The Correlation Contracted Schrödinger Equation: An Accurate Solution of the *G*-Particle-Hole Hypervirial

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ABSTRACT: The equation obtained by mapping the matrix representation of the Schrödinger equation with the 2nd-order correlation transition matrix elements into the 2-body space is the so called correlation contracted Schrödinger equation (CCSE) (Alcoba, Phys Rev A 2002, 65, 032519). As shown by Alcoba (Phys Rev A 2002, 65, 032519) the solution of the CCSE coincides with that of the Schrödinger equation. Here the attention is focused in the vanishing hypervirial of the correlation operator (GHV), which can be identified with the anti-Hermitian part of the CCSE. A comparative analysis of the GHV and the anti-Hermitian part of the contracted Schrödinger equation (ACSE) indicates that the former is a stronger stationarity condition than the latter. By applying a Heisenberg-like unitary transformation to the *G*-particle-hole operator (Valdemoro et al., Phys Rev A 2000, 61, 032507), a good approximation of the expectation value of this operator as well as of the GHV is obtained. The method is illustrated for the case of the Beryllium isoelectronic series as well as for the Li_2 and BeH_2 molecules. The correlation

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energies obtained are within 98.80–100.09% of the full-configuration interaction ones. The convergence of these calculations was faster when using the GHV than with the ACSE.

Key words: reduced density matrix; correlation matrix; *G*-matrix; electronic correlation effects; contracted Schrödinger equation; anti-Hermitian contracted Schrödinger equation

1. Introduction

The seminal works of Husimi [1], Löwdin [2], Mayer [3], Ayres [4], McWeeny [5], and Coulson [6], in the fifties and of Coleman [7] and Garrod and Percus [8] in the early sixties, drew attention on the advantages of using reduced density (RDM) and G-particle-hole matrices in the study of the electronic structure of atoms and molecules. Many and valuable contributions followed these early works which have been reviewed and discussed in the books of Davidson [9] and Coleman and Yukalov [10] as well as in many proceedings and reviews [11–14].

In late years the applicability of the methodology based on the properties of the 2-RDM, and the matrices related to it, has become noteworthy [10, 13, 14]. Thus, several novel approaches shed light on the RDM's theory which, at present, permits an accurate ab-initio study of the electronic structure of fermion systems without having recourse to the *N*-electron wave-function [13, 14]. One of these 2-RDM oriented approaches consists in mapping the matrix representation of the Schrödinger equation from the *N*-electron space into the 2-electron space. The resulting equation was reported in 1987 by Valdemoro [15], who called it second-order contracted Schrödinger equation (2-CSE). This matrix equation is equivalent to Nakatsuji's [16] *density equation* as well as to Cohen and Frishberg's [17] *hierarchy equation* which had been obtained in 1976 by integration over the variables of *N*-2 electrons. An important theorem by Nakatsuji [16], later on confirmed by Mazziotti [18], establishes that there is a one to one correspondence between the solutions of the 2-CSE and of the Schrödinger equation. To solve the 2-CSE, which depends not only on the 2-RDM but also upon the 3- and 4-RDMs, Valdemoro et al. proposed to approximate these high order matrices [19, 20] and solve iteratively the equation. It permitted Colmenero and Valdemoro to report in 1994 [21] the first iterative solution of the 2-CSE. This started a successful line of work which was mainly developed by the groups lead by Nakatsuji, Valdemoro, Mazziotti, Harriman, and Kutzelnigg [18, 22–42].

Recently, Mazziotti [43] proposed a variational method for solving the 2nd-order density hypervirial [44], which this author identified with the anti-Hermitian part of the contracted Schrödinger equation (ACSE). This method yields excellent results [45–49] and, because the ACSE only depends on the 2- and 3-RDM, it is more effective than the 2-CSE methodology.

The correlation contracted Schrödinger equation (CCSE) [50] is an equation related to the 2-CSE where the 2nd-order correlation operators, or equivalently the *G*-particle-hole operators, play a role similar to the 2-body density operators in the 2-CSE. The matrix formed by the expectation values of the correlation operators (2-CM or *G*-matrix) have outstanding orbital and spin properties [51, 52] and it has enough information to calculate the 1- and 2-RDMs and, hence, the electronic energy of the system. Those properties suggested the convenience to investigate whether it was possible to obtain directly the correlation matrices, which determine the solution of the CCSE [50]. Our main objective here is to study how best to solve the *G*-particle-hole hypervirial equation (GHV), to apply this method to the calculation of several electronic systems and to carry out a comparative analysis of the relative strength of the necessary conditions implied respectively by the ACSE and GHV equations.

The article is organized as follows. In the next section, the notation, definitions, and necessary background information are summarized. An Appendix is also given to provide the intermediate steps leading to the formulae that are reported here. In Section 3, we give explicitly the forms of the CCSE and the GHV as well as the description of the method for solving the GHV. In Section 4, a relation linking the ACSE and the GHV is reported and its consequences are discussed. The results obtained in a set of applications of the ACSE and GHV methods are reported in Section 5. The calculations on the Beryllium isoelectronic series as well as of the Li_2 and BeH_2 molecules show that, in these cases, the correlation energies accounted for lie within 98.80% and 100.09% of the full-configuration interaction one. It is also found that the final two-body matrices describing the correlation effects very nearly satisfy the *N*- and

S-representability conditions [7, 52, 53]. In these calculations, both the ACSE and GHV methods yielded equivalent results as far as the energy and properties of the matrices were concerned. However, the GHV rate of convergence was considerably faster than the ACSE one. A brief description of the conclusions of this work is given in the last section.

2. Theoretical Background

Each one of the four interrelated 2-body matrices: the 2-RDM, the hole 2-RDM (2-HRDM), the 2-correlation matrix (2-CM), and the particle-hole *G*-matrix carry all the necessary information about an electronic system [51]. This article describes why the 2-CM, as well as the higher order *n*-CMs, are important and how to obtain an accurate approximation of a matrix corresponding to the solution of the GHV.

2.1. DEFINITION AND BASIC PROPERTIES OF THE CORRELATION MATRICES

To appreciate the relevance of the CMs let us start by recalling [54] that:

$$2!\,{}^2\mathrm{D}_{pq;rs} \equiv {}^1\mathrm{D}_{p;r}\,{}^1\mathrm{D}_{q;s} - \delta_{q,r}\,{}^1\mathrm{D}_{p;s} + {}^2\mathcal{C}_{pq;rs} \tag{1}$$

where

$${}^1\mathrm{D}_{i;j} = \langle \Psi | a_i^\dagger a_j | \Psi \rangle \tag{2}$$

and

$${}^2\mathrm{D}_{ij;kl} = \frac{1}{2!}\langle \Psi | a_i^\dagger a_j^\dagger a_l a_k | \Psi \rangle = \frac{1}{2!}\langle \Psi | {}^2\hat{\Gamma}_{ij;kl} | \Psi \rangle \tag{3}$$

