



# Electron propagator theory: an approach to prediction and interpretation in quantum chemistry

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Electron propagator theory provides a practical means of calculating electron binding energies, Dyson orbitals, and ground-state properties from first principles. This approach to *ab initio* electronic structure theory also facilitates the interpretation of its quantitative predictions in terms of concepts that closely resemble those of one-electron theories. An explanation of the physical meaning of the electron propagator's poles and residues is followed by a discussion of its couplings to more complicated propagators. These relationships are exploited in superoperator theory and lead to a compact form of the electron propagator that is derived by matrix partitioning. Expressions for reference-state properties, relationships to the extended Koopmans's theorem technique for evaluating electron binding energies, and connections between Dyson orbitals and transition probabilities follow from this discussion. The inverse form of the Dyson equation for the electron propagator leads to a strategy for obtaining electron binding energies and Dyson orbitals that generalizes the Hartree–Fock equations through the introduction of the self-energy operator. All relaxation and correlation effects reside in this operator, which has an energy-dependent, nonlocal form that is systematically improvable. Perturbative arguments produce several, convenient (e.g. partial third order, outer valence Green's function, and second-order, transition-operator) approximations for the evaluation of valence ionization energies, electron affinities, and core ionization energies. Renormalized approaches based on Hartree–Fock or approximate Brueckner orbitals are employed when correlation effects become qualitatively important. Reference-state total energies based on contour integrals in the complex plane and gradients of electron binding energies enable exploration of final-state potential energy surfaces. © 2012 John Wiley & Sons, Ltd.

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## INTRODUCTION

Electron propagator theory<sup>1–15</sup> provides a conceptual foundation for the *ab initio* calculation of electron binding energies, one-electron properties, and total energies of molecules. This theory (and its equivalent formulations known as the one-electron

Green's function or equation-of-motion theories) also provides a direct path to interpreting these properties in terms of Dyson orbitals. Whereas the Hartree–Fock equations may be understood in terms of the self-consistent determination of a one-electron potential with Coulomb and exchange components, the generalizations achieved by electron propagator theory through the Dyson equation introduce a correlation potential that is energy dependent and nonlocal. Electron binding energies and Dyson orbitals emerge as eigenvalues and eigenfunctions of one-electron

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equations that include this potential, which is known as the self-energy. Dyson orbitals are related to transition probabilities that pertain to the attachment or removal of a single electron. Summations that involve electron binding energies and corresponding Dyson orbitals may be related to one-electron properties and total energies. *Ab initio* electron propagator methods may be systematically improved by increasing the flexibility of self-energy approximations and by enlargement of basis sets. In electron propagator theory, equations that contain correlated, one-electron operators resemble the Kohn–Sham equations of density-functional theory<sup>16</sup> and also are related to the extended Koopmans's theorem<sup>17</sup> approach. Diagrammatic expression of the self-energy operator establishes a link with many-body theory and the summation of various terms that describe long-range and short-range correlation effects in the random-phase and ladder approximations. Propagator methods derive from multiple-time generalizations of density matrices. Although the Hermitian eigenvalue problem of configuration interaction is defined in Hilbert space, its counterpart in electron propagator theory is defined in Fock space, where states with different numbers of electrons are explicitly coupled.

A self-contained review of electron propagator concepts starts below with a discussion of poles, residues, and their physical significance in terms of electron binding energies and Dyson orbitals. The coupling of the electron propagator to higher propagators leads to the superoperator approach to deriving approximations. Partitioning techniques then establish the structure of the electron propagator matrix. Reference state and transition properties are related to electron binding energies and Dyson orbitals. The inverse form of the Dyson equation provides a correlated generalization of self-consistent field equations. Low-order self-energies that are convenient for calculations on large molecules and renormalized approximations that are capable of higher accuracy and flexibility are presented. Finally, total energy expressions and their gradients are discussed. Approximations that are based on an optimum Slater determinant of the Hartree–Fock or Brueckner types are emphasized here. Alternative approaches that employ multiconfigurational self-consistent fields have been discussed elsewhere.<sup>18–20</sup> The non-Dyson Green's function methods that perform variational–perturbative calculations of total energies and energy differences in Hilbert space are not discussed.<sup>21</sup> Methods that employ a semiempirical Hamiltonian also have been reviewed separately.<sup>22,23</sup>

## ELECTRON PROPAGATOR CONCEPTS

### Spectral Form: Electron Binding Energies and Dyson Orbitals

The molecular electron propagator may be expressed in terms of field operators that annihilate or create electrons in a finite set of orthonormal spin-orbitals with indices  $r, s, t, \dots$ . Let the spectral form for the  $r, s$  element of the electron propagator matrix be

$$G_{rs}(E) = \sum_n U_{nr}^* U_{ns}(E - D_n)^{-1} + \sum_m V_{ms}^* V_{mr}(E - A_m)^{-1},$$

where  $U_{ns} = \langle N - 1, n | a_s | N, 0 \rangle$  and  $V_{mr} = \langle N + 1, m | a_r^\dagger | N, 0 \rangle$ .<sup>11</sup> The indices  $n$  and  $m$  run over states with  $N - 1$  or  $N + 1$  electrons, respectively. The reference state,  $|N, 0\rangle$ , is usually chosen to be the ground state of an  $N$ -electron system with energy  $E_0(N)$ . The poles (values of  $E$  that produce a singularity) occur at  $D_n = E_0(N) - E_n(N - 1)$  or at  $A_m = E_m(N + 1) - E_0(N)$ . Dyson orbitals for electron detachments, defined by

$$\begin{aligned} \varphi_n^{\text{Dyson}}(x_1) &= N^{0.5} \int \Psi_N(x_1, x_2, x_3, \dots, x_N) \\ &\quad \Psi_{n, N-1}^*(x_2, x_3, x_4, \dots, x_N) \\ &\quad \times dx_2 dx_3 dx_4 \dots dx_N, \end{aligned}$$

may be expanded in terms of the spin-orbital basis such that

$$\varphi_n^{\text{Dyson}}(x_1) = \sum_r U_{nr} \varphi_r(x_1).$$

For Dyson orbitals that pertain to electron attachments, where

$$\begin{aligned} \varphi_m^{\text{Dyson}}(x_1) &= (N + 1)^{0.5} \int \\ &\quad \Psi_{m, N+1}(x_1, x_2, x_3, \dots, x_N, x_{N+1}) \\ &\quad \times \Psi_N^*(x_2, x_3, x_4, \dots, x_N, x_{N+1}) \\ &\quad \times dx_2 dx_3 dx_4 \dots dx_N dx_{N+1}, \end{aligned}$$

the corresponding relationship to the residues of the electron propagator matrix elements reads

$$\varphi_m^{\text{Dyson}}(x_1) = \sum_r V_{mr} \varphi_r(x_1).$$

### Propagator Couplings

The electron propagator may be related to other propagators that involve more complex products of field operators. The role of field operators is emphasized in the notation

$$G_{rs}(E) \equiv \langle\langle a_r^\dagger; a_s \rangle\rangle,$$

where the dependence on  $E$  is repressed in the right-hand expression. If each of the bras and kets that appear in the definition of  $G_{rs}(E)$  is an eigenfunction of the many-electron Hamiltonian,  $H$ , then

$$E \langle\langle a_r^\dagger; a_s \rangle\rangle = \sum_n U_{nr}^* U_{ns} [1 + D_n(E - D_n)^{-1}] + \sum_m V_{ms}^* V_{mr} [1 + A_m(E - A_m)^{-1}].$$

Because the sums over  $n$  and  $m$  are assumed to be complete,

$$\sum_n U_{nr}^* U_{ns} = \langle N, 0 | a_r^\dagger a_s | N, 0 \rangle$$

and

$$\sum_m V_{ms}^* V_{mr} = \langle N, 0 | a_s a_r^\dagger | N, 0 \rangle.$$

In the remaining terms of the  $E \langle\langle a_r^\dagger; a_s \rangle\rangle$  expression, a new set of residues that involve the commutator of  $a_s$  with  $H$  may be identified:

$$\begin{aligned} & \sum_n U_{nr}^* U_{ns} D_n (E - D_n)^{-1} \\ &= \sum_n U_{nr}^* \langle N - 1, n | [a_s, H] | N, 0 \rangle (E - D_n)^{-1} \end{aligned}$$

$$\begin{aligned} & \sum_m V_{ms}^* V_{mr} A_m (E - A_m)^{-1} \\ &= \sum_m \langle N, 0 | [a_s, H] | N + 1, m \rangle V_{mr} (E - A_m)^{-1}. \end{aligned}$$

Therefore, the electron propagator may be related to a more complex propagator that depends on  $[a_s, H]$  by writing<sup>1,11</sup>

$$E \langle\langle a_r^\dagger; a_s \rangle\rangle = \langle N, 0 | [a_r^\dagger, a_s] + | N, 0 \rangle + \langle\langle a_r^\dagger; [a_s, H] \rangle\rangle.$$

The latter term is coupled to a yet more complex propagator in which the operator  $[[a_s, H], H]$  appears through

$$\begin{aligned} E \langle\langle a_r^\dagger; [a_s, H] \rangle\rangle &= \langle N, 0 | [a_r^\dagger, [a_s, H]]_+ | N, 0 \rangle \\ &+ \langle\langle a_r^\dagger; [[a_s, H], H] \rangle\rangle. \end{aligned}$$

In general, propagators that involve operators, which change the number of electrons by one ( $\mu^\dagger$  and  $\nu$ ) are subject to the relation

$$E \langle\langle \mu^\dagger; \nu \rangle\rangle = \langle N, 0 | [\mu^\dagger, \nu]_+ | N, 0 \rangle + \langle\langle \mu^\dagger; [\nu, H] \rangle\rangle.$$

Because each propagator is coupled to a higher propagator, the electron propagator may be expressed as a series:

$$\begin{aligned} \langle\langle a_r^\dagger; a_s \rangle\rangle &= E^{-1} \langle N, 0 | [a_r^\dagger, a_s]_+ | N, 0 \rangle \\ &+ E^{-2} \langle N, 0 | [a_r^\dagger, [a_s, H]]_+ | N, 0 \rangle \\ &+ E^{-3} \langle N, 0 | [a_r^\dagger, [[a_s, H], H]]_+ | N, 0 \rangle \\ &+ E^{-4} \langle N, 0 | [a_r^\dagger, [[[a_s, H], H], H]]_+ | N, 0 \rangle \\ &+ \dots \end{aligned}$$

Note that electron propagator matrix elements are determined by commutators with  $H$  and an anticommutator and that density matrices of the reference state,  $|N, 0\rangle$ , suffice to evaluate each term.

