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ORIGINAL PAPER

Drawing information from the ground state G-particle-hole matrix to study electronic excited states

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Abstract Very recently, we have shown the suitability to combine the G-particle-hole Hypervirial (GHV) equation method (Alcoba et al. in Int J Quantum Chem 109:3178, 2009) with the Hermitian Operator (HO) method (Bouten et al. in Nucl Phys A 202:127, 1973) for computing various energy differences of an electronic system spectrum (Valdemoro et al. in J Math Chem 50:492, 2012). The purpose of this paper is to extend our preliminary studies by applying the combined GHV-HO method to obtain the set of ground and low-lying excited states potential energy curves

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of several selected electronic systems. The calculations confirm the reliability of the method.

Keywords G-particle-hole matrix · Reduced density matrix · Excited states · Electronic correlation effects · Hypervirial of the G-particle-hole matrix · Hermitian operator method

1 Introduction

It is well-known that the second-order reduced density matrix (2-RDM) allows to calculate the energy and other fundamental electronic properties of atomic and molecular systems [1–4]. Direct calculation of the 2-RDM without the wave function has emerged through the solutions of the contracted Schrödinger (CSE) [5–15] and Liouville (CLE) [9,11] equations. In the last years our interest has been mainly focused in solving the G-particle-hole hypervirial (GHV) equation [16], which results from the contraction of a particular case of the Liouville equation [16,17]. Although the GHV equation depends upon not only on the 2-RDM but also on the 3-RDM, the 3-RDM can be approximated in terms of the 1- and 2-RDMs [10,12,14,15]. Proceeding in this way, we have recently solved iteratively the GHV equation [16–21]. The accuracy of the results obtained with the GHV method when studying the ground state of molecular systems at equilibrium geometry was excellent when compared with the equivalent Full Configuration Interaction (FCI) quantities [16–18,20].

Very recently, we have shown the suitability to combine the GHV method with the Hermitian Operator (HO) method of Bouten et al. [22,23] for computing electronic excited states of a system [24]. Thus, we reported simple applicative examples of the combined GHV-HO method. These examples constituted a preliminary test showing that, provided that a second-order G-particle-hole matrix corresponding to a conveniently chosen state is known, this combined method can yield accurate energy values for either ground or excited electronic states which would be hard to obtain directly with the GHV. In this paper we extend this preliminary study by applying the combined GHV-HO method to obtain both the ground and the set of low-lying excited states potential energy curves (PEC) of several molecular systems. To perform this work our strategy consists in decomposing the study into two main steps: first one applies the GHV method to study 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 GHV method and implement the HO method to obtain the energy of the excited states in which one is interested and which could not be directly and accurately obtained with the GHV.

The paper is organized as follows: In the next section the notation, definitions and general theoretical background of the GHV and HO methodologies are given. In section three, the results obtained in a set of applications of the combined GHV-HO method on selected molecular systems having singlet, doublet and triplet ground states are reported. The results are compared with those obtained with traditional wave function methods such as single excitation Configuration Interaction (CIS) and FCI. Finally, a brief description of the conclusions of this work is given in the last section.

2 Basic theoretical background

2.1 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 [25] in the occupation number representation as

$$\hat{H} = \frac{1}{2} \sum_{pq;rs} {}^{0}\mathrm{H}_{pq;rs}\, a_p^\dagger a_q^\dagger a_s\, a_r \tag{1}$$

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 orthonormal spin-orbitals, and the matrix ${}^{0}\mathrm{H}$ groups the 1- and 2-electron integrals over the basis set.

In this formalism an element of a p-RDM corresponding to a N-electron state Φ describing the system may be defined as

$$\begin{aligned} p!\, {}^{p}\mathrm{D}_{i_1 i_2 .. i_p; j_1 j_2 \ldots j_p} &= \langle \Phi |\, a_{i_1}^\dagger a_{i_2}^\dagger \ldots a_{i_p}^\dagger a_{j_p} \ldots a_{j_2} a_{j_1}\, | \Phi \rangle \\ &\equiv \langle \Phi |\, {}^{p}\hat{\Gamma}_{i_1 i_2 \ldots i_p; j_1 j_2 \ldots j_p}\, | \Phi \rangle \end{aligned} \tag{2}$$

where ${}^{p}\hat{\Gamma}$ is a p-electron density operator.

