



Electron Propagator Theory: Foundations and Predictions

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Abstract

Electron propagator theory is an efficient means to accurately calculating electron binding energies and associated Dyson orbitals that is systematically improvable and easily interpreted in terms of familiar concepts of valence theory. After a brief discussion of the physical meaning of the poles and residues of the electron propagator, the Dyson quasiparticle equation is derived. Practical approximations of the self-energy operator in common use are defined in terms of the elements of the Hermitian superoperator Hamiltonian matrix. Methods that retain select self-energy terms in all orders of the fluctuation potential include the two-particle-one-hole Tamm–Dancoff approximation, the renormalized third-order method, the third-order algebraic diagrammatic construction, and the renormalized, nondiagonal second-order approximation. Methods based on diagonal second-order and third-order elements of the self-energy matrix, such as the diagonal second-order, diagonal third-order, outer valence Green's function, partial third-order, and renormalized partial third-order approximations, provide efficient alternatives. Recent numerical tests on valence, vertical ionization energies of representative, small molecules, and a comparison of arithmetic and memory requirements provide guidance to users of electron propagator software. A survey of recent applications and extensions illustrates the versatility and interpretive power of electron propagator methodology.



1. INTRODUCTION

Two historical missions have been the constant companions of the field in which Per-Olov Löwdin exercised lasting influence, quantum chemistry. The first is the fulfillment of a reductionist project: to determine molecular properties solely from fundamental constants and equations of physics. The derivation of approximate methods, the design of efficient algorithms and their adaptation to modern computing platforms, and numerical testing of the accuracy of calculations thus enabled are means to producing tools for the prediction of molecular properties. Steady advances on all of these fronts have made quantum chemistry an indispensable part of a chemist's education and have enabled the emergence of a new specialty, computational chemistry. The capabilities of the latter field are especially valuable when competing experimental techniques are costly, unsafe, or slow. These advantages notwithstanding, quantum chemistry is not merely a branch of contemporary computational chemistry because of the former field's second historical mission. As the modern successor of valence theory, quantum chemistry continues to generate concepts of chemical bonding that inform the thinking of specialists who synthesize or characterize new or important forms of matter. These concepts enable the recognition and understanding of patterns of structure, energetics, reactivity, and physical properties and therefore stimulate the formulation and execution of renewed experimental activity. They also inform the education of the next generation of scientists.

There is an inherent tension between these two aspirations. Fulfillment of the first mission inevitably leads to wave function Ansätze, perturbative arguments, density functionals, and parametrization schemes of increasing complexity. Concepts that are products of the second mission, to have any purchase on the minds of experimentalists, must be general and verifiable. Accurate predictions are a necessary condition for influence. However, if such data are not clearly interpreted or if they fail to provide an insight into related systems, their significance may be limited. Qualitative theories based on relatively simple concepts have promoted the recognition of broad patterns of chemical phenomena, but their rigorous numerical realization often leads to inaccurate predictions that undermine their authority.

Theories that are systematically improvable and that generate qualitative concepts with a rigorous foundation therefore have inherent advantages. One such approach to quantum chemistry is based on electron propagator (or one-electron Green's function) theory.¹⁻⁸ An additional advantage arises

from relevance to experiments that have been prominent in the development of quantum theory from its inception: measurements of electron binding energies. Finally, there are advantages of computational economy that are related to the conceptual elegance of the propagator approach to spectra. All of these features of electron propagator theory are related to the Dyson quasiparticle equation, wherein a nonlocal, energy-dependent operator has eigenvalues that are, in principle, exact electron binding energies and corresponding eigenfunctions known as Dyson orbitals that describe how electronic structure changes when an electron is removed or added.

In this review, some fundamental aspects of electron propagator theory's realization in the context of quantum chemistry are discussed. A derivation of the Dyson quasiparticle equation that employs some of Löwdin's most useful concepts and some prominent approximation schemes are presented. Finally, numerical tests that demonstrate the advantages of electron propagator methods for the computational chemist and some recent applications are discussed.