## Superoperator Notation

A succinct expression of the previous equation may be realized through the introduction of a superoperator metric for operators that change the number of electrons by one and accompanying identity and Hamiltonian superoperators.<sup>11,24</sup> The metric is defined by

$$(\mu | \nu) = \langle N, 0 | [\mu^\dagger, \nu]_+ | N, 0 \rangle.$$

The identity and Hamiltonian superoperators are defined, respectively, by

$$\hat{I} \mu = \mu$$

and

$$\hat{H} \mu = [\mu, H].$$

The series expression for the electron propagator matrix elements may be expressed in terms of superoperators as

$$\begin{aligned} \langle\langle a_r^\dagger; a_s \rangle\rangle &= E^{-1} (a_r | a_s) + E^{-2} (a_r | \hat{H} a_s) + E^{-3} (a_r | \hat{H}^2 a_s) \\ &+ E^{-4} (a_r | \hat{H}^3 a_s) + \dots \end{aligned}$$

A compact expression for the electron propagator in terms of the superoperator resolvent,  $(E\hat{I} - \hat{H})^{-1}$ , reads

$$\langle\langle a_r^\dagger; a_s \rangle\rangle = (a_r | (E\hat{I} - \hat{H})^{-1} a_s) = G_{rs}(E).$$

## Partitioning of Operator Spaces

By introducing a row vector of creation operators whose rank,  $R$ , is that of the spin-orbital basis,

$$\mathbf{a}^\dagger = [a_1^\dagger a_2^\dagger a_3^\dagger \dots a_R^\dagger],$$

the electron propagator matrix may be written as

$$\mathbf{G}(E) = (\mathbf{a} | (E\hat{I} - \hat{H})^{-1} \mathbf{a}).$$

The inverse superoperator may be avoided in favor of an inverse matrix through an inner projection that invokes the set of field operator products that change the number of electrons by 1. In addition to the elements of  $\mathbf{a}$  (simple annihilators), this set includes products of  $\tilde{n}$  creators and  $\tilde{n} + 1$  annihilators for  $\tilde{n} = 1, 2, 3, \dots$ . If the latter set is arrayed in a vector,  $\mathbf{w}$ , one may write

$$\mathbf{G}(E) = (\mathbf{a} | \mathbf{w})(\mathbf{w} | (E\hat{I} - \hat{H})^{-1} (\mathbf{w} | \mathbf{a}).$$

The inner projection space<sup>25</sup> may be partitioned into a primary space,  $\mathbf{a}$ , and an orthogonal secondary

space,  $\mathbf{f}$ , which contains triple, quintuple, septuple, and higher products of annihilators and creators. In the superoperator metric,  $(\mathbf{a}\mathbf{a}) = \mathbf{1}_a$ ,  $(\mathbf{f}\mathbf{f}) = \mathbf{1}_f$ ,  $(\mathbf{a}\mathbf{f}) = \mathbf{0}_{\text{axf}}$ , and  $(\mathbf{f}\mathbf{a}) = \mathbf{0}_{\text{fxa}}$ . The partitioned form of the electron propagator matrix is

$$\begin{aligned} G(E) &= [\mathbf{1}_a \mathbf{0}_{\text{axf}}][\mathbf{a}; \mathbf{f} | (E\hat{\mathbf{I}} - \hat{H})\mathbf{a}; \mathbf{f} |^{-1} [\mathbf{1}_a \mathbf{0}_{\text{axf}}]^\dagger \\ &= [\mathbf{1}_a \mathbf{0}_{\text{axf}}][E\hat{\mathbf{I}} - \hat{H}]^{-1} [\mathbf{1}_a \mathbf{0}_{\text{axf}}]^\dagger. \end{aligned}$$

Only the upper-left (primary space) block of the inverse matrix is not annihilated by multiplication with the matrices  $[\mathbf{1}_a \mathbf{0}_{\text{axf}}]$  and  $[\mathbf{1}_a \mathbf{0}_{\text{axf}}]^\dagger$ . Now let the eigenvalues and eigenvectors of the superoperator Hamiltonian matrix,  $\hat{H}$ , be given by  $\hat{H}\Omega = \Omega\omega$ , where  $\Omega^\dagger\Omega = \mathbf{1}$ . An alternative spectral form of the electron propagator may be written as

$$\begin{aligned} G(E) &= [\mathbf{1}_a \mathbf{0}_{\text{axf}}][\Omega(E\mathbf{1} - \omega)^{-1}\Omega^\dagger][\mathbf{1}_a \mathbf{0}_{\text{axf}}]^\dagger \\ &= \Omega_a(E\mathbf{1} - \omega)^{-1}\Omega_a^\dagger. \end{aligned}$$

Eigenvalues of  $\hat{H}$  are poles of the electron propagator, with  $\omega_n = D_n$  for electron detachment energies and  $\omega_m = A_m$  for electron attachment energies. Only the primary-space components of the eigenvectors of  $\hat{H}$ ,  $\Omega_a$ , remain in the latter expression. For electron detachment energies,  $\Omega_{\text{nr}} = U_{\text{nr}}$ , and for electron attachment energies,  $\Omega_{\text{rm}} = V_{\text{mr}}$ .

In electron propagator and equation-of-motion theories, one may obtain electron binding energies and corresponding linear combinations of operators in the primary ( $\mathbf{a}$ ) or secondary ( $\mathbf{f}$ ) spaces by diagonalizing  $\hat{H}$ .<sup>26,27</sup> The entire set of simple annihilators, two-annihilator-one-creator products, three-annihilator-two-creator products, and higher products may contribute to a given operator regardless of reference states that may stipulate occupied and virtual subsets of the orbital spaces. For example, for a final state with  $N - 1$  electrons, the corresponding operator may have primary-space components corresponding to virtual spin orbitals and secondary-space components corresponding to two virtual spin orbitals and one occupied spin orbital. Hilbert-space methods typically restrict such operators to the description of final states with  $N + 1$  electrons.

## Reference-State Properties

Elements of the first-order reduced density matrix of the reference state,  $\rho$ , are related to the electron propagator residues via

$$\begin{aligned} \rho_{\text{rs}} &= \langle N, 0 | a_r^\dagger a_s | N, 0 \rangle = \sum_n U_{\text{nr}}^* U_{\text{ns}} \\ &= \delta_{\text{sr}} - \sum_m V_{\text{ms}}^* V_{\text{mr}}. \end{aligned}$$

In coordinate space, the density operator can be related to the Dyson orbitals through

$$\begin{aligned} \rho(x, x') &= \sum_{\text{rs}} \varphi_r(x) \rho_{\text{rs}} \varphi_s^*(x') \\ &= \sum_n \varphi_n^{\text{Dyson}}(x) \varphi_n^{\text{Dyson}*}(x'). \end{aligned}$$

The latter summation is an exact generalization of the usual Dirac form that pertains to a Slater determinant. In this expression, the number of terms in the summation is larger than the number of electrons, for it considers all final states with  $N - 1$  electrons. In addition, the Dyson orbitals are not necessarily normalized to unity. The norms of the Dyson orbitals are known as pole strengths, where

$$P_n = \int |\varphi_n^{\text{Dyson}}(x)|^2 dx = \sum_r |U_{\text{nr}}|^2$$

for final states with  $N - 1$  electrons or

$$P_m = \int |\varphi_m^{\text{Dyson}}(x)|^2 dx = \sum_r |U_{\text{mr}}|^2$$

for final states with  $N + 1$  electrons. The following rule relates the number of electrons in the reference state to the pole strengths for electron detachments:

$$N = \int \rho(x, x) dx = \sum_n P_n.$$

Reference-state total energies also may be related to poles and residues of the electron propagator by using the identity

$$\begin{aligned} \sum_r \sum_n U_{\text{nr}}^* U_{\text{nr}} D_n &= \sum_r \sum_n \langle N, 0 | a_r^\dagger | N - 1, n \rangle \\ &\quad \times \langle N - 1, n | [a_r, H] | N, 0 \rangle. \end{aligned}$$