Through the application of the fermion algebra and the resolution of the identity operator, it is possible to decompose a p-RDM element into a sum of terms involving lower-order RDM elements and additional terms describing p-body correlation effects [26–32]. Let us consider the decomposition of the 2-RDM which provides the simplest example:

$$2!\, {}^{2}\mathrm{D}_{ij;ml} = {}^{1}\mathrm{D}_{i;m}\, {}^{1}\mathrm{D}_{j;l} - {}^{1}\mathrm{D}_{i;l}\, \delta_{j,m} + \sum_{\Phi' \neq \Phi} \langle \Phi |\, {}^{1}\hat{\Gamma}_{i;m}\, | \Phi' \rangle \langle \Phi' |\, {}^{1}\hat{\Gamma}_{j;l}\, | \Phi \rangle \tag{3}$$

The last term of this equation defines the elements of the second-order correlation matrix (2-CM), or equivalently, of the G-particle-hole matrix, which have the form:

$$\begin{aligned} {}^{2}\mathrm{C}_{ij;ml} &= \langle \Phi |\, {}^{2}\hat{C}_{ij;ml}\, | \Phi \rangle = \sum_{\Phi' \neq \Phi} \langle \Phi |\, {}^{1}\hat{\Gamma}_{i;m}\, | \Phi' \rangle \langle \Phi' |\, {}^{1}\hat{\Gamma}_{j;l}\, | \Phi \rangle \\ &\equiv \langle \Phi |\, {}^{2}\hat{G}_{im;lj}\, | \Phi \rangle = {}^{2}\mathrm{G}_{im;lj} \end{aligned} \tag{4}$$

The ${}^{2}\hat{C}$ and ${}^{2}\hat{G}$ are 2-electron correlation and G-particle-hole operators respectively, which are very different from the 2-electron density operator. These operators are at the center of the GHV and HO methodologies.

2.2 The GHV method

By applying a matrix-contracting mapping involving the G-particle-hole operator to the matrix representation of the hypervirial of the N-electron density operator, one obtains the GHV equation [16], whose compact form is:

$$\left\langle \Phi \left| \left[\hat{H},\ {}^{2}\hat{G}_{im;lj} \right] \right| \Phi \right\rangle = 0 \qquad \forall\, i, j, l, m \tag{5}$$

When developed, this equation depends not only on first- and second-order matrices—such as the 2-RDM or the 2-CM—but also on the third-order correlation matrix whose elements are defined as

$${}^{(3;2,1)}\mathrm{C}_{ijl;pqr} = \sum_{\Psi' \neq \Psi} \langle \Psi | \, {}^{2}\hat{\Gamma}_{ij;pq} \, | \Psi' \rangle \langle \Psi' | \, {}^{1}\hat{\Gamma}_{l;r} \, | \Psi \rangle \tag{6}$$

The explicit form of the GHV equation in term of these 3-CM elements is [16]

$$\begin{aligned} & 2 \sum_{p,q,r} {}^{0}\mathrm{H}_{ir;pq} \, {}^{(3;2,1)}\mathrm{C}_{pqj;mrl} + 2 \sum_{q,r,s} {}^{0}\mathrm{H}_{ql;rs} \, {}^{(3;2,1)}\mathrm{C}_{rsm;jqi} \\ & + 2 \sum_{p,r,s} {}^{0}\mathrm{H}_{rs;pm} \, {}^{(3;2,1)}\mathrm{C}_{ipj;rsl} + 2 \sum_{p,q,r} {}^{0}\mathrm{H}_{pq;jr} \, {}^{(3;2,1)}\mathrm{C}_{lrm;pqi} \\ & + \sum_{p,q,r,s} {}^{0}\mathrm{H}_{rs;pq} \, {}^{(3;2,1)}\mathrm{C}_{pqj;rsl} \, {}^{1}\mathrm{D}_{i;m} - \sum_{p,q,r,s} {}^{0}\mathrm{H}_{pq;rs} \, {}^{(3;2,1)}\mathrm{C}_{rsm;pqi} \, {}^{1}\mathrm{D}_{l;j} = 0 \end{aligned} \tag{7}$$

In order to iteratively solve the GHV equation a set of initial trial N-representable [33] 1- and 2-RDM enter as data to construct an approximate initial 3-CM. The approximation algorithm which is now being used is a recently published modification of Nakatsuji-Yasuda's one [12,13,20]. The deviation from exact fulfilment of the GHV equation gives a second-order error matrix. The iterative method minimizes this error matrix following a modification of Kutzelnigg's [34–36] and Mazziotti's [37] techniques. As a result, an approximated G-particle-hole matrix corresponding to the eigenstate being considered is obtained [16–21].

