

Combining the G -particle-hole hypervirial equation and the hermitian operator method to study electronic excitations and de-excitations

Carmela Valdemoro · Diego R. Alcoba ·
Ofelia B. Oña · Luis M. Tel ·
Encarnación Pérez-Romero

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Abstract The first aim of this paper is to give an overview of the contracted equations theory (Valdemoro in Adv Chem Phys 134. Wiley, New York, 2007) leading to the description of the G -particle-hole Hypervirial equation (GHV) (Alcoba et al. in Int J Quantum Chem 109:3178, 2009; 111:937, 2011; J. Phys. Chem. A 115:2599, 2011; Valdemoro et al. in Int J Quantum Chem 109:2622, 2009; 111:245, 2011). Our second aim here is to show the suitability to combine the GHV method with the Hermitian Operator (HO) method of Bouten et al. (Nucl Phys A 202:127, 1973; 221:173, 1974) for obtaining various energy differences of a system spectrum when the G -particle-hole matrix and the energy of an almost mono-configurational state is known. Two simple applicative examples of the combined GHV-HO performance are reported.

C. Valdemoro (✉)

Instituto de Matemáticas y Física Fundamental, Consejo Superior de Investigaciones Científicas, Serrano 123, 28006 Madrid, Spain
e-mail: c.valdemoro@iff.csic.es

D. R. Alcoba · O. B. Oña

Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, 1428 Buenos Aires, Argentina

D. R. Alcoba

e-mail: qfxaldad@lg.ehu.es

O. B. Oña

e-mail: ofelia@df.uba.ar

D. R. Alcoba

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

L. M. Tel · E. Pérez-Romero

Departamento de Química Física, Facultad de Ciencias Químicas, Universidad de Salamanca, 37008 Salamanca, Spain

L. M. Tel

e-mail: lmtepr@gmail.com

These examples constitute a preliminary test showing that, provided that a G -particle-hole matrix corresponding to a conveniently chosen mainly mono-configurational state is known, this combined method can yield an accurate energy value for a highly correlated state which would be hard to obtain directly with the GHV.

Keywords Correlation matrix · G -particle-hole matrix · Electronic correlation effects · Hypervirial of the G -particle-hole matrix · Hermitian operator method

1 General introduction

To avoid the search for the N -electron wavefunction in the study of the structure of electronic systems, looking instead for the second-order reduced density matrix (2-RDM), has been an old pursuit of mathematicians, physicists and quantum-chemists. There is a large bibliography on this subject which the interested reader may find in the books of Davidson [1] and Coleman and Yukalov [2] as well as in many proceedings and reviews [3–7]. Let us just refer explicitly here to the basic works which were published in the fifties by Husimi [8], Löwdin [9], Mayer [10], McWeeny [11], Ayres [12] and Coulson [13]. These papers and in particular the landmark papers, published in the early sixties by Coleman [14] about the RDMs N -representability conditions and by Garrod and Percus [15] who studied the G -particle-hole matrix, set the basis for subsequent work.

A fruitful line of work in RDM theory consists in looking for the matrix representation in the 2-electron space of the fundamental quantum-mechanical equations, in particular of the Schrödinger (SE) and Liouville (LE) equations and to try to solve them. To this end, two alternative techniques were applied: to integrate these equations over $(N - 2)$ electron variables or to apply a general Matrix Contracting Mapping (MCM) to the N -electron space representation of the equation considered, in order to get its 2-electron space contracted form. The integration technique was simultaneously applied by Nakatsuji [16] and Cohen and Frishberg [17] in 1976. These authors obtained an equation which they named *density equation* (DE) and *hierarchy equation*, respectively. Nakatsuji proved that the DE is equivalent (by the *necessary* and *sufficient* condition) to the SE. The drawback of this equation is that it has a hierarchy character which renders it *operationally* indeterminate [18], since it not only depends on the 2-order RDM but also on the 3- and 4-order RDMs. The matrix contracting technique was applied in 1983 by Valdemoro [19,20] who reported a general form of the MCM. The MCM was first applied to the N -electron representation of a spin-projected-Hamiltonian operator in order to study the properties of this analytically averaged matrix and its corresponding operator [21–25]. Then, in 1986 the MCM was applied to the LE and SE [26] thus generating the contracted Liouville (CLE) and the contracted Schrödinger (CSE) equations. This latter equation was shown to be equivalent to Nakatsuji's integro-differential DE.

Both the CSE and CLE are, like the DE, hierarchy equations, which hindered the development of this line of work until 1992, when Valdemoro [27] proposed an algorithm for approximating the 2-RDM in terms of the 1-RDM. This approach was then extended in order to construct higher-order RDMs in terms of the lower-order ones [28,29]. By replacing into the 2-CSE the approximated expressions for the 3- and

4-RDMs, the 2-CSE could be iteratively solved with a reasonable accuracy in 1994 by Colmenero and Valdemoro [30]. This started a very productive line of work in the groups led respectively by Nakatsuji [31–34], Mazziotti [35–41] and Valdemoro [42–68] which contributed considerably to improve this methodology. In 2009 [69] the MCM was still rendered more general by replacing the auxiliary density matrix involved in the MCM by an N -electron representation of any p -electron operator, which permitted to generate a new set of contracted equations, one of which is the G -particle-hole Hypervirial equation (GHV) with which we are concerned here.

