

Symmetry-adapted formulation of the combined G-particle-hole hypervirial equation and Hermitian operator method

**Diego R. Alcoba, Gustavo E. Massaccesi,
Ofelia B. Oña, Juan J. Torres-Vega, Luis
Lain & Alicia Torre**

Journal of Mathematical Chemistry

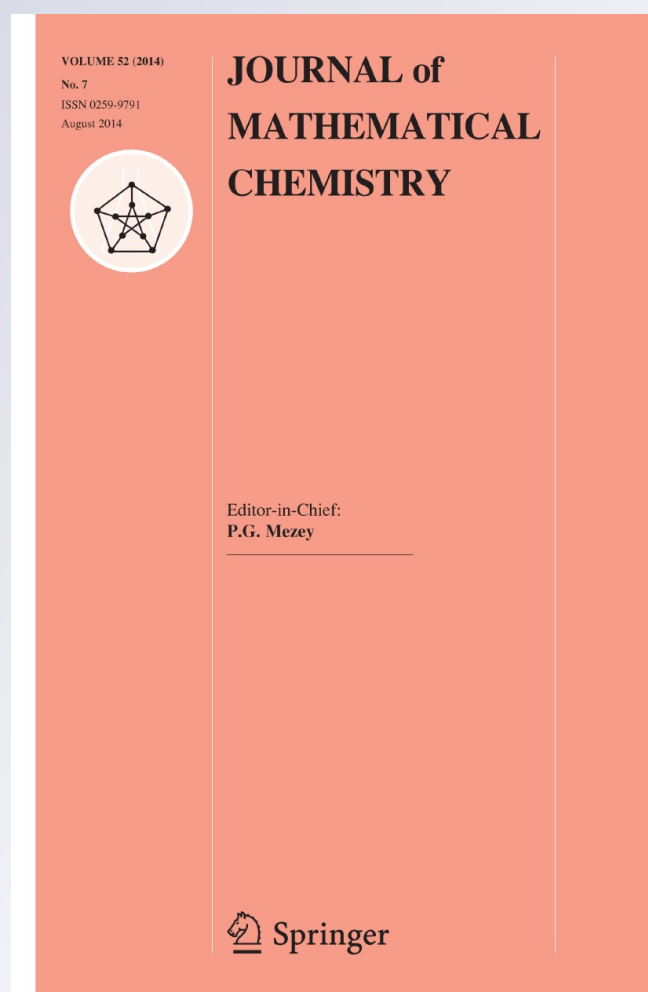
ISSN 0259-9791

Volume 52

Number 7

J Math Chem (2014) 52:1794-1806

DOI 10.1007/s10910-014-0346-9



Your article is protected by copyright and all rights are held exclusively by Springer International Publishing Switzerland. This e-offprint is for personal use only and shall not be self-archived in electronic repositories. If you wish to self-archive your article, please use the accepted manuscript version for posting on your own website. You may further deposit the accepted manuscript version in any repository, provided it is only made publicly available 12 months after official publication or later and provided acknowledgement is given to the original source of publication and a link is inserted to the published article on Springer's website. The link must be accompanied by the following text: "The final publication is available at link.springer.com".

Symmetry-adapted formulation of the combined G-particle-hole hypervirial equation and Hermitian operator method

Diego R. Alcoba · Gustavo E. Massaccesi · Ofelia B. Oña ·
Juan J. Torres-Vega · Luis Lain · Alicia Torre

Received: 17 February 2014 / Accepted: 5 March 2014 / Published online: 15 March 2014
© Springer International Publishing Switzerland 2014

Abstract High accuracy energies of low-lying excited states, in molecular systems, have been determined by means of a procedure which combines the G-particle-hole hypervirial (GHV) equation method (Alcoba et al. in *Int J Quantum Chem* 109:3178, 2009) and the Hermitian operator (HO) one (Bouten et al. in *Nucl Phys A* 202:127, 1973). This work reports a suitable strategy to introduce the point group symmetry within the framework of the combined GHV-HO method, which leads to an improvement of the computational efficiency. The resulting symmetry-adapted formulation

D. R. Alcoba (✉)

Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, 1428 Buenos Aires, Argentina
e-mail: qfxaldad@lg.ehu.es

D. R. Alcoba

Instituto de Física de Buenos Aires, Consejo Nacional de Investigaciones Científicas y Técnicas, Ciudad Universitaria, 1428 Buenos Aires, Argentina

G. E. Massaccesi

Departamento de Ciencias Exactas, Ciclo Básico Común, Universidad de Buenos Aires, Ciudad Universitaria, 1428 Buenos Aires, Argentina

O. B. Oña

Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas, Universidad Nacional de La Plata, CCT La Plata, Consejo Nacional de Investigaciones Científicas y Técnicas, Diag. 113 y 64 (S/N), Sucursal 4, CC 16, 1900 La Plata, Argentina

J. J. Torres-Vega

Departamento de Ciencias Químicas, Facultad de Ciencias Exactas, Universidad Andres Bello, Av. República 275, Santiago de Chile, Chile

L. Lain · A. Torre

Departamento de Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Apdo. 644, E-48080 Bilbao, Spain

has been applied to illustrate the computer timings and the hardware requirements in selected chemical systems of several geometries. The new formulation is used to study the low-lying excited states torsional potentials in the ethylene molecule.

