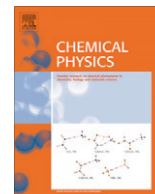




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## Chemical Physics

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# The H<sub>4</sub> model revisited within the framework of the G-particle-hole Hypervirial equation

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## ARTICLE INFO

## Article history:

Available online xxxxx

## Keywords:

Hydrogen aggregates  
G-particle hole Hypervirial equation method  
Reduced density matrices theory  
Electron correlation

## ABSTRACT

In this paper we report the results obtained when calculating the electronic structure of the H<sub>4</sub> molecular system within the framework of the G-particle-hole Hypervirial equation (GHV). This method determines directly the G-particle-hole matrix of the state considered without a previous knowledge of the wavefunction. Our primary aim is to compare the GHV performance with that of other standard *ab initio* methods having as ultimate reference the FCI results, when the system considered is strongly correlated.

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## 1. Introduction

It is well known that the H<sub>4</sub> aggregate is a highly complex system due to its molecular orbital degeneracies leading to different geometries, close-by in energy in its potential energy surface (PES). Moreover, the singlet ground state of this system is clearly multideterminantal. This complexity has motivated that many authors had studied it using different methods. For instance, Paldus et al. [1] as well as Kowalski and Jankowski [2,3] studied this hydrogen model in order to analyse the performance of the Hilbert-space state-universal coupled-cluster (SU-CC) theory. Likewise, Van Voorhis and Head-Gordon [4] applied the variational coupled-cluster (VCCD) to the H<sub>4</sub> aggregate which they considered as a *probe* system in order to test different methodologies. Using the density matrix variational theory (DMVT), which represents a conceptually different approach to those previously mentioned, Nakata et al. [5] studied the ground-state at several geometries and obtained excellent results.

Our aim here is to study the H<sub>4</sub> within the framework of the G-particle-hole Hypervirial equation (GHV) [6–11]. In a similar way to the DMVT, this methodology does not look for the wavefunction of the state considered but it looks directly for the G-particle-hole matrix [12] which, as the 2-order reduced density matrix, determines the energy as well as all the other state

observables of the system [13–15]. Here, we wish to compare the GHV performance with some of the methods applied in the previously mentioned works [1–5] as well as with the FCI values.

For the sake of that comparison, the H<sub>4</sub> system is a very interesting one. It has no more than four electrons, strongly correlated, with possible degeneracies due to the spatial symmetry. Its FCI results are readily accessible. The same system has also been used in the past to test other methodologies whose results are available. Hence, it has been selected as a challenging system to test the new method in the study of a molecular aggregate.

This paper is organized as follows. After a section where the basic notations and definitions are given we dedicate Section 3 to give a brief overview of the GHV method. A description of the different calculations which have been carried out and a discussion of the results obtained are given in Section 4.

## 2. Basic notations and definitions

In second-quantization language and in the occupation number representation [16] the 1- and 2-order reduced density matrices (1- and 2-RDM) corresponding to a state may be described as:

$${}^1D_{ij} = \langle \Phi | a_i^\dagger a_j | \Phi \rangle, \quad {}^2D_{ij,rs} = \frac{1}{2!} \langle \Phi | a_i^\dagger a_j^\dagger a_s a_r | \Phi \rangle \quad (1)$$

where the operator's labels  $i, j, r, s, \dots$  refer to a set of  $2K$  orthonormal spin-orbitals forming the basis and the number of electrons of the system is denoted  $N$ .

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The two other matrices which are at the center of our interest are the 2-order correlation matrix,  ${}^2C$ , and the  $G$ -particle-hole matrix,  $G$ . These matrices are interrelated and, although they have different properties, they describe pure 2-body effects and cannot be factorized in terms of the 1-RDM [14,15,17–19]. The  ${}^2C$  can be defined as:

$${}^2C_{ij;tv} = \sum_{\Phi' \neq \Phi} \langle \Phi | a_i^\dagger a_t | \Phi' \rangle \langle \Phi' | a_j^\dagger a_v | \Phi \rangle \equiv \langle \Phi | a_i^\dagger a_t \hat{Q} a_j^\dagger a_v | \Phi \rangle \quad (2)$$

where the symbol  $\hat{Q}$  represents the orthogonal complement of projector operator  $\hat{P} = |\Phi\rangle\langle\Phi|$ .

The  $G$ -particle-hole matrix elements are the same as those of the  ${}^2C$  although located at different row–column positions in the matrix. Those elements are the expectation values of the corresponding operators.

$$\langle \Phi | {}^2\hat{C}_{ij;tv} | \Phi \rangle \equiv {}^2C_{ij;tv} \equiv G_{it,vj} \equiv \langle \Phi | \hat{G}_{it,vj} | \Phi \rangle \quad (3)$$

It should be also recalled that the 1-RDM can easily be obtained by contracting either the 2-RDM or the  $G$ -particle-hole matrix [13–15].