2.3 The HO method

In the early seventies Bouten, Van Leuven, Mihailovich and Rosina studied the properties of the particle-hole subspace of a state, and reported the so-called Hermitian Operator method [22,23,38–41] as a mean of computing the set of low-lying excited states of an electronic system when one knows the G-particle-hole matrix corresponding to the ground state. In their work [22], Bouten et al. proposed to solve the following equation

$$\hat{H}\,\hat{\mathcal{R}}\,|\Phi\rangle = E_{\Psi}\,|\Psi\rangle \tag{8}$$

where Φ is the (reference) ground state, $\hat{\mathcal{R}}$ is an excitation operator, and Ψ is an excited eigenstate generated by the excitation operator $\hat{\mathcal{R}}$. To this aim, these authors considered the equation

$$\langle \Phi | [\hat{\mathcal{R}}, [\hat{H}, \hat{\mathcal{R}}']] | \Phi \rangle = (E_\Phi - E_\Psi) \langle \Phi | \hat{\mathcal{R}} \hat{\mathcal{R}}' + \hat{\mathcal{R}}' \hat{\mathcal{R}} | \Phi \rangle \tag{9}$$

which is formally equivalent to Eq. (8) and valid when both Φ and Ψ are eigenstates of $\hat{H}$ and the $\hat{\mathcal{R}}'$ operators form a complete set. Then Bouten et al. [22] proposed the following approximated excitation Hermitian Operator for acting on the ground state wavefunction Φ

$$\begin{aligned}\hat{\mathcal{R}} = \sum_{t,v} \Big\{ & q^{(+)}_{t,v} (a^\dagger_t a_v - {}^1\mathrm{D}_{t;v} + a^\dagger_v a_t - {}^1\mathrm{D}_{v;t}) \\ & + i\, q^{(-)}_{t,v} (a^\dagger_t a_v - {}^1\mathrm{D}_{t;v} - a^\dagger_v a_t + {}^1\mathrm{D}_{v;t}) \Big\}\end{aligned} \tag{10}$$

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

By replacing the $\hat{\mathcal{R}}$ one-body excitation operator into the Eq. (9) one obtains the following system of decoupled equations

$$\begin{aligned}\mathcal{H}^{(++)}\, q^{(+)} &= 2\,(E_\Psi - E_\Phi)\, \mathcal{G}^{(++)}\, q^{(+)} \\ \mathcal{H}^{(--)}\, q^{(-)} &= 2\,(E_\Psi - E_\Phi)\, \mathcal{G}^{(--)}\, q^{(-)}\end{aligned} \tag{11}$$

where $\mathcal{G}^{(++)}$ and $\mathcal{G}^{(--)}$ are linear combinations of the G-particle-hole matrix elements corresponding to the reference eigenstate Φ

$$\mathcal{G}^{(\pm\pm)}_{ij;pq} = {}^2\mathrm{G}_{ij;pq} \pm {}^2\mathrm{G}_{ij;qp} \pm {}^2\mathrm{G}_{ji;pq} + {}^2\mathrm{G}_{ji;qp} \tag{12}$$

and the matrices $\mathcal{H}^{(++)}$ and $\mathcal{H}^{(--)}$ have the following form:

$$\begin{aligned}\mathcal{H}^{(\pm\pm)}_{ij;pq} = {} & 4 \sum_{r,s} \Big\{ \tilde{\mathrm{H}}_{jr;ps}\, {}^2\mathrm{D}_{ir;qs} \pm \tilde{\mathrm{H}}_{ir;ps}\, {}^2\mathrm{D}_{jr;qs} \pm \tilde{\mathrm{H}}_{jr;qs}\, {}^2\mathrm{D}_{ir;ps} + \tilde{\mathrm{H}}_{ir;qs}\, {}^2\mathrm{D}_{jr;ps} \Big\} \\ & - 2 \sum_{r} \Big\{ \delta_{q,i}\, (\tilde{\mathrm{H}}\, {}^2\mathrm{D})_{pr;jr} \pm \delta_{q,j}\, (\tilde{\mathrm{H}}\, {}^2\mathrm{D})_{pr;ir} \pm \delta_{p,i}\, (\tilde{\mathrm{H}}\, {}^2\mathrm{D})_{qr;jr} + \delta_{p,j}\, (\tilde{\mathrm{H}}\, {}^2\mathrm{D})_{qr;ir} \Big\} \\ & + 2 \Big\{ (\tilde{\mathrm{H}}\, {}^2\mathrm{D})_{pi;jq} \pm (\tilde{\mathrm{H}}\, {}^2\mathrm{D})_{pj;iq} \pm (\tilde{\mathrm{H}}\, {}^2\mathrm{D})_{qi;jp} + (\tilde{\mathrm{H}}\, {}^2\mathrm{D})_{qj;ip} \Big\}\end{aligned} \tag{13}$$

where

$$\tilde{\mathrm{H}}_{ir;ps} = {}^0\mathrm{H}_{ir;ps} - {}^0\mathrm{H}_{ri;ps} \equiv {}^0\mathrm{H}_{ir;ps} - {}^0\mathrm{H}_{ir;sp} \tag{14}$$

As can be appreciated, the system of equations, Eq. (11), depend only on the 2-RDM, or equivalently on the G-particle-hole matrix, which happens to be the output of solving the GHV equation. That is why, very recently, we proposed a combination of both methods [24]. In the following section we apply this combined method to obtain the set of ground and low-lying excited states potential energy curves of a series of selected electronic systems.