Whereas the right-hand side of the previous equation is the trace of a kind of energy-weighted density matrix, the left-hand side is the expectation value of an operator that includes the one-electron part of the Hamiltonian plus twice the two-electron part:

$$\begin{aligned} \text{Tr}(\mathbf{U}^\dagger \mathbf{D} \mathbf{U}) &= \langle N, 0 | \sum_{\text{rt}} h_{\text{rt}} a_r^\dagger a_t + 0.5 \sum_{\text{rtuv}} \\ &\quad \times \langle r t | uv \rangle a_r^\dagger a_t^\dagger a_v a_u | N, 0 \rangle, \end{aligned}$$

where  $\mathbf{D}$  is a diagonal matrix of electron detachment energies. The total energy of the reference state, therefore, may be obtained by restoring the proper coefficients to the one-electron and two-electron terms in the Hamiltonian:

$$\begin{aligned} \langle N, 0 | H | N, 0 \rangle &= \langle N, 0 | \sum_{\text{rt}} h_{\text{rt}} a_r^\dagger a_t + 0.25 \sum_{\text{rtuv}} \\ &\quad \times \langle r t | uv \rangle a_r^\dagger a_t^\dagger a_v a_u | N, 0 \rangle \\ &= 0.5 \text{Tr}(\mathbf{U}^\dagger \mathbf{D} \mathbf{U}) \\ &\quad + 0.5 \langle N, 0 | \sum_{\text{rs}} h_{\text{rs}} a_r^\dagger a_s | N, 0 \rangle \\ &= 0.5 \sum_r \sum_n U_{\text{nr}}^* U_{\text{nr}} D_n \\ &\quad + 0.5 \sum_{\text{rs}} h_{\text{rs}} \sum_n U_{\text{nr}}^* U_{\text{ns}}. \end{aligned}$$

In the latter expression, the second term is one half of a sum of one-electron matrix elements over Dyson orbitals for electron detachments. The first term comprises electron detachment energies weighted by pole strengths. Therefore,

$$\langle N, 0 | H | N, 0 \rangle = 0.5 \sum_n P_n D_n + 0.5 \sum_n \langle \varphi_n^{\text{Dyson}} | h \varphi_n^{\text{Dyson}} \rangle,$$

where both summations run over final states with  $N - 1$  electrons. In terms of Dyson orbitals that are normalized to unity,  $\Phi$ , the same expression reads

$$\langle N, 0 | H | N, 0 \rangle = 0.5 \sum_n P_n (D_n + \langle \Phi_n^{\text{Dyson}} | h \Phi_n^{\text{Dyson}} \rangle).$$

This generalization of the Hartree–Fock energy expression substitutes pole strengths for occupation numbers and electron-detachment Dyson orbitals for occupied canonical orbitals. It also displays a relationship between electron-detachment and total energies that is exact.

The generalized eigenvalue problem associated with the so-called extended Koopmans's theorem<sup>17</sup> may be expressed as

$$\mathbf{F}^{\text{EKT}} \mathbf{C} = \rho \mathbf{C} \mathbf{D},$$

where the Fock-like matrix

$$F_{rs}^{\text{EKT}} = \langle N, 0 | a_r^\dagger [a_s, H] | N, 0 \rangle$$

may be generated from the one-electron and two-electron density matrices corresponding to the reference state. A symmetric form of this matrix reads

$$\mathbf{F}^{\text{EKT}} = \mathbf{U}^\dagger \mathbf{D} \mathbf{U}.$$

## Transition Probabilities

When bound-continuum transitions occur between an initial,  $N$ -electron bound state,  $|N, \text{initial}\rangle$ , and a final state that is approximated by an antisymmetrized product of a continuum orbital,  $\varphi^{\text{cont}}$ , and a bound state with  $N - 1$  electrons,  $|N - 1, \text{final}\rangle$ , the transition probability,  $\sigma^{\text{if}}$ , is related to the corresponding Dyson orbital according to

$$\sigma^{\text{if}} = \mathbf{K}^{\text{if}} \left| \langle \varphi_{\text{if}}^{\text{Dyson}} | \mathbf{T} \varphi^{\text{cont}} \rangle \right|^2,$$

where  $\mathbf{K}^{\text{if}}$  is a constant and  $\mathbf{T}$  is a transition operator.<sup>28</sup> For example, photoionization cross-sections in the sudden approximation may be determined when  $\mathbf{T}$  describes the interaction between a radiation field and electrons.<sup>3</sup> Penning ionization cross-sections for collisions between excited He

atoms and molecules involve the electron repulsion operator.<sup>29</sup> Transition probabilities that pertain to electron-two-electron scattering experiments invoke probability amplitudes corresponding to Dyson orbitals.<sup>30,31</sup> Approximate intensity ratios in spectra are often generated by assuming the equality of matrix elements between continuum orbitals and Dyson orbitals normalized to unity. Under this assumption, relative intensities become proportional to pole strengths.

## Inverse Form of the Dyson Equation

The structure of the electron propagator matrix, where

$$\mathbf{G}(E) = [\mathbf{1}_a \mathbf{0}_{\text{axf}}] (\mathbf{a}; \mathbf{f} | (E \hat{I} - \hat{H}) \mathbf{a}; \mathbf{f})^{-1} [\mathbf{1}_a \mathbf{0}_{\text{axf}}]^\dagger,$$

implies that the top-left block in the central, inverse matrix is identical to  $\mathbf{G}(E)$ . To determine this inverse matrix, one may write two simultaneous equations:

$$(\mathbf{a} | (E \hat{I} - \hat{H}) \mathbf{a}) \mathbf{G}(E) + (\mathbf{a} | (E \hat{I} - \hat{H}) \mathbf{f}) \mathbf{g}_{\text{fa}}(E) = \mathbf{1}_a,$$

$$(\mathbf{f} | (E \hat{I} - \hat{H}) \mathbf{a}) \mathbf{G}(E) + (\mathbf{f} | (E \hat{I} - \hat{H}) \mathbf{f}) \mathbf{g}_{\text{fa}}(E) = \mathbf{0}_{\text{fxa}}.$$

Because of the orthogonality of the  $\mathbf{a}$  and  $\mathbf{f}$  operator subspaces, solving for  $\mathbf{G}(E)$  yields

$$\mathbf{G}(E) = [(\mathbf{a} | (E \hat{I} - \hat{H}) \mathbf{a}) - (\mathbf{a} | \hat{H} \mathbf{f}) \times (\mathbf{f} | (E \hat{I} - \hat{H}) \mathbf{f})^{-1} (\mathbf{f} | \hat{H} \mathbf{a})]^{-1}.$$

Evaluation of the first term on the right-hand side of the previous equation reveals the presence of a generalized Fock matrix,  $\mathbf{F}^{\text{ref}}$ , which depends on the reference state's one-electron density matrix:

$$\begin{aligned} (a_r | (E \hat{I} - \hat{H}) a_s) &= E \delta_{rs} - h_{rs} - \sum_{tu} \langle r t | s u \rangle \\ &\times \langle N, 0 | a_t^\dagger a_u | N, 0 \rangle \\ &\equiv E \delta_{rs} - F_{rs}^{\text{ref}}. \end{aligned}$$

The inverse electron propagator matrix therefore reads

$$\mathbf{G}^{-1}(E) = E \mathbf{1} - \mathbf{F}^{\text{ref}} - (\mathbf{a} | \hat{H} \mathbf{f}) (\mathbf{f} | (E \hat{I} - \hat{H}) \mathbf{f})^{-1} (\mathbf{f} | \hat{H} \mathbf{a}).$$

The second term on the left-hand side is known as the energy-dependent self-energy matrix,  $\sigma(E)$ , and leads to the inverse form of the Dyson equation,

$$\mathbf{G}^{-1}(E) = E \mathbf{1} - \mathbf{F}^{\text{ref}} - \sigma(E).$$

Whereas poles of the electron propagator occur when  $\det \mathbf{G}(E)$  diverges, an alternative computational strategy for obtaining poles is provided by demanding that  $\det \mathbf{G}^{-1}(E) = 0$ . The latter condition requires that  $\mathbf{G}^{-1}(E)$  have a zero eigenvalue such that

$$[\mathbf{F}^{\text{ref}} + \sigma(E)] \mathbf{C} = \mathbf{C} \mathbf{E}.$$

The latter expression is a generalization of the canonical Hartree–Fock equations, where Coulomb and exchange terms in  $\mathbf{F}^{\text{ref}}$  are potentially subject to a correlated one-electron density matrix and where an energy dependent, nonlocal operator also describes the effects of electron correlation as well as relaxation of orbitals in final states. A pole search may involve diagonalization of the matrix  $\mathbf{F}^{\text{ref}} + \sigma(E)$  for various values of  $E$  until one of the eigenvalues equals  $E$ . Such values of  $E$  are poles. The accompanying eigenvector,  $\mathbf{C}$ , is proportional to the corresponding  $\mathbf{U}$  vector for electron detachments or to the corresponding  $\mathbf{V}$  vector for electron attachments. The pole strength is given by

$$P = [1 - \mathbf{C}^\dagger \sigma'(E) \mathbf{C}]^{-1},$$

where  $\sigma'_{rs}(E) = d\sigma_{rs}(E)/dE$  and  $\mathbf{C}^\dagger \mathbf{C} = 1$ . In the canonical, Hartree–Fock orbital basis,

$$F_{rs}^{\text{ref}} = \varepsilon_r \delta_{rs} + \sum_{tu} \langle rt | |su \rangle \rho_{tu}^{\text{corr}},$$

where the correlation contribution to the one-electron density matrix,  $\rho^{\text{corr}}$ , generates nonvanishing off-diagonal elements of  $\mathbf{F}^{\text{ref}}$  and corrections to the Hartree–Fock orbital energies in the diagonal elements. These terms are sometimes known as the energy-independent self-energy. The uncorrelated electron propagator defined by the Hartree–Fock approximation,  $G_0(E)$ , has a simple structure of poles and residues where

$$[\mathbf{G}_0(E)]_{sr} = (E - \varepsilon_r)^{-1} \delta_{rs}.$$

One may rewrite the inverse Dyson equation in terms of a zeroth-order electron propagator matrix and the total self-energy matrix,  $\Sigma(E)$ , where

$$\mathbf{G}^{-1}(E) = \mathbf{G}_0^{-1}(E) - \Sigma(E).$$

The total self-energy matrix has energy-dependent and energy-independent (or constant) components, where

$$\Sigma(E) = \sigma(E) + \Sigma(\infty).$$

In the limit of  $E$  approaching infinity, only the constant component of the self-energy matrix,

$$\Sigma_{rs}(\infty) = \sum_{tu} \langle rt | |su \rangle \rho_{tu}^{\text{corr}},$$

remains, for the energy-dependent component vanishes. Electron attachment poles at very high  $E$  therefore approach the eigenvalues of  $\mathbf{F}^{\text{ref}}$ .