The operators $a_i^\dagger$ and a_k refer to the creator/annihilator operators associated to a finite set of $2K$ orthonormal spinorbitals and ${}^2\hat{\Gamma}_{ij;kl}$ is a 2-body density operator. Those equations define the elements of the 1-RDM and and 2-RDM, respectively. The ${}^2\mathcal{C}$-matrix is the 2-CM, first member of a family of matrices which will be considered in what follows. From a statistical point of view, the first term of the *r.h.s.* of Eq. (1) describes the product of two independent one-body probabilities whereas the second and third terms represent the exchange-correlation contributions to the 2-RDM. This exchange part is rendered explicit when the Krönecker delta is replaced in Eq. (1) by

$$\delta_{i,j} = {}^1\mathrm{D}_{i;j} + {}^1\bar{\mathrm{D}}_{i;j} \tag{4}$$

where ${}^1\bar{\mathrm{D}}$ is the 1st-order hole-RDM. By so doing, what remains is the 2nd-order cumulant of a moment expansion of the 2-RDM, which accounts for the *statistically irreducible* two-body correlation effects [55–57].

$${}^2\Delta_{pq;rs} = -\,{}^1\mathrm{D}_{p;s}\,{}^1\bar{\mathrm{D}}_{q;r} + {}^2\mathcal{C}_{pq;rs} \tag{5}$$

The form of the ${}^2\mathcal{C}$ matrix is:

$${}^2\mathcal{C}_{pq;rs} = \langle \Psi | a_p^\dagger a_r\, \hat{Q}\, a_q^\dagger a_s | \Psi \rangle \tag{6}$$

where

$$\hat{Q} = \sum_{\Psi' \neq \Psi} |\Psi'\rangle\langle\Psi'| \tag{7}$$

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

The 2-CM describes the simultaneous virtual excitations and de-excitations of two electrons. It can also be interpreted as representing a connected particle-hole pair. Although with a different ordering, the same elements which form the 2-CM appear in the *G*-matrix [58]. Thus,

$${}^2\mathcal{C}_{pq;rs} \equiv {}^2G_{pr;sq} \tag{8}$$

The *G*-matrix has attracted a great deal of attention [59, 60] because it has important properties, i.e. it is a positive semi-definite Hermitian matrix. Moreover, its contractions

$$\sum_p {}^2G_{pr;pq} = -\,{}^1\mathrm{D}_{q;r}(N-1) + N\delta_{q,r} - ({}^1\mathrm{D}^2)_{q;r} \tag{9}$$

$$\sum_p {}^2G_{qp;rp} = (2K - N + 1)\,{}^1\mathrm{D}_{q;r} - ({}^1\mathrm{D}^2)_{q;r} \tag{10}$$

yield the corresponding 1-RDM.

Therefore, the 2nd-order correlation operator

$${}^2\hat{C}_{pq;rs} \equiv a_p^\dagger a_r\, \hat{Q}\, a_q^\dagger a_s \equiv {}^2\hat{G}_{pr;sq} \tag{11}$$

may be considered as a member of a family of $\hat{C}$- or $\hat{G}$-operators [61].

On the other hand, the CM family is more general than the G one, because it includes many matrices whose elements cannot be cast in the form of a positive semidefinite Hermitian *G*-matrix.

Let us now consider the three types of 3-CM which play a relevant role in this article:

$$ {}^{(3;2,1)}\mathcal{C}_{ijm;pqr} = \left\langle \Psi \middle| a_i^{\dagger} a_j^{\dagger} a_q a_p \, \hat{Q} \, a_m^{\dagger} a_r \middle| \Psi \right\rangle \tag{12} $$

$$ {}^{(3;1,1,1)}\mathcal{C}_{ijm;pqr} = \left\langle \Psi \middle| a_i^{\dagger} a_p \, \hat{Q} \, a_j^{\dagger} a_q \, \hat{Q} \, a_m^{\dagger} a_r \middle| \Psi \right\rangle \equiv {}^{(3,1,1,1)}G_{ipj;rmq} \tag{13} $$

$$ {}^{(3;1,2)}\mathcal{C}_{ijm;pqr} = \left\langle \Psi \middle| a_i^{\dagger} a_p \, \hat{Q} \, a_j^{\dagger} \, a_m^{\dagger} a_r a_q \middle| \Psi \right\rangle \tag{14} $$

As can be seen, only the ${}^{(3;1,1,1)}\mathcal{C}$ elements have the same value, although located differently in the matrix, as in the Hermitian ${}^{(3;1,1,1)}G$-matrix.

In what follows, whenever the G-matrix properties are needed, as in Section 3.2, we will resort to this matrix but in general it is convenient to carry out the theoretical developments in terms of the correlation matrices whose row/column labels are the same as the RDM ones from which they derive.

The form of the two different 4-CMs which will be considered here are:

$$ {}^{(4;3,1)}\mathcal{C}_{ijkl;pqrs} = \left\langle \Psi \middle| a_i^{\dagger} a_j^{\dagger} a_k^{\dagger} a_r a_q a_p \hat{Q} a_l^{\dagger} a_s \middle| \Psi \right\rangle \tag{15} $$

$$ {}^{(4;2,1,1)}\mathcal{C}_{pqij;rsml} = \left\langle \Psi \middle| a_p^{\dagger} a_q^{\dagger} a_s a_r \hat{Q} a_i^{\dagger} a_m \hat{Q} a_j^{\dagger} a_l \middle| \Psi \right\rangle \tag{16} $$

and similar definitions for the multiple possibilities.

2.2. THE HAMILTONIAN OPERATOR

The form of the Hamiltonian operator used here is

$$ \hat{H} = \frac{1}{2} \sum_{p,q,r,s} {}^{0}\mathrm{H}_{pq;rs} a_p^{\dagger} a_q^{\dagger} a_s a_r \tag{17} $$

where

$$ {}^{0}\mathrm{H}_{pq;rs} = \frac{\delta_{p,r}\epsilon_{q;s} + \delta_{q,s}\epsilon_{p;r}}{N-1} + \langle pq|rs \rangle \tag{18} $$

The symbol ϵ represents the 1-electron integral matrix whereas the $\langle pq|rs \rangle$ is the 2-electron repulsion integral in the Condon and Shortley notation ($\langle p(1)q(2)|r(1)s(2)\rangle$).

2.3. THE CORRELATION CONTRACTED SCHRÖDINGER EQUATION

Before describing the CCSE it may be convenient to consider first its precursor, the 2nd-order contracted Schrödinger equation (2-CSE). This equation was obtained in 1987 by Valdemoro [15] within the second quantization formalism in the occupation number representation. It is the result of applying a contraction mapping [62, 63] to the matrix representation of the Schrödinger equation in the form

$$ \sum_{\Lambda,\Omega,\Pi} \langle \Lambda|\hat{H}|\Omega\rangle \langle \Omega|\Psi\rangle \langle \Psi|\Pi\rangle \left\langle \Pi \middle| a_i^{\dagger} a_j^{\dagger} a_l a_m \middle| \Lambda \right\rangle = E \sum_{\Lambda,\Pi} \langle \Lambda|\Psi\rangle \langle \Psi|\Pi\rangle \left\langle \Pi \middle| a_i^{\dagger} a_j^{\dagger} a_l a_m \middle| \Lambda \right\rangle \tag{19} $$

where the states Λ, Ω, Π denote the Slater determinants spanning the N-electron space.