Table 1 Energy values (in Hartree) of the low-lying excited states obtained with the CIS, GHV-HO and FCI methods for HF molecule at equilibrium experimental geometry

State	S	CIS	GHV-HO		FCI
			SHO	AHO	
g	0	−98.570758	[−98.596614]	[−98.596614]	−98.596587
1	1	−98.130519	−98.161927	−98.161927	−98.162158
2	1	−98.130519	−98.161927	−98.161927	−98.162158
3	0	−98.066954	−98.117448	−98.117815	−98.117677
4	0	−98.066954	−98.117448	−98.117815	−98.117677
5	1	−98.031928	−98.034245	−98.034245	−98.034014
6	0	−97.686359	−97.729422	−97.698874	−97.729670
7	1	−97.150264	−97.392791	−97.392791	−97.381060

The GHV energy of the ground state is shown in brackets

Table 2 Energy value (in Hartree) of the low-lying excited states obtained with CIS, GHV-HO and FCI methods for NH_2 molecule at equilibrium experimental geometry

State	S	CIS	GHV-HO		FCI
			SHO	AHO	
g	0.5	−54.8344998	[−54.8826217]	[−54.8826217]	−54.8825989
			−54.8826059	−54.8826059	−54.8825989
1	0.5	−54.7386862	−54.7723650	−54.7735464	−54.7804624
2	0.5	−54.4869474	−54.5241723	−54.5241723	−54.5437026
3	1.5	–	−54.3910079	−54.3910079	−54.4019683
4	1.5	–	−54.3742563	−54.3742563	−54.3785791

The GHV energy of the ground state is shown in brackets

Table 3 Energy value (in Hartree) of the low-lying excited states obtained with CIS, GHV-HO and FCI methods for CH_2 molecule at equilibrium experimental geometry

State	S	CIS	GHV-HO		FCI
			SHO	AHO	
g	1	−38.4284080	[−38.4722779]	[−38.4722779]	−38.4723058
			−38.4722412	−38.4722412	−38.4723058
1	0	–	−38.3845545	−38.3845545	−38.3947222
2	0	–	−38.3600523	−38.3600523	−38.3691504
3	0	–	−38.2557676	−38.2557676	−38.2845735
4	1	−38.0319635	−38.0621497	–	−38.0792791
5	1	−38.0135089	–	−38.0558821	−38.0549147
6	0	–	−38.0586867	−38.0586867	−38.0565582
7	1	−37.9637381	–	−38.0199493	−38.0238722

The GHV energy of the ground state is shown in brackets

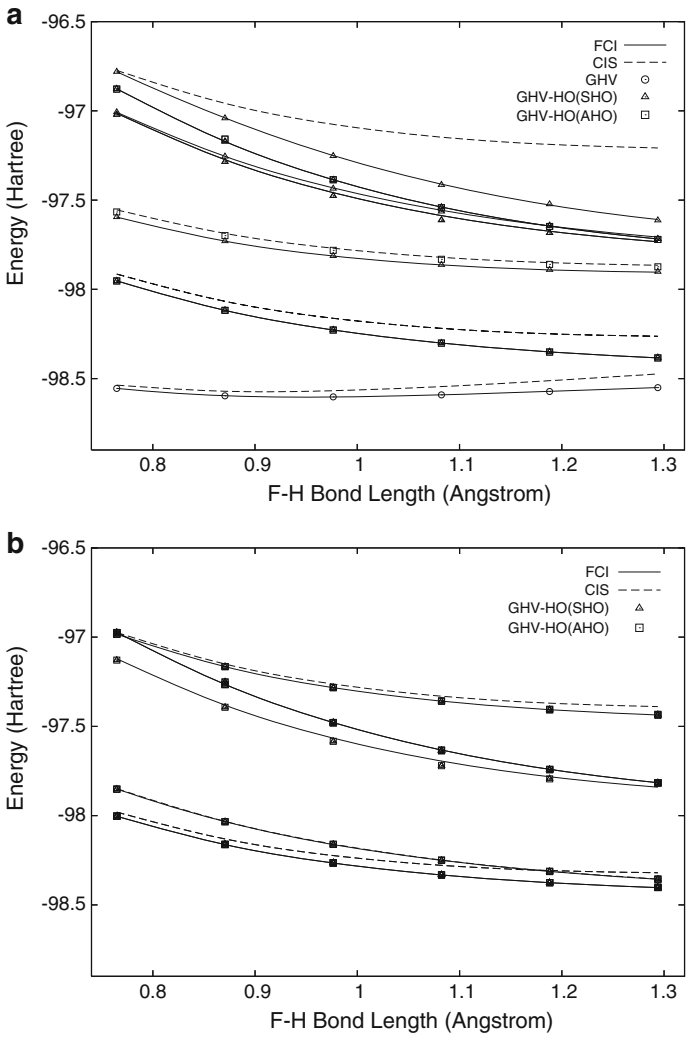

Fig. 1 Energy values (in Hartree) for **a** the ground state and first nine singlet excited states and **b** the first seven triplet excited states of HF as functions of the F-H bond length, respectively. Three of the singlet excited states and two of the triplet excited states are degenerate. The *solid* and *dashed curves* denote the FCI and CIS energy curves respectively, while *triangles*, *squares* and *circles* denote energies computed by means of the GHV-HO method