## SELF-ENERGY APPROXIMATIONS

Practical calculations generally require that approximations be made to the self-energy matrix. Low-order, perturbative methods employ the Møller–Plesset partitioning of the Hamiltonian and identify terms of various orders in the fluctuation potential. For cases where strong orbital relaxation occurs, reference-ensemble density matrices may supplant reference-state density matrices obtained from wavefunctions. Renormalized (or infinite-order) methods also may employ the same partitioning of the Hamiltonian, but with the object of generating all self-energy terms of a given order. Still other approaches depart not from the Hartree–Fock electron propagator, but from reference states generated by multiconfigurational, self-consistent-field wavefunctions.<sup>18</sup>

### Perturbative methods

Hartree–Fock orbital energies are the poles of the zeroth-order electron propagator,  $G_0(E)$ , and provide a point of departure for perturbative corrections that account for final-state orbital relaxation and electron correlation. With the Møller–Plesset partitioning of the Hamiltonian ( $H = H_0 + W$ ), correlation corrections to the reference state's one-electron density matrix,  $\rho^{\text{corr}}$ , from Rayleigh–Schrödinger perturbation theory occur first in second order. Therefore, constant self-energy terms do not appear until third order.

Superoperator matrix elements that occur in the energy-dependent self-energy matrix, where

$$\sigma(E) = (\mathbf{a} | \hat{H} \mathbf{f}) (\mathbf{f} | (E \hat{I} - \hat{H}) \mathbf{f})^{-1} (\mathbf{f} | \hat{H} \mathbf{a}),$$

involve members of  $\mathbf{f}$  that are products of two annihilators and one creator ( $\mathbf{f}_3$ ), three annihilators and two creators ( $\mathbf{f}_5$ ), four annihilators and three creators ( $\mathbf{f}_7$ ), and so on. Elements of  $(\mathbf{a} | \hat{H} \mathbf{f}_3)$  and  $(\mathbf{f}_3 | \hat{H} \mathbf{a})$  depend on the two-electron or lower-order reduced density matrices of the reference state. For Hartree–Fock density matrices, zeroth-order terms vanish, but first-order terms in  $(\mathbf{a} | \hat{H} \mathbf{f}_3)$  and  $(\mathbf{f}_3 | \hat{H} \mathbf{a})$  do appear. Elements of  $(\mathbf{f}_3 | \hat{H} \mathbf{f}_3)$  depend on the three-electron or lower-order density matrices. Here nonzero terms occur in zeroth and first order. Zeroth- and first-order terms vanish for superoperator couplings between  $\mathbf{a}$  and  $\mathbf{f}_{2k+1}$  for  $k > 1$ . Therefore, the first corrections in  $\sigma(E)$  occur in second order:

$$\sigma^{(2)}(E) = (\mathbf{a} | \hat{H} \mathbf{f}_3)_1 (\mathbf{f}_3 | (E \hat{I} - \hat{H}) \mathbf{f}_3)_0^{-1} (\mathbf{f}_3 | \hat{H} \mathbf{a})_1,$$

where the subscripts indicate the order in which the matrix elements have been evaluated. Two-particle-one-hole (2ph) and two-hole-one-particle (2hp)  $\mathbf{f}_3$  operators may couple with simple

annihilators via electron repulsion integrals. Zeroth-order couplings between  $\mathbf{f}_3$  operators occur only in the diagonal elements of  $(\mathbf{f}_3|\hat{H}\mathbf{f}_3)$  and involve orbital energies but not electron repulsion integrals. Elements of the second-order self-energy matrix read:

$$\begin{aligned} \sigma_{pq}^{(2)}(E) = & 0.5 \sum_{aij} \langle pa || ij \rangle (E + \varepsilon_a - \varepsilon_i - \varepsilon_j)^{-1} \\ & \times \langle ij || qa \rangle + 0.5 \sum_{iab} \langle pi || ab \rangle \\ & \times (E + \varepsilon_i - \varepsilon_a - \varepsilon_b)^{-1} \langle ab || qi \rangle, \end{aligned}$$

where  $p$  and  $q$  are general spin-orbital indices,  $i, j$ , and  $k$  are occupied spin-orbital indices and  $a, b$ , and  $c$  are virtual spin-orbital indices. The first term, with its summation over two occupied and one virtual indices, is the 2hp contribution; the second term is its 2ph counterpart.

Self-energy terms in third order may be constant or energy dependent.<sup>32</sup> For the former terms, perturbative corrections to the one-electron density matrix may arise from first-order double substitutions with amplitudes  $t_{ijab} = \langle ij || ab \rangle (\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)^{-1}$ , or from second-order single substitutions where

$$\begin{aligned} |N, 0\rangle = & \{1 + 0.25 \sum_{ijab} t_{ijab} a_a^\dagger a_b^\dagger a_i a_j \\ & + \sum_{ia} (\varepsilon_i - \varepsilon_a)^{-1} [0.5 \sum_{jbc} t_{ijbc} \langle bc || aj \rangle \\ & + 0.5 \sum_{jkb} t_{jkb} \langle ib || jk \rangle] a_a^\dagger a_i + \dots\} |HF\rangle. \end{aligned}$$

Energy-dependent terms arise in two ways. First-order double substitutions occur in the two-electron density matrix of the reference state and, therefore, also appear in formulas for  $(\mathbf{a}|\hat{H}\mathbf{f}_3)_2$  and  $(\mathbf{f}_3|\hat{H}\mathbf{a})_2$ . The inverse matrix  $(\mathbf{f}_3|(E\hat{I} - \hat{H})\mathbf{f}_3)^{-1}_1$  may be expressed as an expansion about its zeroth-order, diagonal part:

$$\begin{aligned} (\mathbf{f}_3|(E\hat{I} - \hat{H})\mathbf{f}_3)^{-1}_1 = & [(\mathbf{f}_3|(E\hat{I} - \hat{H}_0)\mathbf{f}_3)_0^{-1} \\ & - (\mathbf{f}_3|\hat{W}\mathbf{f}_3)_1^{-1}]^{-1} \\ = & (\mathbf{f}_3|(E\hat{I} - \hat{H}_0)\mathbf{f}_3)_0^{-1} \\ & + (\mathbf{f}_3|(E\hat{I} - \hat{H}_0)\mathbf{f}_3)_0^{-1} (\mathbf{f}_3|\hat{W}\mathbf{f}_3)_1 \\ & \times (\mathbf{f}_3|(E\hat{I} - \hat{H}_0)\mathbf{f}_3)_0^{-1} \\ & + (\mathbf{f}_3|(E\hat{I} - \hat{H}_0)\mathbf{f}_3)_0^{-1} (\mathbf{f}_3|\hat{W}\mathbf{f}_3)_1 \\ & \times (\mathbf{f}_3|(E\hat{I} - \hat{H}_0)\mathbf{f}_3)_0^{-1} (\mathbf{f}_3|\hat{W}\mathbf{f}_3)_1 \\ & \times (\mathbf{f}_3|(E\hat{I} - \hat{H}_0)\mathbf{f}_3)_0^{-1} + \dots \end{aligned}$$

Through third order, the energy-dependent part of the self-energy reads

$$\begin{aligned} \sigma_{pq}^{(3)}(E) = & \sigma_{pq}^{(2)}(E) + (\mathbf{a}|\hat{H}\mathbf{f}_3)_2 (\mathbf{f}_3|(E\hat{I} - \hat{H})\mathbf{f}_3)_0^{-1} \\ & \times (\mathbf{f}_3|\hat{H}\mathbf{a})_1 + (\mathbf{a}|\hat{H}\mathbf{f}_3)_1 (\mathbf{f}_3|(E\hat{I} - \hat{H})\mathbf{f}_3)_0^{-1} \\ & \times (\mathbf{f}_3|\hat{H}\mathbf{a})_2 + (\mathbf{a}|\hat{H}\mathbf{f}_3)_1 (\mathbf{f}_3|(E\hat{I} - \hat{H}_0)\mathbf{f}_3)_0^{-1} \\ & \times (\mathbf{f}_3|\hat{W}\mathbf{f}_3)_1 (\mathbf{f}_3|(E\hat{I} - \hat{H}_0)\mathbf{f}_3)_0^{-1} (\mathbf{f}_3|\hat{H}\mathbf{a})_1. \end{aligned}$$

Electron repulsion integrals with four particle, four hole or two particle and two hole indices occur in the formulas for  $(\mathbf{f}_3|\hat{W}\mathbf{f}_3)$ . Ladder and ring terms therefore appear first in the last term of the previous equation and have two energy-dependent denominators.