In order to link our contribution at the 2006 Nice International Conference on *Mathematical Methods for Ab Initio Quantum Chemistry* [70] with the present line of work of our group, the first aim of this paper is to give an overview of the contracted equations theory [7] (Sect. 3) leading to the description of the GHV equation [69, 71–74] (Sect. 4) whose solution yields the G -particle-hole matrix.

The second aim of this work is to obtain directly the set of excitation and de-excitation energies of a given state in terms of the G -particle-hole matrix obtained by solving the GHV equation. There has been a great deal of work on the direct determination of excitation energies in the past [75]. We cannot give here a general view of the field and will just refer here to those papers which in some way are related to our line of work. Let us thus mention the interesting Surjan's proposal [76] for constraining the excited states to be orthogonal to the ground-state being excited. Also, the set of papers which for our purpose are highly relevant were published in the early seventies on the properties of the particle-hole subspace of a state [77–79]. In one of these papers, Rosina [79] reported a 2-RDM based method which has recently been successfully applied by Mazziotti [80, 81]. But it is the paper published in 1973 by the nuclear physicists Bouten, Van Leuven, Mihailovich and Rosina [77] which is at the center of our work here. In this seminal and outstanding paper, the authors propose the Hermitian operator (HO) method for obtaining the transition energies from a ground-state. This paper, if not ignored, was somewhat overlooked for many years because the HO method needs as input data the G -particle-hole matrix of the state being excited and at that time no reliable method for obtaining this matrix had yet been developed. The present situation is now completely different because the GHV equation yields an accurate G -particle-hole matrix whenever the ground or excited state considered is mostly mono-configurational. Therefore, by combining the GHV and the HO method one may not only obtain the excitation energies of the ground-state but also obtain the de-excitations of an excited state. As we describe in Sect. 5, the combined GHV-HO constitutes a powerful tool for an indirect determination of multi-configurational states energy which are otherwise hard to obtain. In Sect. 6, two simple and preliminary test calculations are reported. One of this examples applies particle-hole excitations to the singlet ground-state of the LiH molecule at its equilibrium internuclear distance thus obtaining accurate energy values for the excited states. The other calculation considers the LiH molecule far from equilibrium. In this latter case, the ground-state energy obtained with the GHV equation is not sufficiently accurate. On the other hand, when instead of applying the GHV-HO method upon the ground-state one applies it to the first triplet excited state with spin projection $M_s = 1$ the result obtained is excellent not only for the excited states but also for the ground-state. Some final comments conclude this paper.

2 Notation and theoretical background

2.1 Basic definitions

In second-quantization and in the occupation number representation [82] the 1- and 2-order reduced density matrices (1- and 2-RDM) definitions are, respectively:

$${}^1D_{i;l} = \langle \Phi | a_i^\dagger a_l | \Phi \rangle, \quad {}^2D_{ij;kt} = \frac{1}{2!} \langle \Phi | a_i^\dagger a_j^\dagger a_t a_k | \Phi \rangle = \frac{1}{2!} \langle \Phi | {}^2\hat{\Gamma}_{ij;kt} | \Phi \rangle \quad (1)$$

where the operator's labels refer to the elements of a finite basis set of $2K$ orthonormal spin-orbitals and where ${}^2\hat{\Gamma}$ is the 2-body density operator. The p -order hole reduced density matrices (p -HRDM) result from taking the expectation value of a string of operators where the annihilators are on the left of the creators. The main N -representability conditions [14, 15, 83, 84] that these RDMs must satisfy are:

- The 1- and 2-RDM as well as the 1- and 2-HRDM, denoted by ${}^1\bar{D}$ and ${}^2\bar{D}$, are Hermitian positive semi-definite matrices.
- The 1-RDM is derived from the 2-RDM by contraction. Similarly, the 1-HRDM is derived from the 2-HRDM.
- The fermion algebra imposes a set of inter-relations among the elements of these matrices. The main relation is

$${}^1\bar{D}_{i;l} + {}^1D_{i;l} = \delta_{i;l} \quad (2)$$

which sets the bounds for these positive semi-definite matrices' roots. Many other fermion relations have been reported [48].

Let us now recall that the 2-RDM may be decomposed as [44]:

$$2! {}^2D_{pq;tv} \equiv {}^1D_{p;t} {}^1D_{q;v} - \delta_{q,t} {}^1D_{p;v} + {}^2C_{pq;tv} \quad (3)$$

where

$${}^2C_{pq;tv} = \sum_{\Phi' \neq \Phi} \langle \Phi | a_p^\dagger a_t | \Phi' \rangle \langle \Phi' | a_q^\dagger a_v | \Phi \rangle \equiv \langle \Phi | a_p^\dagger a_t \hat{Q} a_q^\dagger a_v | \Phi \rangle \quad (4)$$

Here \hat{Q} is the orthogonal complement of the projection operator $\hat{P} = |\Phi\rangle \langle \Phi|$ on the space of the state being studied.

The first term of the *r.h.s.* of Eq. (3) describes the product of two independent one-body probabilities. The second and third terms represent the exchange-correlation contributions to the 2-RDM. Hence, the only term which has an irreducible two-body character is the 2C which we denote 2-order correlation matrix (2-CM) [44–68]. Unlike the 2-RDM, from which it is derived, the 2-CM matrix is not a Hermitian positive

semi-definite matrix. There is, however, a closely related 2-order matrix, the G -particle-hole matrix, initially reported and studied by Garrod and Percus [15] such that

$${}^2C_{pq;tv} \equiv G_{pt;vq} \quad (5)$$

which is Hermitian and positive semi-definite. This G -particle-hole property is what is generally called the G N -representability condition [15,84].