3 Results

To assess the performance of the combined GHV-HO methodology, we have carried out a number of calculations on a set of selected molecular systems including HF, H_2O, NH_3, NH_2 and CH_2, at both experimental equilibrium [42] and non-equilibrium geometries. This set has been chosen so as to deal with molecular systems having different bonding patterns and spin-symmetry properties in their ground state.

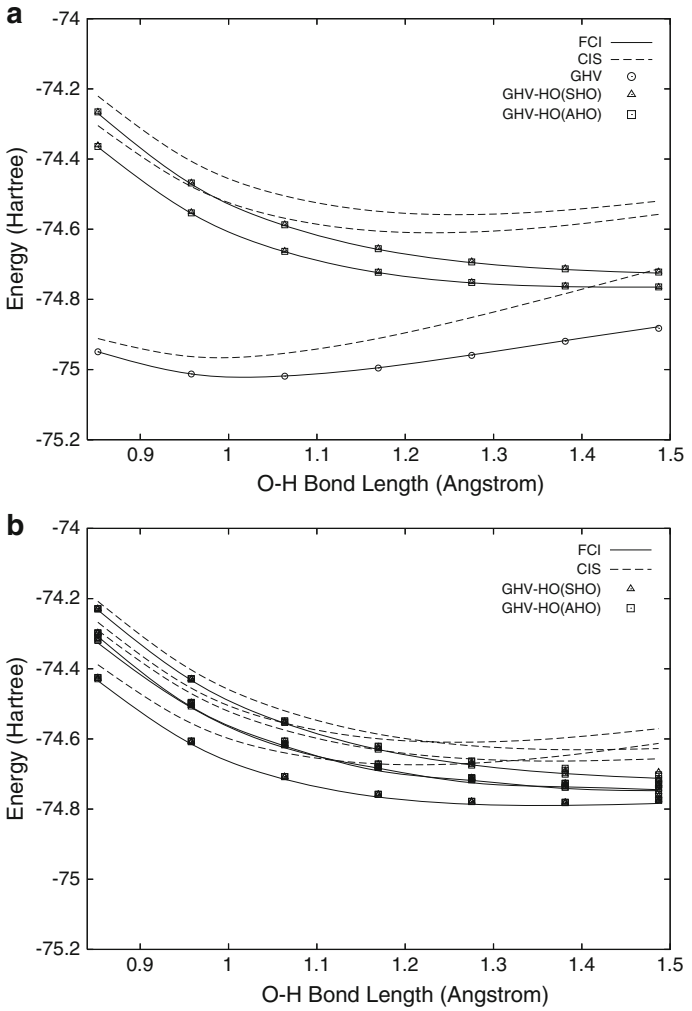

Fig. 2 Energy values (in Hartree) for **a** the ground state and first two singlet excited states and **b** the first four triplet excited states of the totally-symmetric bond stretching mode of H_2O as functions of the O-H bond length, respectively. The *solid* and *dashed curves* denote the FCI and CIS energy curves respectively, while *triangles*, *squares* and *circles* denote energies computed by means of the GHV-HO method

As mentioned above, to perform the calculations our strategy consists in decomposing the study into two main steps. In the first step, one applies the GHV method to study the ground state thus generating an initial accurate G-particle-hole matrix. In all cases, the studied state is the leading member of the multiplet, $M_s = S$, 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. In the second step, we use as data the G-particle-hole matrix obtained with the GHV method and implement the HO method to obtain the energy

