE,[54-56] a very efficient iterative method for solving the GHV equation has been developed.[1,3,4] The accuracy of the results obtained with this method when studying singlet ground- and excited-states with weak to moderate multiconfigurational character of a set of atoms and molecules was excellent compared to the equivalent full configuration interaction (FCI) quantities.[1,3,4] The purpose of the current work is to investigate the behavior of the GHV methodology in the study of high-spin doublet and triplet states occurring in a variety of systems. It must be noted that an alternative approach for treating these systems has been reported within the framework of the ACSE.[60,61] However, this ACSE study of the multiplet states is achieved by spin coupling the open-shell molecules to one or more hydrogen atoms to form auxiliary singlet composite systems which can be solved by existing ACSE algorithms, and, to our knowledge, the direct approach for calculating multiplet states here reported has not yet been carried out.

The paper is organized as follows: In the next section the notation, definitions and general theoretical background of the GHV methodology are given. A set of new theoretical results aiming at optimizing the GHV method accuracy are described in section III. The results obtained in a set of applications of the method are reported in section IV. These calculations show that the correlation energies accounted for lie within 97.6% and 102.1% of the FCI one. It is also found that the calculated two-body matrices describing the correlation effects satisfy closely a set of N- and Spin-representability stringent conditions.[39,50,64-66] The results are compared with those obtained with traditional wave function methods such as single and double excitation configuration interaction, coupled-cluster singles-doubles, and FCI. Finally, a brief description of the conclusions of this work is given in the last section.

II. THEORETICAL OUTLINE

A. General Notation. In what follows, we will consider pairwise-interacting systems composed of fixed number of electrons, N, whose Hamiltonian may be written within second quantization formalism[67] in the occupation number representation as[9]

$$\hat{H} = \frac{1}{2}\sum_{p,q,r,s} {}^0H_{rs;pq} a_p^\dagger a_q^\dagger a_s a_r \tag{1}$$

where $a_p^\dagger$ and a_r are second quantization creation and annihilation operators, the indices refer to members of a finite basis set of $2K$ real orthonormal spin—orbitals, and the second-order matrix ${}^0H$ collects the 1- and 2-electron integrals over the basis set.

In this formalism an element of a p-RDM, ${}^P\mathbf{D}$, corresponding to a N-electron state Φ describing the system may be defined as

$$p!\,{}^P D_{i_1 i_2..i_p;j_1 j_2..j_p} = \langle\Phi| a_{i_1}^\dagger a_{i_2}^\dagger....a_{i_p}^\dagger a_{j_p}.....a_{j_2} a_{j_1}|\Phi\rangle$$

$$\equiv \langle\Phi|{}^P\hat{\Gamma}_{i_1 i_2..i_p;j_1 j_2..j_p}|\Phi\rangle \tag{2}$$

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 Φ considered.

Through the application of the fermion algebra several different, although equivalent, decompositions of a p-RDM can be obtained. Here we focus on the decomposition leading to an expression combining matrices whose labels coincide with those of the p-RDM being decomposed.[1-4,7,25,26,28,38,39,41,43-46,50,52] Let us consider the decomposition of the 2-RDM which provides the simplest example:

$$2!\,{}^2D_{ij;kl} = {}^1D_{i;k}\,{}^1D_{j;l} - \delta_{j,k}\,{}^1D_{i;l} + {}^2C_{ij;kl} \tag{3}$$

The matrix ${}^2\mathbf{C}$ is the second-order correlation matrix.[25,26,38,39,41,46,52] This matrix, which describes two-body correlation effects in the state Φ, is defined as

$$ {}^2C_{ij;kl} = \sum_{\Phi' \neq \Phi} \langle\Phi| a_i^\dagger a_k|\Phi'\rangle\langle\Phi'| a_j^\dagger a_l|\Phi\rangle$$

$$\equiv \langle\Phi| a_i^\dagger a_k \hat{P} a_j^\dagger a_l|\Phi\rangle \tag{4}$$

where $\hat{P}$ is the projection operator upon the complementary space to $|\Phi\rangle\langle\Phi|$. When the elements of the ${}^2\mathbf{C}$ matrix are ordered in such a way that the resulting matrix is a Hermitian, one has the well-known G-particle—hole matrix.[15,68] Thus

$$ {}^2C_{ij;kl} \equiv {}^2G_{ik;lj} \equiv \langle\Phi|{}^2\hat{G}_{ik;lj}|\Phi\rangle \tag{5}$$

where ${}^2\hat{G}$ is the G-particle—hole operator. Both the correlation and G-particle—hole matrices play relevant roles in RDMs theory and GHV methodology.[1,25,26,35,36,38,39,44-46,50,52,65]

B. Form of the Hypervirial Equation for the G-Particle—Hole Operator. The GHV methodology is centered on the solution of the G-particle—hole hypervirial equation, whose compact form is[1-4]

$$\langle\Phi|[{}^2\hat{G}_{im;lj}, \hat{H}]|\Phi\rangle = 0, \ \forall, i,j,l,m \tag{6}$$