Both the  ${}^2C$  and the  $G$  are the lower-order members of two large families, the  $p$ -order correlation matrices ( $p$ -CM) and the  $p$ -order  $G$ -particle-hole matrices ( $p$ -G) [19–22]. Although the matrices of these two families are closely interrelated their properties are drastically different. Thus, the  $p$ -G matrices are symmetric, positive, semi-definite matrices while no  $p$ -CM shares these properties. On the other hand the  $p$ -CM follows the notation of the  $p$ -RDM from which it derives by decomposition. These are the reasons why one may use according to the needs whichever of these two matrices is more convenient.

Let us finish this section by describing the form of the many-body Hamiltonian operator which we find more useful in this methodology [23]:

$$\hat{H} = \frac{1}{2} \sum_{ij,t,v} {}^0H_{ij;tv} a_i^\dagger a_j^\dagger a_v a_t \quad (4)$$

where

$${}^0H_{ij;tv} = \frac{\delta_{it}\epsilon_{j,v} + \delta_{j,v}\epsilon_{it}}{N-1} + \langle ij|tv \rangle \quad (5)$$

and where  $\epsilon$  is the matrix grouping the kinetic and attraction integrals and where  $\langle ij|tv \rangle$  represents a 2-electron integral in the  $\langle 12|12 \rangle$  notation.

### 3. An overview of the GHV method

The GHV method has already been described in detail in [6,8,10]. In consequence, only the main lines of this method will be recalled here.

The GHV equation [6] may be expressed in compact form as:

$$0 = \langle \Phi | [\hat{H}, \hat{G}] | \Phi \rangle \quad (6)$$

When replacing into this equation the operators  $\hat{H}$  and  $\hat{G}$  by relations (4) and (3) respectively and transforming all creator-annihilator strings into their normal product form, one obtains an equation which may be briefly expressed as:

$$0 = \text{Function}({}^0H, ({}^{3;2,1}C)) \quad (7)$$

where an element of the 3-order correlation matrix  $({}^{3;2,1}C)$  may be written as:

$$({}^{3;2,1}C)_{ijm;rst} = \langle \Phi | a_i^\dagger a_j^\dagger a_s a_r \hat{Q} a_m^\dagger a_t | \Phi \rangle \quad (8)$$

Eq. (7) can be solved iteratively by initiating the process with the  $N$ -representable [24] 1- and 2-RDMs which we expect to correspond

to a zero-order wave-function of the state being studied. In order to evaluate the *r.h.s.* of Eq. (7) one needs to approximate the  $({}^{3;2,1}C)$  elements in terms of the 2-order matrices. This is carried out by applying a set of constructing algorithms [8,10] which are a modification of those proposed by Nakatsuji and Yasuda [25,26]. Note that, although Eq. (7) involves a 3-order correlation matrix, due to internal averaging of the different terms, the matrix equation is in fact a 2-order one. Once the GHV equation represented in (7) is established, it can be transformed into a system of differential equations [8] to be solved iteratively. This is done by adapting to the GHV case the unitary transformation of operators technique proposed by Kutzelnigg et al. [27] and in particular by Mazziotti [28–30] for solving other Hypervirial equations. In terms of the quantities obtained at the  $n$ th iteration, the resulting  $G$ -particle-hole matrix error is [6,8,10]:

$$(\Delta G^{(n+1)})_{im;vj} = \langle \Phi | [\hat{A}^{(n)}, \hat{G}_{im;vj}] | \Phi \rangle \quad (9)$$

where

$$\hat{A}^{(n)} = \sum_{i,m,r,j} A_{im,rj}^{(n)} \hat{G}_{im;vj} \quad (10)$$

is the anti-Hermitian operator appearing in the exponent of the unitary operator used in the transformation and the matrix  $A$  is the residual of the GHV equation [6,8,10]. At each iteration, the  $G$ -particle-hole matrix obtained is contracted in order to obtain the corresponding 1-RDM, and the energy is calculated according to the expression [31]:

$$E = \sum_{ij,m,l} {}^0H_{ij,ml} [{}^1D_{im} {}^1D_{jl} - \delta_{j,m} {}^1D_{il} + G_{im;jl}] \quad (11)$$

or, when  $\Psi$  is a singlet state, to the spin-adapted formula [31]:

$$E = \sum_{il} \{ 2\bar{h}_{il}^c - \bar{h}_{il}^x \} {}^1D_{il} - \sum_{ij,l,m} {}^0H_{ij,ml} (2G_{\bar{i}l,m\bar{j}} - G_{\bar{i}m;\bar{l}j}) \quad (12)$$

where the bar over the indices denotes that the spin-orbital has a beta spin and where

$$\bar{h}_{il}^c = \sum_j {}^0H_{ij;lj} \quad \bar{h}_{il}^x = \sum_j {}^0H_{ij;jl}$$

