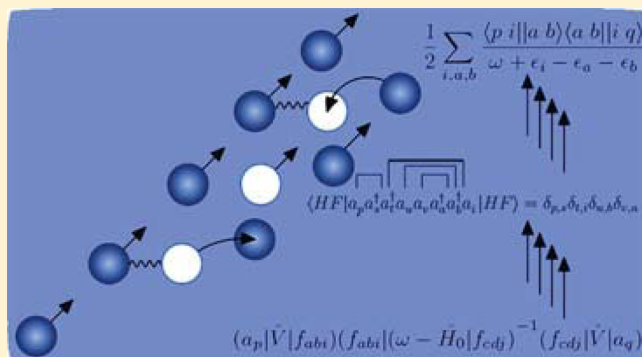


Symbolic Algebra Development for Higher-Order Electron Propagator Formulation and Implementation

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ABSTRACT: Through the use of symbolic algebra, implemented in a program, the algebraic expression of the elements of the self-energy matrix for the electron propagator to different orders were obtained. In addition, a module for the software package Lowdin was automatically generated. Second- and third-order electron propagator results have been calculated to test the correct operation of the program. It was found that the Fortran 90 modules obtained automatically with our algorithm succeeded in calculating ionization energies with the second- and third-order electron propagator in the diagonal approximation. The strategy for the development of this symbolic algebra program is described in detail. This represents a solid starting point for the automatic derivation and implementation of higher-order electron propagator methods.



1. INTRODUCTION

Methods based on electron propagator theory (EPT)^{1–8} have been shown to be among the best choices for the study of molecular ionization, because they give access to detailed information about processes associated with electron addition or removal.^{9,10} These methods are based on an alternative solution of Schrödinger's equation, namely, the use of Green function methodologies from many-body physics.¹ For derivation of the electron propagator formulation, a perturbative approach is used in order to achieve practical computer implementations with different degrees of approximation.² Several methods of EPT are now well-established techniques^{5–7,11–21} for the theoretical description of ionization spectra. The second- and third-order propagators (EP2 and EP3) have been implemented in some software packages (e.g., deMon2k,²² Gaussian²³), and the mathematical expressions have already been reported.¹

Schirmer et al. presented fourth-order formulas on the framework of the algebraic diagrammatic approximation²⁴ (ADC(4)), and several implementations of it have been reported with different approaches,^{25–28} some of which are interfaced to the software packages GAMESS²⁹ and MOL-CAS.³⁰ Despite the importance of EPT, complete fourth-order and higher methods with a superoperator approach³¹ (EP4) have not been implemented, as far as we know. The only implementation beyond third order, that we are aware of, is the partial fourth order presented by Ortiz.³² We are convinced that the implementation of methods with this approach beyond the third order could permit a better understanding of the convergence of the perturbative series for the different cases of ionization phenomena like valence and core electron ionization, proton ionization, etc.

Regarding the formulation of electron propagator, the higher is the order, the more complex the final expression and the process to determine it, because the number of algebraic manipulations increases exponentially with the order. This could be the main reason for the lack of software implementations for the fourth and higher orders.

Some other *ab initio* methods for solving Schrödinger's equation face a similar challenge; their development involves derivation, transformation, and implementation, all of which are daunting tasks of symbolic manipulations. This problem has been solved in some of those methodologies by the development of software packages that make automatic derivation and code implementation into computational quantum chemistry software packages through symbolic algebra methods.^{33,34} The mathematical operations needed in the derivations are performed by computerized systems that can handle higher mathematical constructs. It makes the development of an entire novel class of many-body correlated methods with high complexity and accuracy feasible. These procedures are so intricate that they cannot be handled manually.^{33,35–37} Nowadays, there are software packages that, in addition to the automation of the derivation, also computer-synthesize the electronic structure software codes.^{38–42} However, an approach of the same nature has not been developed for EPT.

In the present manuscript, an algorithm to obtain and handle the high-order electron propagator is described in order to get a module for the computational software package, LOWDIN.⁴³ The algorithm is based in the treatment of propagator formulation by the use of symbolic algebra to get the self-energy matrix in terms of antisymmetrized electron repulsion integrals, for a

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posterior automatic implementation in a module compatible with the LOWDIN software. It is based on the formulation found in the book of Linderberg and Öhrn¹ and on the superoperator approach.³¹ The strategy for the automation is described in detail here. In addition, results of the automatic implementation for EP2 and EP3 are presented and contrasted to the previously reported values.⁴⁴ This development offers a starting point for the automation of the higher orders.

The presentation is organized as follows: In section 2, EPT is summarized, following the superoperator formulation. In section 3, a general strategy to obtain the self-energy explicit formulation for any order is presented. In section 4, details of the implementation in the developed software are provided. In section 5, results of the simplified formulas of EP2 and EP3 are reported. In section 6, results from calculations of ionization potentials of some molecules are shown and compared with previously reported. Finally, in section 7, concluding remarks are given.

2. THEORY

Electron Propagator. The propagator of a particle is a Green function associated with the differential operator of the time-dependent Schrödinger's equation, $G_{pq}(t, t')$. After a Fourier transformation, the time-dependent Green's function is changed to the frequency domain to obtain the so-called "spectral" (or Lehmann) representation of the propagator,^{1,45,46}

$$G_{pq}(\omega) = \sum_n \frac{\langle N|a_p|N+1, n\rangle\langle N+1, n|a_q^\dagger|N\rangle}{\omega + E_n(N-1) - E_0(N)} + \sum_n \frac{\langle N|a_q^\dagger|N-1, n\rangle\langle N-1, n|a_p|N\rangle}{\omega - E_n(N+1) + E_0(N)} \quad (1)$$

where $E_0(N)$ is the energy of the reference state, $|N\rangle$, with N electrons. $E_n(N \pm 1)$ is the energy of the n th state, $|N \pm 1, n\rangle$ of the system with $N \pm 1$ electrons (with external potential unchanged). a_p and a_q^\dagger are the standard annihilation and creation operators of second quantization.⁴⁷ Since we are using atomic units, the numerical value of ω corresponds not only to a frequency but also to a meaningful energy. The poles of the right-hand side of eq 1 will correspond exactly to electron binding energies: electron affinities (EAs) and ionization potentials (IPs).