Keywords G-particle-hole matrix · Reduced density matrix · Hypervirial of the G-particle-hole operator · Hermitian operator method · Point group symmetry

1 Introduction

All the electronic properties of physical interest, including the energy, can be expressed by means of expectation values of one- and two-electron operators. Therefore, the evaluation of these quantities can be implemented using only the second-order reduced density matrix (2-RDM) without recourse to the N -body wave function. Both variational and non-variational approaches have been developed to determine directly the 2-RDM elements for electronic systems. There is a large bibliography on this subject, which the interested reader may find in the Davidson [1] and Coleman and Yukalov [2] books as well as in many proceedings and reviews [3–8]. In the last years our interest has been focused on a non-variational method based on the iterative solution of the G-particle-hole hypervirial equation (GHV) [9], which arises from the contraction of a particular case of the quantum Liouville equation [10]. The accuracy of the results obtained with the GHV method for the ground state of molecular systems at equilibrium geometry was excellent when compared with the Full Configuration Interaction (FCI) procedure counterpart quantities [9, 11–13]. However, the study of the excited states is still a partially open question [14, 15]. The results provided by the GHV method for ground states have recently induced us to study the suitability to combine this method with the Hermitian operator (HO) procedure by Bouten et al. [16, 17] for computing excited state energies. We have calculated directly excited-state energies from the sole knowledge of the ground-state 2-RDM, or, equivalently, from the G-particle-hole matrix, which is obtained by solving the GHV equation [18]. Applications to molecular systems have shown that this combined GHV-HO method can yield accurate energy values not only for excited states but also for some ground states in which the GHV method presents shortcomings [18–20].

The aim of this work is to enhance the efficiency of the combined GHV-HO method by the exploitation of molecular point group symmetry. Following a recent report made within the framework of the GHV method [21], a symmetry-related analysis of the matrices and matrix operations involved in the HO method is performed. This analysis leads to a symmetry-adapted formulation of the combined GHV-HO algorithm for Abelian groups which generates significant computational savings in both floating-point operations and memory storage.

This work has been organized as follows. In the next section we report the notation, the definitions and the general theoretical background of the GHV and HO methods. In Sect. 3 we describe the symmetry-adapted formulation of the GHV-HO method. The performance and efficiency of this new formulation are shown and analyzed for a set of molecules in Sect. 4. Finally, the conclusions of this work are described in the last section.

2 Basic theoretical background

2.1 Notation and definitions

We will consider pairwise-interacting N -electron systems, whose Hamiltonian \hat{H} may be written within second quantization formalism [22] as

$$\hat{H} = \frac{1}{2} \sum_{pq:rs} {}^0H_{rs}^{pq} a^{p\dagger} a^{q\dagger} a_s a_r \quad (1)$$

where $a^{p\dagger}$ and a_r are second quantization creation and annihilation operators, respectively; the indices stand for the elements of a finite basis set of $2K$ orthonormal spin-orbitals. 0H is a second-order matrix which collects the one- and two-electron integrals, ϵ_s^q and $\langle pq|rs \rangle$ (in the $\langle 12|12 \rangle$ notation), respectively, and the Kronecker deltas

$${}^0H_{rs}^{pq} = \frac{\delta_r^p \epsilon_s^q + \delta_s^q \epsilon_r^p}{N - 1} + \langle pq|rs \rangle \quad (2)$$

In this formalism the elements of the first- and second-order reduced density matrices (1- and 2-RDM) [22] and those of the second-order G-particle-hole correlation matrix [23] may be expressed as

$${}^1D_v^t = \langle \Phi | a^{t\dagger} a_v | \Phi \rangle, \quad (3)$$

$${}^2D_{kl}^{ij} = \frac{1}{2!} \langle \Phi | a^{i\dagger} a^{j\dagger} a_l a_k | \Phi \rangle \quad (4)$$

and

$${}^2G_{lj}^{im} = \langle \Phi | {}^2\hat{G}_{lj}^{im} | \Phi \rangle = \sum_{\Phi' \neq \Phi} \langle \Phi | a^{i\dagger} a_m | \Phi' \rangle \langle \Phi' | a^{j\dagger} a_l | \Phi \rangle. \quad (5)$$

where Φ and Φ' are wave functions of the N -electron system. These three matrices, which are related by [24]

$$2! {}^2D_{ml}^{ij} = {}^1D_m^i {}^1D_l^j - {}^1D_l^i \delta_m^j + {}^2G_{lj}^{im} \quad (6)$$

are the basic tools of the GHV and HO methodologies.

2.2 The G-particle-hole hypervirial equation method

Applying a matrix-contracting mapping which involves the G-particle-hole operator 2G to the matrix representation of a particular case of the quantum Liouville equation—the hypervirial of the N -electron density operator—one obtains the GHV equation [9, 10], whose compact form is

$$\left\langle \Phi \left[\left[\hat{H}, {}^2\hat{G}_{lj}^{im} \right] \right] \Phi \right\rangle = 0 \quad (\forall i, j, l, m) \quad (7)$$

and its explicit development leads to [9]

$$\begin{aligned} & \sum_{p,q,r,s} {}^0H_{pq}^{rs} (3;2,1) C_{rsl}^{pqj} {}^1D_m^j - \sum_{p,q,r,s} {}^0H_{rs}^{pq} (3;2,1) C_{pqi}^{rsm} {}^1D_j^l \\ & + 2 \sum_{p,r,s} {}^0H_{pm}^{rs} (3;2,1) C_{rsl}^{ipj} + 2 \sum_{p,q,r} {}^0H_{jr}^{pq} (3;2,1) C_{pqi}^{lrm} \\ & + 2 \sum_{p,q,r} {}^0H_{pq}^{ir} (3;2,1) C_{mrl}^{pqj} + 2 \sum_{q,r,s} {}^0H_{rs}^{ql} (3;2,1) C_{jq_i}^{rsm} = 0 \end{aligned} \quad (8)$$

where

$${}^{(3;2,1)}C_{pqi}^{jlm} = \sum_{\Phi' \neq \Phi} \langle \Phi | a^{i\dagger} a^{j\dagger} a_q a_p | \Phi' \rangle \langle \Phi' | a^{m\dagger} a_l | \Phi \rangle \quad (9)$$

are the elements of a third-order correlation matrix [25].