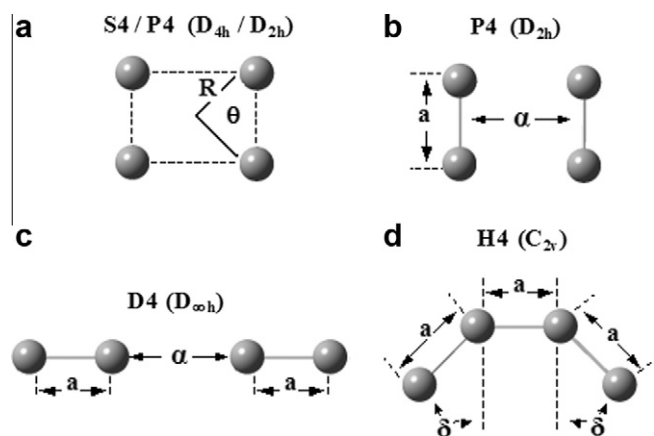
are one-body contractions of the  ${}^0H$  of the coulomb and exchange types respectively. Fehlbeg's method [32] for numerical integration of differential equations is applied in order to accelerate convergence.

### 4. Six H<sub>4</sub> potential-energy curves for planar conformations

In the introduction we have mentioned the studies on the H<sub>4</sub> model by Paldus et al. [1], Kowalski et al. [2,3], Van Voorhis and Head-Gordon [4] and Nakata et al. [5]. Here, in order to evaluate the GHV performance, we have selected the same basic geometries which have been investigated by these authors. These geometries are represented in Fig. 1 where the variable parameters are also shown. As Paldus et al. mentioned in [1], this choice of geometries and parameters permits to break and generate, in a continuous way, orbital and configuration degeneracies when transforming one geometry into another.

#### 4.1. Calculations and results

In order to suitably control the quality of the GHV results, a FCI calculation has been carried out in all cases. The Huzinaga–Dunning DZ basis set [33], which is also the basis set used in the DMVT calculation [5], has been used here. The GAMESS program [34] have been used to calculate the integrals matrix  ${}^0H$  and the initial values of all the matrices required in the GHV method. In the tables



**Fig. 1.** Nuclear conformations and definitions of the variable parameters for the S4 ( $D_{4h}$ ), P4 ( $D_{2h}$ ), D4 ( $D_{\infty h}$ ) and H4 ( $C_{2v}$ ) models.

reported below for the S4 and S4/P4 potential energy curves (PECs) we have omitted the values which were also obtained with the DMVT because within the precision considered here, the values obtained with this method coincide with the FCI ones. The disadvantage of the DMVT is that it is too costly for calculating larger systems and somewhat inadequate for the study of other molecular systems including dissociative species [35].

#### 4.1.1. S4 conformation, $\theta = 90^\circ$ , $R$ variable ( $D_{4h}$ )

A study of the determinant coefficient values in the ground-state wave-function shows that two determinants initially dominate the wave-function but as the  $R$  increases this multireferential character becomes stronger. This, as was previously pointed out [1–3], is what renders difficult the study of the PECs of this system in this conformation.

In Table 1 we compare the errors with respect to the FCI with those of RHF, MP2, CISD, CCSD and the GHV methods for the square stretching dissociation of the H<sub>4</sub>. A column with the FCI values completes the data given in this table. As can be seen, the CCSD and the GHV, which are the two most accurate methods, give errors of the order of 10 mE<sub>h</sub>, the CCSD by excess and the GHV by defect. Up to  $R = 1.6$  Å, the curve is better described by the GHV, after which distance all the calculations give diverging results with respect to the FCI values. The GHV maximum absolute energy error, 16.34 mE<sub>h</sub>, occurs at 2.0 Å.

#### 4.1.2. S4/P4 conformations, $\theta$ variable ( $D_{2h}$ )

Two rectangular conformation PECs with a variable  $\theta$  have been calculated while keeping constant the distance  $R$ .

- $R = 0.869$  Å constant. Here, as  $\theta$  decreases the H<sub>4</sub> aggregate splits into two H<sub>2</sub> moieties. The most stable conformation in this PEC occurs at  $\theta = 50^\circ$  when the internuclear distance at each of the two H<sub>2</sub> moieties is 0.734 Å.

**Table 1**

Errors with respect to the FCI values of the H<sub>4</sub> ground state energy (in mE<sub>h</sub>) obtained with standard methods for the S4 model with  $\theta = 90^\circ$  ( $D_{4h}$ ) and  $R$  variable. The FCI reference values (in E<sub>h</sub>) are given in the last column.

R/Å	RHF	MP2	CISD	CCSD	GHV	FCI
0.6	-103.72	-55.28	-9.87	-4.67	-4.66	-1.951120
0.8	-128.09	-70.78	-9.83	-0.36	-4.61	-2.061044
1.0	-156.21	-86.81	-12.89	4.28	-4.69	-2.068375
1.2	-190.63	-104.37	-19.30	8.93	-7.53	-2.047426
1.4	-230.70	-122.64	-26.67	12.18	-6.93	-2.024629
1.6	-274.49	-139.35	-26.64	12.60	-7.66	-2.008466
1.8	-318.89	-150.84	-21.70	10.58	-11.20	-1.999208
2.0	-360.46	-153.48	-18.35	7.63	-16.34	-1.994539

- $R = 1.738$  Å constant. In this case, the equilibrium is reached for  $\theta = 30^\circ$  and here the internuclear distance at each of the two H<sub>2</sub> moieties is 0.900 Å.