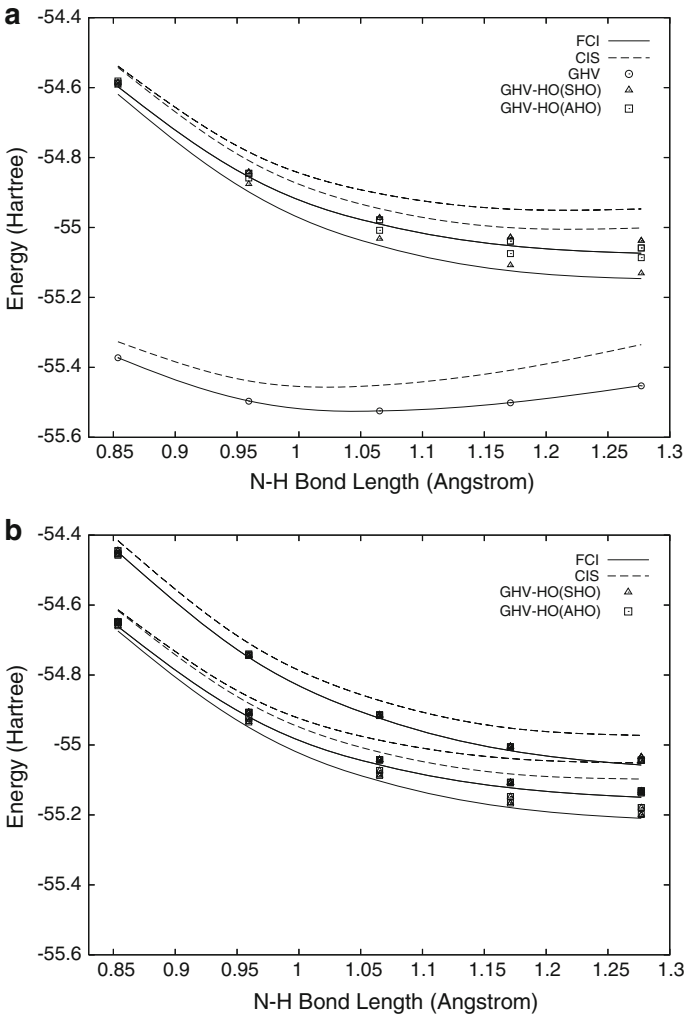

Fig. 3 Energy values (in Hartree) for **a** the ground state and first three singlet excited states and **b** the first four triplet excited states of the totally-symmetric bond stretching mode of NH_3 as functions of the N-H bond length, respectively. The *solid* and *dashed curves* denote the FCI and CIS energy curves respectively, while *triangles*, *squares* and *circles* denote energies computed by means of the GHV-HO method

of the excited states in which one is interested and which could not be directly and accurately obtained with the GHV. All calculations have been performed using minimal (STO-3G) basis sets. For the sake of comparison other usual ab initio calculations have been done for the states considered. In addition to the GHV-HO results, the reported figures include single-reference CIS model results, and FCI ones, which is why a minimal basis set has been employed. The PSI3 quantum chemistry package [43] has been used to calculate the integrals matrix ^{0}H, and the initial values of all the matrices required.

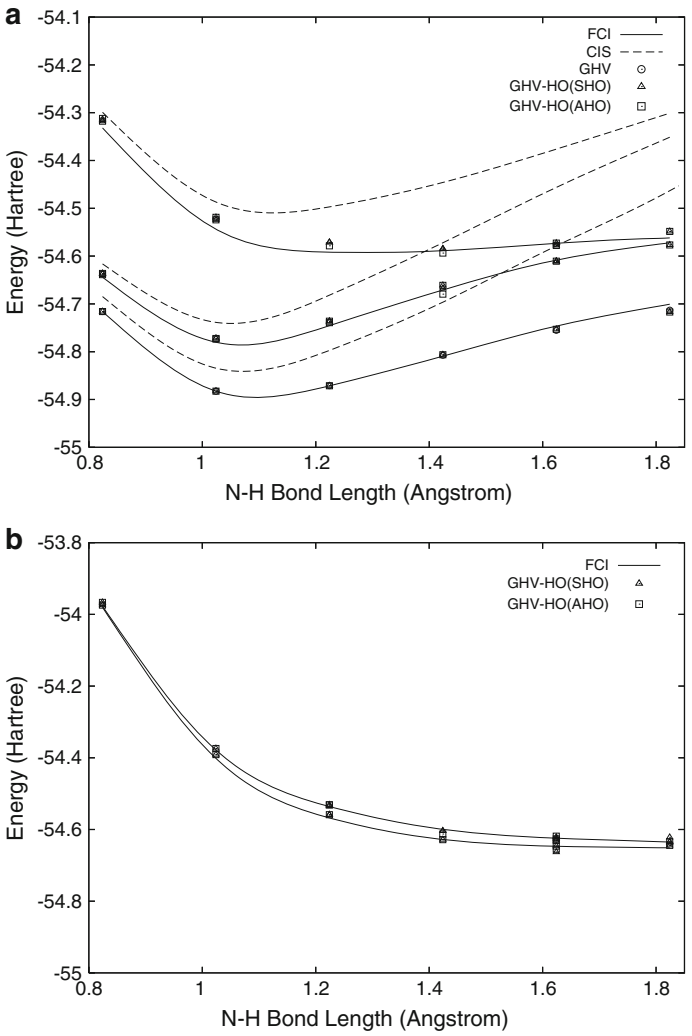

Fig. 4 Energy values (in Hartree) for **a** the ground state and first two doublet excited states and **b** the first two quartet excited states of the totally-symmetric bond stretching mode of NH_2 as functions of the N-H bond length, respectively. The *solid* and *dashed curves* denote the FCI and CIS energy curves respectively, while *triangles*, *squares* and *circles* denote energies computed by means of the GHV-HO method