The operators ${}^2\hat{C}$ and \hat{G} corresponding to these two matrices are defined as:

$${}^2\hat{C}_{pq;tv} = a_p^\dagger a_t \hat{Q} a_q^\dagger a_v = \hat{G}_{pt;vq} \quad (6)$$

The non-vanishing contractions of the G -particle-hole matrix generate the 1-RDM and the 1-HRDM [53,54,85,86].

This brief account of the 1- and 2-order reduced matrices shows that, although each of these matrices has its own identity and its own properties, they are so interrelated that when one knows a 2-order matrix all the other 2- and 1-order matrices can be derived from it [53]. That is why according to the type of information that is available or the formal difficulties of the problem under study, one may choose which of these second-order matrices is more convenient.

For some years our interest has been centered on the G -particle-hole matrix because it is the irreducible 2-body part of the 2-RDM and thus carries the information about that part of the electronic correlation which cannot be expressed in terms of the 1-RDM. Relation (4) shows that this two-body matrix depends on all the system's spectrum virtual transitions of the two electrons involved. It must, however, be recalled here that the second-order cumulant ${}^2\Delta$ [36,87,88],

$${}^2\Delta_{ij;kl} = -{}^1\bar{D}_{j;k} {}^1D_{i;l} + {}^2C_{ij;kl} \equiv {}^2D_{ij;kl} - {}^1D_{i;k} {}^1D_{j;l} + {}^1D_{i;l} {}^1D_{j;k} \quad (7)$$

which has the same symmetry properties than the 2-RDM, plays a similarly active part. Note that the first term of the *r.h.s* under the action of the Hamiltonian will give rise to an electron-hole polarization. That is, the cumulant groups the two terms which describe two-different correlation mechanisms, *i.e.* an electron-hole polarization and the two-electron virtual transitions.

The decomposition of higher-order p -RDMs may be carried out in a similar way as in the 2-RDM case [46]. These decomposition generate a set of structural varieties of p -body CMs and G -matrices describing different p -body correlation effects. Both the p -CM and p - G family of matrices have very interesting properties [44,47,48,51–55,58,59,63–66,68,71]. We will just consider here those 3-CMs which appear in the GHV equations theory.

$${}^{(3;2,1)}C_{ijm;pqt} = \langle \Phi | a_i^\dagger a_j^\dagger a_q a_p \hat{Q} a_m^\dagger a_t | \Phi \rangle \equiv \langle \Phi | {}^{(3;2,1)}\hat{C}_{ijm;pqt} | \Phi \rangle \quad (8)$$

$${}^{(3;1,1,1)}C_{ijm;pqt} = \langle \Phi | a_i^\dagger a_p \hat{Q} a_j^\dagger a_q \hat{Q} a_m^\dagger a_t | \Phi \rangle \equiv \langle \Phi | {}^{(3;1,1,1)}\hat{C}_{ijm;pqt} | \Phi \rangle \quad (9)$$

The numbers appearing in the upper-left label have the following meaning: in the ${}^{(3;2,1)}C$ case, the first one, 3, denotes that it is a 3-CM; the second one, 2, denotes the

order of the density operator preceding the \hat{Q} operator; and the last number denotes the order of the density operator following \hat{Q} . Similar notation follows for the $(3;1,1,1)C$.

2.2 The Hamiltonian operator

The form of the Hamiltonian used here is

$$\hat{H} = \frac{1}{2} \sum_{p,q,t,v} {}^0H_{pq;tv} a_p^\dagger a_q^\dagger a_v a_t \quad (10)$$

where

$${}^0H_{pq;tv} = \frac{\delta_{p,t} \epsilon_{q,v} + \delta_{q,v} \epsilon_{p,t}}{N - 1} + \langle pq|tv \rangle \quad (11)$$

and where $\epsilon_{q,v}$ and $\langle pq|tv \rangle$ are 1- and 2-electron integrals respectively. The 2-electron integrals are written in the $\langle 12|12 \rangle$ notation.

2.3 A state energy and correlation energy

Let us now conclude this section by recalling that the energy of a state Φ , when one knows the 2-RDM of that state, is given by

$$E_\Phi = \sum_{p,q,t,v} {}^0H_{pq;tv} {}^2D_{tv;pq}^\Phi \quad (12)$$

and, since we have seen that the cumulant groups the two types of correlation energy, the *absolute* definition of the correlation energy is

$$\begin{aligned} E_\Phi^{Corr} &= \sum_{p,q,t,v} {}^0H_{pq;tv} {}^2\Delta_{tv;pq}^\Phi \\ &\equiv \sum_{p,q,t,v} {}^0H_{pq;tv} \left({}^2D_{tv;pq}^\Phi - {}^1D_{t;p}^\Phi {}^1D_{v;q}^\Phi + {}^1D_{t;q}^\Phi {}^1D_{v;p}^\Phi \right) \end{aligned} \quad (13)$$

which vanishes when Φ is a Slater determinant. The variationally optimum Slater determinant, the Hartree-Fock approximation, is usually taken as reference in many calculations involving correlation effects.