When developed, this equation is a hierarchy equation, which depends not only on 2-electron matrices—such as the 2-RDM or the ${}^2\mathbf{C}$—but on the 3-RDM or the third-order correlation matrix ${}^{(3;2,1)}\mathbf{C}$ whose elements are defined as

$$ {}^{(3;2,1)}C_{tvj;rsl} = \langle\Phi| a_t^\dagger a_v^\dagger a_s a_r \hat{P} a_j^\dagger a_l|\Phi\rangle \tag{7}$$

The explicit form of the G-particle—hole hypervirial equation in term of these third-order correlation matrix elements is[1]

$$\sum_{t,v,r,s} {}^0H_{rs;tv}\,{}^{(3;2,1)}C_{tvj;rsl}\,{}^1D_{i;m} - \sum_{t,v,r,s} {}^0H_{rs;tv}\,{}^{(3;2,1)}C_{tvm;rsi}\,{}^1D_{j;l}$$

$$+ 2\sum_{t,v,r} {}^0H_{jr;tv}\,{}^{(3;2,1)}C_{lrm;tvi} + 2\sum_{t,v,r} {}^0H_{vr;tl}\,{}^{(3;2,1)}C_{vrm;jti}$$

$$+ 2\sum_{t,v,r} {}^{(3;2,1)}C_{tvj;mrl} + 2\sum_{t,v,r} {}^0H_{vr;tm}\,{}^{(3;2,1)}C_{itj;vrl} = 0 \tag{8}$$

Because of the symmetry properties which interrelate the elements of the third-order cumulant matrix,[24,69] ${}^3\Delta$, it is simpler and hence more convenient to express relation 8 in terms of this matrix.[1,3] To this aim, in our present version of the

computational code, the $^{(3;2,1)}C$ elements are replaced by the following expression:[1,3,4]

$$
\begin{aligned}
^{(3;2,1)}C_{tvj;rsl} = {}& 2\,^1D_{t;l}\,^1D_{v;s}\,^1D_{j;r} - {}^1D_{t;l}\,^1D_{v;r}\,^1D_{j;s} - {}^1D_{t;s}\,^1D_{v;l}\,^1D_{j;r} \\
& - 2\,^1D_{t;l}\,^1D_{v;s}\delta_{j;r} + {}^1D_{t;l}\delta_{v;r}\,^1D_{j;s} + {}^1D_{t;s}\,^1D_{v;l}\delta_{j;r} \\
& - {}^1D_{t;l}\delta_{v;s}\,^1D_{j;r} + {}^1D_{t;l}\,^1D_{v;r}\delta_{j;s} \\
& + {}^1D_{t;l}\delta_{v;s}\delta_{j;r} - {}^1D_{t;r}\delta_{v;r}\delta_{j;s} \\
& + {}^1D_{t;r}\,^2C_{vj;sl} + {}^1D_{v;s}\,^2C_{tj;rl} - {}^1D_{j;s}\,^2C_{tv;rl} \\
& - {}^1D_{v;l}\,^2C_{tj;rs} - {}^1D_{t;s}\,^2C_{vj;rl} - {}^1D_{v;r}\,^2C_{tj;sl} \\
& + {}^1D_{t;l}\,^2C_{vj;rs} + {}^1D_{j;r}\,^2C_{tv;sl} \\
& - \delta_{j;r}\,^2C_{tv;sl} + \delta_{j;s}\,^2C_{tv;rl} + {}^3\Delta_{tvj;rsl}
\end{aligned}
\tag{9}
$$

The next question—to construct the third-order cumulant matrix in terms of the second-order one—is analyzed in the following section.

C. Solution of the G-Particle—Hole Hypervirial Equation.

A very efficient procedure for solving the GHV equation has been developed.[1,3,4] This approach, whose general lines follow the exponential formulation of successive unitary transformations of trial functions (or RDMs) aiming at enforcing the vanishing of the hypervirials of p-electron density operators proposed by Kutzelnigg in refs 34, 62, and 63 and the continuous formulation for solving the ACSE proposed by Mazziotti in ref 54, is based on the stationary condition of the eigenstates of the Hamiltonian against unitary transformations. Thus, eq 6 implies a relation linking RDMs and correlation matrices. It is fulfilled for the exact eigenstates of the Hamiltonian.[1] But, for approximate matrices, its lhs does not vanish. It provides a measure of the deviations from those associated with an eigenstate of the Hamiltonian and gives the error of the approximation. The error diminishes as the matrices approach those of an eigenstate. A unitary operator modifies either the wave function Φ and the elements of the RDMs or, alternatively, since the G-particle—hole operator is related to Φ, the commutator of $2\hat{G}$ and $\hat{H}$. Such a unitary operator can be written as $e^{\lambda \hat{B}}$ provided that $\hat{B}$ is antihermitian. The real parameter λ expresses the extent of the transformation. The transformation operator becomes an identity as the $\hat{B}$ operator or the λ-parameter vanish.