Despite the GHV equation depends not only on first- and second-order reduced density matrices but also on third-order correlation ones, these last matrices can be approximated in terms of the lower-order ones [8, 12, 19, 26–29]. The approximation algorithm which is now being used is modification of Nakatsuji–Yasuda’s one [12, 27]. Following this procedure, a solution of the GHV equation may be obtained by iteratively solving a set of differential equations to minimize the second-order error matrix resulting from the deviation from exact fulfilment of the equation, yielding an approximated G-particle-hole matrix corresponding to the eigenstate being considered [11].

2.3 The Hermitian operator method

In 1973, Bouten et al. studied the properties of the particle-hole subspace of a state reporting the so-called Hermitian operator method [16, 17]. This method allows one to compute the set of low-lying excited states of an electronic system from the sole knowledge of the G-particle-hole matrix corresponding to the ground state. The procedure is based on a relation connecting the ground state Φ (reference) with an excited eigenstate Ψ of the Hamiltonian through an excitation operator \hat{S} :

$$\hat{H} \hat{S} |\Phi\rangle = E_\Psi |\Psi\rangle \quad (10)$$

This relation implies the following equivalent equation

$$\langle \Phi | [\hat{S}, [\hat{H}, \hat{S}']] | \Phi \rangle = (E_\Phi - E_\Psi) \langle \Phi | \hat{S} \hat{S}' + \hat{S}' \hat{S} | \Phi \rangle \quad (11)$$

which has to be solved. To this aim, the authors proposed to approximate the excitation operator as follows, [16]

$$\hat{S} = \sum_{t,v} \{ c_{t,v}^{(+)} (a^{t\dagger} a_v - {}^1D_v^t + a^{v\dagger} a_t - {}^1D_t^v) + i c_{t,v}^{(-)} (a^{t\dagger} a_v - {}^1D_v^t - a^{v\dagger} a_t + {}^1D_t^v) \} \quad (12)$$

where the c symbols represent real coefficients and i is the imaginary unit.

By replacing this definition into Eq. (11), one obtains the following system of decoupled equations for the excitation energies ($E_\Phi - E_\Psi$) and the expansion vectors $c^{(\pm)}$

$$\mathcal{H}^{(\pm\pm)} c^{(\pm)} = 2 (E_\Psi - E_\Phi) \mathcal{G}^{(\pm\pm)} c^{(\pm)} \tag{13}$$

where $\mathcal{G}^{(\pm\pm)}$ are functionals of the G-particle-hole matrix corresponding to the reference eigenstate

$$\mathcal{G}_{pq}^{ij(\pm\pm)} = {}^2G_{pq}^{ij} \pm {}^2G_{qp}^{ij} \pm {}^2G_{pq}^{ji} + {}^2G_{qp}^{ji} \tag{14}$$

and the matrices $\mathcal{H}^{(\pm\pm)}$ have the following form

$$\begin{aligned} \mathcal{H}_{pq}^{ij(L\pm\pm)} = & 4 \sum_{r,s} \left\{ \tilde{H}_{ps}^{jr} {}^2D_{ir}^{qs} \pm \tilde{H}_{ps}^{ir} {}^2D_{jr}^{qs} \pm \tilde{H}_{qs}^{jr} {}^2D_{ir}^{ps} + \tilde{H}_{qs}^{ir} {}^2D_{jr}^{ps} \right\} \\ & - 2 \sum_{r,k,l} \left\{ \delta_i^q \tilde{H}_{kl}^{pr} {}^2D_{jr}^{kl} \pm \delta_j^q \tilde{H}_{kl}^{pr} {}^2D_{ir}^{kl} \pm \delta_i^p \tilde{H}_{kl}^{qr} {}^2D_{jr}^{kl} + \delta_j^p \tilde{H}_{kl}^{qr} {}^2D_{ir}^{kl} \right\} \\ & + 2 \sum_{k,l} \left\{ \tilde{H}_{kl}^{pi} {}^2D_{kl}^{jq} \pm \tilde{H}_{kl}^{pj} {}^2D_{kl}^{iq} \pm \tilde{H}_{kl}^{qi} {}^2D_{kl}^{jp} + \tilde{H}_{kl}^{qj} {}^2D_{kl}^{ip} \right\} \end{aligned} \tag{15}$$

with

$$\tilde{H}_{ps}^{ir} = {}^0H_{ps}^{ir} - {}^0H_{ps}^{ri} \equiv {}^0H_{ps}^{ir} - {}^0H_{sp}^{ir} \tag{16}$$

As can be observed, Eq. (13) constitutes a generalized eigenvalue system which only depends on the 2-RDM, or equivalently on the G-particle-hole matrix, which turns out to be the output of solving the GHV equation. That is fundamental reason why we have proposed to combine the GHV method with the HO one [18]. In the next section we outline an algorithm for exploiting point group symmetry, by which the computational efficiency of the combined GHV-HO method is highly improved.