3 Outlook of the different contracted equations obtained by applying the density and the correlation matrix contracting mapping

In this section an overview is given of the different second-order equations which can be obtained by applying the generalised MCM to the matrix representation of important Quantum-Mechanical N -electron equations.

3.1 The matrix contracting mapping

Let us consider a general matrix expression, represented in the N -electron space, ${}^N M(\Phi, \hat{O})$, where Φ is a N -electron wavefunction and \hat{O} is an operator (*e.g.* the Hamiltonian operator, \hat{H} , the total spin-squared operator, \hat{S}^2 , etc.). This matrix may be contracted into the p -electron space (with $p < N$) by applying to it a linear MCM whose general expression is

$$\sum_{\Lambda, \Omega} {}^N M_{\Lambda; \Omega} \langle \Lambda | {}^p \hat{T}_{\lambda; \gamma} | \Omega \rangle = {}^p M_{\lambda; \gamma} \quad (14)$$

where ${}^p \hat{T}$ is a p -electron operator and $\{\Lambda, \Omega, \dots\}$ and $\{\lambda, \gamma, \dots\}$ represent the elements of complete basis set of states of N and p electrons respectively. As mentioned above, this MCM was reported for ${}^p \hat{T} = {}^2 \hat{\Gamma}$, the second-order density operator, by Valdemoro in 1983 [19,20] and later applied to the matrix representation of the Schrödinger equation, thus obtaining the second-order Contracted Schrödinger Equation (2-CSE) [26]. After some simple algebra one obtains the compact form of this equation:

$$\langle \Phi | \hat{H} {}^2 \hat{\Gamma}_{\lambda; \gamma} | \Phi \rangle = E_{\Phi} {}^2 D_{\lambda; \gamma}^{\Phi} \quad (15)$$

When ${}^p \hat{T} = {}^2 \hat{C}$ one obtains the second-order Correlation Contracted Schrödinger Equation (2-CCSE) [55] whose compact expression is:

$$\langle \Phi | \hat{H} {}^2 \hat{C}_{\lambda; \gamma} | \Phi \rangle = E_{\Phi} {}^2 C_{\lambda; \gamma}^{\Phi} \quad (16)$$

Both the 2-CSE and the 2-CCSE share an important property. Thus, Nakatsuji [16] and later on Mazziotti [35] proved that the CSE is rigorously equivalent to the SE. In the same way as Nakatsuji, Alcoba found the same equivalence [55] between the 2-CCSE and the SE.

We will now analyse what happens when one applies the MCM to the N -electron density Hypervirial equation (N -HV), which is a particular case of the LE. Let us first consider the contraction of this equation, using ${}^p \hat{T} = ({}^3; 1, 1, 1) \hat{C}$, to the 3-electron space. The resulting equation, the 3-GHV, which depends on a 4-CM matrix, can be shown to share with the 2-CSE and 2-CCSE the important property that it is equivalent to the SE [71]. This property has not however been demonstrated for the equation obtained when using MCM with the ${}^p \hat{T} = {}^3 \hat{\Gamma}$ as the auxiliary matrix.

Finally, the two D - and G -particle-hole Hypervirial equations, obtained when the contraction of the N -HV is carried out up to the 2-electron space, the D -Hypervirial equation and the GHV equation, constitute a necessary but not sufficient condition for their solutions to be Hamiltonian eigenstates. Levy and Berthier [89] referred to the D -Hypervirial as the generalized Brillouin condition and Kutzelnigg [90–92] reported how to implement this generalized condition for the construction of correlated wavefunctions. These two equations can also be identified with the anti-Hermitian part of the 2-CSE and 2-CCSE respectively which is why Mazziotti has preferred to call

ACSE the *D*-Hypervirial. This author reported in 2006 an iterative method for solving this equation [93,94] which gave very good results [95–100].

As mentioned above, the 3-order GHV's solutions are exact while no such property has been proven for the 3-order ACSE. Moreover, it has also been shown that, while solving the (2-order) GHV implies that the ACSE [69], the 1-CSE and the 1-HV are also solved, the inverse is not true [69,73]. It follows therefore that the GHV is a more demanding equation than the ACSE.

The main features of these equations are summarised in the Synopsis.

After this schematic overview of the properties of the four main contracted equations which have been obtained by applying the two types of MCM to important matrix relations represented in the *N*-electron space, we now focus on the GHV equation, whose solution yields the *G*-particle-hole correlation matrix.

SYNOPSIS OF THE MAIN CONTRACTED EQUATIONS

The table is organised in the following way:

Acronym	{	Name ${}^p\hat{T}$ operator Conditions implied by the equation Matrices involved Main research groups
2-CSE	{	Contracted Schrödinger equation ${}^2\hat{T} = a_p^\dagger a_q^\dagger a_s a_r$ Necessary and sufficient Depends on the 2-, 3-, 4-RDM Nakatsuji, Cohen, Frishberg, Valdemoro, Mazziotti, Harriman
ACSE	{	{ Anti-Hermitian Contracted Schrödinger equation { 2-order density Hypervirial equation ${}^2\hat{T} = a_p^\dagger a_q^\dagger a_s a_r$ Necessary Depends on the 2-, 3-RDM Mazziotti, Kutzelnigg
2-CCSE	{	Correlation Contracted Schrödinger equation ${}^2\hat{T} = a_p^\dagger a_r \hat{Q} a_q^\dagger a_s$ Necessary and sufficient Depends on the 2-, 3-, 4-CM Alcoba, Valdemoro, Tel, Pérez-Romero
3-GHV	{	Hypervirial of the 3- <i>G</i> -particle-hole or 3-CM operator ${}^3\hat{T} = a_p^\dagger a_s \hat{Q} a_q^\dagger a_r \hat{Q} a_t^\dagger a_u$ Necessary and sufficient Depends on the 2-, 3-, 4-CM Alcoba, Valdemoro, Tel, Pérez-Romero
GHV	{	Hypervirial of the <i>G</i> -particle-hole or 2-CM operator ${}^2\hat{T} = a_p^\dagger a_r \hat{Q} a_q^\dagger a_s$ Necessary, stronger than ACSE Depends on the 2-, 3-CM Alcoba, Valdemoro, Tel, Pérez-Romero

4 Solving the GHV

The compact form of the GHV equation [69] is:

$$\langle \Phi | [\hat{H}, \hat{G}] | \Phi \rangle = 0 \quad (17)$$

When developing this relation one obtains its explicit form,

$$\begin{aligned} & \sum_{p,q,r,s} {}^0H_{rs;pq}^{(3;2,1)} C_{pqj;rs} {}^1D_{i;m} - \sum_{p,q,r,s} {}^0H_{pq;rs}^{(3;2,1)} C_{rsm;pqi} {}^1D_{l;j} \\ & + 2 \sum_{p,r,s} {}^0H_{rs;pm}^{(3;2,1)} C_{ipj;rs} + 2 \sum_{p,q,r} {}^0H_{pq;jr}^{(3;2,1)} C_{lrm;pqi} \\ & + 2 \sum_{p,q,r} {}^0H_{ir;pq}^{(3;2,1)} C_{pqj;mrl} + 2 \sum_{q,r,s} {}^0H_{ql;rs}^{(3;2,1)} C_{rsm;jqi} = 0 \quad (18) \end{aligned}$$

The N -representable and Spin-representable [43] 1- and 2-order matrices corresponding to an approximate mono-configurational eigenstate are taken as trial functions in order to construct the elements of this matrix equation. These trial matrices are the input data for the constructing algorithms yielding the 3-CM or, equivalently, the 3-order cumulant, which is the only approximation introduced. The GHV equation (18) thus constructed does not vanish and yields a 2-order error-matrix A . In order to iteratively solve the GHV equation and reach an accurate approximation of the exact G -particle-hole matrix one proceeds as follows. The function Φ , or alternatively the operator \hat{G} , is transformed through the action of a unitary operator. In this way the problem of solving the vanishing GHV equation can be transformed into finding the solution of a system of differential equations. By adapting to the GHV case the procedures developed by Kutzelnigg [75,90–92] and in particular by Mazziotti [93,94] one obtains [69,72,74]:

$$(\Delta G^{n+1})_{im;l} = \langle \Phi | [\hat{A}^n, \hat{G}_{im;l}] | \Phi \rangle \quad (19)$$

where $(\Delta G)^{n+1}$ is the error of the G -particle-hole, after the n th iteration and

$$\hat{A}^n = \sum_{i,m,l,j} A_{im,lj}^n \hat{G}_{im;l} \quad (20)$$

is the anti-Hermitian operator appearing in the exponent of the unitary operator used in the transformation. Finally, in order to accelerate convergence we apply Fehlberg's method [101, 102]. A detailed description of this methodology is given in [72, 74].

When the state Φ is mostly mono-configurational, which generally is the case in ground-states and in the highest spin projection multiplet states, the accuracy of the G -particle-hole matrix is excellent [69,72–74]. By contracting the G -particle-hole matrix thus obtained the 1- and 2-RDM as well as the energy E_Φ of the state may also be calculated.

5 Obtaining the set of excitation energies in terms of the G -particle-hole matrix

As has been mentioned in the Introduction, in their 1973 work Bouten, Van Leuven, Mihailovich and Rosina [77] reported the HO method for obtaining transition energies to the excited states from the ground-state. The input data needed in the HO method is the G -particle-hole matrix which happens to be the output of solving the GHV equation. That is why we propose here a combination of both methods. Thus, whenever the state to be excited, or de-excited, by the HO is mostly a mono-configurational one, the GHV equation yields a highly accurate G -particle-hole matrix which is what is needed as input in the HO method.

Although the idea of Bouten et al. was to apply the HO upon a system ground-state, we will show here that the HO may also be applied to an excited state, which results in a new and powerful tool for indirectly studying highly correlated states. Thus, since the GHV method is not variational, it permits the study of excited almost mono-configurational states, which allows us to extend the applicability of the combined GHV-HO method to quasi mono-configurational states, were they ground or excited states.