The analysis of the value of the largest determinant coefficient of the FCI wave-function in these two PECs shows that the multi-configurational character diminishes with  $\theta$ . In particular, when  $R = 1.738$  Å the initial value of this coefficient for  $\theta = 90^\circ$  is 0.54; for  $\theta = 75^\circ$  is 0.72 and for  $\theta = 30^\circ$ , which is the equilibrium point, this coefficient value is 0.99. That value indicates that, at that geometry, the wave-function is almost monoconfigurational. In Tables 2 and 3 we report the errors with respect to the FCI values of different methods for these two PECs. The FCI energy values are shown in the last column of these tables. Here also, the CCSD and the GHV are the two methods which give a closer result to the FCI one. It is interesting to note that also here the signs of the CCSD and of the GHV errors, are opposite.

#### 4.1.3. P4 conformation, $a = 1.058$ Å, $\alpha$ variable ( $D_{2h}$ )

In this PEC two H<sub>2</sub> moieties keep constant their internuclear distance at 1.058 Å while varying their separating distance  $\alpha$  (see Fig. 1). As can be appreciated in Table 4, the largest error in all calculations corresponds to the S4 conformation ( $\alpha = 1.058$  Å) which is highly multiconfigurational. Here the CCSD's are the most accurate ones. Although the values obtained with the GHV show slightly higher errors than the CCSD ones, they are of the same order. The CISD's errors are slightly higher than the GHV ones but still acceptable while MP2 and RHF are several orders higher.

#### 4.1.4. Potential energy curve describing the dissociation of the D4, $a = 1.058$ Å (linear, $D_{\infty h}$ ) as the two H<sub>2</sub> moieties separate

The different methods examined perform here in a similar way as in the other PECs. Thus, the CCSD, the GHV and the CISD give accurate results as can be appreciated in Table 5. The larger errors appear at  $\alpha = 0.794$  Å and  $\alpha = 1.058$  Å which correspond to the points with largest orbital degeneracy. The best results are obtained with the CCSD followed by the GHV.

#### 4.1.5. Potential energy curve evolving from the H4 ( $C_{2v}$ ) conformation to the D4 (linear, $D_{\infty h}$ ) conformation

In Table 6 we show the energy errors (in mE<sub>h</sub>), obtained with various standard methods, for H4 ( $C_{2v}$ ). While the distance  $a = 1.058$  Å is kept constant, the  $\delta$  angle varies from 0° to 90°. Thus when  $\delta = 0^\circ$  the conformation is the S4 ( $D_{4h}$ ) and as  $\delta$  augments, the conformation evolves towards D4 (linear,  $D_{\infty h}$ ) conformation which is reached when  $\delta = 90^\circ$ . The FCI energy value (in E<sub>h</sub>) is given in the last column of Table 6. As can be seen the CCSD gives the smallest error for all calculated points of this PEC and, although slightly larger, the values obtained with the GHV are of the same

**Table 2**

Errors with respect to the FCI values of the H<sub>4</sub> ground-state energy (in mE<sub>h</sub>) obtained with standard methods for the S4/P4 model for  $R = 0.869$  Å and  $\theta$  variable. The FCI reference values (in E<sub>h</sub>) are given in the last column.

$\theta$ /Degrees	RHF	MP2	CISD	CCSD	GHV	FCI
90.0	-137.13	-76.15	-10.48	1.22	-4.69	-2.069685
89.9	-136.21	-75.32	-10.38	1.16	-4.31	-2.069691
89.5	-132.66	-72.13	-9.99	0.93	-3.15	-2.069840
89.0	-128.52	-68.43	-9.50	0.68	-1.77	-2.070301
88.0	-121.20	-61.97	-8.55	0.32	-0.22	-2.072098
85.0	-105.36	-48.60	-6.28	-0.12	1.95	-2.083031
80.0	-90.12	-37.14	-4.17	-0.17	1.43	-2.110601
75.0	-80.36	-30.78	-3.01	-0.13	0.73	-2.141413
70.0	-72.87	-26.36	-2.26	-0.10	0.44	-2.172051
60.0	-61.34	-20.10	-1.31	-0.06	0.18	-2.226445
50.0	-52.50	-15.69	-0.78	-0.04	0.13	-2.257406
40.0	-45.20	-12.41	-0.48	-0.03	0.08	-2.226763

**Table 3**

Errors with respect to the FCI values of the H<sub>4</sub> ground-state energy (in mE<sub>h</sub>) obtained with standard methods for the S4/P4 model for R = 1.738 Å and θ variable. The FCI reference values (in E<sub>h</sub>) are given in the last column.