3 Symmetry-adaptation of the GHV-HO method

It is well known that the operations of the symmetry point group of a molecule, group \mathcal{F} , maintain the matrix elements of the second-order electron integral matrix 0H unchanged and therefore, this matrix is an invariant (2,2)-tensor for the group \mathcal{F} [30]. Analogously, if the N -electron wave function Φ belongs to a one-dimensional representation of \mathcal{F} , then the 1- and 2-RDM and the G-particle-hole matrix are invariant (1,1)- and (2,2)-tensors for the symmetry point group, the formers in the particle-particle metric while the latter in the particle-hole metric [30]. Therefore, when the spin-orbitals are symmetry-adapted and ordered according to their irreducible representations, these first- and second-order matrices are sparse, and when \mathcal{F} is Abelian they are also block diagonal. The structure of the symmetry forbidden coefficients in all these matrices is easier to analyze when the group \mathcal{F} possesses an Abelian D_{2h} subgroup, and hence only this kind of groups will be considered hereafter. When the studied electronic system has no Abelian subgroup, an Abelian subgroup will be considered.

The sparsity of all the first- and second-order matrices have been recently exploited within the framework of the GHV method by carrying out a detailed analysis of the matrix operations involved in Eq. (8). This analysis has led to a symmetry-adapted formulation of the GHV algorithm which generates significant computational savings in both floating-point operations and memory storage [21]. Let us now reconsider the analysis for the case of the HO decoupled equations, Eq. (13). In this case, three different types of terms need to be calculated,

$$\sum_{r,s} \tilde{H}_{ps}^{jr} {}^2D_{ir}^{qs} \equiv {}^2Z_{pi}^{qj} \tag{17}$$

$$\sum_{k,l} \tilde{H}_{kl}^{pi} {}^2D_{jq}^{kl} \equiv {}^2W_{jq}^{pi} \tag{18}$$

and

$$\sum_{r,k,l} \delta_i^q \tilde{H}_{kl}^{pr} {}^2D_{jr}^{kl} = \delta_i^q {}^1Y_j^p \equiv {}^2X_{ij}^{qp} \tag{19}$$

with the auxiliary matrix 1Y defined as

$${}^1Y_j^p \equiv \sum_{r,k,l} \tilde{H}_{kl}^{pr} {}^2D_{jr}^{kl} \tag{20}$$

A detailed analysis of the mathematical operations involved in the calculation of these terms reveals that the corresponding auxiliary and final matrices are defined by covariant equations in particle-particle or particle-hole metric, as appropriate. Those matrices can be expressed in terms of elementary tensorial operations as follows:

$${}^2Z = \left(\left(\left(\tilde{H} \otimes {}^2D \right)_{(1,2,3,4) \rightarrow (1,3,4,2)}^{(1,2,3,4) \rightarrow (1,3,4,2)} \right)_{\text{con}} \right)_{\text{con}} \tag{21}$$

$${}^2W = \left(\left(\left(\tilde{H} \otimes {}^2D \right)_{(1,2,3,4) \rightarrow (3,4,1,2)}^{(1,2,3,4) \rightarrow (3,4,1,2)} \right)_{\text{con}} \right)_{\text{con}} \tag{22}$$

$${}^1Y = \left(\left(\left(\left(\tilde{H} \otimes {}^2D \right)_{(1,2,3,4) \rightarrow (1,2,3,4)}^{(1,2,3,4) \rightarrow (1,2,3,4)} \right)_{\text{con}} \right)_{\text{con}} \right)_{\text{con}} \tag{23}$$

$${}^2X = \delta \otimes {}^1Y \tag{24}$$

where

$$(\mathbf{V} \otimes \mathbf{W})_{m_1 \dots m_{v+w}}^{i_1 \dots i_{v+w}} = \mathbf{V}_{m_1 \dots m_v}^{i_1 \dots i_v} \times \mathbf{W}_{m_{v+1} \dots m_{v+w}}^{i_{v+1} \dots i_{v+w}} \tag{25}$$

$$\left(\mathbf{V}_{(1, \dots, v) \rightarrow (\sigma(1), \dots, \sigma(v))}^{(1, \dots, v) \rightarrow (\tau(1), \dots, \tau(v))} \right)_{m_1 \dots m_v}^{i_1 \dots i_v} = \mathbf{V}_{m_{\sigma(1)} \dots m_{\sigma(v)}}^{i_{\tau(1)} \dots i_{\tau(v)}} \tag{26}$$

$$(\mathbf{V}_{\text{con}})_{m_1 \dots m_{v-1}}^{i_1 \dots i_{v-1}} = \sum_x \mathbf{V}_{m_1 \dots m_{v-1} x}^{i_1 \dots i_{v-1} x} \tag{27}$$

The covariance of these equations implies that all the intermediate and final matrices involved in HO method are invariant tensors for the group \mathcal{F} , which retains symmetry

properties of the input density and electron integral matrices. The block structure of these tensors can be applied to efficiently perform the evaluation of the HO operations for each one of the auxiliary operations resulting from Eq. (13). Thus, for instance, the auxiliary matrix 2Z defined in Eq. (17) is a (2,2)-tensor for the group \mathcal{F} whose non-vanishing blocks are associated with irreducible representations $\pi_i, \pi_j, \pi_p, \pi_q$ of \mathcal{F} such that $\pi_i \otimes \pi_j \otimes \pi_p \otimes \pi_q = A$. Hence, one could avoid the evaluation of the symmetry forbidden elements, and calculate the remaining elements as follows

$${}^2Z_{pi}^{qj} = \sum_{\substack{\pi_r, \pi_s \\ \pi_j \otimes \pi_r \otimes \pi_p \otimes \pi_s = A \\ \pi_i \otimes \pi_r \otimes \pi_q \otimes \pi_s = A}} \sum_{r \in \pi_r, s \in \pi_s} \tilde{H}_{ps}^{jr} {}^2D_{ir}^{qs} \quad (\forall p \in \pi_p, q \in \pi_q, i \in \pi_i, j \in \pi_j) \quad (28)$$