2. POLES AND RESIDUES OF THE ELECTRON PROPAGATOR

The exact electron propagator suffices to determine the electron binding energies, Dyson orbitals, one-electron properties, and total energy of an N -electron system.^{1,5} Let $(\chi_r, \chi_s, \chi_t, \chi_u, \dots)$ be a set of orthonormal spin-orbitals where the corresponding field operators obey the following relationships:

$$\begin{aligned} [a_r^\dagger, a_s^\dagger]_+ &= [a_r, a_s]_+ = 0 \\ [a_r^\dagger, a_s]_+ &= \delta_{rs}. \end{aligned}$$

In this notation, the second-quantized Hamiltonian is given by

$$H = \sum_{rs} h_{rs} a_r^\dagger a_s + \frac{1}{4} \sum_{rstu} \langle rs || ut \rangle a_r^\dagger a_s^\dagger a_t a_u,$$

where \mathbf{h} is the matrix of the one-electron operator and where antisymmetrized two-electron integrals in Dirac notation, such that

$$\begin{aligned} \langle rs || ut \rangle &= \langle rs | ut \rangle - \langle rs | tu \rangle \\ \langle rs | tu \rangle &= \int \chi_r^*(1) \chi_s^*(2) g(1, 2) \chi_t(1) \chi_u(2) d(1) d(2), \end{aligned}$$

appear in the last term. Solutions of the Schrödinger equation read

$$H|N, 0\rangle = E_0(N)|N, 0\rangle$$

for the initial, N -electron, ground state and

$$H|N + 1, m\rangle = E_m(N + 1)|N + 1, m\rangle$$

$$H|N - 1, n\rangle = E_n(N - 1)|N - 1, n\rangle$$

for final states with $N \pm 1$ electrons. Elements of the electron propagator matrix, $\mathbf{G}(E)$, are expressed as

$$G_{rs}(E) = \sum_m V_{rm} V_{sm}^* (E - A_m)^{-1} + \sum_n U_{rn}^* U_{sn} (E - D_n)^{-1},$$

where A_m is the m -th electron attachment energy, $E_m(N + 1) - E_0(N)$, D_n is the n -th electron detachment energy, $E_0(N) - E_n(N - 1)$, and where the overlap amplitudes are given by

$$V_{rm} = \langle N + 1, m | a_r^\dagger | N, 0 \rangle$$

$$U_{sn} = \langle N - 1, n | a_s | N, 0 \rangle.$$

Dyson orbitals for electron attachment and detachment which read

$$\begin{aligned} \phi_m(x_1) &= (N + 1)^{1/2} \int dx_2 dx_3 dx_4 \dots dx_{N+1} \Psi_{N+1, m}(x_1, x_2, x_3, \dots, x_{N+1}) \\ &\quad \times \Psi_{N, 0}(x_2, x_3, x_4, \dots, x_{N+1}) \end{aligned}$$

$$\begin{aligned} \phi_n(x_1) &= (N)^{1/2} \int dx_2 dx_3 dx_4 \dots dx_N \Psi_{N, 0}(x_1, x_2, x_3, \dots, x_N) \\ &\quad \times \Psi_{N-1, n}(x_2, x_3, x_4, \dots, x_N) \end{aligned}$$

are related to the overlap amplitudes through

$$\phi_m(x_1) = \sum_r V_{rm}^* \chi_r(x_1)$$

$$\phi_n(x_1) = \sum_r U_{rn} \chi_r(x_1).$$

Whereas the poles of the electron propagator equal electron binding energies, the corresponding residues are related to Dyson orbitals.