When obtaining the 2-CSE, the transition 2-RDMs, $\langle \Pi | a_i^{\dagger} a_j^{\dagger} a_l a_m | \Lambda \rangle$, are the mathematical tools in the contraction of the Schrödinger matrix equation from the N-electron space into the 2-electron reduced space.

When instead of the transition 2-RDMs we perform the same operation with the transition 2-CM $\langle \Phi | {}^{2}\hat{C} | \Phi' \rangle$ one has:

$$ \sum_{\Lambda,\Omega,\Pi} \langle \Lambda|\hat{H}|\Omega\rangle \langle \Omega|\Psi\rangle \langle \Psi|\Pi\rangle \langle \Pi| {}^{2}\hat{C}_{ij;ml} |\Lambda\rangle = E \sum_{\Lambda,\Pi} \langle \Lambda|\Psi\rangle \langle \Psi|\Pi\rangle \langle \Pi| {}^{2}\hat{C}_{ij;ml} |\Lambda\rangle \tag{20} $$

This expression clearly shows that this contracting mapping consists in taking the trace in the N-electron space of the product of the matrix representation of the Schrödinger equation with the transition correlation elements $\langle \Pi | {}^{2}\hat{C}_{ij;ml} | \Lambda \rangle$. Consequently, this equation really is a contracted form of the Schrödinger equation involving the 2-CM which is why we name it "correlation contracted Schrödinger equation" (CCSE). Its compact form is:

$$ \langle \Psi | \hat{H} \, {}^{2}\hat{C}_{ij;ml} | \Psi \rangle = E \, {}^{2}\mathcal{C}_{ij;ml} \equiv E \, {}^{2}G_{im;lj} = \langle \Psi | \hat{H} \, {}^{2}\hat{G}_{im;lj} | \Psi \rangle \tag{21} $$

This equation may be developed in two equivalent ways. The more obvious way is to transform the product $\hat{H} a_i^{\dagger} a_m$ implicitly appearing in (21) into its normal product form with respect to the bare vacuum, which gives the equation [50]:

$$ \sum_{p,q,r} {}^{0}\mathrm{H}_{pq;ir} \, {}^{(3;2,1)}\mathcal{C}_{pqj;mrl} - \sum_{p,q,r} {}^{0}\mathrm{H}_{pq;ri} \, {}^{(3;2,1)}\mathcal{C}_{pqj;mrl} + \sum_{p,q,r,s} {}^{0}\mathrm{H}_{pq;rs} \, {}^{(4;3,1)}\mathcal{C}_{pqij;mrsl} = E \, {}^{2}\mathcal{C}_{ij;ml} \tag{22} $$

Alternatively one may insert in (21) the unit operator after the Hamiltonian operator, thus

$$E\,{}^2\mathcal{C}_{ij;ml} = \langle \Psi | \hat{H}(\hat{P}+\hat{Q})\,{}^2\hat{C}_{ij;ml} | \Psi \rangle$$
$$= E\,{}^2\mathcal{C}_{ij;ml} + \sum_{p,q,r,s} {}^0\mathrm{H}_{pq;rs}\,{}^{(4;2,1,1)}\mathcal{C}_{pqij;rsml} \qquad (23)$$

That is,

$$\sum_{p,q,r,s} {}^0\mathrm{H}_{pq;rs}\,{}^{(4;2,1,1)}\mathcal{C}_{pqij;rsml} = 0 \qquad \forall i,j,m,l \qquad (24)$$

To demand that Eq. (22) be satisfied is equivalent [50] to demand the fulfilment of condition (24). These results show a similar pattern to those involving the 2-body density operator recently discussed [64]. The important question from the applicative point of view is that both forms of the CCSE involve not only the 3-CM but also the 4-CM.

3. Form and Solution of the Hypervirial Equation of the Expectation Value of the Correlation, or *G*-Particle-Hole, Operator

For eigenstates of the Hamiltonian, there are many relations based on the *diagonal* hypervirial theorem, that must vanish. The simplest ones are those constructed with density operators for a given state Ψ such as the 1st- and 2nd-order hypervirial equations (1-HV and 2-HV respectively)

$$\left\langle \Psi \left| \left[a_i^{\dagger} a_l, \hat{H} \right] \right| \Psi \right\rangle = 0 \quad \langle \Psi | [{}^2\hat{\Gamma}_{ij;kl}, \hat{H}] | \Psi \rangle = 0$$

But their vanishing does not necessarily imply for Ψ to be an eigenstate.

Analogously, the anti-Hermitian part of the CCSE (21) is the vanishing hypervirial of the correlation operator (GHV) whose form, for a given state Ψ, is:

$$\langle \Psi | [{}^2\hat{C}_{ij;ml}, \hat{H}] | \Psi \rangle = \langle \Psi | [{}^2\hat{G}_{im;lj}, \hat{H}] | \Psi \rangle = 0 \quad \forall i,j,l,m \qquad (25)$$

The explicit form of this equation in terms of the 1-RDM and of the 3-CM is derived in the Appendix. Here we report its final expression,

$$\sum_{p,q,r,s} {}^0\mathrm{H}_{pq;rs}\,{}^{(3;2,1)}\mathcal{C}_{pqj;rsl}\,{}^1\mathrm{D}_{i;m} - \sum_{p,q,r,s} {}^0\mathrm{H}_{pq;rs}\,{}^{(3;2,1)}\mathcal{C}_{pqm;rsi}\,{}^1\mathrm{D}_{j;l}$$
$$+ 2\sum_{p,q,r} {}^0\mathrm{H}_{pq;jr}\,{}^{(3;2,1)}\mathcal{C}_{lrm;pqi} + 2\sum_{p,q,r} {}^0\mathrm{H}_{pl;qr}\,{}^{(3;2,1)}\mathcal{C}_{qrm;jpi}$$
$$+ 2\sum_{p,q,r} {}^0\mathrm{H}_{pq;ir}\,{}^{(3;2,1)}\mathcal{C}_{pqj;mrl} + 2\sum_{p,q,r} {}^0\mathrm{H}_{pm;qr}\,{}^{(3;2,1)}\mathcal{C}_{ipj;qrl} = 0 \qquad (26)$$

This hypervirial equation does not depend on the 4-CM elements, which is why it is more convenient to attempt to solve it than the CCSE.