In a similar way, the auxiliary matrix 2W defined in Eq. (18) can be evaluated as

$${}^2W_{jq}^{pi} = \sum_{\substack{\pi_k, \pi_l \\ \pi_p \otimes \pi_i \otimes \pi_k \otimes \pi_l = A \\ \pi_k \otimes \pi_l \otimes \pi_j \otimes \pi_q = A}} \sum_{k \in \pi_k, l \in \pi_l} \tilde{H}_{kl}^{pi} {}^2D_{jq}^{kl} \quad (\forall p \in \pi_p, q \in \pi_q, i \in \pi_i, j \in \pi_j) \quad (29)$$

On the other hand, the non-vanishing blocks of elements ${}^1Y_p^j$ in Eq. (20) are associated with irreducible representations π_p, π_j of \mathcal{F} such that $\pi_p \otimes \pi_j = A$, and for each one of these blocks one calculates

$${}^1Y_p^j = \sum_{\substack{\pi_r, \pi_k, \pi_l \\ \pi_p \otimes \pi_r \otimes \pi_k \otimes \pi_l = A \\ \pi_k \otimes \pi_l \otimes \pi_j \otimes \pi_r = A}} \sum_{r \in \pi_r, k \in \pi_k, l \in \pi_l} \tilde{H}_{kl}^{pr} {}^2D_{jr}^{kl} \quad (\forall p \in \pi_p, j \in \pi_j) \quad (30)$$

The remaining matrix operations involved in the calculation and solution of the symmetry-blocked HO generalized eigenvalue equations can be analyzed and evaluated in a similar way. Therefore, it is possible to exploit the block structure of the ordinary density and electron integral matrices entering in the HO equations to improve the efficiency of the HO computations and reduce the memory requirements. In the next section the computational advantages of a symmetry-adapted formulation of the GHV-HO (sa-GHV-HO) method, which results from combining the symmetry-adapted formulations of the GHV (sa-GHV) and HO (sa-HO) algorithms, will be discussed and analyzed.

4 Results and discussion

4.1 Efficiency of the sa-GHV-HO method

To illustrate the computational advantages of the sa-GHV-HO method, we have carried out numerical determinations in small- and medium-sized molecular systems in their

Table 1 Comparison of floating-point operations and memory (in brackets) requirements of the HO computational algorithms: ratios of the non-symmetry-adapted to the symmetry-adapted formulations

System	Subgroup	Irr. rep.	Basis set		
			STO-3G	6-31G	6-31G(d)
NH ₃	C _s	2	3.11	3.29	3.75
			[1.88]	[1.91]	[1.93]
H ₂ O ₂	C ₂	2	4.05	4.27	3.92
			[2.00]	[2.00]	[2.00]
FH	C _{2v}	4	4.78	6.80	9.36
			[2.84]	[3.00]	[3.43]
H ₂ O	C _{2v}	4	6.05	8.32	11.78
			[3.09]	[3.20]	[3.54]
CH ₄	D ₂	4	10.74	14.34	15.61
			[4.00]	[4.00]	[4.00]
C ₂ H ₆	C _{2h}	4	13.72	20.70	18.41
			[3.76]	[3.82]	[3.87]
Li ₂	D _{2h}	8	17.17	30.86	47.97
			[6.35]	[6.72]	[7.30]
C ₂ H ₂	D _{2h}	8	17.55	24.38	46.21
			[5.68]	[6.00]	[6.87]
C ₂ H ₄	D _{2h}	8	21.61	38.52	52.52
			[6.18]	[6.39]	[7.07]

ground states at equilibrium experimental geometries [31] using the basis sets STO-3G, 6-31G and 6-31G(d). These systems have been chosen in order to explore the computational improvements implemented by the algorithms in different point groups. The electron integrals for the sa-GHV and sa-HO methods and their initial values (at a mean-field level of approximation) required for initiating the iterative GHV process have been computed with the PSI3 package [32]. In order to fairly assess the improved performance due to symmetry, two sets of calculations have been carried out using identical algorithms. In first set of calculations we have assumed a C_1 symmetry point group, and in the second one the group assumed corresponds to the largest Abelian subgroup of the symmetry point group describing the full symmetry of the system determined by PSI3 code. Consequently, the gains due to symmetry reflect directly the inherent savings in the symmetry-adapted method.

Table 1 reports the statistics concerning the computational cost and hardware requirements of the HO calculations. That table shows the ratios of the computing time and memory needs between the calculations performed in the largest Abelian subgroup of the symmetry point group described by PSI3 code and those performed in C_1 subgroup. As can be appreciated from the results presented in Table 1, the improvement increases not only with the order of the group but also with the size of the basis set considered. The results show that computational efficiency ranges from 3.11 to 52.52 in floating-points operation rates and from 1.88 to 7.30 in memory allocation. These computed factors of reduction due to symmetry are indeed close to the theoretical estimations in most cases. Thus, considering that the group \mathcal{F} has f irre-

ducible representations, and assuming that the partitioning of molecular spin-orbitals according to irreducible representation is strictly regular, then a straightforward calculation shows that $(2, 2)$ -tensors have f blocks of size $(K^2/f) \times (K^2/f)$, so they have K^4/f^2 non-vanishing coefficients, and the operations involved in calculation and solution of the generalized eigenvalue equations Eq. (13) have a time proportional to $f \times (K^2/f)^3 = K^6/f^2$. As in the GHV method [21], these estimations show that the computational costs of the HO method can be reduced by a factor of f in storage and f^2 in floating-point operations. The asymptotic f and f^2 values are only actually achieved when the symmetry blocking of the orbitals is optimum as can be appreciated from the results presented in Table 1 for the methane molecule. Note that in cases where the dimension of irreducible representation is far from regular, values of $\sim 0.3 f^2$ in computer times and $\sim 0.7 f$ in memory are achieved. This is the case of STO-3G basis set in the acetylene molecule which has 4, 0, 1, 1, 0, 4, 1 and 1 orbitals of $a_g, b_{1g}, b_{2g}, b_{3g}, a_u, b_{1u}, b_{2u}$ and b_{3u} symmetries, respectively.