There is ample computational evidence that the off-diagonal elements of the self-energy matrix in the canonical Hartree–Fock basis are negligible for electron binding energies near the Fermi level in closed-shell molecules. Neglect of these elements leads to the diagonal self-energy approximation (which also has been called the quasiparticle approximation) and to a simple form of the inverse Dyson equation:

$$G^{-1}(E)_{rr} = 0 = E - \varepsilon_r - \Sigma(E)_{rr}.$$

This expression may be iterated with respect to  $E$  to produce a pole. Satisfactory convergence is generally achieved within three iterations when  $\varepsilon_r$  serves as the initial guess for  $E$ .

When the pole is approximated by a canonical orbital energy, the resulting values of  $\varepsilon_r + \Sigma^{(2)}(\varepsilon_r)_{rr}$  and  $\varepsilon_r + \Sigma^{(3)}(\varepsilon_r)_{rr}$  are equal to electron binding energies determined by Møller–Plesset, Rayleigh–Schrödinger perturbation theory with a frozen set of spin orbitals in second order.<sup>11</sup> Pole strengths also are easily evaluated according to  $P_r = (1 - d\Sigma(E)_{rr}/dE)^{-1}$ . Perturbative calculations of this kind are most likely to be valid when pole strengths are close to unity. The value of 0.85 has become an approximate standard of validity for calculations of valence ionization energies and electron affinities performed with low-order, diagonal self-energy methods.<sup>33</sup>

Second-order, diagonal self-energy results for valence ionization energies of closed-shell molecules generally overestimate corrections to Hartree–Fock orbital energies, but third-order results often display the opposite trend. Although root-mean-square errors for the results of Koopmans’s theorem are over 1 eV, their counterparts for the diagonal, third-order self-energy still exceed 0.5 eV. Therefore, various schemes have emerged to provide more accurate results

without requiring significant, additional computational effort.

On the basis of a diagrammatic analysis of the second- and third-order self-energy terms, the outer valence Green's function (OVGF) approximations were devised.<sup>4,5,34,35</sup> In the A version of OVGF, a scaling factor for the third-order terms is introduced, where

$$\Sigma^{\text{OVGF-A}}(E)_{\text{rr}} = \Sigma^{(2)}(E)_{\text{rr}} + (1 + X_r)^{-1} \Sigma^{(3)}(E)_{\text{rr}}.$$

[Note that  $\Sigma^{(2)}(E) = \sigma^{(2)}(E)$ .] In the latter expression, the third-order self-energy matrix elements comprise constant and energy-independent terms such that

$$\begin{aligned} \Sigma^{(3)}(E) &= \Sigma^{(3)}(\infty) + (\mathbf{a}|\hat{H}\mathbf{f}_3)_2(\mathbf{f}_3|(E\hat{I} - \hat{H})\mathbf{f}_3)_0^{-1} \\ &\quad \times (\mathbf{f}_3|\hat{H}\mathbf{a})_1 + (\mathbf{a}|\hat{H}\mathbf{f}_3)_1(\mathbf{f}_3|(E\hat{I} - \hat{H})\mathbf{f}_3)_0^{-1} \\ &\quad \times (\mathbf{f}_3|\hat{H}\mathbf{a})_2 + (\mathbf{a}|\hat{H}\mathbf{f}_3)_1(\mathbf{f}_3|(E\hat{I} - \hat{H}_0)\mathbf{f}_3)_0^{-1} \\ &\quad \times (\mathbf{f}_3|\hat{W}\mathbf{f}_3)_1(\mathbf{f}_3|(E\hat{I} - \hat{H}_0)\mathbf{f}_3)_0^{-1}(\mathbf{f}_3|\hat{H}\mathbf{a})_1 \end{aligned}$$

and the scaling factor reads

$$X_r = -2[(\mathbf{a}|\hat{H}\mathbf{f}_3)_2(\mathbf{f}_3|(E\hat{I} - \hat{H})\mathbf{f}_3)_0^{-1}(\mathbf{f}_3|\hat{H}\mathbf{a})_1]_{\text{rr}} \sigma_{\text{rr}}^{(2)-1}.$$

Another scaled approximation, known as the B version of OVGF, introduces two factors for the 2ph and 2hp contributions to  $\Sigma^{(3)}(E)$ , where

$$\begin{aligned} \Sigma^{\text{OVGF-B}}(E)_{\text{rr}} &= \Sigma^{(2)}(E)_{\text{rr}} + \Sigma^{(3)}(\infty)_{\text{rr}} \\ &\quad + (1 + X_r^{2\text{hp}})^{-1} \Sigma^{(3-2\text{hp})}(E)_{\text{rr}} \\ &\quad + (1 + X_r^{2\text{ph}})^{-1} \Sigma^{(3-2\text{ph})}(E)_{\text{rr}}. \end{aligned}$$

Each of the scaling factors,  $X_r^{2\text{ph}}$  and  $X_r^{2\text{hp}}$ , has the same formula as in the A version, but only 2hp and 2ph terms are included, respectively. The C version of OVGF once again scales the entire third-energy term as in the A version, but with a different factor, where

$$\Sigma^{\text{OVGF-C}}(E)_{\text{rr}} = \Sigma^{(2)}(E)_{\text{rr}} + (1 + X_r^{\text{C}})^{-1} \Sigma^{(3)}(E)_{\text{rr}}$$

and

$$\begin{aligned} X_r^{\text{C}} &= [X_r^{2\text{hp}} \Sigma^{(3-2\text{hp})}(E)_{\text{rr}} + X_r^{2\text{ph}} \Sigma^{(3-2\text{ph})}(E)_{\text{rr}}] \\ &\quad \times [\Sigma^{(3-2\text{hp})}(E)_{\text{rr}} + \Sigma^{(3-2\text{ph})}(E)_{\text{rr}}]. \end{aligned}$$

Root-mean-square errors for the A, B, and C version are all approximately 0.3 eV. The latter figure may be reduced to 0.25 eV by adopting a selection procedure that employs several numerical criteria.<sup>5,35</sup>

An alternative approach employs no scaling factors or numerical parameters and is founded on an asymmetric superoperator metric approximation,

$$\langle \mu | \nu \rangle = \langle \det | [\mu^\dagger, \nu]_+ (1 + T_2) | \det \rangle,$$

where  $|\det\rangle$  is a Slater determinant and  $T_2$  is a double substitution operator.<sup>36,37</sup> After choosing  $|\det\rangle$  to be the Hartree–Fock wavefunction and  $T_2$  to be its first-order, perturbative correction, the asymmetric self-energy through third order reads

$$\begin{aligned} \Sigma(E) &= (\mathbf{a}|\hat{H}\mathbf{f}_3)_1(\mathbf{f}_3|(E\hat{I} - \hat{H})\mathbf{f}_3)_0^{-1}(\mathbf{f}_3|\hat{H}\mathbf{a})_1 \\ &\quad + (\mathbf{a}|\hat{H}\mathbf{f}_3)_1(\mathbf{f}_3|(E\hat{I} - \hat{H})\mathbf{f}_3)_0^{-1}(\mathbf{f}_3|\hat{H}\mathbf{a})_2 \\ &\quad + (\mathbf{a}|\hat{H}\mathbf{f}_3)_1(\mathbf{f}_3|(E\hat{I} - \hat{H}_0)\mathbf{f}_3)_0^{-1} \\ &\quad \times (\mathbf{f}_3|\hat{W}\mathbf{f}_3)_1(\mathbf{f}_3|(E\hat{I} - \hat{H}_0)\mathbf{f}_3)_0^{-1}(\mathbf{f}_3|\hat{H}\mathbf{a})_1. \end{aligned}$$

Note that there is no constant term in the latter expression. In numerical trials on ionization energies of small, closed-shell molecules, the 2ph terms are important in second, but not third order. The bottleneck matrix multiplication in third-order calculations involves the largest block of electron repulsion integrals, those with four virtual-orbital indices. Therefore, omission of third order, 2ph terms may improve efficiency without reducing accuracy for this class of electron binding energies. Diagonal matrix elements of the resulting, partial third-order (P3) self-energy for ionization energies read

$$\begin{aligned} \Sigma^{\text{P3}}(E)_{\text{kk}} &= 0.5 \Sigma_{\text{iab}} \langle ki | ab \rangle (E + \varepsilon_i - \varepsilon_a - \varepsilon_b)^{-1} \\ &\quad \times \langle ab | ki \rangle + 0.5 \Sigma_{\text{aij}} \langle ka | ij \rangle \\ &\quad \times (E + \varepsilon_a - \varepsilon_i - \varepsilon_j)^{-1} W_{\text{kaij}} + 0.5 \Sigma_{\text{aij}} \\ &\quad U_{\text{kaij}}(E) (E + \varepsilon_a - \varepsilon_i - \varepsilon_j)^{-1} \langle ij | ka \rangle, \end{aligned}$$

with the intermediate matrices

$$\begin{aligned} W_{\text{kaij}} &= \langle ka | ij \rangle + 0.5 \Sigma_{\text{bc}} \langle ka | bc \rangle t_{\text{ijbc}}^* \\ &\quad - (1 - P_{\text{ij}}) \Sigma_{\text{bl}} \langle kl | bi \rangle t_{\text{jlab}}^* \end{aligned}$$

$$\begin{aligned} U_{\text{kaij}}(E) &= -0.5 \Sigma_{\text{lm}} \langle ka | lm \rangle (E + \varepsilon_a - \varepsilon_l - \varepsilon_m)^{-1} \\ &\quad \times \langle lm | ij \rangle - (1 - P_{\text{ij}}) \Sigma_{\text{bl}} \langle kb | jl \rangle \\ &\quad \times (E + \varepsilon_b - \varepsilon_j - \varepsilon_l)^{-1} \langle al | bi \rangle. \end{aligned}$$

