Ionization and Double-Excitations within the Framework of the *G*-Particle-Hole Hypervirial Equation Method

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Recently, through the use of one-electron excitation operators, the set of low-lying excited states of several electronic systems was obtained within the framework of the Hermitian Operator method combined with the *G*-particle-hole Hypervirial equation method [Valdemoro et al., *J. Math. Chem.* 2012, 50, 492]. The main aim of this article is to extend our study by including higher-order excitations as well as extended ionization and electron affinity operators. Several examples show the convenience of this extension to improve the accuracy of the results in some relevant cases. Through the use of geminal excitations, the algebra of the formal derivations is considerably simplified. © 2012 Wiley Periodicals, Inc.

General Introduction

To determine directly 1- and 2-body reduced density matrices (RDM) without a previous knowledge of the *N*-electron wavefunction is an old pursuit. Especial mention must be given to the pioneer works by Husimi,[1] Löwdin,[2] Mayer,[3] McWeeny,[4] Ayres,[5] and Coulson.[6] Two remarkable papers in the early sixties—by Coleman[7] about the RDM *N*-representability conditions and by Garrod and Percus[8] about the *G*-particle-hole matrix properties—set a firm foundation for the 2-RDM theory. The interested reader may find general information about the rich bibliography on the 2-RDM theory in Davidson's[9] and Coleman and Yukalov's[10] books as well as in the reviews and proceedings.[11–15] One of the present lines of research, which is yielding many excellent results, is that of looking for the solution of the matrix representation in the 2-electron space of the Schrodinger and Liouville (LE) equations. Several accounts have been given about these contracted/integrated equations.[16–19] The drawback of these contracted equations is that they are operationally indeterminate,[20] because, in an averaged form, they involve high-order RDMs terms. To solve these equations, one must therefore approximate these high-order RDMs in terms of the lower-order ones.[21] This approach permitted Colmenero and Valdemoro[22] to solve iteratively the contracted Schrödinger equation in 1994. This work was further developed by the groups lead by Nakatsuji,[23,24] Mazziotti[25] and Valdemoro.[26] A similar line of thoughts is being now applied to solve the *G*-particle-hole hypervirial equation (GHV),[27–33] which results from a contraction of a particular case of the LE[19,29] and which is one of the equations most used by our group.

Many authors have studied excited states, electron affinity and ionization potential energies.[34–47] Our work partly follows the approaches of Bouten et al.,[39,40] Simons and Smith,[38,47] and Szekeres et al.[42] Thus, Bouten et al.[39,40] studied in the early seventies the properties of the particle-hole subspace of a state and described a so-called Hermitian Operator (HO) method for calculating excited states. A combination of their formulation and the GHV method was carried out in Ref. [32], which yielded excellent results in calculating the low-lying excited states of a series of molecules.

An extension of the said method for higher-order excitations is a necessary but not a trivial matter. A similar consideration applies to the equations of the motion (EOM) method of Simons and Smith,[38,47] which allows one to calculate electron affinities and ionization potentials. The aim of this article is mainly to report the formalism for double-excitations as well as for the electron affinity and ionization potential involving more than a single fermion operator. Thus, analytical close-form expressions for these extended excitations will permit the study of highly correlated states. The geminal algebra developed by Valdemoro et al.[48] has been used to reduce the otherwise excessively large number of algebraic operations and formulae.

The following section deals with the theoretical background on Bouten et al.[39,40] HO equations as well as on Simons and Smith's EOM ones.[38,47] The double excitations formulation together with the final close-form expressions for the double excitations is reported in "Extension of the HO Method: Double

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Excitations" section. The geminal algebra rules are also recalled in this section. A short discussion of the previously obtained results introduces "Simple and Extended Electron Affinity and Ionization Potential Equations" section, to show the advantage of pushing a step further the study of the ionized states and then follows the extended formulation for the electron affinity and ionization potential. Finally, some concluding comments on the structural difficulties of the computational codes are given in "Concluding Comments" section.

Basic Theoretical Background

The main fermion relation is

$$ {}^1D_{i;m} + {}^1\overline{D}_{i;m} = \delta_{i;m} \tag{1} $$

where ${}^1D$ and ${}^1\overline{D}$ represent the 1-RDM and 1-hole RDM (1-HRDM), respectively.

$$ {}^1D_{i;m} = \langle\Phi|\, i^\dagger\, m\, |\Phi\rangle, \qquad {}^1\overline{D}_{i;m} = \langle\Phi|\, m\, i^\dagger\, |\Phi\rangle \tag{2} $$

and where the fermion creation/annihilation operator labels correspond to the spin–orbitals forming a finite basis of $2K$ orthonormal elements spanning the one-electron space. This equation and the positive semidefiniteness of these matrices summarize the ensemble N-representability conditions for the 1-RDM.[7] The 2-RDM may be expressed as:

$$ {}^2D_{ij;mt} = \frac{1}{2!}\,\langle\Phi|\, i^\dagger\, j^\dagger\, t\, m\, |\Phi\rangle \tag{3} $$