5.1 The Hermitian Operator method

In this section we recall the main steps of the HO method which has been implemented into our computational code and whose preliminary results are reported in the following section. Let us start by rewriting the \hat{Q} operator appearing in the G -particle-hole matrix expression, corresponding to a state Φ , in an equivalent form:

$$\hat{Q} = \hat{I} - |\Phi\rangle \langle \Phi| \quad (21)$$

which is an Hermitian and an idempotent operator. Therefore, a G -particle-hole matrix element can be rewritten as:

$$\begin{aligned} G_{pt;vq}^{\Phi} &\equiv \langle \Phi | a_p^{\dagger} a_t (\hat{I} - |\Phi\rangle \langle \Phi|) (\hat{I} - |\Phi\rangle \langle \Phi|) a_q^{\dagger} a_v | \Phi \rangle \\ &= \langle \Phi | (a_p^{\dagger} a_t - {}^1D_{p;t}) (a_q^{\dagger} a_v - {}^1D_{q;v}) | \Phi \rangle \end{aligned} \quad (22)$$

which is the form used in the HO method.

As has been mentioned, the original aim of the HO method was to derive the energies of excited states when one knows the G -particle-hole matrix of this system's ground-state. The work of Bouten, Van Leuven, Mihailovich and Rosina [77] starts by creating Hermitian mono-excitations \hat{S} upon the ground-state, Φ , and then deriving the equations which set the appropriate constraints.

Let us define an excitation operator \hat{S} such that

$$\hat{H} \hat{S} |\Phi\rangle = E_{\Psi} |\Psi\rangle \quad (23)$$

where Ψ is an excited eigenstate generated by the excitation operator \hat{S} . The exact form of \hat{S} is:

$$\hat{S} = |\Phi\rangle\langle\Psi| + |\Psi\rangle\langle\Phi| \quad (24)$$

which is Hermitian and generates:

$$\langle\Phi|(\hat{S}'\hat{H}\hat{S} + \hat{S}\hat{H}\hat{S}')|\Phi\rangle = E_\Psi \langle\Phi|(\hat{S}'\hat{S} + \hat{S}\hat{S}')|\Phi\rangle \quad (25)$$

which is equivalent to

$$\langle\Phi|[\hat{S}', [\hat{H}, \hat{S}]]|\Phi\rangle = (E_\Psi - E_\Phi) \langle\Phi|(\hat{S}'\hat{S} + \hat{S}\hat{S}')|\Phi\rangle \quad (26)$$

valid for any operator \hat{S}' and, particularly, when $\hat{S}' = \hat{S}$.

Bouten et al. [77] proposed to approximate \hat{S} as:

$$\hat{S} = \sum_{t,v} \left\{ c_{t,v}^+ (a_t^\dagger a_v - {}^1D_{t;v} + a_v^\dagger a_t - {}^1D_{v;t}) + i c_{t,v}^- (a_t^\dagger a_v - {}^1D_{t;v} - a_v^\dagger a_t + {}^1D_{v;t}) \right\} \quad (27)$$

where the c symbols represent real coefficients. That is, the action upon Φ of the mono-excitation operator followed by the implicit projector \hat{Q} generates a state Ψ orthogonal to Φ . Replacing this definition into (26) one obtains the matrix equation

$$\begin{pmatrix} \mathcal{H}^{(++)} & \mathcal{H}^{(+-)} \\ \mathcal{H}^{(-+)} & \mathcal{H}^{(--)} \end{pmatrix} \begin{pmatrix} c^+ \\ c^- \end{pmatrix} = 2(E_\Psi - E_\Phi) \begin{pmatrix} \mathcal{G}^{(++)} & \mathcal{G}^{(+-)} \\ \mathcal{G}^{(-+)} & \mathcal{G}^{(--)} \end{pmatrix} \begin{pmatrix} c^+ \\ c^- \end{pmatrix} \quad (28)$$

In the case considered here, all the elements appearing in equation (26) are real. In consequence, as Bouten et al. pointed out [77], one obtains a system of two decoupled equations:

$$\mathcal{H}^{(++)} c^+ = 2(E_\Psi - E_\Phi) \mathcal{G}^{(++)} c^+ \quad (29a)$$

$$\mathcal{H}^{(--)} c^- = 2(E_\Psi - E_\Phi) \mathcal{G}^{(--)} c^- \quad (29b)$$

where $\mathcal{G}^{(++)}$ and $\mathcal{G}^{(--)}$ are functionals of the G -particle-hole matrix corresponding to state Φ . Since the G -particle-hole is a symmetric and positive semi-definite matrix, the $\mathcal{G}^{(++)}$ and $\mathcal{G}^{(--)}$ may be expressed as:

$$\mathcal{G}_{ij;pq}^{(++)} = G_{ij;pq} + G_{ij;qp} + G_{ji;pq} + G_{ji;qp} \quad (30a)$$

$$\mathcal{G}_{ij;pq}^{(--)} = G_{ij;pq} - G_{ij;qp} - G_{ji;pq} + G_{ji;qp} \quad (30b)$$

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

$$\mathcal{H}_{ij;pq}^{(++)} = \langle \Phi | \left[a_i^\dagger a_j - {}^1D_{i;j} + a_j^\dagger a_i - {}^1D_{j;i}, \right. \\ \left. [\hat{H}, a_p^\dagger a_q - {}^1D_{p;q} + a_q^\dagger a_p - {}^1D_{q;p}] \right] | \Phi \rangle \quad (31a)$$

$$\mathcal{H}_{ij;pq}^{(--)} = \langle \Phi | \left[a_i^\dagger a_j - {}^1D_{i;j} - a_j^\dagger a_i + {}^1D_{j;i}, \right. \\ \left. [\hat{H}, a_p^\dagger a_q - {}^1D_{p;q} - a_q^\dagger a_p + {}^1D_{q;p}] \right] | \Phi \rangle \quad (31b)$$