Superoperators. The superoperator approach allows us to handle approximations of eq 1, the formalism discussed here has been presented in several previous publications.^{1,3,15,21}

First, eq 1 is multiplied by ω and invoking the identity $\omega(\omega + a)^{-1} = 1 - a(\omega + a)^{-1}$, we obtain

$$\omega G_{pq}(\omega) = \sum_n \langle N|a_p|N+1, n\rangle\langle N+1, n|a_q^\dagger|N\rangle \times \left(1 - \frac{-E_n(N+1) + E_0(N)}{\omega - E_n(N+1) + E_0(N)}\right) + \sum_n \langle N|a_q^\dagger|N-1, n\rangle\langle N-1, n|a_p|N\rangle \times \left(1 - \frac{E_n(N-1) - E_0(N)}{\omega + E_n(N-1) - E_0(N)}\right) \quad (2)$$

If we take into account that the bracketed terms are eigenstates of the Hamiltonian, the following relations are obtained:

$$\langle N|a_p|N+1, n\rangle[E_n(N+1) - E_0(N)] = \langle N|[a_p, H]_-|N+1, n\rangle \quad (3)$$

$$\langle N-1, n|a_p|N\rangle[E_0(N) - E_n(N-1)] = \langle N-1, n|[a_p, H]_-|N\rangle \quad (4)$$

Hence, eq 2 could be rewritten in terms of commutators,

$$\omega G_{pq}(\omega) = \langle N|[a_p, a_q^\dagger]_+|N\rangle + \sum_n \frac{\langle N|[a_p, H]_-|N+1, n\rangle\langle N+1, n|a_q^\dagger|N\rangle}{\omega - E_n(N+1) + E_0(N)} + \sum_n \frac{\langle N|a_q^\dagger|N-1, n\rangle\langle N-1, n|[a_p, H]_-|N\rangle}{\omega + E_n(N-1) - E_0(N)} \quad (5)$$

or in the Zubarev notation:¹

$$\omega\langle\langle a_p; a_q^\dagger \rangle\rangle = \langle[a_p, a_q^\dagger]_+\rangle + \langle\langle[a_p, H]_-; a_q^\dagger\rangle\rangle_E \quad (6)$$

Later, this procedure is employed iteratively over the last term of eq 6:

$$\langle\langle a_p; a_q^\dagger \rangle\rangle = \omega^{-1}\langle[a_p, a_q^\dagger]_+\rangle + \omega^{-2}\langle\langle[a_p, H]_-; a_q^\dagger\rangle\rangle + \omega^{-3}\langle\langle[[a_p, H]_-, H]_-; a_q^\dagger\rangle\rangle + \dots \quad (7)$$

$$= \omega^{-1}\langle[a_p, a_q^\dagger]_+\rangle + \omega^{-2}\langle[a_p, [H, a_q^\dagger]_-]_+\rangle + \omega^{-3}\langle[a_p, [H, [H, a_q^\dagger]_-]_+]\rangle + \dots \quad (8)$$

In this point, it is convenient to introduce a more compact notation for the treatment of the second quantization operators. A linear vectorial space of field operators (linear combinations of products of elementary second quantization operators), $\{X\}$, is proposed with the consequent definition of the corresponding superoperators acting on this space.¹ For a given operator O , a superoperator \hat{O} is defined that can act on any field operator, X , as follows:³

$$\hat{O}X = [O, X]_- = OX - XO \quad (9)$$

For completeness, an identity superoperator (\hat{I}) is defined by

$$\hat{I}X = X \quad (10)$$

Except for the identity, the definition of any superoperator \hat{O} requires the existence of the corresponding second quantization operator, O . The inner product of any two operators in this space is defined by the next equation:

$$(Y|Z) \equiv \langle N|[Y^\dagger, Z]_+|N\rangle = \langle N|Y^\dagger Z + ZY^\dagger|N\rangle \quad (11)$$

Note that this definition is made with respect to $|N\rangle$, the exact wave function for the reference state of the N -electron system. With this approach, eq 7 is reduced to

$$\langle\langle a_p; a_q^\dagger \rangle\rangle = \omega^{-1}(a_p^\dagger|a_q^\dagger) + \omega^{-2}(a_p^\dagger|\hat{H}|a_q^\dagger) + \omega^{-3}(a_p^\dagger|\hat{H}^2|a_q^\dagger) + \dots \quad (12)$$

If we utilize a geometric series, the electron propagator matrix (\mathbf{G}) is given by

$$\mathbf{G}(\omega) = (\mathbf{a}^\dagger(\omega\hat{I} - \hat{H})^{-1}|\tilde{\mathbf{a}}^\dagger) \quad (13)$$

where \mathbf{a}^\dagger is a column vector whose components are simple annihilation operators

$$\mathbf{a}^\dagger = \begin{bmatrix} a_1^\dagger \\ \vdots \\ a_n^\dagger \end{bmatrix} \quad (14)$$

and $\hat{\mathbf{a}}^\dagger$ is the transpose (row vector) of \mathbf{a}^\dagger . The superoperator $(\omega\hat{I} - \hat{H})^{-1}$ is known as the resolvent.¹