In Tables 1, 2 and 3 we report the energy values of the calculations carried out at equilibrium geometry with the CIS, the GHV-HO, and the FCI methods for several low-lying excited states of HF, NH_2 and CH_2 having singlet, doublet and triplet ground states respectively. In these tables we report both the energy eigenvalues of the HO equation corresponding to $\mathcal{H}^{(++)}$, i.e. to the symmetric particle-hole subspace, which are denoted by the symbol SHO, and those obtained within the anti-symmetric subspace, which are denoted by the symbol AHO. The calculations show that in general these two sets of eigenvalues are close to each other. However, it is interesting to

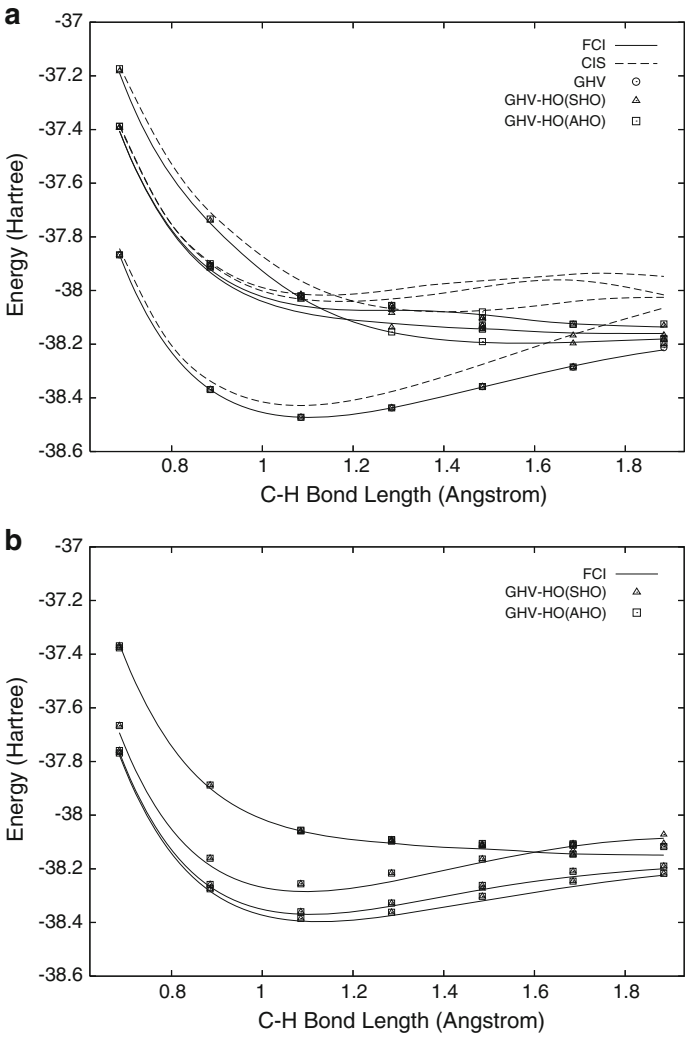

Fig. 5 Energy values (in Hartree) for **a** the ground state and first three triplet excited states and **b** the first four singlet excited states of the totally-symmetric bond stretching mode of CH_2 as functions of the C-H bond length, respectively. The *solid* and *dashed curves* denote the FCI and CIS energy curves respectively, while *triangles*, *squares* and *circles* denote energies computed by means of the GHV-HO method

note that in some cases only one of these eigenvalues is available. This is probably due to the fact that the use of a mono-excitation operator, Eq. (10) may not be sufficient for some states [24]. Also, due to similar reasons, slightly different energy values have been obtained for different members of some non-singlet excited states. Hence, we only report the values of the leading members of these states. The calculations show that the accuracy of the results obtained with the GHV-HO for these systems is far better than that of the CIS calculations. Thus, for the HF molecule, the CIS energy error relative to FCI lies within $2.09\,10^{-3}$ and $2.31\,10^{-1}$ Hartree, while for the GHV-

HO method the error lies between 1.38 10^{-4} and 3.08 10^{-2} Hartree. Although the GHV-HO energy errors for the NH_2 and CH_2 molecules are larger than those for the HF one, they are clearly still smaller than those resulting from CIS calculations. This CI method takes explicitly into account the same excitations than the HO method and therefore, its inferior performance must be due to the fact that the HO method profits of the knowledge of correlated ground state G-particle-hole matrix.