θ/Degrees	RHF	MP2	CISD	CCSD	GHV	FCI
90.0	-305.27	-148.07	-23.15	11.38	-9.63	-2.001469
89.9	-304.76	-147.91	-23.23	11.26	-9.49	-2.001469
89.5	-302.70	-147.24	-23.55	10.80	-8.99	-2.001488
89.0	-300.14	-146.41	-23.99	10.20	-8.74	-2.001545
88.0	-295.08	-144.75	-24.96	9.01	-7.60	-2.001771
85.0	-280.21	-139.73	-28.67	5.53	-5.36	-2.003270
80.0	-255.70	-130.51	-37.13	1.62	-2.78	-2.008003
75.0	-230.87	-119.65	-42.57	0.35	-0.98	-2.015271
70.0	-205.72	-107.23	-34.51	0.07	0.05	-2.025517
60.0	-156.46	-79.81	-19.45	-0.01	0.81	-2.058411
50.0	-113.12	-53.64	-8.97	-0.01	0.53	-2.113761
40.0	-79.97	-33.12	-3.46	0.00	0.15	-2.193770
30.0	-57.97	-19.75	-1.21	0.00	0.02	-2.281126
20.0	-44.05	-12.31	-0.45	0.00	-0.03	-2.265302

**Table 4**

Errors with respect to the FCI values of the H<sub>4</sub> ground-state energy (in mE<sub>h</sub>) obtained with standard methods for the P4 model for α = 1.058 Å and α variable. The FCI reference values (in E<sub>h</sub>) are given in the last column.

α/Å	RHF	MP2	CISD	CCSD	GHV	FCI
0.794	-63.22	-20.06	-1.37	-0.18	0.19	-2.091125
0.953	-83.55	-33.90	-3.61	-0.65	1.35	-2.056263
1.058	-121.67	-66.82	-9.61	-1.54	-4.71	-2.047746
1.164	-93.45	-40.64	-4.73	-0.48	1.18	-2.075871
1.270	-84.75	-33.66	-3.48	-0.21	1.29	-2.110929
1.588	-75.82	-28.48	-2.63	-0.09	0.32	-2.182053
2.646	-69.19	-26.27	-2.18	-0.01	0.08	-2.233339
3.704	-68.60	-26.17	-2.15	0.00	0.06	-2.235382

**Table 5**

Errors with respect to the FCI values of the H<sub>4</sub> ground-state energy (in mE<sub>h</sub>) obtained with standard methods for the D4 model for α = 1.058 Å and α variable. The FCI reference values (in E<sub>h</sub>) are given in the last column.

α/Å	RHF	MP2	CISD	CCSD	GHV	FCI
0.794	-75.77	-27.31	-1.98	-0.60	1.74	-2.188525
1.058	-68.92	-24.68	-1.81	-0.31	0.86	-2.214929
1.588	-68.08	-25.03	-2.06	-0.16	0.24	-2.230760
2.646	-68.74	-26.07	-2.16	-0.02	0.08	-2.235443
3.704	-68.60	-26.16	-2.15	0.00	0.07	-2.235426
4.233	-68.58	-26.17	-2.15	0.00	0.06	-2.235402

**Table 6**

Errors with respect to the FCI values of the H<sub>4</sub> ground-state energy (in mE<sub>h</sub>) obtained with standard methods for the H4 model for α = 1.058 Å and angle δ variable (C<sub>2v</sub>). The FCI reference values (in E<sub>h</sub>) are given in the last column.

δ/degrees	RHF	MP2	CISD	CCSD	GHV	FCI
0.0	-121.67	-66.82	-9.61	-1.54	-4.71	-2.047746
15.0	-80.68	-32.00	-3.05	-0.34	1.53	-2.128004
30.0	-73.23	-27.49	-2.28	-0.32	0.95	-2.176595
45.0	-70.48	-25.77	-1.99	-0.30	0.83	-2.198710
60.0	-69.41	-25.05	-1.87	-0.30	0.81	-2.208967
75.0	-69.01	-24.76	-1.82	-0.31	0.84	-2.213587
90.0	-68.92	-24.68	-1.81	-0.31	0.86	-2.214929

order. The CISD's errors although larger are still acceptable; this is not the case for the RHF nor for the MP2.

#### 4.1.6. Permanent electric dipole and quadrupole values in the H<sub>4</sub> (C<sub>2v</sub>) conformation

The permanent dipole (μ) and (traceless) quadrupole (Q) moments as well as the *r.m.s.* deviation of the 1-RDM with respect to the corresponding FCI matrix can be considered suitable tests

for the *N*- and spin-representability [19,24,36–38] of the 1-RDM as well as for its accuracy. Therefore these quantities have been calculated for the H<sub>4</sub> (C<sub>2v</sub>) conformation and their values are reported in Table 7 for the various standard approaches. In both cases it is assumed that the molecular system H<sub>4</sub> lies in the (y,z) plane, so that the *x*-axis is perpendicular to the molecular plane. The coordinate origin is at the center of mass of the molecular system, and the molecule is oriented in a way shown in Fig. 2. According to this choice, the only nonvanishing dipole and quadrupole components are μ<sub>z</sub>, Q<sub>xx</sub>, Q<sub>yy</sub>, and Q<sub>zz</sub>.