There are several ways of decomposing the 2-RDM in terms that involve just 1-RDM and 1-HRDM elements and pure 2-body terms. Thus,

$$ 2!\,{}^2D_{pq;tv} \equiv {}^1D_{p;t}\,{}^1D_{q;v} - \delta_{q,t}\,{}^1D_{p;v} + {}^2C_{pq;tv} \tag{4a} $$

$$ \equiv {}^1D_{p;t}\,{}^1D_{q;v} - {}^1D_{q;t}\,{}^1D_{p;v} - {}^1\overline{D}_{q;t}\,{}^1D_{p;v} + {}^2C_{pq;tv} \tag{4b} $$

$$ \equiv {}^1D_{p;t}\,{}^1D_{q;v} - {}^1D_{q;t}\,{}^1D_{p;v} + {}^2\Delta_{pq;tv} \tag{4c} $$

where

$$ {}^2C_{pq;tv} = \sum_{\Phi'\neq\Phi} \langle\Phi|\, p^\dagger\, t\, |\Phi'\rangle\, \langle\Phi'|\, q^\dagger\, v\, |\Phi\rangle \equiv \langle\Phi|\, \hat{C}_{pq;tv}\, |\Phi\rangle \tag{5} $$

is an element of the 2-order correlation matrix,[48–51] which does not contribute to the trace of the 2-RDM. The symbol ${}^2\Delta$ represents the second-order cumulant[52–56] that groups two terms, which generate two correlation mechanisms under the action of the Hamiltonian: an electron–hole polarization and the pure 2-body correlation effects generated by virtual electron excitations/de-excitations.[48–50,57,58]

The G-particle-hole matrix,[8] which is defined as:

$$ {}^2G_{pt;vq} \equiv {}^2C_{pq;tv} \tag{6} $$

can also be considered a correlation matrix, because it is a pure 2-body matrix.[48,51] Note that, although the two ${}^2G$ and ${}^2C$ matrices share the same elements, these elements occupy

different positions in each matrix. Hence, these two matrices have different properties; in particular, the G-particle-hole matrix is a positive semidefinite matrix whose contraction into the 1-body space generates the 1-RDM.[57,59,60]

In a similar way, higher-order p-body correlation matrices are obtained by decomposing the higher-order p-RDMs.[48,51]

The GHV

Let us contract the LE into the 2-body space with a correlation contracting mapping, in the following way[29]:

$$ \sum_{\Lambda,\Omega} \langle\,\Lambda\,|\,[\,\hat{H},\,|\,\Phi\,\rangle\langle\,\Phi'\,|\,]\,|\,\Omega\,\rangle\,\langle\,\Omega\,|\,{}^2\hat{G}_{im;lj}\,|\,\Lambda\,\rangle $$
$$ = \langle\,\Phi'\,|\,[\,\hat{H},\,{}^2\hat{G}_{im;lj}\,]\,|\,\Phi\,\rangle \tag{7} $$

which vanishes for $\Phi = \Phi'$ and becomes the compact expression of the GHV equation. Taking into account that the many-body Hamiltonian operator may be expressed as

$$ \hat{H} = \frac{1}{2}\sum_{p,q,m,v} {}^0H_{pq;mv}\, p^\dagger\, q^\dagger\, v\, m \tag{8} $$

where ${}^0H$ groups the one- and two-electron integrals,[61] and bringing all the operator strings that are implicit in this compact equation to their normal product form, one obtains the explicit form of the GHV equation[27]:

$$ 2\sum_{p,r,s} {}^0H_{rs;pm}\,{}^{(3;2,1)}C_{ipj;rsl} + 2\sum_{p,q,r} {}^0H_{pq;jr}\,{}^{(3;2,1)}C_{lrm;pqi} $$
$$ + 2\sum_{p,q,r} {}^0H_{ir;pq}\,{}^{(3;2,1)}C_{pqj;mrl} + 2\sum_{q,r,s} {}^0H_{ql;rs}\,{}^{(3;2,1)}C_{rsm;jqi} $$
$$ + \sum_{p,q,r,s} {}^0H_{rs;pq}\,{}^{(3;2,1)}C_{pqj;rsl}\,{}^1D_{i;m} - \sum_{p,q,r,s} {}^0H_{pq;rs}\,{}^{(3;2,1)}C_{rsm;pqi}\,{}^1D_{l;j} = 0 \tag{9} $$

where

$$ {}^{(3;2,1)}C_{rsm;jqi} = \sum_{\Phi'\neq\Phi} \langle\Phi|\, a_r^\dagger\, a_s^\dagger\, a_q\, a_j\, |\Phi'\rangle\, \langle\Phi'|\, a_m^\dagger\, a_i\, |\Phi\rangle \tag{10} $$

describes an element of the 3-order correlation matrix. These equations are iteratively solved following a similar procedure to those reported in Refs. [62–65]. As a result, an approximated G-particle-hole matrix corresponding to the eigenstate being considered is obtained.[27,29]