For the general many-body case it can be shown that:

$$\mathcal{H}_{ij;pq}^{(\pm\pm)} = +4 \sum_{r,s} \left\{ \tilde{H}_{jr;ps} {}^2D_{ir;qs} \pm \tilde{H}_{ir;ps} {}^2D_{jr;qs} \pm \tilde{H}_{jr;qs} {}^2D_{ir;ps} + \tilde{H}_{ir;qs} {}^2D_{jr;ps} \right\} \\ - 2 \sum_r \left\{ \delta_{q,i} (\tilde{H}^2D)_{pr;jr} \pm \delta_{q,j} (\tilde{H}^2D)_{pr;ir} \pm \delta_{p,i} (\tilde{H}^2D)_{qr;jr} + \delta_{p,j} (\tilde{H}^2D)_{qr;ir} \right\} \\ + 2 \left\{ (\tilde{H}^2D)_{pi;jq} \pm (\tilde{H}^2D)_{pj;iq} \pm (\tilde{H}^2D)_{qi;jp} + (\tilde{H}^2D)_{qj;ip} \right\} \quad (32)$$

where

$$\tilde{H}_{ir;ps} = {}^0H_{ir;ps} - {}^0H_{ri;ps} \equiv {}^0H_{ir;ps} - {}^0H_{ir;sp} \quad (33)$$

As can be appreciated, only second-order matrices are involved in these final formulae.

Note that in order to solve the system of the two uncoupled equations (29) one must first remove from the G -particle-hole matrix, which is the metric matrix in the particle-hole space, its zero valued roots and then solve the resulting generalized eigenvalue problem. In what follows the solutions of the equation corresponding to the $\mathcal{H}^{(++)}$, *i.e.* to the symmetric particle-hole subspace are denoted by the symbol SHO, and those obtained within the anti-symmetric subspace are denoted by the symbol AHO.

It is also important to check the accuracy of the expectation values of the \hat{S}^2 and \hat{M}_s operators. This is achieved by replacing the Hamiltonian operator by \hat{S}^2 in equations (23)–(33), which is easily carried out by replacing the 0H elements by the corresponding elements of the matrix representation of \hat{S}^2 and the energy difference by the difference in the $S(S + 1)$ values of the two states Ψ and Φ . In order to determine this difference one uses the same coefficients c^+ and c^- obtained when solving the system of equations corresponding to the Hamiltonian. Similar considerations follow for the \hat{M}_s operator.

6 Determining the energy of the LiH molecule states at two different internuclear distances with the combined GHV-HO method

Here we will report the results obtained in the study of the energy spectrum of the LiH molecule. The basis set used is the STO-3G. The PSI3 program [103] has been used to calculate the integrals matrix 0H and the initial values of all the matrices

required. As mentioned above, there are two different possible approaches aiming at describing different but overlapping particle-hole subspaces. Thus, we will first consider the case which Bouten et al. had in mind when they developed their HO method. That is, when the particle-hole excitation operators act on the ground-state. Another possibility exists: to extend the original HO method by having the particle-hole excitation operators act upon an already excited state. That is, the choice of the state studied with the GHV determines the G -particle-hole matrix entering into the HO equations and consequently determines the states of the spectrum whose energy will be obtained. These states are the elements of the particle-hole subspace of the G -particle-hole matrix state. It all, therefore, hinges on choosing the system almost mono-configurational states so that an accurate GHV can be obtained with the GHV method and then apply the HO method in order to obtain the energy of the strongly correlated states of the spectrum which could otherwise be hard to obtain.

6.1 The G -particle-hole matrix corresponds to the singlet LiH ground-state

In this first example the particle-hole excitation operators act upon the singlet ground-state of the LiH molecule at its experimental equilibrium internuclear distance, 1.595 Angstrom [104]. In these conditions, the state is almost mono-configurational and, as could be expected, the GHV gives an excellent result with an energy value error of only 2.300×10^{-5} Hartree. Using the G -particle-hole matrix corresponding to this state, the energy of the excited states of this particle-hole subspace have been calculated. In Table 1, we report the energy errors of the calculations carried out with the CIS, the SHO and the AHO methods. The corresponding FCI energy values are also reported in this table.

The results shown in Table 1 indicate that

- The accuracy of the CIS results is rather poor. This CI method takes explicitly into account the same excitations than the HO method, therefore the CIS inferior performance must be due to the fact that the HO method profits of the knowledge of correlated ground-state G -particle-hole matrix.
- The SHO performs slightly better than the AHO except for states 5 and 6 which are the highest singlet mono-excited states of the spectrum.
- It is interesting to note that the results for the triplet states are better than those obtained for singlets.
- The slightly different energy values obtained for different members of some of the triplets is due to the fact that in order to describe well some of these states, particularly those with $M_s = 0$, higher-order excitations are needed.

The calculation of the expectation value of the \hat{S}^2 operator has also yielded in all these cases excellent results with errors lower than 10^{-4} .