While the electronic dipole moments obtained with the GHV as well as with the CCSD compare well with the FCI value, the situation changes when considering the quadrupole moments and the *r.m.s.* deviation. Thus for δ = 0°, which corresponds to the S4 (D<sub>4h</sub>) conformation, the 1-RDM *r.m.s.* deviation is significant and, what is more, the cartesian components of the quadrupole tensor are far from the FCI results. The calculations show that, for the S4 conformation, the space symmetry is broken.

On the other hand, when the angle δ augments, and consequently the orbitals degeneracy disappears, the values obtained both for the quadrupole moments and for the 1-RDM *r.m.s.* deviation compare well with the FCI values.

#### 4.2. General comments on the GHV performance and the symmetry problem

In the first part of this section we have reported and compared the results obtained with the RHF, the MP2, the CISD, the CCSD and the GHV methods for the six PECs considered. Clearly the RHF and the MP2 performance is rather poor and, although the CISD performs much better, the results obtained with this method are not as good as the CCSD and GHV ones. The method which in general yields the lowest absolute energy errors is the CCSD but the GHV performance can really be considered comparable to the CCSD one. Thus, when examining the maximum absolute energy errors (MAE) of these two methods, the results show that both PECs follow rather faithfully the FCI curve; the different MAE values in mE<sub>h</sub> occurring for the square planar (D<sub>4h</sub>) conformation are given in the following list.

	R = 0.748 Å	R = 0.869 Å	R = 1.6 Å	R = 1.738 Å	R = 2.0 Å
CCSD	1.54	1.22	12.60	11.38	-
GHV	4.71	4.69	-	9.63	16.34

Let us conclude our comments concerning the energy by noting that the most stable of the H<sub>4</sub> conformations examined corresponds to the S4/P4 with R = 1.738 Å and θ = 30°. At this geometry the FCI energy value is -2.281126 E<sub>h</sub> while that obtained with the GHV is -2.281141 E<sub>h</sub>, which can be considered excellent. Evidently, this H<sub>4</sub> structure is very close to that of two parallel hydrogen molecules separated by the distance R.

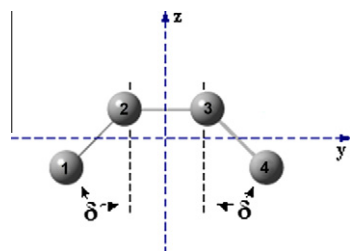
Let us now consider the results obtained for the non-vanishing quadrupole components for the S4 square planar conformation. It is clear that the GHV results resulting from the calculated 1-RDM, and consequently the matrix itself, do not correctly describe the symmetry properties of this H<sub>4</sub> geometry. Our initial trial G-particle-hole matrix is derived from the RHF wave-function and, since the RHF results show an extreme lack of symmetry of the quadrupole components, we think that this is at the root of the GHV errors.

In the GHV method the *N*- and spin-representability of the initial G-particle-hole matrix (and hence of the 2-RDM and 2-HRDM) is, in principle, maintained during the iterations. The only intrinsic source of error of the method derives from the approximation algorithms used at present for evaluating the 3-order cumulant

**Table 7**

Nonvanishing cartesian components of dipole ( $\mu$ , in D) and (traceless) quadrupole ( $Q$ , in Buckingham) moments, and *r.m.s.* deviation of 1-RDM with respect to the FCI value in the H4 ( $C_{2v}$ ) conformation of H<sub>4</sub> obtained with standard methods for  $a = 1.058 \text{ \AA}$  and  $\delta$  (in degrees) variable.