The Bouten et al. HO method

To calculate excited states, Bouten et al.[39,40] proposed to solve the equation

$$ \hat{H}\,\hat{S}\,|\Phi\rangle = E_\Psi\,|\Psi\rangle. \tag{11} $$

To this aim, these authors start with the equation

$$ \langle\Phi|\,[\,\hat{S},\,[\,\hat{H},\,\hat{S}'\,]\,]\,|\Phi\rangle = (E_\Psi - E_\Phi)\,\langle\Phi|\,\hat{S}\,\hat{S}' + \hat{S}'\,\hat{S}\,|\Phi\rangle, \tag{12} $$

which is formally equivalent to Eq. (11) for $\hat{S} = |\Psi\rangle\langle\Phi| + |\Phi\rangle\langle\Psi|$ and valid when both Φ and Ψ are eigenstates of $\hat{H}$ and

the $\widehat{S'}$ operators form a complete set. Then Bouten et al. propose the following approximated excitation HO for acting on the ground state wavefunction Φ

$$\widehat{S} = \sum_{t,v} \left\{ c^{(+)}_{t;v} \left(t^\dagger v - {}^1D_{t;v} + v^\dagger t - {}^1D_{v;t} \right) \right.$$
$$\left. + i\, c^{(-)}_{t;v} \left(t^\dagger v - {}^1D_{t;v} - v^\dagger t + {}^1D_{v;t} \right) \right\} \qquad (13)$$

where the c symbols represent real coefficients, the fermion operators represent spin–orbitals, and i is the imaginary unit. Note that the terms $|\Phi| \widehat{S}\widehat{S'} + \widehat{S'}\widehat{S}|\Phi\rangle$ involve elements of the G-particle-hole matrix, due to the $t^\dagger v - {}^1D_{t;v}$ type of operator structure in the definition of the $\widehat{S}$ operator. Bouten et al. showed that by substituting the $\widehat{S}$ 1-body excitation operator into Eq. (12) one obtains the following system of decoupled equations:

$$\mathcal{H}^{(++)} c^{(+)} = 2 \left(E_\Psi - E_\Phi \right) \mathcal{G}^{(++)} c^{(+)} \qquad (14a)$$
$$\mathcal{H}^{(--)} c^{(-)} = 2 \left(E_\Psi - E_\Phi \right) \mathcal{G}^{(--)} c^{(-)} \qquad (14b)$$

where $\mathcal{G}^{(++)}$ and $\mathcal{G}^{(--)}$ are functionals of the G-particle-hole matrix corresponding to the reference eigenstate Φ. Defining $\tilde{H}_{ir;ps} = {}^0H_{ir;ps} - {}^0H_{ri;ps} \equiv {}^0H_{ir;ps} - {}^0H_{ir;sp}$ one obtains

$$\mathcal{H}^{(++)}_{ij;pq} = +4 \left\{ \tilde{H}_{jr;ps}\,{}^2D_{ir;qs} + \tilde{H}_{ir;ps}\,{}^2D_{jr;qs} \right.$$
$$\left. + \tilde{H}_{jr;qs}\,{}^2D_{ir;ps} + \tilde{H}_{ir;qs}\,{}^2D_{jr;ps} \right\}$$
$$- 2 \left\{ \delta_{q,i}\,(\tilde{H}\,{}^2D)_{pr;jr} + \delta_{q,j}\,(\tilde{H}\,{}^2D)_{pr;ir} \right.$$
$$\left. + \delta_{p,i}\,(\tilde{H}\,{}^2D)_{qr;jr} + \delta_{p,j}\,(\tilde{H}\,{}^2D)_{qr;ir} \right\}$$
$$+ 2 \left\{ (\tilde{H}\,{}^2D)_{pi;jq} + (\tilde{H}\,{}^2D)_{pj;iq} + (\tilde{H}\,{}^2D)_{qi;jp} + (\tilde{H}\,{}^2D)_{qj;ip} \right\}$$
$$(15a)$$

$$\mathcal{H}^{(--)}_{ij;pq} = +4 \left\{ \tilde{H}_{jr;ps}\,{}^2D_{ir;qs} - \tilde{H}_{ir;ps}\,{}^2D_{jr;qs} \right.$$
$$\left. - \tilde{H}_{jr;qs}\,{}^2D_{ir;ps} + \tilde{H}_{ir;qs}\,{}^2D_{jr;ps} \right\}$$
$$- 2 \left\{ \delta_{q,i}\,(\tilde{H}\,{}^2D)_{pr;jr} - \delta_{q,j}\,(\tilde{H}\,{}^2D)_{pr;ir} \right.$$
$$\left. - \delta_{p,i}\,(\tilde{H}\,{}^2D)_{qr;jr} + \delta_{p,j}\,(\tilde{H}\,{}^2D)_{qr;ir} \right\}$$
$$+ 2 \left\{ (\tilde{H}\,{}^2D)_{pi;jq} - (\tilde{H}\,{}^2D)_{pj;iq} - (\tilde{H}\,{}^2D)_{qi;jp} + (\tilde{H}\,{}^2D)_{qj;ip} \right\}$$
$$(15b)$$