4.2 Application of the sa-GHV-HO method to describe the low-lying excited states torsional potentials in the ethylene molecule

As an application of the proposed algorithms, we have studied the low-lying excited state potential energy curves (PEC) in the ethylene molecule, which demands a high computational cost without the symmetry adaptation. To perform this work our strategy has consisted in decomposing the study into two main steps. In the first one, one applies the sa-GHV method to describe the PEC of a ground state thus generating an initial set of accurate G-particle-hole matrices. In the second step, we use as data the G-particle-hole matrices obtained with the sa-GHV method and implement the sa-HO method to obtain the energy of the excited states in which one is interested and which could not be directly obtained with the GHV. All these calculations have been performed using minimal STO-3G basis sets. In addition to the sa-GHV/sa-GHV-HO results, the reported Fig. 1 includes restricted HF, single-reference CIS model results, and FCI ones, which is reason why a minimal basis set has been employed. The PSI3 quantum chemistry package has been used to calculate the integrals matrix 0H , and the initial values of all the matrices required.

The ethylene molecule in its ground state belongs to the symmetry point group D_{2h} ; the partially twisted ethylene belongs to the symmetry point group D_2 and that 90° twisted one to C_{2v} . Although at the equilibrium geometry (D_{2h}) the ethylene molecule is a well-behaved closed-shell molecule whose π -valence ground state can be described accurately by single-reference methods, it becomes a diradical at 90° twisted, when the π -bond is completely broken. Thus, at the twisted geometry the ground state ethylene molecule is two-configurational. As mentioned above, the first step to use our algorithms was to apply the sa-GHV method to study the ground state thus generating an initial accurate G-particle-hole matrix. This state was well approximated producing a cusplless PEC close to the FCI one. Our results show two of the most important low-lying excited states of ethylene molecule reviewed by Merer and Mulliken in their early experimental work [33], T (lowest triplet) and T_R (triplet Rydberg). These two states could be accurately obtained by single excitations from

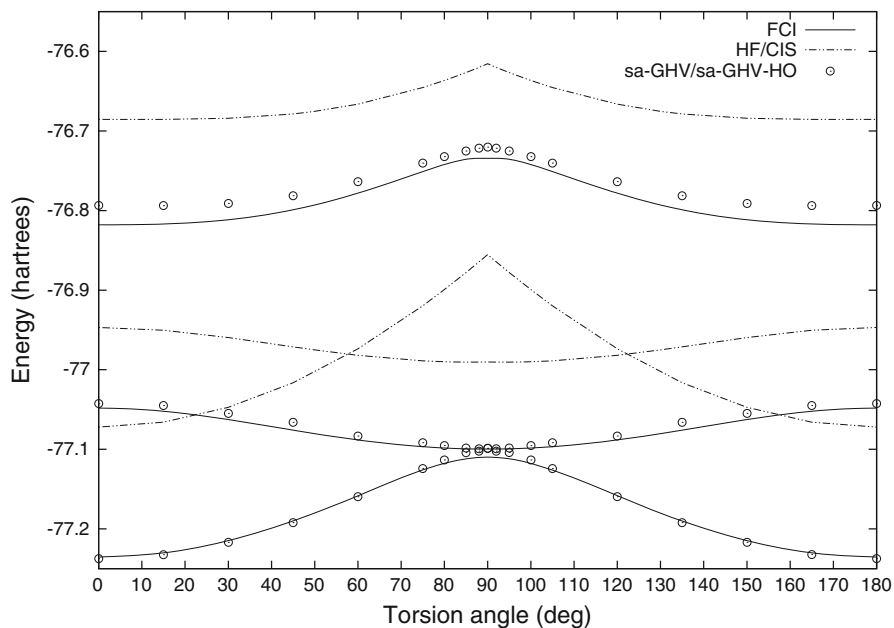


Fig. 1 Ethylene torsion, minimal basis set. Energy values (in hartrees) for the ground state and first two triplet excited states of ethylene as functions of the torsional angle. The *solid* and *dashed* curves denote the FCI and HF/CIS energy curves, respectively, while *circles* denote energies computed by means of the sa-GHV and sa-GHV-HO methods

N (the ground state). We have calculated the PEC of these states as functions of the torsional angle between the planes of the two methylene groups.

Figure 1 shows a comparison of the ground and two low-lying triplet excited states described by the sa-GHV/sa-GHV-HO, HF/CIS and FCI methods. We report the energy eigenvalues of only one HO equation corresponding to either $\mathcal{H}^{(++)}$ or $\mathcal{H}^{(--)}$, i.e. to the symmetric or antisymmetric particle-hole subspace. Table 2 presents the energy errors relative to FCI method, the maximum absolute errors (MAE) and the nonparallelity errors (NPE). The GHV energy error relative to FCI for the ground state lies within $1.29 \cdot 10^{-3}$ and $1.11 \cdot 10^{-2}$ hartrees. The ground state is two-configurational near 90° so the algorithms for the construction of higher-order matrices are not entirely accurate and as a result, the errors are slightly higher at the barrier. However, the NPE and MAE of the GHV method for the ground state reported in Table 2 are an order of magnitude lower than those of the HF method. The excellent performance of the GHV method for the ground state reported also in Ref. [21] is retained when we apply the sa-GHV-HO method to generate excited states. As can be appreciated the accuracy of the results obtained with the sa-GHV-HO for the ethylene molecule is far better than that of the CIS calculations. Thus, the CIS energy error relative to FCI lies near $1.00 \cdot 10^{-1}$ hartrees, while for the sa-GHV-HO method the error lies between $3.98 \cdot 10^{-4}$ and $9.82 \cdot 10^{-3}$ hartrees for the first excited state and between $9.77 \cdot 10^{-3}$ and $2.44 \cdot 10^{-2}$ hartrees for the second excited state. CIS method explicitly take into account the same excitations than the HO one and therefore, its inferior performance must be