3. DERIVATION OF THE DYSON QUASIPARTICLE EQUATION

A generalized notation for propagators with field operators or field operator products that change the number of electrons by one, designated by μ^\dagger and ν , may be introduced such that

$$\langle\langle \mu^\dagger; \nu \rangle\rangle = \sum_m V'_{\mu m} V'^*_{\nu m} (E - A_m)^{-1} + \sum_n U'_{\mu n} U'^*_{\nu n} (E - D_n)^{-1}$$

$$V'_{\mu m} = \langle N + 1, m | \mu^\dagger | N, 0 \rangle$$

$$U'_{\nu n} = \langle N - 1, n | \nu | N, 0 \rangle.$$

In this notation,

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

A generalized propagator defined in terms of μ^\dagger and ν may be related to a more complicated propagator through

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

Let a binary product and an accompanying metric matrix for the operators be defined by

$$(\mu | \nu) = \langle N, 0 | [\mu^\dagger, \nu]_+ | N, 0 \rangle = \text{Tr}(\rho [\mu^\dagger, \nu]_+),$$

where

$$\rho = |N, 0\rangle \langle N, 0|.$$

(In his lectures for aspiring quantum chemists, Löwdin often discussed the axioms, such as Hermitian symmetry, that a binary product must satisfy.)⁹ Hamiltonian and identity superoperators^{7,10} then may be defined by

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

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

A chain of propagators may be generated, where for example

$$\begin{aligned} E\langle\langle a_r^\dagger; a_s \rangle\rangle &= \langle N, 0 | [a_r^\dagger, a_s]_+ | N, 0 \rangle + \langle\langle a_r^\dagger; [a_s, H] \rangle\rangle \\ &= (a_r | a_s) + \langle\langle a_r^\dagger; \hat{H}a_s \rangle\rangle \\ E\langle\langle a_r^\dagger; \hat{H}a_s \rangle\rangle &= \langle N, 0 | [a_r^\dagger, \hat{H}a_s]_+ | N, 0 \rangle + \langle\langle a_r^\dagger; [[a_s, H], H] \rangle\rangle \\ &= (a_r | \hat{H}a_s) + \langle\langle a_r^\dagger; \hat{H}^2 a_s \rangle\rangle \\ E\langle\langle a_r^\dagger; \hat{H}^\xi a_s \rangle\rangle &= \langle N, 0 | [a_r^\dagger, \hat{H}^\xi a_s]_+ | N, 0 \rangle + \langle\langle a_r^\dagger; [\hat{H}^\xi a_s, H] \rangle\rangle \\ &= (a_r | \hat{H}^\xi a_s) + \langle\langle a_r^\dagger; \hat{H}^{\xi+1} a_s \rangle\rangle. \end{aligned}$$

The electron propagator therefore may be written as a series, where

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

or in terms of the superoperator resolvent, $(E\hat{I} - \hat{H})^{-1}$, such that

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

A projection technique discussed by Löwdin¹¹ may be used to replace the superoperator resolvent by an inverse matrix expressed in a complete manifold of operators, \mathbf{w} , such that

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

This substitution yields the following form of the electron propagator matrix:

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

where \mathbf{a} is a column vector of annihilation operators. The operator manifold, \mathbf{w} , may be partitioned into a primary space of simple field operators, \mathbf{a} , and an orthogonal, secondary space with higher field operator products, \mathbf{f} , where

$$\begin{aligned} |\mathbf{w}\rangle &= |\mathbf{a}; \mathbf{f}\rangle, \\ (\mathbf{a}|\mathbf{a}) &= \mathbf{1}_a, (\mathbf{a}|\mathbf{f}) = \mathbf{0}_{a \times f}, (\mathbf{f}|\mathbf{a}) = \mathbf{0}_{f \times a}, (\mathbf{f}|\mathbf{f}) = \mathbf{1}_f. \end{aligned}$$

After partitioning,

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

Only the upper left block of the inverse matrix is needed because of the orthogonalization of the primary and secondary operator spaces. Now let $\hat{\mathbf{H}} = (\mathbf{a}; \mathbf{f} | \hat{H} \mathbf{a}; \mathbf{f})$. After solving the Hermitian eigenvalue equation,

$$\hat{\mathbf{H}}\mathbf{\Omega} = \mathbf{\Omega}\boldsymbol{\omega},$$

the electron propagator matrix reads

$$\mathbf{G}(E) = [\mathbf{1}_a \mathbf{0}_{a \times f}] [\mathbf{\Omega}(E\mathbf{1} - \boldsymbol{\omega})^{-1} \mathbf{\Omega}^\dagger] [\mathbf{1}_a \mathbf{0}_{a \times f}]^\dagger.$$