where only 2-order matrices are involved. Hence, since

$$\mathcal{H}^{(++)} c^{(+)} = 2 \left(E_\Psi - E_\Phi \right) \mathcal{G}^{(++)} c^{(+)} \qquad (16a)$$
$$\mathcal{H}^{(--)} c^{(-)} = 2 \left(E_\Psi - E_\Phi \right) \mathcal{G}^{(--)} c^{(-)}, \qquad (16b)$$

the matrices $\mathcal{H}^{(++)}$ and $\mathcal{H}^{(--)}$ can be cast into functionals of the G-particle-hole matrix corresponding to the reference eigenstate Φ, and

$$\mathcal{G}^{(++)} = \mathcal{F}^{(+)}({}^2G) \qquad (17a)$$
$$\mathcal{G}^{(--)} = \mathcal{F}^{(-)}({}^2G) \qquad (17b)$$

one may set and solve the HO equations; thus determining part of the system spectrum provided that one knows the G-particle-hole matrix of Φ.

The Simons et al. EOM method

In the early seventies, Simons and Smith[38] proposed a method for the calculation of electron affinities and ionization potentials. These quantities link two states of a system with different number of electrons. The method is based on the relations:

$$\hat{H}\,\widehat{S}\,|\Phi(N)\rangle = E_\Psi\,|\Psi(N-1)\rangle \qquad (18a)$$
$$\hat{H}\,\widehat{S}^\dagger\,|\Phi(N)\rangle = E_\Psi\,|\Psi(N+1)\rangle, \qquad (18b)$$

which implies that the following equations

$$\langle \Phi | \widehat{S}\,[\hat{H},\,\widehat{S'}^\dagger]\,|\,\Phi \rangle = \Delta E^+ \langle \Phi | \widehat{S}\,\widehat{S'}^\dagger | \Phi \rangle \qquad (19)$$

and

$$\langle \Phi | [\hat{H},\,\widehat{S'}^\dagger]\,\widehat{S}|\,\Phi \rangle = \Delta E^- \langle \Phi | \widehat{S'}^\dagger\,\widehat{S} | \Phi \rangle \qquad (20)$$

have to be solved. ΔE^+ and ΔE^- denote electron affinity and ionization potential energies, respectively. By expanding the $\widehat{S}$ operator in the basis spanned by the set of $\widehat{S'}$ operators, these two equations become linear and can be combined as follows[42,47]:

$$\langle \Phi | [\widehat{S},\,[\hat{H},\,\widehat{S'}^\dagger]]_+\,|\Phi \rangle = \Delta E \langle \Phi | \widehat{S}\,\widehat{S'}^\dagger + \widehat{S'}^\dagger\,\widehat{S} | \Phi \rangle, \qquad (21)$$

where ΔE denotes either electron affinity or ionization potential energies. The latter equation permits to approximately evaluate the energy differences of Eqs. (19) and (20) and to reduce the computational cost, because the anticommutation implies a cancellation of the higher-order matrices. In what follows, we will consider this equation in the study of electron affinity and ionization potential.

Extension of the HO Method: Double Excitations

To solve Bouten et al. equations (14), the G-particle-hole matrix of the reference state was needed as input data. It is, therefore, evident that the GHV and the HO methods are particularly well suited to be combined. Recently, we showed that the combination of these two methods could indeed be very effective.[32] Thus, the low-lying states of a set of molecules were determined and, what is still more stricking, we showed that by starting from the lowest triplet ($M_s = 1$) state of LiH—which even at a far from equilibrium geometry can be considered monoconfigurational—a correct energy value for the singlet ground state could be obtained. It should be emphasized that no particular spin-flip operator such as Krylov's one[66] is involved here. The HO method generates a spectrum of states with various spin symmetries, because the operators involve spin–orbitals without restrictions. These excellent results are however limited given that the method proposed by Bouten et al. considers only monoexcitations. The formalism must, therefore, be

extended so as to study those highly correlated excited states of interest, which cannot be reached with single excitations from a state that can be accurately treated with the GHV method, that is, states having a single dominant Slater determinant. The first singlet excited state of the BeH_2, of the same symmetry as the ground state, is one of these states—as the corresponding function of this state is a clearly multideterminantal one.[30] In this section, we describe the main lines of these extended derivations and their final close-form analytical expressions.