The 2-electron density operator transforms as

$$
^2\hat{\Gamma}'_{ij;kl} = e^{\lambda \hat{B}}\,^2\hat{\Gamma}'_{ij;kl}\,e^{-\lambda \hat{B}}
$$

whereas the transformation of the G-particle—hole operator is of the form

$$
^2\hat{G}'_{im;lj} = e^{\lambda \hat{B}}\,^2\hat{G}_{il;mj}\,e^{-\lambda \hat{B}}
$$

The 2-RDM and the G-particle—hole matrix elements are transformed accordingly. The first-order variation of any of their elements

$$
\frac{d^2D_{im;lj}}{d\lambda} = \langle \Psi | [\hat{B}, {}^2\hat{\Gamma}_{ij;kl}] | \Psi \rangle_\lambda
\tag{10}
$$

$$
\frac{d^2G_{im;lj}}{d\lambda} = \langle \Psi | [\hat{B}, {}^2\hat{G}_{im;lj}] | \Psi \rangle_\lambda
\tag{11}
$$

is the expectation value of the commutator of the corresponding operator with $\hat{B}$.

Now the problem is 2-fold: Propose an adequate antihermitian $\hat{B}$ operator and find a numerical solution to the differential equation 11.

Here, the $\hat{B}$ operator has been chosen in a way similar to that used by Mazziotti[54] for solving the ACSE. Both, Mazziotti's and the relation here proposed, can be traced back at least to the work of Kutzelnigg[34] in 1979. In that paper, the author makes use of a Newton—Raphson-type method to generate a transformation leading to the vanishing of the hypervirials of the density operators.

$$
\hat{B} = \sum_{p,q,r,s} B_{pr;sq}\,^2\hat{G}_{pr;sq}
\tag{12}
$$

where the coefficients

$$
B_{pr;sq} = \langle \Psi | {}^2\hat{G}_{pr;sq}, \hat{H} | \Psi \rangle
\tag{13}
$$

In that way the $\hat{B}$ operator is antihermitian by construction. The coefficients $B_{pr;sq}$ become smaller as residual in GHV equation, the lhs of eq 6, vanishes, and the unitary transformation $e^{\lambda \hat{B}}$ becomes an identity one.

As has been discussed,[1] this exponent of the transformation operator can be considered to represent an effective or mean G-particle—hole hypervirial operator since it includes an operational trace over one electron variable. This approximation constitutes a very powerful operative procedure which renders feasible the calculations in terms only of 3-order and lower-order matrices while preserving the essence of the theory and causing the enforcement of the GHV stationary condition.

Although the $\hat{B}$ operator has been calculated in the form described above, in order to take advantage of the antisymmetry properties under permutation of indices of the RDMs, eq 10 has been preferred over eq 11 for the numerical solution. At this point, it must be noted that Mazziotti's continuous formulation proposed in ref 54 differs from the one reported here, as it uses a different algorithm than the one given by eqs 12 and 13.

For the integration of the differential equation eq 10 an adaptive variable step method due to Fehlberg[70] has been used.[3] The integration of the differential equation is carried out until either the least-squares error of the GHV equation, or the least-squares error of its contraction into the 1-electron space, the first-order contracted Schrödinger equation,[32,38] ceases to decrease.[1,3]

The computational efficiency of the GHV method has recently been significantly enhanced through the use of sum factorization and matrix—matrix multiplication at computational costs of K^6 in floating point operations and K^4 in storage, where K is the number of orbitals forming the basis set.[3] For the sake of comparison, MP2, CCSD, and CCSD(T) methods scale in floating point operations as K^5, K^6, and K^7, respectively. At present, solving the GHV equations is slower than solving the CCSD ones because the present CCSD codes only compute excitations from a single-reference wave function which lowers the computational cost.

III. NEW THEORETICAL RESULTS AND SPIN-REPRESENTABILITY CONDITIONS

Recently we have realized that the performance of the construction algorithms for the third-order cumulants, $^3\Delta$, used previously for studying singlet states was not sufficiently accurate for doublet and triplet states. This motivated our search for an improved version of these algorithms which would prove adequate in the treatment of high spin-multiplicity states. This set of new constructing algorithms is reported here. Another new theoretical result presented in this section concerns the explicit expression of the spin-representability conditions that a G-particle—hole matrix corresponding to a triplet state must satisfy.

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Table 1. Energy Errors, in Units of E_h, of Various High-Spin Doublet Ground States from GHV Methodology (m-NY Algorithm) Compared with Those from Several Standard *ab Initio* Methods[a]

system	state	ROHF	SDCI	CCSD	CCSD(T)	GHV	FCI
B	^2S	1.277×10^{-2}	5.000×10^{-8}	5.000×10^{-8}	5.000×10^{-8}	-1.100×10^{-6}	-24.1143052
C^+	^2S	1.250×10^{-2}	5.000×10^{-8}	5.000×10^{-8}	5.000×10^{-8}	-1.200×10^{-6}	-36.5565514
N^{2+}	^2S	1.237×10^{-2}	5.000×10^{-8}	5.000×10^{-8}	5.000×10^{-8}	2.500×10^{-6}	-51.6147425
OH	$^2\Pi$	1.010×10^{-1}	3.494×10^{-3}	8.743×10^{-4}	3.157×10^{-4}	2.423×10^{-4}	-75.4628553
NH_2	$^2B_1$	1.050×10^{-1}	4.395×10^{-3}	1.276×10^{-3}	3.636×10^{-4}	6.196×10^{-4}	-55.6351826
CH_3	$^2A_2''$	9.925×10^{-2}	4.310×10^{-3}	1.359×10^{-3}	3.146×10^{-4}	8.675×10^{-4}	-39.6426085
CH	$^2\Pi$	6.740×10^{-2}	2.480×10^{-3}	1.078×10^{-3}	3.002×10^{-4}	7.682×10^{-4}	-38.3175616
NO	$^2\Pi$	2.386×10^{-1}	1.997×10^{-2}	7.844×10^{-3}	2.214×10^{-3}	-5.020×10^{-3}	-129.407249[b]