3.1. APPROXIMATING THE HIGH-ORDER CORRELATION MATRICES

Let us now consider the terms appearing in Eq. (26). These terms depend on the 3-CM elements which in principle we do not know. To solve this problem an approximative evaluation of this matrix is being developed but, until this task is accurately achieved, one can replace the direct evaluation of the 3-CM elements in terms of the antisymmetric 3rd-order cumulant, ${}^3\Delta$ [55–57] and lower order matrices

$$\begin{aligned}
{}^{(3;2,1)}\mathcal{C}_{ijk;pqr} &= 2\,{}^1\mathrm{D}_{i;r}\,{}^1\mathrm{D}_{j;q}\,{}^1\mathrm{D}_{k;p} - {}^1\mathrm{D}_{i;r}\,{}^1\mathrm{D}_{j;p}\,{}^1\mathrm{D}_{k;q} \\
&\quad - {}^1\mathrm{D}_{i;q}\,{}^1\mathrm{D}_{j;r}\,{}^1\mathrm{D}_{k;p} - 2\,{}^1\mathrm{D}_{i;r}\,{}^1\mathrm{D}_{j;q}\delta_{k;p} \\
&\quad + {}^1\mathrm{D}_{i;r}\delta_{j;p}\,{}^1\mathrm{D}_{k;q} + {}^1\mathrm{D}_{i;q}\,{}^1\mathrm{D}_{j;r}\delta_{k;p} \\
&\quad - {}^1\mathrm{D}_{i;r}\delta_{j;q}\,{}^1\mathrm{D}_{k;p} + {}^1\mathrm{D}_{i;r}\,{}^1\mathrm{D}_{j;p}\delta_{k;q} \\
&\quad + {}^1\mathrm{D}_{i;r}\delta_{j;q}\delta_{k;p} - {}^1\mathrm{D}_{i;r}\delta_{j;p}\delta_{k;q} \\
&\quad + {}^1\mathrm{D}_{i;p}\,{}^2\mathcal{C}_{jk;qr} + {}^1\mathrm{D}_{j;q}\,{}^2\mathcal{C}_{ik;pr} - {}^1\mathrm{D}_{k;q}\,{}^2\mathcal{C}_{ij;pr} \\
&\quad - {}^1\mathrm{D}_{j;r}\,{}^2\mathcal{C}_{ik;pq} - {}^1\mathrm{D}_{i;q}\,{}^2\mathcal{C}_{jk;pr} - {}^1\mathrm{D}_{j;p}\,{}^2\mathcal{C}_{ik;qr} \\
&\quad + {}^1\mathrm{D}_{i;r}\,{}^2\mathcal{C}_{jk;pq} + {}^1\mathrm{D}_{k;p}\,{}^2\mathcal{C}_{ij;qr} \\
&\quad - \delta_{k;p}\,{}^2\mathcal{C}_{ij;qr} + \delta_{k;q}\,{}^2\mathcal{C}_{ij;pr} + {}^3\Delta_{ijk;pqr} \qquad (27)
\end{aligned}$$

Valdemoro et al. [27] solve this problem by proposing an approximation to the cumulant matrix ${}^3\Delta$ based on the role played by the frontier electrons, the so called VTP functional. To define the frontier orbitals in this context, these authors consider the configuration which is expected to dominate in the state under study. Then, the set of frontier spin-orbitals is formed by the highest-occupied spin-orbital (HOMO) and lowest empty spin-orbital (LUMO) within each molecular-orbital symmetry.

The approximations used for the elements of ${}^3\Delta$ are:

$$ {}^3\Delta_{i_oj_ek_e;p_eq_er_o} = \frac{1}{6}\left({}^2\Delta_{i_ol;p_eq_e}{}^2\Delta_{j_ek_e;lr_o}\right) \qquad (l = \text{HOMO}) \tag{28} $$

and

$$ {}^3\Delta_{i_ej_ok_o;p_oq_or_e} = -\frac{1}{6}\left({}^2\Delta_{i_el;p_oq_o}{}^2\Delta_{j_ok_o;lr_e}\right) \qquad (l = \text{LUMO}) \tag{29} $$

where the o's and e's denote occupied and empty (or unoccupied) spin-orbitals, and ${}^2\Delta$ is given in Eq. (5). The remaining elements of ${}^3\Delta$ are set to zero.

The VTP reconstruction contains many contributions from higher orders of perturbation theory via the 1-RDM and 2-body correlation matrix and, thus, may be described as highly renormalized [65]. The CCSE requires a 2nd-order correction of the 3-body correlation matrix functional to generate 2nd-order 2-body correlation matrices and energies, but the GHV can produce 2nd-order 2-body correlation matrices and 3rd-order energies from only a 1st-order reconstruction of the 3-body correlation matrix.

3.2. SOLUTION OF THE GHV

At this stage, it is more convenient to refer to the G-matrix rather than to the 2-CM because the symmetry and eigenvalues properties of the G-matrix render more obvious the arguments proposed here.

Because of Eq. (21) one has

$$ \frac{1}{E}\langle\Psi|\hat{H}\,{}^2\hat{G}_{im;lj}|\Psi\rangle = {}^2_lG_{im;lj} \tag{30} $$

and

$$ \frac{1}{E}\langle\Psi|\,{}^2\hat{G}_{im;lj}\hat{H}|\Psi\rangle = {}^2_rG_{im;lj} \tag{31} $$

where the subscripts l/r indicate that the matrix is the result of the Hamiltonian operating on the left/right of ${}^2\hat{G}$. Hence,

$$ \frac{1}{E}\langle\Psi|[\hat{H},\,{}^2\hat{G}_{im;lj}]|\Psi\rangle = A_{im;lj} \tag{32} $$

where $A = {}^2_lG - {}^2_rG$ represents the error of the G-matrix when its hypervirial does not vanish.

Let us now consider a Heisenberg-like unitary transformation of the operator ${}^2\hat{G}$, which can be represented by the exponential of an anti-Hermitian operator $\hat{A}$. According to the well-known Campbell-Baker-Hausdorff relation [66, 67], such transformation can be rewritten as

$$ \begin{aligned} e^{\hat{A}}\,{}^2\hat{G}_{im;lj}e^{-\hat{A}} &= {}^2\hat{G}_{im;lj} + [\hat{A},{}^2\hat{G}_{im;lj}] \\ &\quad + \frac{1}{2!}[\hat{A},[\hat{A},{}^2\hat{G}_{im;lj}]] + \frac{1}{3!}[\hat{A},[\hat{A},[\hat{A},{}^2\hat{G}_{im;lj}]]] + \cdots \end{aligned} \tag{33} $$

The expectation value of both sides of Eq. (33) is equivalent to a Taylor series for ${}^2\hat{G}$ with respect to a common variable of $\hat{A}$ and ${}^2\hat{G}$ [67].

Let us now identify $\hat{A}$ with the operator whose representation is the G-error

$$ \hat{A} = \sum_{i,m,l,j} A_{im;lj}\,{}^2\hat{G}_{im;lj} \equiv \sum_{i,m,l,j}\hat{A}_{im;lj} \tag{34} $$

which is anti-Hermitian by construction.

In view of this definition, the product $E\hat{A}$ can be considered to represent an *effective* or *mean* hypervirial operator which approximates the three-body hypervirial operator—which includes an operatorial trace over one electron variable– by a connected particle-hole pair operator. Although arising from different arguments, this approximation is rather similar to that proposed by Mazziotti [43] when solving the ACSE and constitutes a very powerful operative procedure which renders feasible the calculation of the expectation value $\langle\Psi|[\hat{A},\,{}^2\hat{G}_{im;lj}]|\Psi\rangle$ in terms only of 3-body correlation matrices while preserving the essence of the theory.

Because the A-matrix is the difference of two approximate positive G-matrices, the expectation value of the operator series (33) must be convergent. In practice, it may be convenient, in order to accelerate convergence, to replace the factor $\frac{1}{E}$ by an infinitesimal one, ϵ, in units of an inverse of energy.