Extended form of the $\widehat{S}$ excitation operators

To reduce the rather large number of terms and be, therefore, capable of obtaining close-form analytic expressions for the equations, we have had recourse to geminal algebra.[48] In what follows, the Greek letters represent geminal creator/annihilator operators, whereas the Latin letters represent single fermion operators participating in the geminals.

As an extension of the single excitation operators given in Eq. (13), the double excitation operator takes the form:

$$\widehat{S} = \sum_{\lambda,\gamma} \{ c_{\lambda;\gamma}^{(+)} (\lambda^\dagger \gamma - {}^2D_{\lambda;\gamma} + \gamma^\dagger \lambda - {}^2D_{\gamma;\lambda})$$
$$+ i\, c_{\lambda;\gamma}^{(-)} (\lambda^\dagger \gamma - {}^2D_{\lambda;\gamma} - \gamma^\dagger \lambda + {}^2D_{\gamma;\lambda}) \} \qquad (22)$$

where

$$\lambda^\dagger \equiv \lambda_1^\dagger \lambda_2^\dagger \quad (\lambda_1^\dagger < \lambda_2^\dagger) \quad \text{and} \quad \gamma \equiv \gamma_2 \gamma_1 \quad (\gamma_1 < \gamma_2) \qquad (23)$$

is a nonredundant definition of geminals.

The geminal algebra rules The geminal algebra rules are

$$\gamma \lambda^\dagger = \delta_{\lambda,\gamma} + \lambda^\dagger \gamma - \sum_{i,j} {}^1D_{i;j}^{\lambda\gamma} i^\dagger j \qquad (24a)$$

$$i \lambda^\dagger = \sum_t \langle t\, i \mid \lambda \rangle t^\dagger + \lambda^\dagger i \qquad (24b)$$

$$\gamma i^\dagger = \sum_t \langle \gamma \mid i\, t \rangle t + i^\dagger \gamma \qquad (24c)$$

where

$${}^1D_{i;j}^{\lambda\gamma} \equiv \langle \lambda \mid i^\dagger j \mid \gamma \rangle$$

$$\langle t\, i \mid \lambda \rangle = \delta_{\lambda_1,i} \delta_{\lambda_2,t} - \delta_{\lambda_1,t} \delta_{\lambda_2,i}$$

Hamiltonian in the geminal basis The Hamiltonian operator in the geminal notation takes the form:

$$\hat{H} = \sum_{\tau,\mu} {}^0H_{\tau;\mu}\, \tau^\dagger \mu \qquad (25)$$

where

$${}^0H_{\tau;\mu} = {}^0H_{\tau_1 \tau_2; \mu_1 \mu_2} - {}^0H_{\tau_1 \tau_2; \mu_2 \mu_1}. \qquad (26)$$

The Hamiltonian thus expressed in the geminal basis is the same as that given in Eq. (8).

Explicit form of the double excitation HO equation

The inclusion of the above-mentioned Hamiltonian operator in the expression

$$\langle \Phi \mid [\lambda^\dagger \gamma, [\hat{H}, \eta^\dagger \chi]] \mid \Phi \rangle \qquad (27)$$

gives way to the following set of terms gathered according to the order of the RDM they involve. In what follows, λ, γ, η and χ are fixed indices, and a sum is implied over all the other indices.

Two-electron terms

$${}^0H_{\gamma;\eta} \langle \Phi \mid \lambda^\dagger \chi \mid \Phi \rangle + {}^0H_{\chi;\lambda} \langle \Phi \mid \eta^\dagger \gamma \mid \Phi \rangle$$
$$- {}^0H_{\chi;\mu} \delta_{\gamma,\eta} \langle \Phi \mid \lambda^\dagger \mu \mid \Phi \rangle - {}^0H_{\tau;\eta} \delta_{\lambda,\chi} \langle \Phi \mid \tau^\dagger \gamma \mid \Phi \rangle \qquad (28)$$