6.2 The G -particle-hole matrix corresponds to the first triplet LiH state at a large internuclear distance

At an internuclear distance of 4.595 Angstrom, the energy error in the evaluation of the ground-state with the GHV method is 9.876×10^{-3} Hartree, which is not suffi-

Table 1 Errors with respect to the FCI values of the LiH energy spectrum (in Hartree) obtained with CIS and the GHV-HO method from the G -particle-hole matrix of the ground-state

State	S, M_S	CIS	SHO	AHO	FCI
g	0,0	-2.037×10^{-2}	–	–	–7.882402
1	1,1	-3.404×10^{-2}	-2.460×10^{-4}	-1.025×10^{-3}	–7.766418
	1,0	-3.404×10^{-2}	-1.025×10^{-3}	-2.560×10^{-4}	–7.766418
	1,–1	-3.404×10^{-2}	-2.560×10^{-4}	-1.025×10^{-3}	–7.766418
2	0,0	-5.265×10^{-2}	-2.186×10^{-3}	-1.931×10^{-2}	–7.749216
3	1,1	-3.364×10^{-2}	-3.980×10^{-4}	-3.990×10^{-4}	–7.716454
	1,0	-3.364×10^{-2}	-1.304×10^{-3}	-1.302×10^{-3}	–7.716454
	1,–1	-3.364×10^{-2}	-3.980×10^{-4}	-3.990×10^{-4}	–7.716454
4	1,1	-3.364×10^{-2}	-3.990×10^{-4}	-1.304×10^{-3}	–7.716454
	1,0	-3.364×10^{-2}	-1.304×10^{-3}	-1.302×10^{-3}	–7.716454
	1,–1	-3.364×10^{-2}	-3.990×10^{-4}	-1.304×10^{-3}	–7.716454
5	0,0	-6.085×10^{-2}	-1.625×10^{-3}	-8.240×10^{-4}	–7.696952
6	0,0	-6.085×10^{-2}	-1.625×10^{-3}	-8.240×10^{-4}	–7.696952
7	1,1	-1.182×10^{-2}	-9.900×10^{-5}	-5.430×10^{-4}	–7.482612
	1,0	-1.182×10^{-2}	-5.430×10^{-4}	-1.090×10^{-4}	–7.482612
	1,–1	-1.182×10^{-2}	-1.090×10^{-4}	-5.430×10^{-4}	–7.482612

The LiH internuclear distance is the experimental one, 1.595 Angstrom

The GHV energy error of the ground-state is -2.300×10^{-5} Hartree

ciently accurate. This is due to the fact that at this distance the ground-state is already multi-configurational.

This second example is therefore a good test for our proposal for an extension of Botten et al. HO method. Therefore, in this calculation the HO excitation/de-excitation operators act upon the first triplet state, with $M_S = 1$, of the LiH molecule. In general the first multiplets with the highest spin projection are described by an almost single-configurational wave-function even at large internuclear distances, and, as was expected, the GHV gave in this case an energy value with an error of 2.200×10^{-6} Hartree. Using the G -particle-hole matrix corresponding to this state, the energy of the mono-excited states have been calculated with the HO method. The results thus obtained jointly with the FCI ones are reported in Table 2. These results indicate that

- The first and most important result is that the energy value error in the singlet ground-state diminishes by three orders of magnitude with respect to the GHV result.
- Another striking observation is that here, both the SHO and the AHO show a similar performance.
- Here again the results for the triplet states are better than those obtained for singlets.

The expectation values of the \hat{S}^2 operator for the ground-state and for all the triplet states are excellent. However, the three excited singlets have an incorrect $\langle \hat{S}^2 \rangle$ (0.9938, 1.0001 and 1.0001). It is also interesting to note that the 3 and 4 triplets

Table 2 Errors with respect to the FCI values of the LiH energy spectrum (in Hartree) obtained with the GHV-HO method from the G -particle-hole matrix of the first triplet state with $M_S = 1$

State	S, M_S	SHO	AHO	FCI
g	0,0	-9.000×10^{-6}	-9.000×10^{-6}	-7.782873
1	1,0	-2.000×10^{-6}	-2.000×10^{-6}	-7.782353
2	0,0	-1.138×10^{-3}	-1.138×10^{-3}	-7.698426
3	1,1	-1.930×10^{-4}	-1.930×10^{-4}	-7.697223
4	1,1	-1.930×10^{-4}	-1.930×10^{-4}	-7.697223
5	0,0	-1.660×10^{-4}	-1.660×10^{-4}	-7.697194
6	0,0	-1.660×10^{-4}	-1.660×10^{-4}	-7.697194
7	1,1	-1.930×10^{-4}	-1.930×10^{-4}	-7.696503

The LiH internuclear distance is 4.595 Angstrom

The GHV energy errors of the singlet ground-state and the first triplet state with $M_S = 1$ are -9.876×10^{-3} Hartree and -2.200×10^{-6} Hartree, respectively

become degenerate as well as the 5 and 6 singlet states at this close to dissociation internuclear distance. This degeneracy is of the π type.

7 Concluding comments

The two preliminary examples just reported indicate the relevance of the combined GHV-HO method not only in the calculation of almost single-configurational ground and excited states but also in the study of strongly correlated states which, at present, cannot be accurately studied except with very costly treatments. We realise that this is just a preliminary test of the applicative possibilities of the GHV-HO combined method. We are aware that calculations of strongly correlated states with extended basis sets must be carried out in order to ascertain that this approach is fully reliable. Another related matter, which needs to be prospected is to understand whether the eigenvectors of the generalized eigensystem have a clear physical significance.

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