(A spin-orbital permutation operator is denoted by  $P_{\text{ij}}$ .) Correlation effects are represented in the second and third terms of the  $W_{\text{kaij}}$  intermediate, which arises from the superoperator Hamiltonian's coupling between simple field ( $a_k$ ) and 2hp ( $a^\dagger_a a_i a_j$ ) operators and first-order, perturbative corrections to the



reference-state's two-electron density matrix. Ladder and ring terms are generated, respectively, by the first and second terms in the  $U$  intermediate. The bottleneck contraction for the calculation of diagonal, P3 self-energy matrix elements occurs in the second term of the  $W$  intermediate. This is the only term in which electron repulsion integrals with three virtual-orbital indices appear. No integrals with four virtual-orbital indices are needed. For ionization energies of closed-shell molecules, P3 results produce root-mean-square errors that are slightly smaller than those of the OVGf methods. Similar self-energy formulas with a reversal of roles between occupied and virtual orbital indices pertain to electron attachment energies. An extension of the P3 self-energy, known as P3+,<sup>38</sup> produces accurate electron detachment energies of small, closed-shell anions and applies the  $(1 + X_r^{2ph})^{-1}$  scaling factor of the OVGf B approximation to the  $U$  intermediate and to the second and third terms of the  $W$  intermediate.

Diagonal self-energy approximations that are based on perturbative corrections to canonical, Hartree–Fock orbital energies have been widely used for calculating the lowest ionization energies and largest electron affinities of molecules and for calculating the lowest electron detachment energies of anions. In these cases, the effects of final-state orbital relaxation and electron correlation have similar magnitudes. Relaxation and correlation terms in the self-energy may be identified systematically.<sup>39</sup> However, for ionization energies of core levels, relaxation effects are considerably larger and dominate the corrections that must be made to the results of Koopmans's theorem. The second-order, third-order, OVGf, P3, and P3+ methods discussed above generally fail to produce predictions for core ionization energies that are appreciably more accurate than canonical, Hartree–Fock orbital energies.

To tackle such cases, the transition operator method (TOM)<sup>40</sup> has been employed to generate an orbital whose energy recovers large relaxation effects and which offers an improved reference for diagonal, perturbative self-energy calculations. TOM self-consistent field calculations are based on a Fock matrix that depends on spin-orbital occupation numbers:

$$F_{rs}^{\text{TOM}} = h_{rs} + \sum_t \langle rt | st \rangle n_t.$$

In the usual Hartree–Fock equations, spin-orbital occupation numbers are unity or zero for occupied and virtual orbitals, respectively. This choice is modified

for a single spin-orbital, that has an occupation number of 0.5. The resulting spin-orbital's energy provides an excellent approximation to  $\Delta$ SCF, differences of self-consistent field results for core and outer-valence electron binding energies.

To accommodate this transition spin-orbital and its energy, reference density matrices may be chosen to correspond to ensembles instead of pure states.<sup>41–43</sup> Grand-canonical Hartree–Fock (GCHF) theory,<sup>44</sup> which permits spin-orbital occupation numbers between zero and unity, provides such flexibility. The resulting density matrices, when used with general expressions for superoperator Hamiltonian matrix elements between  $a$  and  $f_3$  operators, produce the following, generalized form of the second-order self-energy matrix:

$$\begin{aligned} \Sigma^{(\text{TOEP2})}(E)_{pq} = & 0.5 \sum_{\text{aij}} \langle pa | ij \rangle (E + \varepsilon_a - \varepsilon_i - \varepsilon_j)^{-1} \\ & \times \langle ij | qa \rangle n_i n_j (1 - n_a) + 0.5 \sum_{\text{iab}} \\ & \times \langle pi | ab \rangle (E + \varepsilon_i - \varepsilon_a - \varepsilon_b)^{-1} \\ & \times \langle ab | qi \rangle (1 - n_a)(1 - n_b) n_i. \end{aligned}$$

(TOEP2 stands for transition-operator, second-order electron propagator.) Summations in the latter equation refer to spin orbitals obtained from a single GCHF calculation. For each final state, a separate GCHF calculation is performed with a single spin orbital that has an occupation number of 0.5. In diagonal self-energy calculations that are based on TOM spin orbitals, the same, simplified form of the inverse Dyson equation is employed, where

$$E = \varepsilon_p^{\text{TOM}} + \Sigma_{pp}^{(\text{TOEP2})}(E).$$

TOEP2 results provide improvements to TOM orbital energies that reduce average absolute errors to about 1 eV. For valence ionization energies of closed-shell molecules, TOEP2 performs much better than diagonal, second-order theory based on ordinary Hartree–Fock orbitals. Average absolute errors are approximately 0.35 eV. The TOEP2 method therefore provides a useful description of core and outer-valence ionization energies.

## Renormalized methods

Renormalized methods procure self-energy terms in all orders of the fluctuation potential by considering the eigenvalues and eigenvectors of the superoperator Hamiltonian matrix, where  $\hat{H}\Omega = \Omega\omega$ . For example, in the two-particle-one-hole Tamm–Dancoff approximation (2ph TDA),<sup>2,4</sup> the self-energy is based on the following choices for superoperator matrix elements

that involve  $\mathbf{a}$  and  $\mathbf{f}_3$  operators:

$$\Sigma^{2\text{ph TDA}}(E) = (\mathbf{a}|\hat{H}\mathbf{f}_3)_1(\mathbf{f}_3|(E\hat{I} - \hat{H})\mathbf{f}_3)_1^{-1}(\mathbf{f}_3|\hat{H}\mathbf{a})_1.$$

Expansion of the inverse matrix about its zeroth-order part sufficed above to produce third-order ring and ladder terms. Retention of the entire inverse matrix generates ring and ladder terms in all orders and also produces mixed ring-ladder terms starting in fourth order. Solving the Dyson equation for its poles and residues with this self-energy approximation is equivalent to diagonalizing  $\hat{H}$  such that the operator manifold is restricted to  $\mathbf{a}$  and  $\mathbf{f}_3$  with all matrix elements being evaluated in first order. For typical closed-shell molecules, there will be several ionization energies for which the pole strength,

$$P_n = \sum_r |\Omega_{rn}|^2,$$

where  $\Omega_{rn}$  is the element pertaining to spin-orbital  $r$  in the  $n$ th eigenvector of  $\hat{H}$ , is close to unity. In these cases, the Koopmans description of final states may retain its qualitative validity, provided that a single  $\Omega_{rn}$  element is dominant. However, for many more states, the more numerous  $\mathbf{f}_3$  components of their eigenvectors make the largest contributions to the norm,  $\Omega^\dagger\Omega = 1$ . When 2hp components dominate in this way, the final state is said to be a shake-up, or a correlation state, with no Koopmans counterpart. Couplings between 2hp operators in the  $\mathbf{f}_3$  manifold and inner-valence orbitals in the  $\mathbf{a}$  manifold are generally so strong that the Koopmans picture of final states is obliterated, with many low pole strengths distributed over the ionization energy spectrum above 25 eV. This breakdown of the simple molecular-orbital picture for higher valence ionization energies typifies photoelectron spectra of closed-shell molecules.<sup>45</sup> The 2ph TDA self-energy is capable of producing a qualitatively reasonable description of this effect. Its first-order treatment of  $\hat{H}$  yields a matrix with  $h + 2\text{hp}$  and  $p + 2\text{ph}$  configuration interaction blocks that are coupled through nonzero matrix elements between  $p$  and 2hp operators and between  $h$  and 2ph operators. (First-order matrix elements between 2hp and 2ph operators vanish.) Therefore, the 2ph TDA improves, respectively, on  $h + 2\text{hp}$  and  $p + 2\text{ph}$  configuration interaction treatments of final states pertaining to electron detachment and attachment energies with a correlated description of the reference state's energy.