Table 2 Energy errors (hartrees) of the two lowest triplet excited states and ground state for ethylene torsional potentials using STO-3G basis set

Angle (deg)	HF/CIS			sa-GHV _{isa} -GHV-HO			FCI		
	N	T	T _R	N	T	T _R	N	T	T _R
0	1.633 [-1]	1.013 [-1]	1.325 [-1]	-2.118 [-3]	5.571 [-3]	2.437 [-2]	-77.235361	-77.048184	-76.817992
15	1.643 [-1]	1.018 [-1]	1.315 [-1]	-2.182 [-3]	7.127 [-3]	2.304 [-2]	-77.230147	-77.052176	-76.816906
30	1.675 [-1]	1.031 [-1]	1.275 [-1]	-2.191 [-3]	7.779 [-3]	2.064 [-2]	-77.214742	-77.062633	-76.811611
45	1.736 [-1]	1.047 [-1]	1.204 [-1]	-1.999 [-3]	9.815 [-3]	1.758 [-2]	-77.190031	-77.075940	-76.799033
60	1.846 [-1]	1.063 [-1]	1.119 [-1]	-1.292 [-3]	4.878 [-3]	1.445 [-2]	-77.158314	-77.088256	-76.778162
75	2.063 [-1]	1.079 [-1]	1.055 [-1]	1.821 [-3]	4.965 [-3]	1.065 [-2]	-77.125967	-77.096723	-76.751004
80	2.183 [-1]	1.084 [-1]	1.056 [-1]	4.206 [-3]	3.077 [-3]	9.770 [-3]	-77.117583	-77.098376	-76.742097
85	2.341 [-1]	1.089 [-1]	1.089 [-1]	7.853 [-3]	9.990 [-4]	1.020 [-2]	-77.111926	-77.099380	-76.735464
88	2.458 [-1]	1.092 [-1]	1.143 [-1]	1.086 [-2]	-2.729 [-3]	1.258 [-2]	-77.110240	-77.099663	-76.734360
90	2.546 [-1]	1.094 [-1]	1.188 [-1]	1.112 [-2]	-3.982 [-4]	1.403 [-2]	-77.109913	-77.099717	-76.734348
MAE	2.546 [-1]	1.094 [-1]	1.325 [-1]	1.112 [-2]	9.815 [-3]	2.437 [-2]	-	-	-
NPE	0.09	0.01	0.03	0.01	0.01	0.01	-	-	-

Numbers in square brackets indicate powers of 10. Geometry used: R_{CC}=1.339 Å, R_{CH}=1.086 Å, α(HCH) = 117.6°

due to the fact that the HO method profits of the knowledge of correlated ground state G-particle-hole matrix.

5 Concluding remarks

In this work we have outlined a scheme to introduce the point group symmetry in the GHV-HO framework. The proposed algorithm provides a procedure for exploiting the sparseness of the matrices involved in the calculations due to symmetry which leads to an efficient computational implementation. The cpu and memory requirements for calculations using this approach are not limited by the total number of spin-orbitals constituting the basis set but rather by the maximum number of spin-orbitals belonging to the irreducible representations of the symmetry point group the molecular system. Hence, large molecules belonging to high symmetries no longer represent a formidable computational obstacle. We highlight that the reported strategy for exploiting symmetry within the GHV-HO method may also accelerate other RDM-oriented approaches such as the contracted Schrödinger equation method [7, 8, 27, 34–37] and the equation-of-motion techniques [18–20, 38–43].

Acknowledgments This report has been financially supported by the Projects UBACYT 20020100100197 and 20020100100502 (Universidad de Buenos Aires, Argentina), PIP N. 11220090100061, 11220090100369 and 11220080100398 (Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina), DI-407-13/I(Universidad Andres Bello, Chile), and GIU12/09 and UFI11/07 (Universidad del País Vasco). We thank the Universidad del País Vasco for allocation of computational resources.