[a] Errors are measured relative to FCI. [b] Frozen core approximation: The two lowest doubly occupied molecular orbitals frozen.

A. Constructing Algorithms Suitable for Multiplet States. There are several suitable approaches for constructing the third-order cumulant matrices, $^3\Delta$, in terms of the second-order ones[3,18,23,25−27] when the electronic state has weak to moderate multiconfigurational character and is well approximated by a single Slater determinant. Here we report a new algorithm for approximating $^3\Delta$ when treating high-spin doublet and triplet states. This new algorithm is a modified version of the Nakatsuji-Yasuda one[18] and is here denoted as m-NY. It has the following form:

$$^3\Delta_{i\bar{j}k;pq\bar{r}} \approx \hat{\mathscr{A}} \sum_{\bar{t}} {}^2\Delta_{i\bar{k};p\bar{t}} ({}^1D_{t;t}^{(*)} - {}^1\overline{D}_{t;t}^{(*)})^2 \Delta_{\bar{j}t;q\bar{r}}$$

$$+ \hat{\mathscr{A}}' \sum_{t} {}^2\Delta_{ij;pt} ({}^1D_{t;t}^{(*)} - {}^1\overline{D}_{t;t}^{(*)})^2 \Delta_{t\bar{k};q\bar{r}}$$

$$^3\Delta_{i\bar{j}\bar{k};pq\bar{r}} \approx \hat{\mathscr{A}} \sum_{t} {}^2\Delta_{ij;t\bar{q}} ({}^1D_{t;t}^{(*)} - {}^1\overline{D}_{t;t}^{(*)})^2 \Delta_{t\bar{k};p\bar{r}}$$

$$+ \hat{\mathscr{A}}' \sum_{\bar{t}} {}^2\Delta_{\bar{j}\bar{k};t\bar{q}} ({}^1D_{t;t}^{(*)} - {}^1\overline{D}_{t;t}^{(*)})^2 \Delta_{it;p\bar{r}} \quad (14)$$

where the bar over an index indicates that the spin−orbital has a β spin, $\hat{\mathscr{A}}$ and $\hat{\mathscr{A}}'$ are antisymmetrizer operators, $^1D^{(*)}$ and $^1\overline{D}^{(*)}$ are the 1-RDM and the first-order hole RDM (1-HRDM)[14] corresponding to a Hartree−Fock reference calculation, and $^2\Delta$ is the second-order cumulant matrix,[24,69] which is related to the second-order correlation matrix as follows:[25]

$$^2\Delta_{ij;kl} = -\overline{D}_{j,k} {}^1D_{i;l} + {}^2C_{ij;kl} \quad (15)$$

The remaining elements of $^3\Delta$ are set to zero.

B. The G-Particle−Hole Matrix Spin-Representability Conditions. The G-particle−hole matrix corresponding to a state with a given S and S_z spin quantum-numbers can be decomposed[52,65] in terms of different spin components, $_{(S',S_z')}{}^2G$, resulting from the splitting of the $\hat{P}$ operator in eq 4. These spin-component matrices have to be positive, and in some cases negative, semidefinite.[65] It is important to realize that the well-known N-representability condition, which imposes that $^2\mathbf{G} \geq 0$,[15] does not necessarily imply that the necessary properties of the spin-components of the G-particle−hole matrix are satisfied.[65] In other words, the constraints imposed on the separate spin-components are far more demanding than those imposed on the whole matrix.

a. A New Set of Necessary Spin-Representability Conditions for Triplet States. From the relations reported in refs[52] and,[65] we have derived the following *necessary conditions* linking the different spin-components of the G-particle−hole matrix when the state is a triplet with $S_z = 1$

$$_{(2,2)}^{2}G_{i\bar{l};m\bar{j}} = {}^2G_{i\bar{l};m\bar{j}} \quad (16a)$$

$$_{(2,0)}^{2}G_{i\bar{l};m\bar{j}} = \frac{1}{6} {}^2G_{i\bar{l};\overline{m}j} \quad (16b)$$

$$_{(1,1)}^{2}G_{i\bar{l};m\bar{j}} = -\frac{1}{4}{}_{(2,2)}^{2}G_{i\bar{l};\overline{m}j} + {}^1D_{i;l}{}^1D_{j;m} - {}^1D_{i;m}\delta_{j;l} - 2!{}^2D_{ij;lm} \quad (16c)$$