The 2ph TDA does not suffice to generate all third-order terms in the self-energy and is not capable of accurate predictions of outer-valence ionization energies. To recover all of these terms through improvements to  $\hat{H}$ , the  $(\mathbf{a}|\hat{H}\mathbf{a})$  block must be correct through

third order and the  $(\mathbf{a}|\hat{H}\mathbf{f}_3)$  and  $(\mathbf{f}_3|\hat{H}\mathbf{a})$  blocks must be correct through second order. The corresponding 3+ self-energy has constant and energy-dependent parts:

$$\begin{aligned}\Sigma^{(3+)}(E) &= \Sigma^{(3)}(\infty) + \sigma^{3+}(E) \\ &= \Sigma^{(3)}(\infty) + [(\mathbf{f}_3|\hat{H}\mathbf{a})_1 + (\mathbf{a}|\hat{H}\mathbf{f}_3)_2] \\ &\quad \times (\mathbf{f}_3|(E\hat{I} - \hat{H})\mathbf{f}_3)_1^{-1}[(\mathbf{f}_3|\hat{H}\mathbf{a})_1 + (\mathbf{a}|\hat{H}\mathbf{f}_3)_2].\end{aligned}$$

As in the 2ph TDA, ring, ladder, and mixed ring-ladder terms are retained in all orders of the fluctuation potential in the 3+ approximation and, therefore, a qualitatively reasonable description of correlation states is conserved. In addition, the second-order description of couplings between the  $\mathbf{a}$  and  $\mathbf{f}_3$  operator manifolds that is necessary for accurate treatment of valence electron binding energies is present.

Several attempts at improving the 3+ self-energy focus on the constant term, which depends on the reference state's one-electron density matrix. By extending the argument of the electron propagator matrix into the complex plane, such that

$$\begin{aligned}G_{rs}(E) &= \lim_{\eta \rightarrow 0} [\sum_n U_{nr}^* U_{ns}(E - D_n - i\eta)^{-1} \\ &\quad + \sum_m V_{ms}^* V_{mr}(E - A_m + i\eta)^{-1}],\end{aligned}$$

one may express this density matrix as

$$\rho = (1/2\pi i) \int_C \mathbf{G}(E) dE,$$

where the  $C$  contour encloses all electron detachment poles but no electron attachment poles. A series expansion for  $\mathbf{G}(E)$  may be obtained by inverting both sides of the inverse Dyson equation

$$[\mathbf{G}^{-1}(E)]^{-1} = [\mathbf{G}_0^{-1}(E) - \Sigma(E)]^{-1},$$

so that

$$\begin{aligned}\mathbf{G}(E) &= \mathbf{G}_0(E) + \mathbf{G}_0(E)\Sigma(E)\mathbf{G}_0(E) \\ &\quad + \mathbf{G}_0(E)\Sigma(E)\mathbf{G}_0(E)\Sigma(E)\mathbf{G}_0(E) + \dots \\ &= \mathbf{G}_0(E) + \mathbf{G}_0(E)\Sigma(E)\mathbf{G}(E).\end{aligned}$$

After making the approximation

$$\rho = (1/2\pi i) \int_C [\mathbf{G}_0(E) + \mathbf{G}_0(E)\Sigma(E)\mathbf{G}_0(E)] dE$$

where  $\Sigma(E)$  is approximated according to

$$\Sigma(E) = \Sigma(\infty) + \sigma^{3+}(E),$$

**TABLE 1** |  $\hat{H}$  Matrix Elements in ADC(4)

$\hat{H}_{XY}$	$Y = a$	$Y = f_3$	$Y = f_5$
$X = a$	4	3	2
$X = f_3$	3	2	1
$X = f_5$	2	1	0

one may recover all contributions to  $\rho$  through third order in the fluctuation potential.<sup>5,46</sup> Therefore, the constant contribution to the self-energy matrix is correct through fourth order. Many higher-order terms in  $\rho$  also are included in this scheme, which includes a renormalized, energy-dependent self-energy matrix that is correct through third order and an energy-independent self-energy matrix that is correct through fourth order. This approximation is known as the third-order, algebraic, diagrammatic construction, or ADC(3),<sup>4</sup> although other similar schemes for the determination of the constant part of the self-energy matrix have been associated with the same name. ADC(3) calculations on outer-valence ionization energies of closed-shell molecules produce root-mean-square errors of approximately 0.3 eV.

Renormalized self-energies that are correct through fourth order require introduction of the  $f_5$  operator manifold. In addition,  $\hat{H}_{XY}$  matrix elements must be calculated through the orders in the fluctuation potential that are shown in Table 1. A similar approach to calculating the constant part of the self-energy matrix through fifth order is adopted in the ADC(4) method.<sup>47</sup>

Another approach to renormalized self-energies employs the asymmetric superoperator metric that was invoked in the derivation of the P3 method. Only first-order perturbative corrections to the Hartree–Fock determinant are needed in computing reference-state density matrices. In calculations on electron detachment energies, superoperator matrix elements are evaluated through the orders shown in Table 2.<sup>38</sup>

Electron binding energies are obtained as eigenvalues of the matrix  $\frac{1}{2}(\hat{H} + \hat{H}^\dagger)$ . This approximation recovers all self-energy terms that occur in the P3 method and also includes 2hp ring and ladder terms in all orders. Because of the latter renormalization and the recovery of all second-order terms, this method has been designated the renormalized, second-order method or NR2. It has proven to be an efficient means of describing outer-valence electron detachment energies and correlation states when large basis sets are required.<sup>48</sup>

**TABLE 2** |  $\hat{H}$  Matrix Elements in NR2

$\hat{H}_{XY}$	$Y = 1h$	$Y = 1p$	$Y = 2hp$	$Y = 2ph$
$X = 1h$	0	0	2	1
$X = 1p$	0	0	1	1
$X = 2hp$	1	1	1	0
$X = 2ph$	1	1	0	0

**TABLE 3** |  $\hat{H}$  Matrix Elements in BD-T1

$\hat{H}_{XY}$	$Y = 1h$	$Y = 1p$	$Y = 2hp$	$Y = 2ph$
$X = 1h$	0	1	2	2
$X = 1p$	1	0	2	2
$X = 2hp$	1	1	2	2
$X = 2ph$	1	1	2	2

Additional renormalizations may be incorporated through the use of Brueckner orbitals and double substitution amplitudes that are produced in a Brueckner-doubles, coupled-cluster calculation.<sup>49</sup> The resulting superoperator metric becomes  $(\mu|\nu) = \langle \text{Brueckner} | [\mu, \nu]_+ \exp(T_2) | \text{Brueckner} \rangle$ , where the Brueckner determinant now defines the set of occupied spin-orbitals. In this basis, the primary-space superoperator (i.e., Fock operator) couplings between occupied and virtual spin-orbitals no longer vanish, even in the semicanonical basis that diagonalizes the Fock operator in the occupied-occupied and virtual-virtual blocks. The  $T_2$  amplitudes occur in formulas for the primary-secondary and secondary-secondary blocks so that the  $\hat{H}$  matrix now has the structure shown in Table 3.

The first Brueckner-doubles, triple field-operator method (BD-T1)<sup>6,50–54</sup> neglects the 2hp–2ph couplings that appear first in second order and, as in the NR2 method, obtains electron binding energies through diagonalization of a Hermitized matrix. The BD-T1 method has proven to be remarkably versatile. Average errors for valence ionization energies of small, closed-shell molecules are less than 0.2 eV. Electron detachment energies of small, closed-shell anions are accurate to within 0.1 eV. Core ionization energies have average errors of less than 1 eV. Even ionization energies of molecules with large diradical character have been accurately calculated with the BD-T1 method.

Several methods for obtaining a small number of the eigenvalues and eigenvectors of large, symmetric matrices have been successfully employed in

renormalized calculations. Davidson's method<sup>55</sup> was originally developed for configuration interaction calculations where only the lowest eigenvalues are needed. However, this strategy was successfully applied to valence electron binding energies that lie in the middle of the eigenvalue spectrum of  $\hat{H}$ .<sup>26,27</sup> Lanczos methods for obtaining eigenvalues and eigenvectors also have been implemented in 2ph-TDA and ADC(3) calculations.<sup>56</sup>

## Total Energies and Energy Gradients

Just as it is possible to express the one-electron density matrix in terms of a contour integral that involves the electron propagator matrix, a total energy of the reference state may be expressed in a similar way:

$$\langle H \rangle = \text{Tr}[(4\pi i)^{-1} \int_C (\mathbf{h} + E\mathbf{1})\mathbf{G}(E)dE],$$

where  $\mathbf{h}$  is the matrix of the one-electron (kinetic energy plus nuclear attraction) operator. The unperturbed Hamiltonian of Møller–Plesset theory is related to  $\mathbf{h}$  through

$$\mathbf{h} = \mathbf{H}_0 - \mathbf{v},$$

where  $\mathbf{v}$  is the Coulomb-exchange operator. Perturbative contributions to total energies in order  $n$ , therefore, may be expressed as<sup>57</sup>

$$E^{(n)} = \text{Tr}[(4\pi i)^{-1} \int_C (\mathbf{H}_0 + E\mathbf{1})\mathbf{G}^{(n)}(E)dE] - \text{Tr}[(4\pi i)^{-1} \int_C \mathbf{v}\mathbf{G}^{(n-1)}(E)dE].$$

The zeroth-order propagator matrix, where  $\mathbf{G}_0(E) = \mathbf{G}^{(0)}(E)$ , suffices to evaluate the Hartree–Fock total energy,

$$\begin{aligned} \langle H \rangle_{\text{HF}} &= E^{(0)} + E^{(1)} \\ &= \text{Tr}[(4\pi i)^{-1} \int_C (\mathbf{h} + E\mathbf{1})\mathbf{G}_0(E)dE], \end{aligned}$$

for  $\Sigma^{(1)}(E)$  and  $\mathbf{G}^{(1)}(E)$  vanish. The second-order term in the total energy requires the second-order electron-propagator expression generated by the Dyson equation:

$$\mathbf{G}^{(2)}(E) = \mathbf{G}_0(E) + \mathbf{G}_0(E)\Sigma^{(2)}(E)\mathbf{G}_0(E).$$