Using the internal projection technique introduced by Löwdin, direct treatment of the resolvent is avoided:⁴⁸

$$\mathbf{G}(\omega) = (\mathbf{a}^\dagger \hat{\mathbf{h}})(\mathbf{h} \omega \hat{I} - \hat{H} \hat{\mathbf{h}})^{-1}(\mathbf{h} \hat{\mathbf{a}}^\dagger) \quad (15)$$

where \mathbf{h} is a column vector that contains the complete set of field operators that modify the total number of electrons by one, $\{\hat{a}_p^\dagger\} \cup \{\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_x\} \cup \{\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_x \hat{a}_z\} \cup \dots$. All the elements of \mathbf{h} are required to be orthonormal. It is also convenient to decompose the projection space into a primary space contained on vector \mathbf{a}^\dagger and a complementary space, \mathbf{f} , for the rest of the elements. While \mathbf{a}^\dagger includes simple creation or annihilation operators, \mathbf{f} contains operators associated with ionizations coupled to single excitations, double excitations and so on. Hence, the propagator matrix can be rewritten as

$$\mathbf{G}(\omega) = \begin{bmatrix} \mathbf{1} & \mathbf{0} \end{bmatrix} \begin{bmatrix} (\mathbf{a}^\dagger \omega \hat{I} - \hat{H} \hat{\mathbf{a}}^\dagger) & -(\mathbf{a}^\dagger \hat{H} \hat{\mathbf{f}}) \\ -(\mathbf{f} \hat{H} \hat{\mathbf{a}}^\dagger) & (\mathbf{f} \omega \hat{I} - \hat{H} \hat{\mathbf{f}}) \end{bmatrix}^{-1} \begin{bmatrix} \mathbf{1} \\ \mathbf{0} \end{bmatrix} \quad (16)$$

The poles are at the values of ω that are equal to the eigenvalues of the super-Hamiltonian matrix.¹ Thus, we are faced with a regular eigenvalue problem:

$$\begin{bmatrix} (\mathbf{a}^\dagger \hat{H} \hat{\mathbf{a}}^\dagger) & (\mathbf{a}^\dagger \hat{H} \hat{\mathbf{f}}) \\ (\mathbf{f} \hat{H} \hat{\mathbf{a}}^\dagger) & (\mathbf{f} \hat{H} \hat{\mathbf{f}}) \end{bmatrix} \begin{bmatrix} \mathbf{C}_a \\ \mathbf{C}_f \end{bmatrix} = \omega \begin{bmatrix} \mathbf{C}_a \\ \mathbf{C}_f \end{bmatrix} \quad (17)$$

Self-Energy. For the calculation of \mathbf{C}_a only, a smaller eigenvalue problem can be formulated:⁴⁸

$$\{(\mathbf{a}^\dagger \hat{H} \hat{\mathbf{a}}^\dagger) + (\mathbf{a}^\dagger \hat{H} \hat{\mathbf{f}})(\mathbf{f} \omega \hat{I} - \hat{H} \hat{\mathbf{f}})^{-1}(\mathbf{f} \hat{H} \hat{\mathbf{a}}^\dagger)\} \mathbf{C}_a = \omega \mathbf{C}_a \quad (18)$$

where the matrix depends on its own eigenvalues, ω . The Möller–Plesset⁴⁹ partition is used for the Hamiltonian,

$$H = H^{(0)} + V \quad (19)$$

where $H^{(0)}$ is the Fock operator and V is the fluctuation potential. Equation 18 can be expressed in the following form:

$$[\boldsymbol{\varepsilon} + \boldsymbol{\Sigma}(\omega)] \mathbf{C}_a = \omega \mathbf{C}_a \quad (20)$$

where $\boldsymbol{\varepsilon}$ is a diagonal matrix that contains Hartree–Fock canonical orbital energies as its nonzero entries. The matrix, $\boldsymbol{\Sigma}(\omega)$, holds the dependency on the eigenvalues of the problem, ω , and is, therefore, known as the self-energy matrix:

$$\boldsymbol{\Sigma}(\omega) = (\mathbf{a}^\dagger \hat{V} \hat{\mathbf{a}}^\dagger) + (\mathbf{a}^\dagger \hat{V} \hat{\mathbf{f}})(\mathbf{f} \omega \hat{I} - \hat{H} \hat{\mathbf{f}})^{-1}(\mathbf{f} \hat{V} \hat{\mathbf{a}}^\dagger) \quad (21)$$

Since all the second quantization operators are eigenoperators of the Fock superoperator it is also true that $(\mathbf{a}^\dagger \hat{H}_0 \hat{\mathbf{f}}) = \mathbf{0}$. This has been used to simplify the formulations above.

3. ALGORITHM PROPOSED FOR AUTOMATION

Equation 20 shows that, if the expression of the self-energy matrix is obtained, the eigenvalues (ω) can be obtained by solving a eigenvalue problem and iterating until self-consistency. It is common practice to neglect the off-diagonal elements of the self-energy matrix in the calculation of electron binding energies for molecular systems.^{2,13} Even for the cases where eq 17 is solved directly, the super-Hamiltonian matrix has an approximate nature and the different approximation levels are defined by the accuracy of the corresponding self-energy matrix. Hence, the principal objective for the new symbolic

algebra package is to obtain the explicit formulation of the self-energy matrix elements. Below, we will follow a top-down description of our strategy.

Building the Self-Energy Matrix. After eq 21, it follows that self-energy matrix for a given order n (this is the only input that must be provided by the user to the new symbolic algebra package) is given by

$$\begin{aligned} \Sigma^{[n]}(\omega) &= (\mathbf{a}^\dagger \hat{V} \hat{\mathbf{a}}^\dagger)^{[n]} \\ &+ \sum_{m=0}^{m=n} \sum_{l=0}^{l=n-m} (\mathbf{a}^\dagger \hat{V} \hat{\mathbf{f}})^{[m]} ((\mathbf{f} \omega \hat{I} - \hat{H} \hat{\mathbf{f}})^{-1})^{[l]} (\mathbf{f} \hat{V} \hat{\mathbf{a}}^\dagger)^{[n-m-l]} \end{aligned} \quad (22)$$