Three-electron terms

$$- {}^0H_{\tau;\eta} {}^1D_{t;v}^{\tau\gamma} \langle \Phi \mid t^\dagger \lambda^\dagger \chi\, v \mid \Phi \rangle - {}^0H_{\tau;\lambda} {}^1D_{t;v}^{\tau\chi} \langle \Phi \mid t^\dagger \eta^\dagger \gamma\, v \mid \Phi \rangle$$
$$- {}^0H_{\gamma;\mu} {}^1D_{t;v}^{\mu\eta} \langle \Phi \mid t^\dagger \lambda^\dagger \chi\, v \mid \Phi \rangle - {}^0H_{\chi;\mu} {}^1D_{t;v}^{\eta\gamma} \langle \Phi \mid t^\dagger \eta^\dagger \gamma\, v \mid \Phi \rangle$$
$$+ {}^0H_{\chi;\mu} {}^1D_{t;v}^{\eta\gamma} \langle \Phi \mid t^\dagger \lambda^\dagger \mu\, v \mid \Phi \rangle + {}^0H_{\tau;\eta} {}^1D_{t;v}^{\lambda\chi} \langle \Phi \mid t^\dagger \tau^\dagger \gamma\, v \mid \Phi \rangle$$
$$+ {}^0H_{\tau;\mu} {}^1D_{t;v}^{\tau\gamma} \delta_{\gamma,\eta} \langle \Phi \mid t^\dagger \lambda^\dagger \mu\, v \mid \Phi \rangle + {}^0H_{\tau;\mu} {}^1D_{t;v}^{\eta\mu} \delta_{\lambda,\chi} \langle \Phi \mid t^\dagger \tau^\dagger \gamma\, v \mid \Phi \rangle$$
$$+ {}^0H_{\tau;\mu} {}^1D_{t;s}^{\tau\gamma} {}^1D_{s;v}^{\eta\mu} \langle \Phi \mid t^\dagger \lambda^\dagger \chi\, v \mid \Phi \rangle - {}^0H_{\tau;\mu} {}^1D_{s;v}^{\tau\gamma} {}^1D_{t;s}^{\eta\mu} \langle \Phi \mid t^\dagger \lambda^\dagger \mu\, v \mid \Phi \rangle$$
$$+ {}^0H_{\tau;\mu} {}^1D_{t;s}^{\tau\chi} {}^1D_{s;v}^{\lambda\mu} \langle \Phi \mid t^\dagger \eta^\dagger \gamma\, v \mid \Phi \rangle - {}^0H_{\tau;\mu} {}^1D_{t;s}^{\eta\mu} {}^1D_{s;v}^{\lambda\chi} \langle \Phi \mid t^\dagger \tau^\dagger \gamma\, v \mid \Phi \rangle \qquad (29)$$

Four-electron terms

$$+ {}^0H_{\tau;\mu} {}^1D_{s;t}^{\eta\mu} {}^1D_{r;v}^{\tau\gamma} \langle \Phi \mid r^\dagger s^\dagger \lambda^\dagger \chi\, t\, v \mid \Phi \rangle$$
$$+ {}^0H_{\tau;\mu} {}^1D_{s;t}^{\lambda\mu} {}^1D_{r;v}^{\tau\chi} \langle \Phi \mid r^\dagger s^\dagger \eta^\dagger \gamma\, t\, v \mid \Phi \rangle$$
$$+ {}^0H_{\tau;\mu} {}^1D_{r;v}^{\tau\chi} {}^1D_{s;t}^{\eta\gamma} \langle \Phi \mid r^\dagger s^\dagger \lambda^\dagger \mu\, v\, t \mid \Phi \rangle$$
$$+ {}^0H_{\tau;\mu} {}^1D_{t;v}^{\lambda\chi} {}^1D_{s;r}^{\eta\mu} \langle \Phi \mid \tau^\dagger s^\dagger t^\dagger r\, v\, \gamma \mid \Phi \rangle$$
$$+ {}^0H_{\tau;\mu} {}^1D_{r;s}^{\eta\mu} \langle t\, s \mid \lambda \rangle \langle \Phi \mid \tau^\dagger r^\dagger t^\dagger \gamma\, \chi \mid \Phi \rangle$$
$$+ {}^0H_{\tau;\mu} {}^1D_{r;s}^{\chi\tau} \langle t\, s \mid \gamma \rangle \langle \Phi \mid \eta^\dagger \lambda^\dagger \mu\, t\, r \mid \Phi \rangle$$
$$+ {}^0H_{\tau;\mu} {}^1D_{r;s}^{\gamma\eta} \langle t\, s \mid \mu \rangle \langle \Phi \mid \tau^\dagger \lambda^\dagger \chi\, r\, t \mid \Phi \rangle$$
$$+ {}^0H_{\tau;\mu} {}^1D_{r;s}^{\lambda\chi} \langle t\, s \mid \tau \rangle \langle \Phi \mid \eta^\dagger t^\dagger r^\dagger \mu\, \gamma \mid \Phi \rangle \qquad (30)$$

For the sake of simplicity, the contributions to the left-hand side (LHS) of Eq. (12), which can be easily obtained from these terms by interchanging $\lambda \leftrightarrow \gamma$ and $\eta \leftrightarrow \chi$ have not been explicitly given. When this interchange is carried out, the sign of the expression may or may not change, depending on whether the equation being considered is obtained within the symmetric or antisymmetric particle-hole subspace.

Simple and Extended Electron Affinity and Ionization Potential Equations

Simple electron affinity and ionization potential equations

We report in Table 1 a set of calculations on Be, B, C^+, and N^{2+}, carried out with the simple operators $\widehat{S}$ proposed by Simons and Smith.[38,47] The simplest ionization operator is:

$$\widehat{S} = \sum_t c_t\, t \qquad (31)$$

Table 1. Calculated ionization potentials and electron affinities (ΔE) in Hartrees.