$\delta/\text{Degrees}$	Method	$\mu_z$	$Q_{xx}$	$Q_{yy}$	$Q_{zz}$	<i>r.m.s.</i>
0.0	HF	0.0000	0.835	-3.974	3.138	$1.129 \cdot 10^{-2}$
	MP2	0.0000	0.825	-3.790	2.965	$9.439 \cdot 10^{-3}$
	CISD	0.0000	0.770	-0.896	0.127	$1.516 \cdot 10^{-3}$
	CCSD	0.0000	0.774	-0.378	-0.396	$6.39210^{-4}$
	GHV	0.0000	0.798	-2.277	1.479	$3.870 \cdot 10^{-3}$
	FCI	0.0000	0.769	-0.385	-0.385	
15.0	HF	-0.0275	0.365	-2.819	2.455	$5.499 \cdot 10^{-3}$
	MP2	-0.0121	0.363	-2.700	2.337	$3.604 \cdot 10^{-3}$
	CISD	-0.0155	0.382	-2.356	1.975	$5.381 \cdot 10^{-4}$
	CCSD	-0.0057	0.388	-2.306	1.918	$9.112 \cdot 10^{-5}$
	GHV	-0.0043	0.393	-2.312	1.919	$4.832 \cdot 10^{-5}$
	FCI	-0.0066	0.390	-2.306	1.916	
45.0	HF	-0.1409	-0.253	-0.596	0.849	$4.895 \cdot 10^{-3}$
	MP2	-0.0894	-0.200	-0.628	0.828	$2.477 \cdot 10^{-3}$
	CISD	-0.0774	-0.147	-0.603	0.750	$3.532 \cdot 10^{-4}$
	CCSD	-0.0658	-0.134	-0.612	0.746	$4.541 \cdot 10^{-5}$
	GHV	-0.0651	-0.128	-0.620	0.748	$8.452 \cdot 10^{-5}$
	FCI	-0.0660	-0.130	-0.618	0.748	
75.0	HF	-0.0925	-0.635	1.120	-0.485	$5.230 \cdot 10^{-3}$
	MP2	-0.0561	-0.496	0.853	-0.357	$2.328 \cdot 10^{-3}$
	CISD	-0.0445	-0.404	0.687	-0.283	$3.285 \cdot 10^{-4}$
	CCSD	-0.0398	-0.383	0.646	-0.263	$5.339 \cdot 10^{-5}$
	GHV	-0.0389	-0.374	0.629	-0.255	$4.640 \cdot 10^{-5}$
	FCI	-0.0396	-0.378	0.637	-0.259	
90.0	HF	0.0000	-0.696	1.393	-0.696	$5.290 \cdot 10^{-3}$
	MP2	0.0000	-0.539	1.077	-0.539	$2.318 \cdot 10^{-3}$
	CISD	0.0000	-0.439	0.877	-0.439	$3.266 \cdot 10^{-4}$
	CCSD	0.0000	-0.416	0.831	-0.416	$5.620 \cdot 10^{-5}$
	GHV	0.0000	-0.407	0.813	-0.407	$3.659 \cdot 10^{-5}$
	FCI	0.0000	-0.411	0.822	-0.411	



**Fig. 2.** Molecular orientation of the H4 ( $C_{2v}$ ) model. The coordinate origin is at the center of mass of the H<sub>4</sub> aggregate.

needed for constructing the GHV equation. These algorithms are extremely accurate when the state under study is only moderately multiconfigurational but otherwise their accuracy diminishes [9,39]. But, in the calculations reported above, in particular for the S4 square planar conformation, we are inclined to think that errors are mainly due to the choice of the initial trial *G*-particle-hole matrix which was deduced from an RHF calculation. Thus, the value obtained for the S4 quadrupole moment components at the RHF level of accuracy do not show up the space symmetry and, as we stated in [9], the solution of the GHV equation will correspond to a Hamiltonian eigenstate provided the trial matrix initiating the iterative procedure satisfies all the invariants of the system such as *N*- and spin-representability, space symmetry properties, etc. The question of how to determine the initial *G*-particle-hole matrix when studying a highly degenerate state is now being investigated.

### Acknowledgements

This work has been financially supported by the Spanish Ministerio de Educación y Ciencia under project FIS2007-62006, by the

Universidad de Buenos Aires under projects X-017 and X-079 and Argentine Consejo Nacional de Investigaciones Científicas y Técnicas under project PIP No. 11220090100061. Financial support from the Spanish Dirección General de Universidades e Investigación de la Comunidad de Madrid under Grant No. S2009/ESP/1691 and Program MODELICO-CM and from projects LIMA and N4E (European Commission FP7-ICT-2009-4-248909-LIMA and FP7-ICT-2009-4-248855-N4E) is also acknowledged.

### References

- [1] J. Paldus, P. Piecuch, L. Pylypov, B. Jeziorowski, Phys. Rev. A 47 (1993) 2738.
- [2] K. Kowalski, K. Jankowski, Chem. Phys. Lett. 290 (1998) 180; K. Kowalski, K. Jankowski, Phys. Rev. Lett. 81 (1998) 1195.
- [3] K. Jankowski, K. Kowalski, J. Chem. Phys. 110 (1999) 3714; K. Jankowski, K. Kowalski, J. Chem. Phys. 110 (1999) 9345; K. Jankowski, K. Kowalski, J. Chem. Phys. 111 (1999) 2940; K. Jankowski, K. Kowalski, J. Chem. Phys. 111 (1999) 2952.
- [4] T. Van Voorhis, M. Head-Gordon, J. Chem. Phys. 113 (2000) 8873.
- [5] M. Nakata, M. Ehara, H. Nakasutji, J. Chem. Phys. 116 (2002) 5432.
- [6] D.R. Alcoba, C. Valdemoro, L.M. Tel, E. Pérez-Romero, Int. J. Quantum Chem. 109 (2009) 3178.
- [7] C. Valdemoro, D.R. Alcoba, L.M. Tel, E. Pérez-Romero, Int. J. Quantum Chem. 109 (2009) 2622.
- [8] D.R. Alcoba, L.M. Tel, E. Pérez-Romero, C. Valdemoro, Int. J. Quantum Chem. 111 (2011) 937.
- [9] C. Valdemoro, D.R. Alcoba, L.M. Tel, E. Pérez-Romero, Int. J. Quantum Chem. 111 (2011) 245.
- [10] D.R. Alcoba, C. Valdemoro, L.M. Tel, E. Pérez-Romero, O.B. Oña, J. Phys. Chem. A 115 (2011) 2599.
- [11] C. Valdemoro, D.R. Alcoba, O.B. Oña, L.M. Tel, E. Pérez-Romero, J. Math. Chem. (2011), doi:10.1007/s10910-011-9810-y.
- [12] C. Garrod, J.K. Percus, J. Math. Phys. 5 (1964) 1756.
- [13] C. Garrod, M. Rosina, J. Math. Phys. 10 (1975) 1855.
- [14] C. Valdemoro, L.M. Tel, D.R. Alcoba, E. Pérez-Romero, F.J. Casquero, Int. J. Quantum Chem. 90 (2002) 1555.
- [15] C. Valdemoro, D.R. Alcoba, L.M. Tel, Int. J. Quantum Chem. 93 (2003) 212.
- [16] P.R. Surjan, Second Quantized Approach to Quantum Chemistry: An Elementary Introduction, Springer-Verlag, Berlin, Heidelberg, 1989.