The order of the self-energy, which is by definition the order of the propagator approximation that is in use, can be determined if we manage to deal with the reciprocal included in eq 22. For that purpose, the following expansion is employed by Linderberg and Öhrn:¹

$$\begin{aligned} ((\mathbf{f} \omega \hat{I} - \hat{H} \hat{\mathbf{f}})^{-1}) &= ((\mathbf{f} \omega \hat{I} - \hat{H} \hat{\mathbf{f}})^{[0]} + \sum_{j=1}^{\infty} (\mathbf{f} \omega \hat{I} - \hat{H} \hat{\mathbf{f}})^{[j]})^{-1} \\ &= ((\mathbf{f} \omega \hat{I} - \hat{H} \hat{\mathbf{f}})^{[0]})^{-1} \\ &- ((\mathbf{f} \omega \hat{I} - \hat{H} \hat{\mathbf{f}})^{[0]})^{-1} \\ &\times \sum_{j=1}^{\infty} (\mathbf{f} \omega \hat{I} - \hat{H} \hat{\mathbf{f}})^{[j]} ((\mathbf{f} \omega \hat{I} - \hat{H} \hat{\mathbf{f}})^{-1}) \\ &= ((\mathbf{f} \omega \hat{I} - \hat{H} \hat{\mathbf{f}})^{[0]})^{-1} \\ &- ((\mathbf{f} \omega \hat{I} - \hat{H} \hat{\mathbf{f}})^{[0]})^{-1} \\ &\times \sum_{j=1}^{\infty} (\mathbf{f} \omega \hat{I} - \hat{H} \hat{\mathbf{f}})^{[j]} ((\mathbf{f} \omega \hat{I} - \hat{H} \hat{\mathbf{f}})^{[0]})^{-1} \\ &+ ((\mathbf{f} \omega \hat{I} - \hat{H} \hat{\mathbf{f}})^{[0]})^{-1} \\ &\times \sum_{j=1}^{\infty} (\mathbf{f} \omega \hat{I} - \hat{H} \hat{\mathbf{f}})^{[j]} ((\mathbf{f} \omega \hat{I} - \hat{H} \hat{\mathbf{f}})^{[0]})^{-1} \\ &\times ((\mathbf{f} \omega \hat{I} - \hat{H} \hat{\mathbf{f}})^{-1}) \end{aligned} \quad (23)$$

In eq 22, the maximum order of l is the propagator order minus 2. For example, in the treatment of second and third order, only the first two terms of the expansion in eq 23 are needed.

Evaluation of Inner Products to Different Orders. Equation 22 is our recipe to produce self-energy matrices of different orders; it provides inner products in the superoperator space. After identifying the action of a couple of superoperators (namely, \hat{V} and $\hat{H}^{(0)}$), the task reduces to the evaluation of inner products.

Inner products were defined with respect to the exact wave function, according to eq 11. Rayleigh–Schrödinger perturbation theory⁵⁰ will produce different orders of approximation for the wave function and, therefore, for the inner products,

$$(Y|Z) = (Y|Z)^{[0]} + (Y|Z)^{[1]} + (Y|Z)^{[2]} + \dots \quad (24)$$

where $[n]$ is the perturbation order. The sum of the different orders of perturbation of the wave function on both sides of the bracket defines the order of the inner product,

$$(X|Y)^{[n]} = \sum_{m=0}^n (X|Y)^{(m,n-m)} = \sum_{m=0}^n \langle m|[X^\dagger, Y]_+|n-m \rangle \quad (25)$$

where the superscripts (m,l) denote the perturbational orders of the left-side and right-side wave functions in the inner

product. Note that a given order of a inner product might involve many of these types of expectation values.

For the evaluation of eq 22 to different orders, it should be considered that the operator of the fluctuation potential, V , increases the order of the bracketed term by one:

$$(\mathbf{a}^\dagger|\hat{V}|\mathbf{f})^{[n]} = \sum_{m=0}^{n-1} (\mathbf{a}^\dagger|\hat{V}|\mathbf{f})^{(m,n-1-m)} \quad (26)$$

The handling of some inner products requires one to include an adequate \mathbf{f} term. For second- and third-order propagators, the products of two annihilators and one creator (triple products, $f_{v,w,x}$) are enough. For higher orders of the self-energy matrix, quintuple products are required. The triple products $f_{v,w,x}$ satisfy the following requirements: $(f_{v,w,x}|f_{v,w,x}) = 1$ and $(a_p^\dagger|f_{v,w,x}) = 0$. Both inner products must be expanded into a perturbational series. For the first one, this leads one to address two types of $f_{v,w,x}$ in the case of integer occupation numbers: the two-particle-one-hole (2ph) and the two-hole-one-particle (2hp) operators. For the second one, it is needed to deal with some terms of the perturbational series: $(a_p^\dagger|f_{v,w,x})^{[0]}$, which is already zero, and $(a_p^\dagger|f_{v,w,x})^{[1]}$, which needs the restrictions of $\delta_{p,v} = 0$ and $\delta_{p,w} = 0$. Analogous restrictions should be enforced in higher orders.

Evaluation of Wave Function to Different Orders. The Hartree–Fock state, $|\text{HF}\rangle$, is used as a reference state on which second quantization operators act to produce the different contributions to the perturbation expansion. Single and multiple excitations of all orders are considered:

$$|N\rangle = (1 + \sum_{i,a} \tau_i^a a_a^\dagger a_i + \sum_{a>b} \sum_{i>j} \tau_{ij}^{ab} a_a^\dagger a_i a_b^\dagger a_j + \dots)|\text{HF}\rangle \quad (27)$$

where the expansion coefficients (τ) are excitation amplitudes and they will have contributions from the different perturbational orders, l . The indices i and j refer to occupied spin orbitals, while a and b are used to label virtual spin orbitals. Third order requires complete double excitations,

$$|1\rangle = \sum_{a>b} \sum_{i>j} \tau_{ij}^{ab} a_a^\dagger a_i a_b^\dagger a_j |\text{HF}\rangle \quad (28)$$

with an amplitude τ_{ij}^{ab} given by

$$\tau_{ij}^{ab} = \frac{\langle ab||ij\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} \quad (29)$$

and partial single excitation term of second-order perturbation, $|2'\rangle$, that can be obtained from the first-order double excitation amplitudes,

$$|2'\rangle = \frac{1}{2} \sum_{a,i} \left[\sum_{b,c,j} \frac{\langle aj||bc\rangle}{\varepsilon_a - \varepsilon_i} \tau_{ij}^{bc} - \sum_{b,j,k} \frac{\langle jk||ib\rangle}{\varepsilon_a - \varepsilon_i} \tau_{jk}^{ab} \right] a_a^\dagger a_i |\text{HF}\rangle \quad (30)$$