$$_{(1,1)}^{2}G_{i\bar{l};\overline{m}j} = +\frac{1}{4}{}_{(2,2)}^{2}G_{i\bar{l};\overline{m}j} - {}_{(2,2)}^{2}G_{jl;\overline{m}i} + {}^1\overline{D}_{i;l}{}^1D_{j;\overline{m}} \quad (16d)$$

$$_{(1,1)}^{2}G_{i\bar{l};mj} = +\frac{1}{4}{}_{(2,2)}^{2}G_{i\bar{l};\overline{m}j} - {}_{(2,2)}^{2}G_{im;lj} + {}^1D_{i;l}{}^1\overline{D}_{j;m} \quad (16e)$$

$$_{(1,1)}^{2}G_{i\bar{l};\overline{m}j} = -\frac{1}{4}{}_{(2,2)}^{2}G_{i\bar{l};\overline{m}j} + {}^1D_{i;l}{}^1D_{j;\overline{m}} - {}^1D_{i;\overline{m}}\delta_{j;l} - 2!{}^2D_{ij;\overline{l}m} \quad (16f)$$

$$_{(1,0)}^{2}G_{i\bar{l};mj} = \frac{1}{2}\left({}_{(1,1)}^{2}G_{i\bar{l};mj} - {}_{(1,1)}^{2}G_{i\bar{l};\overline{m}j} - {}_{(1,1)}^{2}G_{\bar{i}\bar{l};mj} + {}_{(1,1)}^{2}G_{\bar{i}\bar{l};\overline{m}j}\right)$$
$$+ \frac{1}{2}\left({}^1D_{i;l} - {}^1D_{\bar{i};\bar{l}}\right)\left({}^1D_{j;m} - {}^1D_{\bar{j};\overline{m}}\right) \quad (16g)$$

and

$$_{(0,0)}^{2}G_{i\bar{l};m\bar{j}} = {}^2G_{i\bar{l};m\bar{j}} - {}_{(1,0)}^{2}G_{i\bar{l};m\bar{j}} - {}_{(2,0)}^{2}G_{i\bar{l};m\bar{j}} \quad (16h)$$

All the spin-components can be obtained in terms of the G-particle−hole matrix spin-blocks. The resulting spin-representability conditions which these components must satisfy are:

$$_{(1,1)}^{2}\mathbf{G} \geq 0 \quad _{(1,0)}^{2}G_{\alpha\beta;\alpha\beta} \geq 0 \quad _{(2,2)}^{2}G_{\beta\alpha;\beta\alpha} \geq 0 \quad _{(0,0)}^{2}G_{\alpha\beta;\alpha\beta} \geq 0 \quad (17)$$

b. The Spin-Representability Conditions Taken into Account in the Calculations Here Reported. The conditions that the spin-components of the G-particle−hole matrix have to fulfill in the doublet case have been already described and analyzed[66] in detail. This previously published set of conditions, which for brevity are not recalled here, are applied in the calculations reported in the following section.

The new triplet spin-representability conditions collected in eq 17 jointly with the doublet ones just mentioned constitute an essential set of very stringent spin-representability conditions aimed at testing (but not constraining) the resulting G-particle−hole matrices calculated with the GHV methodology.

Table 2. Energy Errors, in Units of E_h, of Various High-Spin Triplet Ground States from GHV Methodology (m-NY Algorithm) Compared with Those from Several Standard *ab Initio* Methods[a]

system	state	ROHF	SDCI	CCSD	CCSD(T)	GHV	FCI
B^+	^3S	1.299×10^{-2}	5.000×10^{-8}	5.000×10^{-8}	5.000×10^{-8}	-3.000×10^{-7}	-23.6053196
C^{2+}	^3S	1.279×10^{-2}	5.000×10^{-8}	5.000×10^{-8}	5.000×10^{-8}	2.000×10^{-7}	-35.3043096
N^{3+}	^3S	1.268×10^{-2}	5.000×10^{-8}	5.000×10^{-8}	5.000×10^{-8}	1.200×10^{-6}	-49.3628128
O	^3P	6.117×10^{-2}	1.256×10^{-3}	4.449×10^{-4}	9.380×10^{-5}	5.490×10^{-5}	-74.8394081
NH	$^3\Sigma^-$	7.464×10^{-2}	1.932×10^{-3}	6.558×10^{-4}	2.142×10^{-4}	3.616×10^{-4}	-55.0130005
CH_2	$^3B_1$	7.484×10^{-2}	2.249×10^{-3}	8.813×10^{-4}	2.611×10^{-4}	7.258×10^{-4}	-38.9811685
B_2	$^3\Sigma_g^-$	1.631×10^{-1}	1.952×10^{-2}	1.338×10^{-2}	2.846×10^{-3}	3.983×10^{-3}	-49.2211366
O_2	$^3\Sigma_g^-$	2.588×10^{-1}	1.252×10^{-2}	7.235×10^{-3}	3.106×10^{-4}	-4.607×10^{-3}	-149.7867936^b

[a] Errors are measured relative to FCI. [b] Frozen core approximation: The two lowest doubly occupied molecular orbitals frozen.