The sequence of operations in the procedure used in the calculations which are reported in Section 5 consists in an iterative calculation which may be summarized as follows:

$$ {}^2G^{(n)}_{im;lj} = {}^2G^{(n-1)}_{im;lj} + \langle\Psi|[\hat{A}^{(n-1)},{}^2\hat{G}_{im;lj}]|\Psi\rangle \tag{35} $$

It is important to note that the primary aim is to approximate the G-matrix and, as a consequence, to satisfy the GHV, which is only approximately achieved at convergence. The G-matrix obtained after each iteration is then contracted in order to obtain the corresponding 1-RDM [52]. Then, by applying Eq. (1) one has

$$E = \sum_{i,j,m,l}^{2K} {}^{0}\mathrm{H}_{ij,ml} \left[{}^{1}\mathrm{D}_{i;m}{}^{1}\mathrm{D}_{j;l} - \delta_{j,m}{}^{1}\mathrm{D}_{i;l} + {}^{2}G_{im;lj} \right] \quad (36)$$

or, when Ψ is a state with null z-component of the electronic spin, the spin-adapted formula for the energy is [68]:

$$E = \sum_{i,l}^{K} \{2\mathrm{h}^{c}_{i;l} - \mathrm{h}^{x}_{i,l}\}^{1}\mathrm{D}_{i;l} - \sum_{i,j,l,m}^{K} {}^{0}\mathrm{H}_{ij;ml} \left(2\,{}^{2}G_{i\bar{l};m\bar{j}} - {}^{2}G_{i\bar{m};l\bar{j}} \right) \quad (37)$$

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

$$\mathrm{h}^{c}_{i;l} = \sum_{j} {}^{0}\mathrm{H}_{ij;lj} \qquad \mathrm{h}^{x}_{i;l} = \sum_{j} {}^{0}\mathrm{H}_{ij;jl}$$

are one-body contractions of the ${}^{0}\mathrm{H}$ of the coulomb and exchange types respectively.

4. Theoretical Comparative Analysis of the ACSE and GHV Equations

It is now well established that it is more convenient to attempt to solve the ACSE rather than the 2-CSE and that, similarly, it is far easier to solve the GHV than the CCSE. Mazziotti [46] as well as the authors of this article (Valdemoro, C.; Tel, L. M.; Pérez-Romero, E.; Alcoba, D. R. Unpublished results) have tried whether a set of accurate RDM/CM matrices corresponding to multireference self-consistent and configuration interaction functions satisfied the ACSE/GHV conditions with negative results. A reasonable conjecture has been, therefore, that these equations are only satisfied by the matrices corresponding to an eigenstate of the Hamiltonian [69]. Nevertheless, because this is just a conjecture, the more demanding is the condition that we impose, the more plausible is the conjecture. This is the question which is analysed in this section.

When we recently analysed the possible sufficiency of the ACSE condition [64] we found that

$$\begin{aligned} \langle \Psi | [{}^{2}\hat{\Gamma}_{ij;ml}, \hat{H}] | \Psi \rangle &= \sum_{p,q,r,s} {}^{0}\mathrm{H}_{pq;rs} ({}^{(4;2,2)}G_{ijml;rspq} - {}^{(4;2,2)}G_{pqrs;mlij}) \\ &\equiv {}^{(4;2,2)}_{r}\Theta_{ij;ml} - {}^{(4;2,2)}_{l}\Theta_{ij;ml} = 0 \end{aligned} \quad (38)$$

where the r/l subscripts indicate that the Hamiltonian operator acts on the right/left respectively of the 2-body density operator ${}^{2}\hat{\Gamma}$.

Because Alcoba showed that the ${}^{(4;2,2)}\Theta$ terms vanish *iff* they correspond to a Hamiltonian eigenstate, the fulfilment of any of them is equivalent to the fulfilment of the 2-CSE. For the ACSE solution to correspond to an eigenstate, the relation ${}^{(4;2,2)}_{r}\Theta - {}^{(4;2,2)}_{l}\Theta$ should only cancel when each of these two Θ-terms vanishes. Very recently, Davidson (Private Communication, July 2008) has proved that this is not the case, as relation (38) presents solutions others than those corresponding to eigenstates, thus rendering the conjecture concerning the ACSE void.

When a similar analysis is applied to the CCSE and the GHV, the situation, in spite of an apparent similarity, is different. Thus one has

$$\begin{aligned} \langle \Psi | [{}^{2}\hat{G}_{im;lj}, \hat{H}] | \Psi \rangle &= \langle \Psi | [{}^{2}\hat{C}_{ij;ml}, \hat{H}] | \Psi \rangle \\ &= \sum_{p,q,r,s} {}^{0}\mathrm{H}_{pq;rs} \left({}^{(4;1,1,2)}\mathcal{C}_{ijpq;mlrs} - {}^{(4;2,1,1)}\mathcal{C}_{pqij;rsml} \right) \\ &\equiv {}^{(4;1,1,2)}\Theta_{ij,ml} - {}^{(4;2,1,1)}\Theta_{ij,ml} = 0 \end{aligned} \quad (39)$$

which is the condition for the GHV to be satisfied.

The answer to the question of whether this condition can be fulfilled when neither of the two Θ matrices vanishes is still open. Nevertheless, when comparing the formal structures of (39) and (38), it follows that the GHV condition is stronger than the ACSE one. Thus, while in the ACSE the ${}_{r}\Theta$ as well as the ${}_{l}\Theta$ depend *on the same* Hermitian ${}^{(4;2,2)}G$-matrix, in the GHV case the two Θ terms depend *on two different* non-Hermitian correlation matrices with many more degrees of freedom. It renders the probability of both non-null Θ matrices being equal considerably smaller than in the ACSE case. The following theorems confirm this expectation.

Theorem. For quantum systems, with only pairwise interactions, the 1-, 2-, and 3-RDM derived from the 2- and 3-CM satisfying the GHV, also satisfy the 1st-order contracted Schrödinger equation (1-CSE) [16, 17], which derive from contraction of the Schrödinger equation onto the space of one particle. In general, the converse is false.

Proof. By contracting the GHV onto the one particle space,

$$\sum_{p,q,r,s} {}^{0}\mathrm{H}_{pq;rs} {}^{(3;2,1)}\mathcal{C}_{pqj;rsl} = 0 \quad (40)$$

TABLE I

The ground-state energies from the GHV with VTP 3-body (correlation matrix) reconstruction are compared with the energies from the ACSE with VTP 3-body (density matrix) reconstruction as well as Hartree–Fock (HF) and full configuration interaction (FCI) wave function methods, for isoelectronic series in double-ζ basis sets and molecules in minimal basis sets.

	Energy (hartree)			
	Wave function methods		Contracted equation methods	
System	FCI	HF	ACSE	GHV
Be	−14.5871556	−14.5723689	−14.5871461	−14.5871552
B^{+}	−24.2484047	−24.2338257	−24.2484062	−24.2484069
C^{+2}	−36.4148907	−36.4007173	−36.4148954	−36.4148737
N^{+3}	−51.0837830	−51.0698086	−51.0837898	−51.0837257
O^{+4}	−68.2519572	−68.2381775	−68.2519629	−68.2519703
Li_2	−14.8470867	−14.8323167	−14.8469091	−14.8470472
BeH_2	−15.7640945	−15.7345453	−15.7638044	−15.7638136

which is a condition equivalent to the 1-CSE [50]. Hence, the set of solutions of the GHV is a *subset* of those of the 1-CSE. Furthermore, as the set of solutions of the 1-CSE is a subset of those of the 1-HV, the set of GHV solutions is also a subset of those of the 1-HV. ■

As a consequence, it follows that

Theorem. For quantum systems, with only pairwise interactions, the 2- and 3-CM which satisfy the GHV also satisfy the ACSE. In general, the converse is false.