Here, ε_i represents the i th Hartree–Fock spin-orbital energy and $\langle p\ q||s\ r\rangle$ is an antisymmetrized electron repulsion integral in Dirac notation.⁵¹

Mapping Superoperator Bracketed Terms to Hartree–Fock-Based Expectation Values. Besides the substitution of the different corrections to the wave function, the algorithm should also consider the substitution of the adequate expressions for the reference Hamiltonian (Fock operator),

$$H^{(0)} = \sum_p \varepsilon_p a_p^\dagger a_p \quad (31)$$

and the fluctuation operator,

$$V = \sum_{r,s,t,u} \langle r\ s||u\ t\rangle \left[\frac{1}{4} a_r^\dagger a_s^\dagger a_t a_u - \delta_{s,t} \langle n_s \rangle a_r^\dagger a_t \right] \quad (32)$$

where $\langle n_s \rangle$ is the occupation number of spin-orbital s .

These operators should then be taken into account for the evaluation of superoperator bracketed terms. Consider, for example, an element required for eq 26:

$$\begin{aligned} (a_p^\dagger|\hat{V}|f_{v,w,x})^{(0,1)} &= \frac{1}{16} \sum_{r,s} \sum_{t,u} \sum_{a,b} \sum_{i,j} \frac{\langle r\ s||u\ t\rangle \langle a\ b||i\ j\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} \\ &\times \langle \text{HF} | a_j^\dagger a_b a_i^\dagger a_a [a_p^\dagger a_s^\dagger a_t a_u, a_v^\dagger a_w^\dagger a_x]_- | \text{HF} \rangle \\ &- \frac{1}{4} \sum_{r,s} \sum_{t,u} \sum_{a,b} \sum_{i,j} \frac{\langle r\ s||u\ t\rangle \langle a\ b||i\ j\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} \\ &\times \langle \text{HF} | a_j^\dagger a_b a_i^\dagger a_a [a_p^\dagger a_s^\dagger a_t a_u, a_v^\dagger a_w^\dagger a_x]_- | \text{HF} \rangle \delta_{s,t} \langle n_q \rangle \\ &= \frac{1}{16} \sum_{r,s} \sum_{t,u} \sum_{a,b} \sum_{i,j} \frac{\langle r\ s||u\ t\rangle \langle a\ b||i\ j\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} \\ &\times \langle \text{HF} | a_j^\dagger a_b a_i^\dagger a_a a_p^\dagger a_s^\dagger a_t a_u a_v^\dagger a_w^\dagger a_x | \text{HF} \rangle + \dots \end{aligned} \quad (33)$$

Evaluation of Hartree–Fock-Based Expectation Values. Once the bracketed terms were defined with respect to $|\text{HF}\rangle$, they are simplified using the Fermi vacuum and Wick's theorem. Wick's theorem^{52,53} provides a recipe for generating normal ordered chains of particle operators or, in this case, quasi-particle operators, because it is used in the reference state $|\text{HF}\rangle$ (Fermi vacuum). A normal ordered product (enclosed by two colons) has all annihilation operators on the left and all creation operators on the right. Wick's theorem of a quasi-particle operator product $ABC\dots XYZ$, can be written in the following form:

$$ABC\dots XYZ = :ABC\dots XYZ: + \sum_{\text{singles}} \overbrace{:ABC\dots XYZ:} + \sum_{\text{doubles}} \overbrace{:ABC\dots XYZ:} + \dots \quad (34)$$

where the lines above the operators represent contractions, and the labels “singles” and “doubles” refer to the number of contractions performed in all possible ways. The contraction of two operators is defined as the difference between the operator product and the normal ordered chain; for this reason, the nonzero contractions and their results are $\overline{a_i^\dagger a_j} = \delta_{ij}$ and $\overline{a_a a_b^\dagger} = \delta_{ab}$. We use this method because the non-fully contracted normal products vanish, leaving a sum over all possible full contracted products. In addition, a sign for each term must be included in order to adjust the number of commutations that must be performed to get the term, $(-1)^p$, where p is the number of interchanges needed to perform each contraction between two contiguous operators. The term p can be obtained graphically using the number of times that the contraction lines cross. As an illustration, it is presented in the following example:

$$\begin{aligned} \langle \text{HF} | a_i^\dagger a_a a_j^\dagger a_k a_b^\dagger a_l | \text{HF} \rangle &= \langle \text{HF} | a_i^\dagger a_a a_j^\dagger a_k a_b^\dagger a_l | \text{HF} \rangle + \langle \text{HF} | a_i^\dagger a_a a_j^\dagger a_k a_b^\dagger a_l | \text{HF} \rangle \\ &= -\delta_{i,k} \delta_{j,l} \delta_{a,b} + \delta_{i,l} \delta_{j,k} \delta_{a,b} \end{aligned} \quad (35)$$

In summary, the bracketed terms can be simplified by using Wick's theorem in a series of Kronecker deltas. Back

substitution and further manipulations, taking advantage of permutation symmetry in integrals for simplifying the final expressions, are then performed in order to arrive at the self-energy formulations for each order.