Table 3. Root-Mean-Square Deviations on Various Quantities Obtained via GHV Methodology (m-NY Algorithm) from their Exact (FCI) Counterparts for High-Spin Doublet Ground States

system	state	1-HV	1-CSE	2-HV	2-GHV
B	^2S	3.178×10^{-6}	1.999×10^{-6}	3.373×10^{-5}	4.409×10^{-5}
C^+	^2S	5.064×10^{-6}	3.125×10^{-6}	4.194×10^{-5}	5.480×10^{-5}
N^{2+}	^2S	2.399×10^{-6}	1.493×10^{-6}	3.745×10^{-5}	4.895×10^{-5}
OH	$^2\Pi$	1.218×10^{-4}	6.246×10^{-4}	1.146×10^{-4}	1.740×10^{-4}
NH_2	$^2B_1$	5.495×10^{-5}	4.899×10^{-4}	8.806×10^{-5}	1.297×10^{-4}
CH_3	$^2A_2''$	4.396×10^{-5}	3.252×10^{-4}	6.431×10^{-5}	9.303×10^{-5}
CH	$^2\Pi$	7.096×10^{-5}	5.561×10^{-4}	1.019×10^{-4}	1.561×10^{-4}
NO	$^2\Pi$	1.604×10^{-4}	2.597×10^{-3}	1.212×10^{-4}	2.291×10^{-4}

Table 4. Root Mean Square Deviations on Various Quantities Obtained via GHV Methodology (m-NY Algorithm) from Their Exact (FCI) Counterparts for High-Spin Triplet Ground States

system	state	1-HV	1-CSE	2-HV	2-GHV
B^+	^3S	5.750×10^{-8}	9.948×10^{-7}	1.299×10^{-7}	3.973×10^{-7}
C^{2+}	^3S	2.624×10^{-8}	6.382×10^{-7}	7.902×10^{-8}	2.528×10^{-7}
N^{3+}	^3S	8.563×10^{-8}	4.530×10^{-7}	5.737×10^{-8}	1.800×10^{-7}
O	^3P	1.830×10^{-4}	7.290×10^{-4}	1.621×10^{-4}	2.503×10^{-4}
NH	$^3\Sigma^-$	7.267×10^{-5}	6.579×10^{-4}	1.365×10^{-4}	2.026×10^{-4}
CH_2	$^3B_1$	5.092×10^{-5}	4.668×10^{-4}	9.714×10^{-5}	1.414×10^{-4}
B_2	$^3\Sigma_g^-$	1.247×10^{-4}	4.350×10^{-3}	1.551×10^{-4}	3.154×10^{-4}
O_2	$^3\Sigma_g^-$	1.650×10^{-4}	4.044×10^{-3}	1.949×10^{-4}	4.510×10^{-4}

Table 5. $\langle \hat{N}_\alpha \rangle$, $\langle \hat{N}_\beta \rangle$, $\langle \hat{S}_z \rangle$ and $\langle \hat{S}^2 \rangle$ Calculated for the 2-RDM by the GHV Methodology (m-NY Algorithm) for High-Spin Doublet Ground States

system	state	$\langle \hat{N}_\alpha \rangle$	$\langle \hat{N}_\beta \rangle$	$\langle \hat{S}_z \rangle$	$\langle \hat{S}^2 \rangle$
B	^2S	3.000 000	2.000 000	0.500 000	0.750 000
C^+	^2S	3.000 000	2.000 000	0.500 000	0.750 000
N^{2+}	^2S	3.000 000	2.000 000	0.500 000	0.750 000
OH	$^2\Pi$	5.000 075	4.000 023	0.500 026	0.750 350
NH_2	$^2B_1$	5.000 091	4.000 025	0.500 032	0.750 530
CH_3	$^2A_2''$	5.000 077	4.000 018	0.500 029	0.750 790
CH	$^2\Pi$	4.000 063	3.000 032	0.500 016	0.750 270
NO	$^2\Pi$	8.000 291	7.000 496	0.499 898	0.750 539

Table 6. $\langle \hat{N}_\alpha \rangle$, $\langle \hat{N}_\beta \rangle$, $\langle \hat{S}_z \rangle$ and $\langle \hat{S}^2 \rangle$ Calculated for the 2-RDM by the GHV Methodology (m-NY Algorithm) for High-Spin Triplet Ground States

system	state	$\langle \hat{N}_\alpha \rangle$	$\langle \hat{N}_\beta \rangle$	$\langle \hat{S}_z \rangle$	$\langle \hat{S}^2 \rangle$
B^+	^3S	3.000 000	1.000 000	1.000 000	2.000 000
C^{2+}	^3S	3.000 000	1.000 000	1.000 000	2.000 000
N^{3+}	^3S	3.000 000	1.000 000	1.000 000	2.000 000
O	^3P	5.000 075	3.000 002	1.000 036	2.000 198
NH	$^3\Sigma^-$	5.000 113	3.000 007	1.000 053	2.001 126
CH_2	$^3B_1$	5.000 114	3.000 001	1.000 053	2.001 656
B_2	$^3\Sigma_g^-$	6.002 079	4.000 863	1.000 608	2.007 229
O_2	$^3\Sigma_g^-$	9.000 135	7.000 825	0.999 655	2.003 115