	Transition	ΔE (Eq. (21))	ΔE (FCI)
B	$^2S \rightarrow \,^3S + e^-$	0.50925	0.50899
	$^2S + e^- \rightarrow \,^1S$	0.44508	0.44526
C^+	$^2S \rightarrow \,^3S + e^-$	1.25260	1.25224
	$^2S + e^- \rightarrow \,^1S$	0.22102	0.22117
N^{2+}	$^2S \rightarrow \,^3S + e^-$	2.25235	2.25193
	$^2S + e^- \rightarrow \,^1S$	0.11319	0.11307
Be	$^1S \rightarrow \,^2S + e^-$	0.21668	0.30447
	$^1S + e^- \rightarrow \,^2P$	0.21285	0.23757

which in general is a much too simple expression. This choice of excitation, together with Eqs. (19) and (20), generates the equations recently discussed in Ref. [67] within the framework of the extended Koopman's theorem. The procedure here described is a different alternative. The one-electron basis set for Be has been the standard STO-6G. For B, C, and N, double-ζ s-type Gaussian-type orbitals (GTOs) by Huzinaga[68] and Dunning[69] were used. The 1-body matrices corresponding to the correlated state undergoing the ionization, entering as input data into these calculations, have been obtained by solving the GHV equation. In addition, and to assess the accuracy of the method, a set of Full Configuration-Interaction (FCI) calculations for the ionization potential and electron affinity have been carried out. These reference values are reported in the last column of Table 1. As can be seen, while the accuracy of the results is satisfactory for B, C^+, and N^{2+}, the errors in the electron affinity and in the ionization potential of the Beryllium atom are much too large. These results clearly indicate that the ionization operator $\widehat{S}$ must have an extended form. This is why it was decided to obtain the explicit form of these extended equations, to be able to compute with sufficient accuracy these important quantities.

Extended electron affinity and ionization potential equations

The electron affinity and ionization extended operators take the form:

$$\widehat{S} = \sum_{\gamma, p} c_{\gamma;p} \, p^\dagger \, \gamma. \tag{32}$$

The form of the Hamiltonian is:

$$\hat{H} = \sum_{r,s} {}^0 h_{r;s} \, r^\dagger \, s + \sum_{\tau, \mu} {}^0 H_{\tau;\mu} \, \tau^\dagger \, \mu, \tag{33}$$

where the 1-body integrals ^0h are not included in the 2-body matrix ^0H, as in the double excitation case.

The equation that has to be explicitly evaluated and solved is, therefore,

$$\sum_{\gamma, p} \langle \Phi \mid [\, p^\dagger \, \gamma, \, [\hat{H}, \, \lambda^\dagger \, i \,]]_+ \mid \Phi \rangle \, c_{\gamma;p}$$
$$= \Delta E \sum_{\gamma, p} \langle \Phi \mid (\, p^\dagger \, \gamma \, \lambda^\dagger \, i \, + \, \lambda^\dagger \, i \, p^\dagger \, \gamma \,) \mid \Phi \rangle \, c_{\gamma;p} \tag{34}$$

In what follows, and for the sake of clarity, we present separately the one-, two- and three-electron terms arising from the development of

$$\langle \Phi \mid [\, p^\dagger \, \gamma, \, [\hat{H}, \, \lambda^\dagger \, i \,]]_+ \mid \Phi \rangle, \tag{35}$$

which contributes to the LHS of Eq. (34).

One-electron terms

$$- \, {}^0 h_{i;s} \, \delta_{\lambda, \gamma} \, \langle \Phi \mid p^\dagger \, s \mid \Phi \rangle \, - \, {}^0 h_{r;s} \, {}^1 D_{s;r}^{\lambda \gamma} \, \langle \Phi \mid p^\dagger \, i \mid \Phi \rangle$$
$$+ \, {}^0 H_{\gamma;\lambda} \, \langle \Phi \mid p^\dagger \, i \mid \Phi \rangle \tag{36}$$