For electron detachment and attachment energies, $\omega_n = D_n$ and $\omega_m = A_m$, respectively. The elements of $\mathbf{\Omega}$ from the primary operator space provide the residues, where $\Omega_{sm} = V_{sm}$ and $\Omega_{sn} = U_{sn}$. Solving for the upper left block of $(\mathbf{a}; \mathbf{f} | (\hat{E}\mathbf{1} - \hat{H}) \mathbf{a}; \mathbf{f})^{-1}$ yields

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

For orthogonalized operator spaces,

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

Because the first term in the inverse matrix involves a generalized Fock operator, F , where

$$(\mathbf{a}_s | \hat{H} \mathbf{a}_r) = h_{rs} + \sum_{tu} \langle \mathbf{r} \mathbf{t} | \mathbf{s} \mathbf{u} \rangle \langle \mathbf{N}, 0 | \mathbf{a}_t^\dagger \mathbf{a}_u | \mathbf{N}, 0 \rangle = F_{rs},$$

the inverse of the electron propagator matrix may be written as follows:

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

A reference electron propagator, G_0 , whose poles and residues are defined by eigenvalues and eigenfunctions of a Hermitian one-electron operator, H_0 , may be expressed as

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

The reference and exact electron propagators therefore may be related to each other by

$$\mathbf{G}^{-1}(\mathbf{E}) = \mathbf{G}_0^{-1}(\mathbf{E}) - (\mathbf{F}^t - \mathbf{H}_0) - (\mathbf{a}|\hat{\mathbf{H}}\mathbf{f})(\mathbf{f}|(\mathbf{E}\hat{\mathbf{I}} - \hat{\mathbf{H}})\mathbf{f})^{-1}(\mathbf{f}|\hat{\mathbf{H}}\mathbf{a}).$$

The second and third terms are, respectively, the energy-independent and energy-dependent parts of the self-energy matrix, $\mathbf{\Sigma}(\mathbf{E})$:

$$\begin{aligned}\mathbf{F}^t - \mathbf{H}_0 &= \mathbf{\Sigma}(\infty) \\ (\mathbf{a}|\hat{\mathbf{H}}\mathbf{f})(\mathbf{f}|(\mathbf{E}\hat{\mathbf{I}} - \hat{\mathbf{H}})\mathbf{f})^{-1}(\mathbf{f}|\hat{\mathbf{H}}\mathbf{a}) &= \mathbf{\sigma}(\mathbf{E}) \\ \mathbf{\Sigma}(\infty) + \mathbf{\sigma}(\mathbf{E}) &= \mathbf{\Sigma}(\mathbf{E}).\end{aligned}$$

The energy-independent term is given an argument of ∞ to emphasize that the limit of $\mathbf{\Sigma}(\mathbf{E})$ as $|\mathbf{E}|$ increases without bound is $\mathbf{\Sigma}(\infty)$. The inverse form of the Dyson equation reads

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

The regular form of the Dyson equation is

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

Poles of the electron propagator are values of \mathbf{E} where

$$\det \mathbf{G}^{-1}(\mathbf{E}) = 0.$$

These values correspond to solutions of

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

The latter equation may be solved self-consistently with respect to \mathbf{E} . The energy-dependent, nonlocal $\mathbf{\sigma}(\mathbf{E})$ operator and the one-electron density matrix that determines the Fock operator may be systematically improved until exact electron binding energies result. The energy dependence of the $\mathbf{\sigma}(\mathbf{E})$ operator implies that the number of poles is larger than the dimension of the corresponding matrix. The associated eigenfunctions determined by \mathbf{C} are proportional to the Dyson orbitals. The norm of the Dyson orbital corresponding to the electron detachment energy D_n , known as its pole strength, is given by

$$P_n = \langle \phi_n | \phi_n \rangle = [1 - \mathbf{C}_n^\dagger \mathbf{\sigma}'(\mathbf{E}) \mathbf{C}_n]^{-1},$$