Proof. To prove this statement let us rearrange the second-quantized operators appearing in Eq. (38), one has:

$$\begin{aligned}&\langle\Psi|[\hat{H},a_i^{\dagger}a_j^{\dagger}a_la_m]|\Psi\rangle\\&\quad={}^{1}\mathrm{D}_{j;l}\langle\Psi|\hat{H}a_i^{\dagger}a_m|\Psi\rangle-{}^{1}\mathrm{D}_{i;m}\langle\Psi|a_j^{\dagger}a_l\hat{H}|\Psi\rangle\\&\qquad-\delta_{j;m}\langle\Psi|[\hat{H},a_i^{\dagger}a_l]|\Psi\rangle+\langle\Psi|[\hat{H},{}^{2}\hat{\mathrm{C}}_{ij;ml}]|\Psi\rangle\qquad(41)\end{aligned}$$

Hence, as the set of the GHV solutions is a subset of those of the 1-HV, and of the solutions of the 1-CSE, it follows that the RDMs derived from the 2- and 3-CM satisfying the GHV also satisfy the ACSE which is what had to be proven. In general, the converse is false. Thus, a wavefunction of the type considered in (Davidson, E. R. Private Communication, July 2008), which is not a Hamiltonian eigenstate, yields 2- and 3-RDM (and the corresponding 2- and 3-CM) which satisfy the ACSE, but not the GHV. ■

Consequently, the iterative algorithm solves the GHV, the ACSE and the 1-CSE in an approximate and simultaneous way.

5. Some Numerical Results

As a test of the possibilities that the GHV method may provide for the study of the electronic structure of atoms and molecules, a few numerical calculations have been performed. The iterative process has been initiated at the Hartree–Fock (HF) level and has continued until no further decrease in the energy is attained or the root-mean-square deviations between RDMs in successive iterations fall below a preset accuracy limit.

The calculations have been performed on the Beryllium isoelectronic atoms and on the Li_2 and BeH_2 molecules. Bond lengths of Li_2 and of linear BeH_2 molecules have been taken as of 5.50 a_0 and 2.54 a_0, respectively. A double-ζ [70] basis set has been used in the atoms and ions calculations and for the molecules we used a minimal basis set. Electron integrals have been computed with the SMILES [71] program.

In Table I, we report the singlet ground-state energies obtained for these electronic systems with the GHV and the ACSE methods. In these calculations the VTP functional reconstruction of the 3-body correlation matrix was applied.

The results show that the GHV with VTP reconstruction produces 99.05–100.09% of the correlation

TABLE II

N-representability defect of the 2-RDM, 2-HRDM, ${}_{\{0,0\}}^{\ 2}G$, and ${}_{\{1,0\}}^{\ 2}G$ given by the deviations from the positive-/negative-semidefiniteness.

				N-representability error (lowest/highest eigenvalue)			
System	Method	Iteration	ϵ	2-RDM	2-HRDM	${}_{\{0,0\}}^{\ 2}G$	${}_{\{1,0\}}^{\ 2}G$
Be	ACSE	10,000	3.30 [–4]	–2.29 [–6]	–1.58 [–6]	–1.24 [–6]	1.20 [–6]
	GHV	2,500	3.30 [–4]	–3.02 [–6]	–6.52 [–7]	–2.90 [–5]	–1.54 [–6]
Li_2	ACSE	1,100	2.50 [–2]	1.81 [–6]	–8.03 [–5]	–6.64 [–5]	1.96 [–5]
	GHV	250	2.50 [–2]	2.04 [–4]	–9.69 [–5]	–4.72 [–5]	1.32 [–4]
BeH_2	ACSE	2,000	2.50 [–3]	–2.25 [–5]	–1.95 [–6]	–1.65 [–5]	7.93 [–6]
	GHV	1,000	2.50 [–3]	–2.28 [–5]	–4.47 [–6]	–9.46 [–4]	9.57 [–6]

energy which slightly improves upon the 98.80–100.05% recovered by the ACSE with VTP reconstruction.

As a test of accuracy a variety of related matrices are reported. Most of the results quoted in Tables II, III, and IV should vanish for an exact full-configuration-interaction (FCI) calculation. The deviations are, hence, a measure of the error or defect upon convergence of the iterative processes. The quoted values of the ${}^{2}G$-matrix are split into contributions from different spin states [52] in its defining Eqs. (6) and (8). The labels indicating the contributions are given as left-lower indices in the form ${}_{\{S',M'\}}^{\ 2}G$. Because the states studied are singlets, the only possible contributions to ${}^{2}G$ arise from other singlets, ${}_{\{0,0\}}^{\ 2}G$, or from triplets, ${}_{\{1,0\}}^{\ 2}G$.

The selected value of the ϵ parameter, mentioned in Section 3.2, although not fully optimized, represents a compromise between lengthy calculations and the guarantee of convergence.

The Tables II–IV just mentioned show that a steady convergence for the ACSE, 1-CSE, 1-HV, and GHV is observed in every case studied. On the other hand, for a similar convergence, a much smaller number of iterations is enough for the GHV case in comparison with the ACSE.

We finish this account of the applicative results by showing in Figures 1 and 2, the smooth convergence of the process in the Beryllium atom and BeH_2 molecule, respectively. These figures display the resulting energies as a function of the number of iterations. The HF and FCI results are also included for reference. As can be seen, for the Beryllium atom the GHV recovers 99.99 % of the correlation energy by converging to 0.4 microhartree above the FCI energy, whereas for BeH_2 the GHV recovers 99.05 % of the correlation energy by converging to 0.3 millihartree above the FCI energy.

6. Conclusions

In this article, we have studied the G-particle-hole hypervirial equation. The GHV is the anti-Hermitian

TABLE III

Deviations from the FCI results of the 1-RDM, 2-RDM, ${}_{\{0,0\}}^{\ 2}G$, and ${}_{\{1,0\}}^{\ 2}G$ at convergence of the iterative process.

				Root-mean-square deviation (from FCI values)			
System	Method	Iteration	ϵ	1-RDM	2-RDM	${}_{\{0,0\}}^{\ 2}G$	${}_{\{1,0\}}^{\ 2}G$
Be	HF	—	—	2.91 [–3]	5.01 [–3]	2.81 [–3]	2.79 [–3]
	ACSE	10,000	3.30 [–4]	8.68 [–4]	8.16 [–4]	4.45 [–4]	4.36 [–4]
	GHV	2,500	3.30 [–4]	7.07 [–4]	7.66 [–4]	4.26 [–4]	4.14 [–4]
Li_2	HF	—	—	2.92 [–2]	2.89 [–2]	1.67 [–2]	1.37 [–2]
	ACSE	1,100	2.50 [–2]	2.06 [–3]	1.61 [–3]	8.99 [–4]	6.59 [–4]
	GHV	250	2.50 [–2]	2.72 [–3]	2.12 [–3]	1.19 [–3]	8.56 [–4]
BeH_2	HF	—	—	4.57 [–3]	4.38 [–3]	2.58 [–3]	2.48 [–3]
	ACSE	2,000	2.50 [–3]	4.12 [–4]	2.73 [–4]	1.58 [–4]	1.51 [–4]
	GHV	1,000	2.50 [–3]	3.23 [–4]	2.57 [–4]	1.23 [–4]	1.12 [–4]

TABLE IV
Deviations from the FCI results of the 1-HV, 1-CSE, ACSE, and GHV at convergence of the iterative process.