- [17] C. Valdemoro, M.P. de Lara-Castells, E. Pérez-Romero, L.M. Tel, *Adv. Quantum Chem.* 31 (1999) 37.
- [18] C. Valdemoro, in: D.A. Mazziotti (Ed.), *Reduced-Density-Matrix Mechanics with Applications to Many-Electron Atoms and Molecules*, *Adv. Chem. Phys.*, 134, Wiley, New York, 2007. and references therein.
- [19] D.R. Alcoba, in: D.A. Mazziotti (Ed.), *Reduced-Density-matrix Mechanics with Applications to Many-electron Atoms and Molecules*, *Adv. Chem. Phys.*, 134, Wiley, New York, 2007. and references therein.
- [20] C. Valdemoro, L.M. Tel, E. Pérez-Romero, *Phys. Rev. A* 61 (2000) 032507.
- [21] C. Valdemoro, D.R. Alcoba, L.M. Tel, E. Pérez-Romero, *Int. J. Quantum Chem.* 85 (2001) 214.
- [22] D.R. Alcoba, C. Valdemoro, *Phys. Rev. A* 64 (2001) 062105.
- [23] C. Valdemoro, *Phys. Rev. A* 31 (1985) 2114;  
C. Valdemoro, *Phys. Rev. A* 31 (1985) 2123.
- [24] A.J. Coleman, *Rev. Mod. Phys.* 35 (1963) 668.
- [25] H. Nakatsuji, K. Yasuda, *Phys. Rev. Lett.* 76 (1996) 1039.
- [26] K. Yasuda, H. Nakatsuji, *Phys. Rev. A* 56 (1997) 2648.
- [27] W. Kutzelnigg, H. Reitz, S. Durmaz, S. Koch, *Proc. Indian Acad. Sci.* 96 (1986) 177.
- [28] D.A. Mazziotti, *Phys. Rev. Lett.* 97 (2006) 143002.
- [29] D.A. Mazziotti, *Phys. Rev. A* 75 (2007) 022505.
- [30] D.A. Mazziotti, *J. Chem. Phys.* 126 (2007) 184101.
- [31] C. Valdemoro, L.M. Tel, E. Pérez-Romero, in: C. King, M. Bylicki, J. Karwowski (Eds.), *Symmetry, Spectroscopy and SCHUR*, Nicolaus Copernicus University Press, 2006.
- [32] E. Fehlbberg, NASA Technical Report, R287, 1968.;  
E. Fehlbberg, NASA Technical Report, R315, 1969.
- [33] S. Huzinaga, *J. Chem. Phys.* 42 (1965) 1293;  
T.H. Dunning Jr., *J. Chem. Phys.* 53 (1970) 2823;  
T.H. Dunning, P.H. Hay, in: H.F. Schaeffer III (Ed.), *Method of Electronic Structure Theory*, Plenum Press, New York, 1977.
- [34] M.W. Schmidt, K.K. Baldrige, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S. Su, T.L. Windus, M. Dupuis, J.A. Monomery, *J. Comput. Chem.* 14 (1993) 1347.
- [35] H. Van Aggelen, P. Bultinck, B. Verstichel, D. Van Neck, P. Ayers, *Phys. Chem. Chem. Phys.* 1 (2009) 5558.
- [36] E. Pérez-Romero, L.M. Tel, C. Valdemoro, *Int. J. Quantum Chem.* 61 (1997) 55.
- [37] D.R. Alcoba, C. Valdemoro, *Int. J. Quantum Chem.* 102 (2005) 629;  
D.R. Alcoba, C. Valdemoro, *Int. J. Quantum Chem.* 106 (2006) 2999.
- [38] D.R. Alcoba, C. Valdemoro, L.M. Tel, E. Pérez-Romero, *Phys. Rev. A* 77 (2008) 042508.
- [39] C. Valdemoro, L.M. Tel, D.R. Alcoba, E. Pérez-Romero, *Theor. Chem. Acc.* 118 (2007) 503.