where

$$\sigma'_{rs}(E) = d\sigma_{rs}(E)/dE$$

is evaluated at the n th pole, $E_n = D_n$, and $\mathbf{C}_n^\dagger \mathbf{C}_n = 1$. Valid pole strengths vary between zero and unity. A generalized form of the Dyson quasiparticle equation at self-consistency reads

$$[\mathbf{F} + \sigma(D_n)]\phi_n = D_n\phi_n$$

for electron detachments. For electron attachments, where pole strengths are obtained from

$$P_m = \langle \phi_m | \phi_m \rangle = [1 - \mathbf{C}_m^\dagger \sigma'(E) \mathbf{C}_m]^{-1},$$

the Dyson quasiparticle equation at self-consistency is

$$[\mathbf{F} + \sigma(A_m)]\phi_m = A_m\phi_m.$$



4. APPROXIMATIONS IN THE DYSON QUASIPARTICLE EQUATION

Approximations to the exact \mathbf{F} and $\sigma(E)$ matrices may be defined in terms of the manifold of operators retained in the secondary space, \mathbf{f} , and the reference-state density matrices (ie, ρ density operators) used to evaluate matrix elements of the Hamiltonian superoperator, \hat{H} . The union of all 2hp, 2ph, 3h2p, 3p2h, 4h3p, 4p3h, ... operators (ie, Manne's $\mathbf{f}_3, \mathbf{f}_5, \mathbf{f}_7, \dots, \mathbf{f}_{2N+1}$ operator manifolds) suffices for a complete \mathbf{f} space provided that the defining reference determinant that distinguishes particles (ie, p or virtual orbitals with indices a, b, c, \dots) from holes (ie, h or occupied orbitals with indices i, j, k, \dots) is not orthogonal to the exact reference state, $|N, 0\rangle$.¹² The non-redundant members of the \mathbf{a} , \mathbf{f}_3 , and \mathbf{f}_5 operator manifolds are shown in Table 1. For a complete operator manifold, no improvements over this single determinant are needed in $|N, 0\rangle$ to produce exact eigenvalues of \hat{H} and poles of $\mathbf{G}(E)$. This principle is similar to Löwdin's conclusion that the poles of the resolvent's expectation value, $\langle 0 | (E1 - H)^{-1} | 0 \rangle$, are the same for exact and approximate $|0\rangle$ provided that the approximate reference state is not orthogonal to its exact counterpart.^{11,13,14} Therefore, it is possible to obtain exact poles of $\mathbf{G}(E)$ using an approximate reference state that consists of a single determinant. However, to obtain exact residues of $\mathbf{G}(E)$, the reference state also must be exact.

Table 1 Operator Manifolds

	General Operator	$nh(n-1)p$ Operator	Indices ^a	$np(n-1)h$ Operator	Indices ^a
a	a_p	a_i	i occ	a_a	a vir
f₃	$a_p^\dagger a_q a_r$	$a_a^\dagger a_i a_j$	$i < j$ occ a vir	$a_i^\dagger a_a a_b$	$a < b$ occ i vir
f₅	$a_p^\dagger a_q^\dagger a_r a_s a_t$	$a_a^\dagger a_b^\dagger a_i a_j a_k$	$i < j < k$ occ $a < b$ vir	$a_i^\dagger a_j^\dagger a_a a_b a_c$	$a < b < c$ vir $i < j$ occ

^a i, j, k, l occupied; a, b, c, d virtual.

Improvements over a single-determinant approximation for the reference state may reduce the need for higher \mathbf{f}_w operators and also restore the Hermiticity of $\hat{\mathbf{H}}$, a property which can be lost when approximate choices for $|N, 0\rangle$ are made. A study of the effects of perturbative improvements over Hartree–Fock reference states credits Linderberg with the observation that non-Hermitian terms in $\hat{\mathbf{H}}$ may be expressed as

$$\begin{aligned} (Y|\hat{H}X) - (X|\hat{H}Y)^* &= \text{Tr}(\rho[X, Y^\dagger]_+ H - \rho H[X, Y^\dagger]_+) \\ &= \text{Tr}([H, \rho][X, Y^\dagger]_+), \end{aligned}$$