4. SYMBOLIC ALGEBRA ALGORITHM: IMPLEMENTATION

The program begins by choosing the propagator order to be computed. Then, eq 22 is used to identify the necessary sets of inner products for the arrays \mathbf{a}^\dagger and \mathbf{f} . The required matrices of inner products are obtained by appropriate inner products for representative individual elements,

$$(a_{u1}^\dagger | \hat{V} | a_{p25} a_{h26}^\dagger a_{h27}^\dagger)^{(0,1)} (a_{p25} a_{h26}^\dagger a_{h27}^\dagger | \hat{L} \omega - \hat{H}_0 | a_{p29} a_{h30}^\dagger a_{h31}^\dagger)^{-1} (a_{p29} a_{h30}^\dagger a_{h31}^\dagger | \hat{V} | a_{u2}^\dagger)^{(0,0)} + \dots \quad (36)$$

Spin-orbitals are labeled, depending on their origin, with a subindex composed of a letter and a number. Letters “h”, “p”, and “u” indicate that the operator corresponds to an occupied orbital, an unoccupied orbital, and a general spin orbital, respectively. Those coming from the primary space will be identified with numbers 1 and 2 added as subindices. Next bigger numbers are used for the fluctuation operator, excitations of the wave function corrections, and the secondary space spin-orbital labels, in that order. The starting points for each of them are chosen accordingly to the perturbation corrections of each term, in order to avoid the overlapping of indices between inner products. The next step is to reduce inner products to expectation values by means of eq 25. For example,

$$(a_{u1}^\dagger | \hat{V} | a_{p25} a_{h26}^\dagger a_{h27}^\dagger)^{(0,1)} = \langle \text{HF} | [a_{u1} [V, a_{p25} a_{h26}^\dagger a_{h27}^\dagger]_-]_+ | 1 \rangle \quad (37)$$

In this case, the numerical index for operators coming from complementary space starts at 25. In this point, the wave function perturbation ($|1\rangle$) and the superoperator (\hat{V}) are inserted to get

$$\begin{aligned} & \frac{1}{16} \sum_{\substack{18,20 \\ 17,19 \\ 3,4,5,6}} \frac{\langle 3 \ 4 | 5 \ 6 \rangle \langle 17 \ 19 | 18 \ 20 \rangle}{(-\epsilon_{17} + \epsilon_{18} - \epsilon_{19} + \epsilon_{20})} \\ & \times \langle 0 | [a_{u1} [a_{u3}^\dagger a_{u4}^\dagger a_{u5}^\dagger, a_{p25} a_{h26}^\dagger a_{h27}^\dagger]_-]_+ a_{p17}^\dagger a_{h18}^\dagger a_{p19}^\dagger a_{h20}^\dagger | 0 \rangle \\ & - \frac{1}{4} \sum_{\substack{18,20 \\ 17,19 \\ 3,4,5,6}} \frac{\langle 34 | 56 \rangle \langle 1719 | 1820 \rangle}{(-\epsilon_{17} + \epsilon_{18} - \epsilon_{19} + \epsilon_{20})} \\ & \times \langle 0 | [a_{u1} [a_{u3}^\dagger a_{u5}^\dagger, a_{p25} a_{h26}^\dagger a_{h27}^\dagger]_-]_+ a_{p17}^\dagger a_{h18}^\dagger a_{p19}^\dagger a_{h20}^\dagger | 0 \rangle \delta_{h4,6} \quad (38) \end{aligned}$$

Note that numerical labels for the fluctuation operator start at 3, while those for the excitation operator begin at 17. This labeling policy proved to be very useful for identifying the origin of errors that appeared during the development of the symbolic algebra code. Note also that summation index is only the numerical part of the operator labels. Character labels are only used for simplification of expressions based on Kronecker deltas. For example, $\delta_{h4,6}$ will be nonzero only for a single case when 6 corresponds to a given occupied spin-orbital. In printed formulas, the summation indexes are organized in the following form: the first level (top) for occupied orbitals, the second one for unoccupied orbitals, and the last one to both spin-orbital cases.

After commutation and anticommutation are performed, expectation values will be computed using Wick's theorem. For each bracketed term, it is carried out a full contraction. This process is made by getting all possible combinations of pairs of operators, while they are constructed all the zero contractions are discarded and many Kronecker deltas are nullified because of the orthonormality of the primary and complementary spaces. Expressions like the following are obtained at this point of the symbolic algebra processing:

$$\begin{aligned} & -\frac{1}{16} \sum_{\substack{18,20 \\ 17,19 \\ 3,4,5,6}} \frac{\langle 3 \ 4 | 5 \ 6 \rangle \langle 17 \ 19 | 18 \ 20 \rangle}{(-\epsilon_{17} + \epsilon_{18} - \epsilon_{19} + \epsilon_{20})} \\ & \times (-\delta_{p25,3} \delta_{h26,6} \delta_{h27,18} \delta_{h20,4} \delta_{p17,5} \delta_{p19,1} + \dots) + \dots \quad (39) \end{aligned}$$

Later, Kronecker deltas will cancel many of the summations,

$$-\frac{1}{16} \sum_{\substack{20,26,27 \\ 25,17}} \frac{\langle 20 \ 25 | 17 \ 26 \rangle \langle 1 \ 17 | 20 \ 27 \rangle}{(-\epsilon_{17} + \epsilon_{27} - \epsilon_1 + \epsilon_{20})} (1 - \langle n_1 \rangle) + \dots \quad (40)$$

At this point, the permutational symmetry properties of the antisymmetrized integrals are used to achieve further simplification. Since, so far, the computation time has not been an issue for us, the space and spin symmetry are not considered, in order to obtain simple final expression. In addition, it is made via reduction, by joining terms that are almost identical but have different occupation nature requirements of 1 or 2. The reduced inner products are multiplied if the starting term has such form. Finally, label permutations are performed to find equivalent terms in order to decrease the number of them.

The program writes the output in LaTeX;⁵⁴ one has the reduced formulation of the self-energy matrix, and the rest of them have intermediate steps of the process.