In Figs. 1, 2, 3, 4 and 5, we report calculations for the simultaneous bond-breaking potential energy curves of HF, H_2O, NH_3, NH_2 and CH_2 molecules, where multiconfigurational wavefunction effects are important. Figures 1, 2 and 3 show a comparison of the ground and low-lying singlet and triplet excited states PECs for HF and the totally-symmetric bond stretching mode of H_2O and NH_3 molecules, calculated by the GHV-HO, CIS and FCI methods. As can be appreciated, the GHV-HO method

Table 4 Maximum absolute (MAE) and nonparallelity (NPE) errors (in Hartree) for the GHV-HO potential energy curves of HF, H_2O, NH_3, NH_2 and CH_2 molecules

System	MAE			NPE		
	Ground	Excited states		Ground	Excited states	
		Min	Max		Min	Max
HF	5.21×10^{-4}	5.00×10^{-4} (1st triplet)	3.16×10^{-2} (3rd singlet)	5.19×10^{-4}	5.00×10^{-4} (1st triplet)	1.83×10^{-2} (4th Triplet)
	$[7.59 \times 10^{-2}]$	$[2.40 \times 10^{-3}]$ (3rd triplet)	$[4.01 \times 10^{-1}]$ (9th singlet)	$[5.72 \times 10^{-2}]$	$[1.27 \times 10^{-3}]$ (3rd triplet)	$[3.93 \times 10^{-1}]$ (9th singlet)
H_2O	4.45×10^{-3}	2.10×10^{-3} (1st singlet)	1.84×10^{-2} (4th triplet)	4.41×10^{-3}	8.00×10^{-4} (2nd singlet)	1.47×10^{-2} (4th triplet)
	$[1.65 \times 10^{-1}]$	$[8.49 \times 10^{-2}]$ (4th triplet)	$[2.07 \times 10^{-1}]$ (1st singlet)	$[1.28 \times 10^{-1}]$	$[5.23 \times 10^{-2}]$ (2nd triplet)	$[1.56 \times 10^{-1}]$ (2nd singlet)
NH_3	8.26×10^{-4}	1.33×10^{-2} (3rd triplet)	5.99×10^{-2} (1st singlet)	8.21×10^{-4}	2.00×10^{-3} (2nd triplet)	2.80×10^{-2} (1st singlet)
	$[1.17 \times 10^{-1}]$	$[8.48 \times 10^{-2}]$ (4th triplet)	$[1.45 \times 10^{-1}]$ (1st singlet)	$[7.15 \times 10^{-2}]$	$[5.02 \times 10^{-2}]$ (4th triplet)	$[6.79 \times 10^{-2}]$ (1st singlet)
NH_2	1.25×10^{-2}	8.70×10^{-3} (1st doublet)	2.49×10^{-2} (2nd doublet)	1.25×10^{-2}	4.10×10^{-3} (1st doublet)	2.33×10^{-2} (2nd doublet)
	$[2.38 \times 10^{-1}]$	$[2.21 \times 10^{-1}]$ (1st doublet)	$[2.61 \times 10^{-1}]$ (2nd doublet)	$[2.06 \times 10^{-1}]$	$[1.93 \times 10^{-1}]$ (1st doublet)	$[2.28 \times 10^{-1}]$ (2nd doublet)
CH_2	8.35×10^{-3}	1.44×10^{-2} (4th singlet)	3.16×10^{-2} (3rd singlet)	8.34×10^{-3}	1.25×10^{-2} (2nd singlet)	3.14×10^{-2} (3rd singlet)
	$[1.56 \times 10^{-1}]$	$[1.55 \times 10^{-1}]$ (3rd triplet)	$[2.02 \times 10^{-1}]$ (1st triplet)	$[1.33 \times 10^{-1}]$	$[1.29 \times 10^{-1}]$ (3rd triplet)	$[1.78 \times 10^{-1}]$ (1st triplet)

Errors for the CIS potential energy curves (in brackets) are shown for comparison

reproduces well the FCI curves, showing that the accuracy of the GHV-HO energies obtained at the equilibrium geometry is retained along the PECs. On the contrary, the deviation of the CIS curves from the FCI ones are large even at intermediate internuclear distances. The accuracy of these methods may be examined more quantitatively in Table 4, which presents the nonparallelity errors (NPE), computed as the difference between the maximum and minimum errors found over the curves, along with the maximum absolute errors (MAE). Comparisons of the potential energy curves for the totally-symmetric bond stretching mode of NH_2 and CH_2 are shown in Figs. 4 and 5, and errors are given in Table 4. Again, the GHV-HO method simulates well the FCI curves. However, the errors are relatively larger than those of the former molecules. In spite of this, GHV-HO still represents a definite quantitative advantage over CIS results.

4 Conclusions

The GHV-HO method has been applied successfully, for the first time, to the calculation of both the ground and the low-lying excited states potential energy curves of molecular systems having singlet and non-singlet ground states. The results, which are clearly more accurate than those of the CIS method and reproduce well the FCI results, underline the importance of developing this combined technique in the study of excited states. The method may be extended in order to improve the accuracy of the results when the states are dominated by two or more particle excitations, as well as in order to treat ionization and electron attachment. These tasks are currently being carried out in our laboratories [44].

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