where ρ is a general density operator.¹⁵ For example, one may choose ρ to be a pure-state density operator: $\rho = |N, 0\rangle\langle N, 0|$. The usual assumptions of perturbation theory, where

$$\begin{aligned} H &= H_0 + \lambda V, \\ [H_0, \rho_0] &= 0 \end{aligned}$$

and

$$\rho = \rho_0 + \lambda \rho_1 + \lambda^2 \rho_2 + \dots,$$

imply that

$$[H_0, \rho_k] + [V, \rho_{k-1}] = 0.$$

If ρ is correct through order n , then the non-Hermitian terms are of order $n+1$:

$$(Y|\hat{H}X) - (X|\hat{H}Y)^* = \text{Tr}([V, \rho_n][X, Y^\dagger]_+).$$

This conclusion also is valid for the polarization propagator, where a commutator replaces the anticommutator in the definition of the superoperator metric.

For all choices of ρ , non-Hermitian terms vanish when X and Y pertain to the primary (\mathbf{a}) operator space, for $\left[a_p^\dagger, a_q \right]_+ = \delta_{pq}$. These terms also equal zero when X is an $nh(n-1)p$ operator and Y is an $n'p(n'-1)h$ operator (where n and $n' = 1, 2, 3, \dots$), as the anticommutator term, $[X, Y^\dagger]_+$, vanishes in such cases.

First-order non-Hermitian terms may appear when ρ is based on a single Slater determinant. When X is an $nh(n-1)p$ operator and Y is an $(n+1)hnp$ operator, the anticommutator yields a combination of single-replacement operators and therefore the non-Hermitian terms vanish through first order only when the reference determinant satisfies Brillouin's condition. For example, the expression

$$\left(a_a^\dagger a_j a_k | \hat{H} a_i \right) - \left(a_i | \hat{H} a_a^\dagger a_j a_k \right) = (1 - P_{jk}) \delta_{ik} F_{aj}$$

is equal to zero when Hartree-Fock orbitals are assumed. (When X is an $np(n-1)h$ operator and Y is an $(n+1)pnh$ operator, the same conclusion is reached.) However, when X is an $nh(n-1)p$ operator and Y is an $(n+2)h(n+1)p$ operator, $[X, Y^\dagger]_+$ becomes a combination of double-replacement operators. Nonvanishing, first-order terms in the $(\mathbf{a} | \hat{H} \mathbf{f}_5)$ matrix therefore appear. For example,

$$\left(a_a^\dagger a_b^\dagger a_j a_k a_l | \hat{H} a_i \right) - \left(a_i | \hat{H} a_a^\dagger a_b^\dagger a_j a_k a_l \right) = (1 - P_{lk} - P_{lj}) \delta_{il} \langle jk || ab \rangle.$$

These terms are cancelled when first-order corrections to ρ are included. The resulting zero matrix is identical to the adjoint of the $(\mathbf{f}_5 | \hat{H} \mathbf{a})$ matrix. Blocks of \hat{H} that are more remote from the diagonal, where $nh(n-1)p$ and $(n+m)h(n+m-1)p$ operators or $np(n-1)h$ and $(n+m)p(n+m-1)h$ operators with $m > 2$ are coupled, have matrix elements that vanish through first order and therefore there are no corresponding non-Hermitian terms. Diagonal blocks pertaining to $nh(n-1)p$ and $np(n-1)h$ operators also have no non-Hermitian terms in first order.

An alternative strategy that originates in equation-of-motion theory³ is to introduce a density operator, derive \hat{H} and solve for eigenvalues of the

Hermitized matrix, $1/2(\hat{\mathbf{H}} + \hat{\mathbf{H}}^\dagger)$. Disconnected terms that may appear in $\hat{\mathbf{H}}$ should be removed before the Hermitization step.