5. RESULTS FOR FORMULATION: EP2 AND EP3

For the second-order electron propagator (EP2), the following formulation was obtained:

$$\Sigma_{i,j}^{[2]} = \frac{1}{2} \sum_{\substack{a, \\ p,q}} \frac{\langle i \ a | p \ q \rangle \langle p \ q | j \ a \rangle}{(\omega + \epsilon_a - \epsilon_p - \epsilon_q)} + \frac{1}{2} \sum_{\substack{a,b, \\ p}} \frac{\langle i | p | a \rangle \langle a | b | j \rangle}{(\omega + \epsilon_p - \epsilon_a - \epsilon_b)} \quad (41)$$

Note that, for the sake of comparison with the formulation found in the work of Linderberg and Öhrn,¹ here, i and j are used to label general spin-orbitals and a and b are used to label occupied spin-orbitals. For the third-order electron propagator (EP3), $\Sigma_{ij}^{[3]}$, the following contributions were produced by the symbolic algebra code:

$$\begin{aligned}
& -\frac{1}{2} \sum_{a,b,c,p,q} \frac{\langle i \text{ allj } p \rangle \langle q \text{ pllbc } \rangle \langle b \text{ clq } a \rangle}{(-\varepsilon_q + \varepsilon_b - \varepsilon_p + \varepsilon_c)(-\varepsilon_p + \varepsilon_a)} \\
& + \frac{1}{2} \sum_{a,b,p,q,r} \frac{\langle i \text{ allj } p \rangle \langle q \text{ rllb } a \rangle \langle b \text{ pllq } r \rangle}{(-\varepsilon_q + \varepsilon_b - \varepsilon_r + \varepsilon_a)(-\varepsilon_p + \varepsilon_a)} \\
& + \frac{1}{2} \sum_{a,b,c,p,q} \frac{\langle i \text{ allj } b \rangle \langle p \text{ qllb } c \rangle \langle p \text{ qlc } a \rangle}{(-\varepsilon_q + \varepsilon_c - \varepsilon_p + \varepsilon_b)(-\varepsilon_p + \varepsilon_c - \varepsilon_q + \varepsilon_a)} \\
& - \frac{1}{2} \sum_{a,b,p,q,r} \frac{\langle i \text{ pllq } q \rangle \langle p \text{ rlla } b \rangle \langle r \text{ qla } b \rangle}{(-\varepsilon_r + \varepsilon_b - \varepsilon_p + \varepsilon_a)(-\varepsilon_r + \varepsilon_a - \varepsilon_q + \varepsilon_b)} \\
& - \frac{1}{2} \sum_{a,b,c,p,q} \frac{\langle i \text{ pllq } a \rangle \langle q \text{ pllbc } \rangle \langle b \text{ clq } a \rangle}{(-\varepsilon_q + \varepsilon_b - \varepsilon_p + \varepsilon_c)(-\varepsilon_p + \varepsilon_a)} \\
& + \frac{1}{2} \sum_{a,b,p,q,r} \frac{\langle i \text{ pllq } a \rangle \langle q \text{ rllb } a \rangle \langle b \text{ pllq } r \rangle}{(-\varepsilon_q + \varepsilon_b - \varepsilon_r + \varepsilon_a)(-\varepsilon_p + \varepsilon_a)} \\
& - \sum_{a,b,c,p,q,r} \frac{\langle i \text{ allp } q \rangle \langle b \text{ qlq } r \rangle \langle r \text{ pllq } a \rangle}{(\omega + \varepsilon_a - \varepsilon_p - \varepsilon_q)(-\varepsilon_p + \varepsilon_a - \varepsilon_r + \varepsilon_b)} \\
& + \frac{1}{4} \sum_{a,b,p,q} \frac{\langle i \text{ allp } q \rangle \langle b \text{ clq } a \rangle \langle p \text{ qlqb } c \rangle}{(\omega + \varepsilon_a - \varepsilon_p - \varepsilon_q)(-\varepsilon_q + \varepsilon_b - \varepsilon_p + \varepsilon_c)} \\
& - \sum_{a,b,c,p,q} \frac{\langle i \text{ plla } b \rangle \langle q \text{ allj } c \rangle \langle q \text{ pllc } b \rangle}{(\omega + \varepsilon_p - \varepsilon_a - \varepsilon_b)(-\varepsilon_p + \varepsilon_b - \varepsilon_q + \varepsilon_c)} \\
& + \frac{1}{4} \sum_{a,b,p,q,r} \frac{\langle i \text{ plla } b \rangle \langle q \text{ rllj } p \rangle \langle q \text{ rlla } b \rangle}{(\omega + \varepsilon_p - \varepsilon_a - \varepsilon_b)(-\varepsilon_q + \varepsilon_a - \varepsilon_r + \varepsilon_b)} \\
& + \frac{1}{4} \sum_{a,b,c,p,q,r} \frac{\langle i \text{ pllq } r \rangle \langle q \text{ rlla } b \rangle \langle a \text{ blq } p \rangle}{(-\varepsilon_q + \varepsilon_a - \varepsilon_r + \varepsilon_b)(\omega + \varepsilon_p - \varepsilon_a - \varepsilon_b)} \\
& - \sum_{a,b,p,q} \frac{\langle i \text{ allp } b \rangle \langle p \text{ qla } c \rangle \langle b \text{ clq } q \rangle}{(-\varepsilon_q + \varepsilon_c - \varepsilon_p + \varepsilon_a)(\omega + \varepsilon_q - \varepsilon_b - \varepsilon_c)} \\
& + \sum_{a,b,c,p,q,r} \frac{\langle i \text{ plla } q \rangle \langle p \text{ rlla } b \rangle \langle r \text{ qlq } b \rangle}{(-\varepsilon_r + \varepsilon_b - \varepsilon_p + \varepsilon_a)(\omega + \varepsilon_b - \varepsilon_r - \varepsilon_q)} \\
& + \frac{1}{4} \sum_{a,b,p,q} \frac{\langle i \text{ allb } c \rangle \langle p \text{ qlb } c \rangle \langle p \text{ qlq } a \rangle}{(-\varepsilon_q + \varepsilon_b - \varepsilon_p + \varepsilon_c)(\omega + \varepsilon_a - \varepsilon_p - \varepsilon_q)} \\
& + \frac{1}{4} \sum_{a,b,c,p,q,r,s} \frac{\langle i \text{ allp } q \rangle \langle p \text{ qlr } s \rangle \langle r \text{ slq } a \rangle}{(\omega + \varepsilon_a - \varepsilon_p - \varepsilon_q)(\omega + \varepsilon_a - \varepsilon_r - \varepsilon_s)} \\
& - \sum_{a,b,p,q,r} \frac{\langle i \text{ allp } q \rangle \langle p \text{ blla } r \rangle \langle q \text{ rllj } b \rangle}{(\omega + \varepsilon_a - \varepsilon_q - \varepsilon_p)(\omega + \varepsilon_b - \varepsilon_q - \varepsilon_r)} \\
& - \sum_{a,b,c,p,q} \frac{\langle i \text{ plla } b \rangle \langle a \text{ qlp } c \rangle \langle c \text{ blq } q \rangle}{(\omega + \varepsilon_p - \varepsilon_a - \varepsilon_b)(\omega + \varepsilon_q - \varepsilon_c - \varepsilon_b)} \\
& - \frac{1}{4} \sum_{a,b,c,p,d} \frac{\langle i \text{ plla } b \rangle \langle a \text{ blld } d \rangle \langle c \text{ dlq } p \rangle}{(\omega + \varepsilon_p - \varepsilon_a - \varepsilon_b)(\omega + \varepsilon_p - \varepsilon_c - \varepsilon_d)}
\end{aligned}
\tag{42}$$