IV. RESULTS

The GHV methodology has been used for the study of the electronic structure of several atoms and simple molecules in both neutral and ionic forms, including B, B^+, C^+, C^{2+}, N^{2+}, N^{3+}, O, OH, NH_2, CH_3, CH, NO, NH, CH_2, B_2, and O_2. Only the lowest lying doublet- or triplet-states of a given symmetry have been studied. In all cases, the studied state is the leading member of the multiplet, $S_z = S$, which generally has the weakest multiconfigurational character. In that way, the state is well approximated by a single Slater determinant and the algorithms for the construction of higher-order matrices perform well. The one-electron basis sets for the B, C, and N atoms have been double-ζ quality s-type GTOs proposed by Huzinaga and Dunning.[71,72] The calculations on the O atom and on the molecular systems OH, NH_2, CH_3, CH, NO, NH, CH_2, B_2, and O_2 have been performed under the standard 6-31G basis set. The geometries of the molecular systems are the experimental ones.[73] The PSI3 program[74] has been used to calculate the integrals matrix ^0H, the orthonormal MOs, and the initial values of all the matrices required for the iterative GHV process.

A previous ROHF calculation provides the starting point for the iterative solution of the GHV equation. For the sake of comparison other usual *ab initio* calculations have been done for the states considered. The reported figures include ROHF, SDCI, CCSD, CCSD(T), and FCI in addition to the GHV results. To render FCI calculation on the largest systems NO and O_2 feasible, it has been performed within a *frozen core* approximation, where the inner core spin—orbitals have been assumed to be fully "occupied" in every configuration. Tables 1 and 2 present the energy results for doublet and for triplet states, respectively. The calculations show that the correlation energies which are accounted for within the GHV methodology lie within

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Table 7. N- and Spin-Representability Deviations of Two-Body Matrices Obtained via GHV Methodology (m-NY Algorithm) for High-Spin Doublet Ground States

system	state	2-RDM	2-HRDM	$_{(\frac{1}{2},\frac{1}{2})}^{2}G$	$_{(\frac{1}{2},-\frac{1}{2})}^{2}G$	$_{(\frac{3}{2},\frac{3}{2})}^{2}G$
B	^2S	-8.857×10^{-10}	-1.964×10^{-9}	-1.079×10^{-8}	-5.629×10^{-10}	-2.692×10^{-9}
C^+	^2S	-3.256×10^{-10}	-7.811×10^{-10}	-9.364×10^{-10}	-1.144×10^{-10}	-7.474×10^{-10}
N^{2+}	^2S	-1.800×10^{-10}	-4.556×10^{-10}	-6.416×10^{-10}	-7.117×10^{-11}	-9.220×10^{-11}
OH	$^2\Pi$	-5.639×10^{-6}	-2.575×10^{-5}	-7.765×10^{-4}	-4.173×10^{-4}	-1.363×10^{-6}
NH_2	$^2B_1$	-7.951×10^{-6}	-8.923×10^{-6}	-9.267×10^{-4}	-4.423×10^{-4}	-7.241×10^{-7}
CH_3	$^2A_2''$	-4.377×10^{-6}	-6.308×10^{-6}	-1.837×10^{-3}	-7.247×10^{-4}	-8.470×10^{-7}
CH	$^2\Pi$	-7.096×10^{-5}	-1.020×10^{-5}	-6.133×10^{-4}	-2.425×10^{-4}	-3.327×10^{-5}
NO	$^2\Pi$	-1.325×10^{-3}	-9.998×10^{-4}	-2.937×10^{-3}	-9.150×10^{-5}	-2.342×10^{-4}

Table 8. N- and Spin-Representability Deviations of Two-Body Matrices Obtained via GHV Methodology (m-NY Algorithm) for High-Spin Triplet Ground States

system	state	2-RDM	2-HRDM	$_{(0,0)}^{2}G$	$_{(1,0)}^{2}G$	$_{(1,1)}^{2}G$	$_{(2,2)}^{2}G$
B^+	^3S	-1.941×10^{-9}	-1.811×10^{-9}	-3.356×10^{-8}	-3.000×10^{-10}	-2.271×10^{-9}	-1.728×10^{-9}
C^{2+}	^3S	-9.367×10^{-10}	-6.905×10^{-10}	-2.440×10^{-8}	-1.202×10^{-10}	-9.331×10^{-10}	-7.646×10^{-10}
N^{3+}	^3S	-6.538×10^{-10}	-6.223×10^{-10}	-1.620×10^{-7}	-5.147×10^{-11}	-6.882×10^{-10}	-5.910×10^{-10}
O	^3P	-5.925×10^{-5}	-3.213×10^{-5}	-9.385×10^{-3}	-7.926×10^{-5}	-2.093×10^{-4}	-2.141×10^{-6}
NH	$^3\Sigma^-$	-8.738×10^{-5}	-4.507×10^{-5}	-2.464×10^{-2}	-1.107×10^{-3}	-1.657×10^{-3}	-3.120×10^{-6}
CH_2	$^3B_1$	-8.322×10^{-5}	-6.195×10^{-5}	-3.128×10^{-2}	-9.312×10^{-4}	-1.484×10^{-3}	-1.047×10^{-6}
B_2	$^3\Sigma_g^-$	-2.039×10^{-3}	-4.067×10^{-3}	-2.634×10^{-2}	-1.940×10^{-3}	-5.237×10^{-3}	-2.332×10^{-3}
O_2	$^3\Sigma_g^-$	-2.322×10^{-3}	-2.992×10^{-3}	-3.252×10^{-2}	-1.573×10^{-3}	-5.220×10^{-3}	-4.784×10^{-6}