References

1. E.R. Davidson, *Reduced Density Matrices in Quantum Chemistry* (Academic Press, New York, 1976)
2. A.J. Coleman, V.I. Yukalov, *Reduced Density Matrices: Coulson's Challenge* (Springer, New York, 2000)
3. *Reduced Density Matrices with Applications to Physical and Chemical Systems*, eds. by A.J. Coleman, R.M. Erdahl. Queen's Papers on Pure and Applied Mathematics—No. 11 (Queen's University, Kingston, ON, 1968)
4. *Reduced Density Matrices with Applications to Physical and Chemical Systems II*, eds. by R.M. Erdahl. Queen's Papers on Pure and Applied Mathematics—No. 40 (Queen's University, Kingston, ON, 1974)
5. *Density Matrices and Density Functionals*, eds. by R.M. Erdahl, V. Smith. Proceedings of the A.J. Coleman Symposium, Kingston, ON, 1985 (Reidel, Dordrecht, 1987)
6. *Many-electron Densities and Reduced Density Matrices*, ed. by J. Cioslowski (Kluwer, Dordrecht, 2000)
7. *Reduced-Density-matrix Mechanics with Applications to Many-electron Atoms and Molecules*, ed. by D.A. Mazziotti. Adv. Chem. Phys. vol. 134 (Wiley, New York, 2007) and references therein
8. D.A. Mazziotti, Chem. Rev. **112**, 244 (2012) and references therein
9. D.R. Alcoba, C. Valdemoro, L.M. Tel, E. Pérez-Romero, Int. J. Quantum Chem. **109**, 3178 (2009)
10. C. Valdemoro, D.R. Alcoba, L.M. Tel, E. Pérez-Romero, Int. J. Quantum Chem. **109**, 2622 (2009)
11. D.R. Alcoba, L.M. Tel, E. Pérez-Romero, C. Valdemoro, Int. J. Quantum Chem. **111**, 937 (2011)
12. D.R. Alcoba, C. Valdemoro, L.M. Tel, E. Pérez-Romero, O. Oña, J. Phys. Chem. A **115**, 2599 (2011)
13. C. Valdemoro, D.R. Alcoba, O.B. Oña, L.M. Tel, E. Pérez-Romero, J.M. Oliva, Chem. Phys. **399**, 59 (2012)
14. C. Valdemoro, D.R. Alcoba, L.M. Tel, E. Pérez-Romero, Int. J. Quantum Chem. **111**, 245 (2011)
15. D.R. Alcoba, C. Valdemoro, L.M. Tel, Comput. Theor. Chem. **1003**, 55 (2013)
16. M. Bouten, P. Van Leuven, M.V. Mihailovich, M. Rosina, Nucl. Phys. A **202**, 127 (1973)
17. M. Bouten, P. Van Leuven, M.V. Mihailovich, M. Rosina, Nucl. Phys. A **221**, 173 (1974)

18. C. Valdemoro, D.R. Alcoba, O.B. Oña, L.M. Tel, E. Pérez-Romero, *J. Math. Chem.* **50**, 492 (2012)
19. C. Valdemoro, D.R. Alcoba, L.M. Tel, *Int. J. Quantum Chem.* **112**, 2965 (2012)
20. D.R. Alcoba, O.B. Oña, C. Valdemoro, L.M. Tel, G.E. Massaccesi, *J. Math. Chem.* **50**, 2478 (2012)
21. G.E. Massaccesi, D.R. Alcoba, O.B. Oña, *J. Math. Chem.* **50**, 2155 (2012)
22. P.R. Surjan, *Second Quantized Approach to Quantum Chemistry: An Elementary Introduction* (Springer, Berlin, 1989)
23. C. Garrod, J.K. Percus, *J. Math. Phys.* **5**, 1756 (1964)
24. M.V. Mihailovic, M. Rosina, *Nucl. Phys. A* **130**, 386 (1969)
25. D.R. Alcoba, C. Valdemoro, *Phys. Rev. A* **64**, 062105 (2001)
26. F. Colmenero, C. Pérez del Valle, C. Valdemoro, *Phys. Rev. A* **47**, 971 (1993)
27. H. Nakatsuji, K. Yasuda, *Phys. Rev. Lett.* **76**, 1039 (1996)
28. D. Mazziotti, *Phys. Rev. A* **60**, 3618 (1999)
29. C. Valdemoro, L.M. Tel, E.P. Pérez-Romero, in *Many-electron Densities and Density Matrices*, ed. by J. Cioslowski (Kluwer, Boston, 2000)
30. L.M. Tel, E. Pérez-Romero, F.J. Casquero, C. Valdemoro, *Phys. Rev. A* **67**, 052504 (2003)
31. *NIST Computational Chemistry Comparison and Benchmark Database*, ed. by R.D. Johnson III. NIST Standard Reference Database No. 101 (National Institute of Standard and Technology, 2006). <http://srdata.nist.gov/cccbdb>
32. T.D. Crawford, C.D. Sherrill, E.F. Valeev, J.T. Fermann, R.A. King, M.L. Leininger, S.T. Brown, C.L. Janssen, E.T. Seidl, J.P. Kenny, W.D. Allen, *J. Comput. Chem.* **28**, 1610 (2007)
33. A.J. Merer, R.S. Mulliken, *Chem. Rev.* **69**, 639 (1969)
34. F. Colmenero, C. Valdemoro, *Int. J. Quantum Chem.* **51**, 369 (1994)
35. D.A. Mazziotti, *Phys. Rev. A* **57**, 4219 (1998)
36. C. Valdemoro, L.M. Tel, E. Pérez-Romero, A. Torre, *J. Mol. Struct. (Theochem)* **537**, 1 (2001)
37. D.R. Alcoba, F.J. Casquero, L.M. Tel, E. Pérez-Romero, C. Valdemoro, *Int. J. Quantum Chem.* **102**, 620 (2005)
38. Z. Szekeres, A. Szabados, M. Kállay, P.R. Surjan, *Phys. Chem. Chem. Phys.* **3**, 696 (2001)
39. D.A. Mazziotti, *Phys. Rev. A* **68**, 052501 (2003)
40. J.D. Farnum, D.A. Mazziotti, *Chem. Phys. Lett.* **400**, 90 (2004)
41. J. Simons, *Adv. Quantum Chem.* **50**, 213 (2005). and references therein
42. D. Vanfleteren, P.D. Van Neck, P.W. Ayers, R.C. Morrison, P. Bultinck, *J. Chem. Phys.* **130**, 194104 (2009)
43. H. van Aggelen, B. Verstichel, G. Acke, M. Degroote, P. Bultinck, P.W. Ayers, D. Van Neck, *Comput. Theor. Chem.* **1003**, 50 (2013)