which agrees with the formulation already reported.¹

6. RESULTS FOR CODE GENERATION: FORTRAN 90 IMPLEMENTATION FOR LOWDIN

The symbolic algebra code was extended to automatically construct a module in the LOWDIN quantum chemistry package

Table 1. Results Obtained with the New Module, Compared to Previously Reported Values

molecule	orbital	kT (eV)	EP2 ^a (eV)	EP2-auto (eV)	EP3 ^a (eV)	EP3-auto (eV)
B ₂ H ₆	1b _{3g}	12.851	12.21	12.209	12.305	12.30
CH ₄	1t ₂	14.804	14.07	14.061	14.372	14.37
C ₂ H ₄	1b _{3u}	10.244	10.33	10.329	10.517	10.52
	1b _{3g}	13.773	12.75	12.747	13.167	13.17
	3a _g	15.945	14.48	14.482	14.980	14.98
	1b _{2u}	17.479	15.89	15.882	16.407	16.41
	2b _{1u}	21.524	19.34	19.335	19.787	19.79
HCN	1π	13.487	13.68	13.677	13.586	13.58
HNC	1π	14.127	13.74	13.746	14.112	14.11
NH ₃	3a ₁	11.597	10.17	10.167	11.010	11.01
N ₂	1π _u	16.471	17.05	17.049	16.455	16.45
	3σ _g	17.166	15.02	15.022	15.918	15.92
	2σ _u	21.395	18.20	18.197	19.895	19.89
CO	5σ	15.092	14.06	14.056	13.977	13.98
	1π	17.282	16.37	16.371	17.359	17.36
H ₂ CO	2b ₂	11.992	9.94	9.940	11.532	11.53
H ₂ O	1b ₁	13.730	11.50	11.500	13.084	13.08
	1a ₁	15.760	13.86	13.862	15.336	15.34
	1b ₂	19.209	18.08	18.085	19.141	19.14
HF	1π	17.501	14.70	14.709	16.830	16.83
	3σ	20.682	18.94	18.945	20.478	20.48
F ₂	1π _g	18.053	14.20	14.205	16.519	16.52
	3σ _g	20.482	20.46	20.470	21.157	21.15
	1π _u	22.053	17.35	17.358	20.120	20.12

^aReference values taken from Flores-Moreno et al.⁴⁴

for evaluation of the self-energy matrix. The module uses the diagonal approximation,¹ which neglects the off-diagonal terms in the self-energy matrix; hence, the poles are obtained from

$$\omega_p = \varepsilon_p + \sum_{pp} (\omega_p) \tag{43}$$

where ω_p is an electron binding energy, which is obtained using the Newton–Raphson method.

The module uses a Hartree–Fock solution made by LOWDIN, then the spin–orbital molecular functions and their energies are obtained. Afterward, the module gets information about the repulsion integral by making a call to a module of LOWDIN; they then are saved, antisymmetrized, in a proper way. The next step is to perform each summation based on the Newton–Raphson algorithm, which uses Koopmans’ theorem⁵⁵ as a first guess of

ω . This algorithm is used as a first approach because it is the safest way to perform an implementation.

By using the second- and third-order electron propagator module in Fortran 90 included in LOWDIN, the results of the implementation made with the symbolic algebra software were tested with a set of molecules for which EP2 and EP3 results were previously reported.⁴⁴ Results of the new module are compared with those previously reported in Table 1, where we used the geometries from the work of Ortiz⁹ and cc-pVTZ basis set⁵⁶ as described in the work of Flores Moreno et al.⁴⁴ These results make us confident of our automatized approach. Further research for developing the formulation and coding for higher-order propagator methods is underway in our laboratory and will be reported in another paper.

7. CONCLUSIONS

So far, the use of computerized symbolic algebra in the treatment of the formulation for the EPT methods have been shown to be more efficient than the treatment by hand. It would have been a difficult and cumbersome task if it were performed by hand. Also, considering that the second- and third-order formulation and implementation were treated successfully, the automatic implementation of higher-order propagator theory seems feasible through the use of computerized symbolic algebra. In addition, the implementation in other software packages may be reached by an easy connection of the appropriate routines for access to Hartree–Fock energies and coefficients and electron repulsion integrals. However, further work in the automatic code generator is needed to reduce the use of computer resources. Great benefits are expected for the further development of electron and proton propagator methodologies.

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Notes

The authors declare no competing financial interest.

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