Two-electron terms

$$- \, {}^0 h_{r;s} \, \langle \gamma \mid r \, t \rangle \, \langle x \, s \mid \lambda \rangle \, \langle \Phi \mid p^\dagger \, x^\dagger \, t \, i \mid \Phi \rangle$$
$$- \, {}^0 h_{i;p} \, \langle \Phi \mid \lambda^\dagger \, \gamma \mid \Phi \rangle \, + \, {}^0 h_{r;s} \, {}^1 D_{s;t}^{\lambda \gamma} \, \langle \Phi \mid r^\dagger \, p^\dagger \, t \, i \mid \Phi \rangle$$
$$+ \, {}^0 h_{r;s} \, \langle x \, s \mid \lambda \rangle \, \delta_{i,p} \, \langle \Phi \mid r^\dagger \, x^\dagger \, \gamma \mid \Phi \rangle \, + \, {}^0 h_{i;s} \, {}^1 D_{t;v}^{\lambda \gamma} \, \langle \Phi \mid p^\dagger \, t^\dagger \, v \, s \mid \Phi \rangle$$
$$+ \, \delta_{i,p} \, {}^0 H_{\tau;\lambda} \, \langle \Phi \mid \tau^\dagger \, \gamma \mid \Phi \rangle \, - \, {}^0 H_{\tau;\lambda} \, {}^1 D_{t;v}^{\tau \gamma} \, \langle \Phi \mid p^\dagger \, t^\dagger \, v \, i \mid \Phi \rangle$$
$$- \, {}^0 H_{\gamma;\mu} \, {}^1 D_{t;v}^{\lambda \mu} \, \langle \Phi \mid p^\dagger \, t^\dagger \, v \, i \mid \Phi \rangle \, - \, {}^0 H_{\tau;\mu} \, \delta_{\lambda,\gamma} \, \langle t \, i \mid \tau \rangle \, \langle \Phi \mid p^\dagger \, t^\dagger \, \mu \mid \Phi \rangle$$
$$+ \, {}^0 H_{\tau;\mu} \, {}^1 D_{t;x}^{\lambda \gamma} \, \langle x \, i \mid \tau \rangle \, \langle \Phi \mid p^\dagger \, t^\dagger \, \mu \mid \Phi \rangle$$
$$+ \, {}^0 H_{\tau;\mu} \, {}^1 D_{x;t}^{\tau \gamma} \, {}^1 D_{t;v}^{\lambda \mu} \, \langle \Phi \mid p^\dagger \, x^\dagger \, v \, i \mid \Phi \rangle \tag{37}$$

Three-electron terms

$$- \, {}^0 H_{\tau;\mu} \, {}^1 D_{t;v}^{\lambda \mu} \, \langle \gamma \mid t \, x \rangle \, \langle \Phi \mid p^\dagger \, \tau^\dagger \, x \, v \, i \mid \Phi \rangle$$
$$+ \, {}^0 H_{\tau;\mu} \, {}^1 D_{i;t}^{\tau \gamma} \, \langle \Phi \mid p^\dagger \, \lambda^\dagger \, t \, \mu \mid \Phi \rangle$$
$$- \, {}^0 H_{\tau;\mu} \, {}^1 D_{t;v}^{\lambda \mu} \, {}^1 D_{x;s}^{\tau \gamma} \, \langle \Phi \mid p^\dagger \, x^\dagger \, t^\dagger \, s \, v \, i \mid \Phi \rangle$$
$$- \, {}^0 H_{\tau;\mu} \, \delta_{i,p} \, {}^1 D_{t;v}^{\lambda \mu} \, \langle \tau^\dagger \, t^\dagger \, v \, \gamma \mid \Phi \rangle$$
$$+ \, {}^0 H_{\tau;\mu} \, {}^1 D_{t;p}^{\lambda \mu} \, \langle \Phi \mid \tau^\dagger \, t^\dagger \, i \, \gamma \mid \Phi \rangle$$
$$- \, {}^0 H_{\tau;\mu} \, \langle x \, i \mid \tau \rangle \, \langle s \, p \mid \mu \rangle \, \langle \Phi \mid \lambda^\dagger \, x^\dagger \, s \, \gamma \mid \Phi \rangle$$
$$- \, {}^0 H_{\tau;\mu} \, {}^1 D_{t;v}^{\lambda \gamma} \, \langle x \, i \mid \tau \rangle \, \langle \Phi \mid p^\dagger \, t^\dagger \, x^\dagger \, v \, \mu \mid \Phi \rangle \tag{38}$$

Concluding Comments

The set of relations given above constitute a complete set of algorithms that permit to have access to all the relevant ions and spectrum states of a system, provided that one knows the 3- or 4-body G-particle-hole matrices of one of the states of this system for Eqs. (36)–(38) and (28)–(30), respectively. Various methods have been in the past used to estimate 3- and 4-body matrices from lower-order ones.[21,23,26,31,50,51,55,56,70,71] Thus, the information provided by the HO method for single excitations has now been extended, and double excitations from a given reference state are now possible. Similarly, the algorithms that we report here allow us to obtain the ionization potential and electron affinities of a system far more accurately than if the excitation operator is formed by just a one-electron operator, as is the case in the calculations shown in Table 1.

Although coding the theoretical expressions given above is not a trivial matter, we expect to soon have the codes, particularly those needed for calculating the electron affinity and the ionization potential. There are several subtle matters, partly due to the large number of formulae, which implies a great debugging effort; and partly due to the need to handle simultaneously geminal and single fermion labels, while optimizing

the number of operations using fast summation and matrix–matrix multiplication.

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