				Root-mean-square deviation (from FCI values)			
System	Method	Iteration	ϵ	1-HV	1-CSE	ACSE	GHV
Be	HF	—	—	6.33 [–9]	3.17 [–9]	1.33 [–2]	4.34 [–2]
	ACSE	10,000	3.30 [–4]	2.22 [–4]	7.87 [–4]	1.47 [–3]	4.89 [–4]
	GHV	2,500	3.30 [–4]	1.49 [–4]	7.77 [–4]	3.36 [–3]	7.95 [–4]
Li_2	HF	—	—	3.29 [–8]	1.65 [–8]	3.76 [–3]	3.67 [–3]
	ACSE	1,100	2.50 [–2]	4.16 [–5]	1.24 [–3]	7.84 [–4]	5.71 [–4]
	GHV	250	2.50 [–2]	2.89 [–5]	1.22 [–3]	7.95 [–4]	5.98 [–4]
BeH_2	HF	—	—	7.97 [–8]	3.01 [–8]	1.40 [–3]	4.47 [–3]
	ACSE	2,000	2.50 [–3]	9.90 [–5]	6.11 [–5]	2.29 [–4]	8.58 [–5]
	GHV	1,000	2.50 [–3]	2.79 [–5]	6.30 [–5]	5.10 [–4]	1.99 [–4]

part of the CCSE, that is, the relation connecting these two equations is similar to that connecting the ACSE with the 2-CSE. The GHV has very important properties which emphasize its practical utility: (i) it only depends on the 3-order correlation matrices, 3-CM, (ii) it yields second-order accuracy from only first-order reconstruction of the 3-CM from the 2-CM, and (iii) it guarantees that the 1-CSE, the 1-HV, and the ACSE are satisfied. The iterative algorithm proposed to solve the GHV appears to be more efficient than that proposed in the ACSE solution. The GHV algorithm yields correlation energies in the range 99.05–100.09% while leading in a direct way to a quasi *N*- and *S*-representable 2-CM without making any call to the *N*-electron wave-function. In summary, the direct calculation of the 2-CM through the GHV method offers new possibilities for an accurate calculation of many electrons systems. Our next project is to work towards an optimization of the 3-CM reconstruction algorithms as well as improving the present GHV computational implementation in order to accelerate convergence.

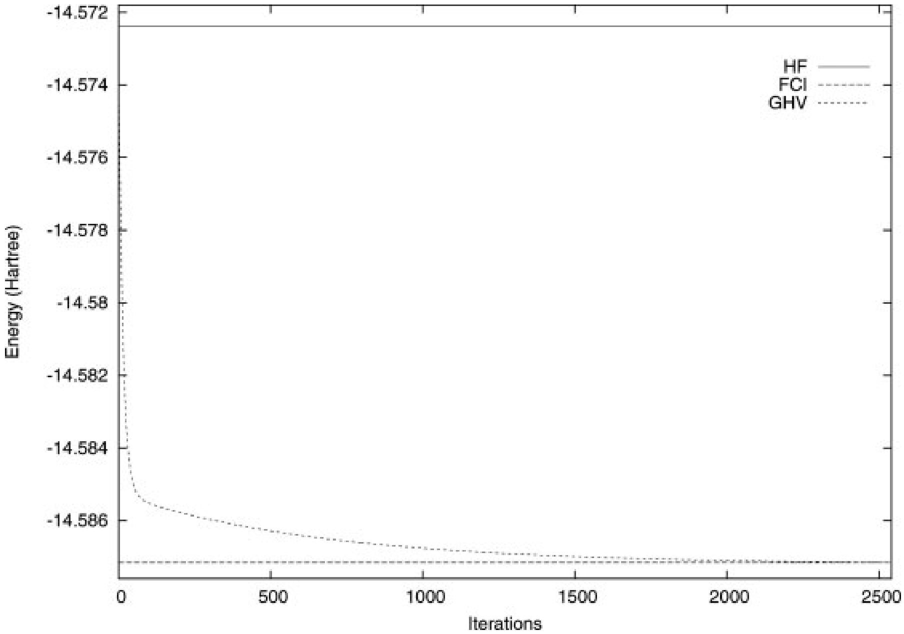

FIGURE 1. For Be the GHV energy converges to 0.4 μE_h above the FCI energy.

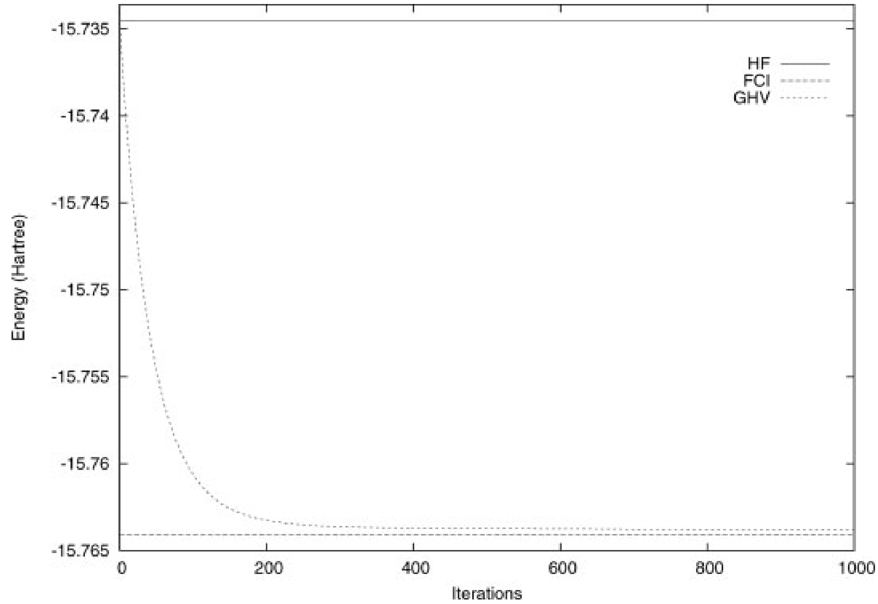

FIGURE 2. For BeH_2 the GHV energy converges to 0.3 mE_h above the FCI energy.

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Appendix: Main Steps in the Derivation of the GHV Equation

The hypervirial relation

$$\langle\Psi|[{}^2\hat{C}_{ij;ml},\hat{H}]|\Psi\rangle = \langle\Psi|{}^2\hat{C}_{ij;ml}\,\hat{H}|\Psi\rangle - \langle\Psi|\hat{H}\,{}^2\hat{C}_{ij;ml}|\Psi\rangle \tag{A.1}$$

should vanish for eigenstates.