[Because  $\Sigma^{(1)}(E)$  vanishes, the second-order term  $\mathbf{G}_0(E)\Sigma^{(1)}(E)\mathbf{G}_0(E)\Sigma^{(1)}(E)\mathbf{G}_0(E)$  also vanishes.] By combining total energies of  $N$ -electron reference states determined in this way (e.g., second-order perturbation theory) with electron binding energies calculated with one of the self-energy approximations discussed above, one may obtain total ener-

gies for states with  $N \pm 1$  electrons that are defined completely in terms of electron propagator concepts.<sup>58–60</sup>

To optimize geometries of such states, gradients of the reference-state energy and of the electron binding energies are needed.<sup>58</sup> The latter may be derived for methods based on Hartree–Fock orbitals by noting that a pole of the electron propagator obeys the relation

$$E_{\text{pole}} = \mathbf{C}^\dagger[\boldsymbol{\epsilon} + \Sigma(E_{\text{pole}})]\mathbf{C}.$$

After differentiating with respect to a one-electron perturbation,  $\alpha$ , one finds that

$$\begin{aligned} E_{\text{pole}}^\alpha &= \mathbf{C}^\dagger \alpha [\boldsymbol{\epsilon} + \Sigma(E_{\text{pole}})]\mathbf{C} + \mathbf{C}^\dagger [\boldsymbol{\epsilon} + \Sigma(E_{\text{pole}})]\mathbf{C}^\alpha \\ &\quad + \mathbf{C}^\dagger [\boldsymbol{\epsilon}^\alpha + \Sigma^\alpha(E_{\text{pole}}) + E_{\text{pole}}^\alpha \boldsymbol{\sigma}'(E)]\mathbf{C} \end{aligned}$$

and consequently that

$$\begin{aligned} E_{\text{pole}}^\alpha [1 - \mathbf{C}^\dagger \boldsymbol{\sigma}'(E)\mathbf{C}] &= \mathbf{C}^\dagger \alpha \mathbf{C} E_{\text{pole}} + \mathbf{C}^\dagger \mathbf{C}^\alpha E_{\text{pole}} \\ &\quad + \mathbf{C}^\dagger [\boldsymbol{\epsilon}^\alpha + \Sigma^\alpha(E_{\text{pole}})]\mathbf{C}. \end{aligned}$$

Because  $\mathbf{C}^\dagger \mathbf{C} = 1$ , the first two terms on the right-hand side of the previous equation vanish, leaving

$$E_{\text{pole}}^\alpha = \mathbf{P}\mathbf{C}^\dagger [\boldsymbol{\epsilon}^\alpha + \Sigma^\alpha(E_{\text{pole}})]\mathbf{C}.$$

Only derivatives of orbital energies, derivatives of self-energy matrix elements, and pole strengths are needed.<sup>60</sup> For renormalized methods, where poles are obtained as eigenvalues of the superoperator Hamiltonian matrix such that  $\hat{H}\Omega = \Omega E_{\text{pole}}$  and  $\Omega^\dagger \Omega = 1$ , the energy gradients are obtained from

$$E_{\text{pole}}^\alpha = \Omega^\dagger \hat{H}^\alpha \Omega.$$

## SURVEY OF RECENT APPLICATIONS

Various diagonal, self-energy approximations such as OVGf and P3 have been implemented in the Gaussian program suites (see [www.gaussian.com](http://www.gaussian.com) and [www.auburn.edu/cosam/JVOrtiz](http://www.auburn.edu/cosam/JVOrtiz) for more information) by V. G. Zakrzewski and the author since the 1994 version.

Many applications of *ab initio* electron propagator methods to neutral and anionic carbon clusters, fullerenes, porphyrins, phthalocyanines, nucleic acid fragments, polycyclic aromatic hydrocarbons, organometallics, and other organic compounds have been reported and reviewed recently by the author

and his collaborators.<sup>61–93</sup> In collaboration with Martínez and coworkers<sup>94–102</sup> and Zein<sup>103,104</sup> photoelectron spectra of metal-oxide clusters anions have been assigned and patterns of electronic structure and reactivity have been analyzed with the aid of Dyson orbitals. Unusual patterns of bonding and spectra in double Rydberg anions, multiply-charged anions and diffusely bound anions have been predicted and interpreted.<sup>105–113</sup> Relationships between electron binding energies, Dyson orbitals, and transport along molecular wires have been established in collaboration with Dahnovsky and coworkers.<sup>114–118</sup> Qualitatively important effects of aqueous solvation on the electronic structure of halide solutions have been demonstrated with the aid of solvent modeling performed by Canuto and coworkers.<sup>119,120</sup> In Seabra et al.,<sup>121,122</sup> Dyson orbitals have been used to calculate photoionization intensities and angular dependencies with transition operators that surpass the dipole approximation. In Martín and coworkers,<sup>123–125</sup> electron propagator calculations on the Rydberg states of small radicals have provided quantum defects that may be used to determine photoionization intensities as a function of photon energy.

Deleuze et al. have made extensive use of electron propagator methods in studies of the electron binding energies of carbon clusters<sup>126–128</sup> and polycyclic aromatic hydrocarbons.<sup>33,129,130</sup> The same techniques have been applied successfully to electron momentum spectra.<sup>131–135</sup> Ohno and coworkers<sup>136–138</sup> have combined Penning ionization experiments with electron propagator calculations to obtain novel insights into chemical bonding.

Close et al.<sup>139–142</sup> have employed the P3 approximation to determine electron binding energies of isolated and microhydrated nucleic-acid bases, nucleotides, and amino acids.

Pérez-González and Galano<sup>143</sup> have related P3 predictions of ionization energies to the propensity of edaravone derivatives to scavenge free radicals.

Mishra and coworkers have applied several electron propagator approximations to the study of nitrogen-rich anionic rings,<sup>144,145</sup> interactions between functional groups in cyclic compounds<sup>146–148</sup> and tautomers of nucleic-acid bases.<sup>149</sup>

Boldyrev and coworkers' interpretations of anion photoelectron spectra by Wang and coworkers have disclosed the existence of several novel patterns of chemical bonding, including aromaticity in metallic clusters, planar tetracoordination by carbon, and superhalogenic electron affinities.<sup>150–155</sup> In this work, routine use is made of electron propagator methods in the assignment of these spectra and in the qualitative interpretation of chemical bonding.

Trofimov and coworkers have employed the OVGf and ADC(3) methods to advantage in studies of vibronic structure in photoelectron spectra,<sup>156</sup> electron momentum spectroscopy of saturated hydrocarbons,<sup>157</sup> photoelectron spectra of substituted organic compounds,<sup>158,159</sup> purines and pyrimidines,<sup>160–163</sup> and donor–acceptor relationships in silatranes.<sup>164</sup>

## EMERGING TECHNIQUES

The generalized formulas for BD-T1  $\hat{H}$  matrix elements that are based on a semicanonical set of reference spin orbitals (i.e., those that diagonalize the occupied–occupied and virtual–virtual blocks of the Fock matrix) also are suitable for use with Kohn–Sham orbitals. The performance of several renormalized self-energies that include ring and ladder terms has been evaluated with Kohn–Sham orbitals generated with several density functionals.<sup>165</sup>

Improved virtual orbitals for electron propagator calculations may be obtained by retaining only some of the eigenvectors of the virtual–virtual block of the density-difference matrix for a second-order, diagonal self-energy calculation.<sup>166,167</sup> The latter matrix is an intermediate that is formed in the evaluation of gradients of electron binding energies.<sup>58–60</sup> For calculations on large molecules, 50% reductions in the dimension of the virtual orbital space produce only minor discrepancies with regular calculations.

Resolution-of-the-identity techniques show considerable promise for improving the efficiency of electron propagator calculations.<sup>168,169</sup> A related approach which employs the Cholesky decomposition of the matrix of the two-electron repulsion operator also has appeared.<sup>170</sup>

Links between concepts of electron propagator theory, especially Dyson orbitals, and those of density-functional theory, such as Fukui functions, have been examined recently.<sup>171</sup>

## CONCLUSIONS

The electron propagator's structure of poles and residues provides a computationally powerful and conceptually concise approach to interpreting molecular spectra and chemical bonding. In electron propagator theory, relationships between electron binding energies, Dyson orbitals, one-electron properties, and total energies are simple to state and provide convenient generalizations of concepts that arise naturally in one-electron theories. The association of electron

binding energies to Dyson orbitals and pole strengths is an especially flexible interpretive tool.

Relaxation and correlation effects may be described by systematic improvements to the self-energy or superoperator Hamiltonian matrices. Diagonal self-energy approximations that are based on low-order terms provide an efficient and accurate means to predicting the smallest electron detachment energies and the largest electron affinities of molecular species. Extensions of these concepts that account for large orbital-relaxation effects in final states enable consideration of core binding energies. Renormalized methods that are somewhat less efficient are capable of describing complex correlation effects in

the inner-valence region where Koopmans final states are no longer discernible. They also offer an accurate depiction of valence electron binding energies. By employing renormalized reference states, it is possible to produce versatile methods that are applicable in all energy regions from core ionization energies to electron affinities. Total energies may be generated from the electron propagator by performing contour integrations in the complex plane that include all electron-detachment poles. By combining reference-state total energies with electron binding energies, it is possible to obtain final-state total energies that may be optimized with the aid of corresponding gradients.

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