97.6% and 102.1% of the FCI one. Since the GHV methodology is not a variational one, it may happen that a particular result falls slightly below the FCI value; in fact, this is generally due to a slight N- or spin-representability defect of the 2-RDM or 3-RDM. Indeed, the GHV methodology is dependent on the approximation used when evaluating the higher-order matrices in terms of the lower-order ones. That is why, in the study of states other than singlet states, it was proven necessary, after a detailed analysis, that the new $^3\Delta$ approximation algorithm, eq 14, had to be used.

Upon convergence, the GHV equation provides excellent results for the energies of the atoms in neutral and ionic form. It must be noted that since only s-type basis sets are used for B, C and N atoms, doublet states of the five-electron atoms are not the ground ^2P state but the excited ^2S states. For the same reason the triplet states of the four-electron atoms are of the ^3S symmetry rather than the ^3P. Computationally, as a benchmark for the methodology, such S states are easier to calculate than the P states. The larger systems energies obtained with the GVH, the CCSD and CCSD(T) methods when compared with the FCI ones are in most cases very accurate and clearly much better than the values obtained with the SDCI treatment. Both the CCSD-(T) and GHV yield better results than the CCSD method. The accuracy of the CCSD(T) and GHV results is of the same order, although the CCSD(T)'s errors are in general somewhat lower than the GHV ones. The most unfavorable cases are the triplet O_2 and the doublet NO where the GHV error is slightly negative due to deviation from N- and S-representability of the 2-RDM and G-matrix spin-components. These results clearly establish that the iterative solution of the GHV equation is as highly reliable in the study of doublet and triplet states as it has proven to be in the closed-shell singlet case.

In order to further assess the accuracy of the results obtained via the solution of the GHV equation, various quantities in addition to the energy have been calculated. Tables 3 and 4

collect the root-mean-square deviations of the first-order density hypervirial (1-HV), the first-order CSE (1-CSE), the second-order density hypervirial (2-HV) and the second-order correlation hypervirial, or, equivalently, the second-order G-particle–hole hypervirial (2-GHV) matrices from their exact counterpart. These deviations are reliable measures of the calculations accuracy. Here again, the smaller the system the better the results. The largest deviations which have been found for the 1-CSE are due to the fact that the approximation of the higher order matrices, although very accurate, is not an exact one. The quantities which measure the deviations of the resulting one- and two-body matrices from the N- and Spin-representability have also been calculated. These quantities are reported in Tables 5, 6, 7 and 8. The expectation values of the numbers of α and β spin electrons, $\langle \hat{N}_\alpha \rangle$ and $\langle \hat{N}_\beta \rangle$, and those of the operators $\hat{S}_z$ and $\hat{S}^2$, $\langle \hat{S}_z \rangle$ and $\langle \hat{S}^2 \rangle$, are summarized in Tables 7 and 8 for the doublet and triplet states, respectively. These quantities are correct for atoms and slightly deviate from the exact values for molecules, although the present approximate decoupling technique does not include any restrictive conditions for the number of the electrons and spins. The D and Q N-representability conditions[8,9,15] and the G Spin-representability conditions indicate that the 2-RDM, the 2-HRDM, and the different spin-components of the G-particle–hole matrix must be Hermitian and positive semidefinite. The lowest eigenvalues of these matrices provide a measure of the fulfillment of those conditions. The relevant eigenvalues are collected in Tables 7 and 8 for the doublet and triplets, respectively. In general the deviations from the positivity of the matrices involved is very small. The only slightly poor results appear in the $_{(0,0)}^{2}G$ of the NH, CH_2, B_2, and O_2 triplet states. It should be pointed out that these latter results could easily be optimized by carrying out a N- and Spin-representability purification of the 2-RDM.[48,50,52,65,66] 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.

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V. CONCLUDING REMARKS

The RDMs of a variety of atoms and molecules in doublet and triplet states have been successfully calculated in a direct way by a theoretically and computationally extended version of the GHV methodology and without any use of the wave function. Generally speaking, the quality of the solutions for the studied systems in high-spin doublet and triplet states are similar to those previously reported for systems in singlet states.[1,3,4] As seen from the Results, the present method and the solution algorithm, although very good, are not yet complete, and there is need for some future improvement. Nonetheless, the results presented here constitute a landmark within the GHV approach in theoretical chemistry as they are its first direct application to doublet and triplet states.

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