- Let us consider the first term of the *r.h.s.* of this equation in terms of the fermion operators and the operator $\hat{Q}$,

$$\sum_{p,q,r,s} \left\langle\Psi\middle|a_i^\dagger a_m\,\hat{Q}\,a_j^\dagger a_l\,a_p^\dagger a_q^\dagger a_s a_r\middle|\Psi\right\rangle {}^0\mathrm{H}_{rs;pq} \tag{A.2}$$

Move the pair $a_j^\dagger a_l$ to the far right of the chain of creators-annihilators by means of the fermion anticommutation relations.

$$\begin{aligned}
&\left\langle\Psi\middle|a_i^\dagger a_m\,\hat{Q}\,a_j^\dagger a_l\,a_p^\dagger a_q^\dagger a_s a_r\middle|\Psi\right\rangle {}^0\mathrm{H}_{rs;pq}\\
&\quad= \left\langle\Psi\middle|a_i^\dagger a_m\,\hat{Q}\,a_j^\dagger a_q^\dagger a_s a_r\middle|\Psi\right\rangle {}^0\mathrm{H}_{rs;lq}\\
&\qquad- \left\langle\Psi\middle|a_i^\dagger a_m\,\hat{Q}\,a_j^\dagger a_p^\dagger a_s a_r\middle|\Psi\right\rangle {}^0\mathrm{H}_{rs;pl}\\
&\qquad+ \left\langle\Psi\middle|a_i^\dagger a_m\,\hat{Q}\,a_p^\dagger a_q^\dagger a_r a_l\middle|\Psi\right\rangle {}^0\mathrm{H}_{rj;pq}\\
&\qquad- \left\langle\Psi\middle|a_i^\dagger a_m\,\hat{Q}\,a_p^\dagger a_q^\dagger a_s a_l\middle|\Psi\right\rangle {}^0\mathrm{H}_{js;pq}\\
&\qquad+ \left\langle\Psi\middle|a_i^\dagger a_m\,\hat{Q}\,a_p^\dagger a_q^\dagger a_s a_r\,\hat{I}\,a_j^\dagger a_l\middle|\Psi\right\rangle {}^0\mathrm{H}_{rs;pq}
\end{aligned} \tag{A.3}$$

Notice the identity operator $\hat{I}$ inserted in the last term to give way for the next step.

- Perform a similar transformation on the second term in Eq. (A.1)

$$\sum_{p,q,r,s} {}^0\mathrm{H}_{rs;pq}\left\langle\Psi\middle|a_p^\dagger a_q^\dagger a_s a_r\,a_i^\dagger a_m\,\hat{Q}\,a_j^\dagger a_l\middle|\Psi\right\rangle \tag{A.4}$$

moving the pair $a_i^\dagger a_m$ to the left of $\hat{H}$

$$\begin{aligned}
&{}^0\mathrm{H}_{rs;pq}\left\langle\Psi\middle|a_p^\dagger a_q^\dagger a_s a_r\,a_i^\dagger a_m\,\hat{Q}\,a_j^\dagger a_l\middle|\Psi\right\rangle\\
&\quad= {}^0\mathrm{H}_{is;pq}\left\langle\Psi\middle|a_p^\dagger a_q^\dagger a_s a_m\,\hat{Q}\,a_j^\dagger a_l\middle|\Psi\right\rangle\\
&\qquad- {}^0\mathrm{H}_{ri;pq}\left\langle\Psi\middle|a_p^\dagger a_q^\dagger a_r a_m\hat{Q}\,a_j^\dagger a_l\middle|\Psi\right\rangle\\
&\qquad+ {}^0\mathrm{H}_{rs;pm}\left\langle\Psi\middle|a_i^\dagger a_p^\dagger a_s a_r\,\hat{Q}\,a_j^\dagger a_l\middle|\Psi\right\rangle
\end{aligned}$$

$$
\begin{aligned}
&- {}^{0}\mathrm{H}_{rs;mq}\langle\Psi|a_i^{\dagger}a_q^{\dagger}a_s a_r\,\hat{Q}\,a_j^{\dagger}a_l|\Psi\rangle\\
&+ {}^{0}\mathrm{H}_{rs;pq}\langle\Psi|a_i^{\dagger}a_m\,\hat{I}\,a_p^{\dagger}a_q^{\dagger}a_s a_r\,\hat{Q}\,a_j^{\dagger}a_l|\Psi\rangle \quad \text{(A.5)}
\end{aligned}
$$

- Let us now develop the last terms on the *r.h.s.* of both (A.3) and (A.5) replacing $\hat{I}$ by $\hat{P}+\hat{Q}$. Thus,

$$
\begin{aligned}
&\langle\Psi|a_i^{\dagger}a_m\,\hat{Q}\,\hat{H}\,\hat{I}\,a_j^{\dagger}a_l|\Psi\rangle\\
&\quad = \langle\Psi|a_i^{\dagger}a_m\,\hat{Q}\,\hat{H}\,|\Psi\rangle\langle\Psi|a_j^{\dagger}a_l|\Psi\rangle\\
&\qquad + \langle\Psi|a_i^{\dagger}a_m\,\hat{Q}\,\hat{H}\,\hat{Q}\,a_j^{\dagger}a_l|\Psi\rangle\\
&\langle\Psi|a_i^{\dagger}a_m\,\hat{I}\,\hat{H}\,\hat{Q}\,a_j^{\dagger}a_l|\Psi\rangle\\
&\quad = \langle\Psi|a_i^{\dagger}a_m|\Psi\rangle\langle\Psi|\hat{H}\,\hat{Q}\,a_j^{\dagger}a_l|\Psi\rangle\\
&\qquad + \langle\Psi|a_i^{\dagger}a_m\,\hat{Q}\,\hat{H}\,\hat{Q}\,a_j^{\dagger}a_l|\Psi\rangle
\end{aligned}
$$

The symmetry ${}^{0}\mathrm{H}_{pq;rs} = {}^{0}\mathrm{H}_{qp;sr}$ of the Hamiltonian matrix permits to collect all terms in Eq. (A.1) in the form

$$
\begin{aligned}
&\sum_{p,q,r,s} {}^{0}\mathrm{H}_{rs;pq}\,{}^{(3;2,1)}\mathcal{C}_{pqj;rsl}\,{}^{1}\mathrm{D}_{i;m} - \sum_{p,q,r,s} {}^{(3;1,2)}\mathcal{C}_{ipq;mrs}\,{}^{0}\mathrm{H}_{rs;pq}\,{}^{1}\mathrm{D}_{j;l}\\
&\quad + 2\sum_{p,r,s} {}^{0}\mathrm{H}_{rs;pm}\,{}^{(3;2,1)}\mathcal{C}_{ipj;rsl} - 2\sum_{p,q,r} {}^{(3;1,2)}\mathcal{C}_{ipq;mlr}\,{}^{0}\mathrm{H}_{rj;pq}\\
&\quad + 2\sum_{p,q,r} {}^{0}\mathrm{H}_{ir;pq}\,{}^{(3;2,1)}\mathcal{C}_{pqj;mrl} - 2\sum_{q,r,s} {}^{(3;1,2)}\mathcal{C}_{ijq;mrs}\,{}^{0}\mathrm{H}_{rs;lq} = 0
\end{aligned}
\quad \text{(A.6)}
$$

which, for the real case, reduces to the form given in Eq. (26).

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