The Manne operator manifold is orthonormal when ρ is obtained from a single determinant. However, when other density operators are employed, the superoperator overlap matrix may no longer be diagonal, ie, $\langle X|Y\rangle \neq \delta_{XY}$. To retain the usual form of $\sigma(E)$ where E-dependence occurs only in the $(\mathbf{f}|(E\hat{\mathbf{I}} - \hat{\mathbf{H}})\mathbf{f})^{-1}$ matrix, orthogonalized secondary operator spaces must be introduced. A convenient technique is to employ a symmetric orthogonalization, where, for example, the operator $a_a^\dagger a_i a_j = f_{aij}$ is replaced by

$$f'_{aij} = a_a^\dagger a_i a_j - \frac{1}{2} \sum_b (a_b | a_a^\dagger a_i a_j) a_b - \frac{1}{2} \sum_{bkl} (a_b^\dagger a_k a_l | a_a^\dagger a_i a_j) a_b^\dagger a_k a_l + \dots$$

Several widely used approximations retain all terms in $\mathbf{F}^t + \sigma(E)$ through a certain order of the fluctuation potential. When Hartree–Fock orbitals are assumed, one-electron density matrix elements, $\langle N, 0 | a_s^\dagger a_s | N, 0 \rangle$ or P_{rs} , have vanishing contributions in first order. Nonzero terms in \mathbf{P} appear in second and higher orders. Therefore, correlation contributions to \mathbf{F} begin in third order,⁴ where for real orbitals

$$\begin{aligned} \Sigma_{pq}^{(3)}(\infty) &= \Sigma_{rs} \langle pr || qs \rangle P_{rs}^{(2)} \\ P_{ij}^{(2)} &= -\frac{1}{2} \sum_{abk} t_{jab}^{(1)} t_{ikab}^{(1)} \\ P_{ab}^{(2)} &= \frac{1}{2} \sum_{ijc} t_{ijac}^{(1)} t_{ijbc}^{(1)} \\ P_{ia}^{(2)} &= (\epsilon_i - \epsilon_a)^{-1} \left[\sum_{jbc} t_{ijbc}^{(1)} \langle bc || aj \rangle + \sum_{jkb} t_{jkab}^{(1)} \langle ib || jk \rangle \right] \\ P_{ai}^{(2)} &= P_{ia}^{(2)} \\ t_{ijab}^{(1)} &= \langle ij || ab \rangle (\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)^{-1}. \end{aligned}$$

Whereas the $P_{ij}^{(2)}$ and $P_{ab}^{(2)}$ terms arise from products of first-order, double-replacement amplitudes, the $P_{ia}^{(2)}$ term involves their second-order, single-replacement counterparts.

For most bases other than the canonical, Hartree–Fock orbitals, F , contains exchange as well as correlation terms. For example, in a canonical, Kohn–Sham basis,

$$\Sigma_{pq}(\infty) = -\Sigma_i \langle pi | iq \rangle - [\nu_{xc}]_{pq} + \Sigma_{rs} \langle pr || qs \rangle (P_{rs} - \delta_{rs} n_r),$$

where matrix elements of the exchange–correlation potential (ν_{xc}) occur in the second-term and spin–orbital occupation numbers, n_r , appear in the last term. The term in parentheses may be set to zero by assuming that the density matrix of the reference determinant is close to exact. In this case, the role of $\Sigma_{pq}(\infty)$ is to recover the usual exchange operator in the Dyson quasiparticle equation.

To define approximate forms of $\sigma(E)$, one may specify \mathbf{f} operator manifolds and the density matrices that are used to evaluate matrix elements of \hat{H} . For example, the two-particle-one-hole Tamm–Dancoff approximation (2ph-TDA)¹⁶ for the self-energy is defined by an operator manifold that includes \mathbf{a} and \mathbf{f}_3 in combination with a Hartree–Fock (ie, zero order) reference state:

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

For the Hartree–Fock reference state, couplings between 2hp and 2ph operators equal zero and enable a separation of $\sigma(E)$ into two terms:

$$\begin{aligned} \sigma^{2ph-TDA}(E) &= (\mathbf{a} | \hat{H} \mathbf{f}_{2hp})_0 (\mathbf{f}_{2hp} | (E\hat{I} - \hat{H}) \mathbf{f}_{2hp})_0^{-1} (\mathbf{f}_{2hp} | \hat{H} \mathbf{a})_0 \\ &\quad + (\mathbf{a} | \hat{H} \mathbf{f}_{2ph})_0 (\mathbf{f}_{2ph} | (E\hat{I} - \hat{H}) \mathbf{f}_{2ph})_0^{-1} (\mathbf{f}_{2ph} | \hat{H} \mathbf{a})_0. \end{aligned}$$

When the usual Møller–Plesset choice for \hat{H}_0 is made, zeroth order contributions to the primary–secondary couplings vanish and resulting first-order expressions read

$$\begin{aligned} (a_a^\dagger a_j | \hat{H} a_p)_0 &= \langle pa || ji \rangle \\ (a_i^\dagger a_a a_b | \hat{H} a_p)_0 &= \langle pi || pa \rangle. \end{aligned}$$

Through first order in V , the 2hp–2hp and 2ph–2ph couplings are given by

$$\begin{aligned} (a_a^\dagger a_j | \hat{H} a_b^\dagger a_k a_l)_0 &= \delta_{ab} \delta_{ik} \delta_{jl} (\epsilon_i + \epsilon_j - \epsilon_a) - \delta_{ab} \langle kl || ij \rangle \\ &\quad + (1 - P_{ij})(1 - P_{kl}) \delta_{ik} \langle al || bj \rangle, \end{aligned}$$

for $i < j$, $k < l$, and

$$\begin{aligned} \left(a_i^\dagger a_a a_b | \hat{H} a_j^\dagger a_c a_d \right)_0 &= \delta_{ij} \delta_{ac} \delta_{bd} (\varepsilon_a + \varepsilon_b - \varepsilon_i) \\ &+ \delta_{ij} \langle cd || ab \rangle - (1 - P_{ab})(1 - P_{cd}) \delta_{ac} \langle id || jb \rangle, \end{aligned}$$

for $a < b$, $c < d$. The latter terms generate ring, ladder, and mixed ring–ladder diagrams in all orders of V . Because the Hartree–Fock reference state generates no energy-independent terms,

$$\sigma^{2\text{ph-TDA}}(\mathbf{E}) = \Sigma^{2\text{ph-TDA}}(\mathbf{E}).$$

The chief arithmetic bottleneck in 2ph-TDA calculations arises from matrix multiplications that involve 2ph–2ph couplings. These contractions scale as ov^4 , where o is the number of occupied orbitals and v is the number of virtual orbitals.

By ignoring the first-order terms in $\left(a_a^\dagger a_i a_j | \hat{H} a_b^\dagger a_k a_l \right)_0$ and $\left(a_i^\dagger a_a a_b | \hat{H} a_j^\dagger a_c a_d \right)_0$, the self-energy expression becomes

$$\begin{aligned} \Sigma^{(2)}(\mathbf{E}) &= (\mathbf{a} | \hat{H} \mathbf{f}_{2\text{hp}})_0 (\mathbf{f}_{2\text{hp}} | \mathbf{E} \hat{I} - \hat{H}_0 \mathbf{f}_{2\text{hp}})_0^{-1} (\mathbf{f}_{2\text{hp}} | \hat{H} \mathbf{a})_0 \\ &+ (\mathbf{a} | \hat{H} \mathbf{f}_{2\text{hp}})_0 (\mathbf{f}_{2\text{hp}} | (\mathbf{E} \hat{I} - \hat{H}_0) \mathbf{f}_{2\text{hp}})_0^{-1} (\mathbf{f}_{2\text{hp}} | \hat{H} \mathbf{a})_0 \end{aligned}$$

and the matrix elements acquire their familiar, second-order form:

$$\begin{aligned} \Sigma_{pq}^{(2)}(\mathbf{E}) &= \Sigma_{a_i < j} \langle qa || ji \rangle (\mathbf{E} + \varepsilon_a - \varepsilon_i - \varepsilon_j)^{-1} \langle ji || pa \rangle \\ &+ \Sigma_{i_a < b} \langle qi || ba \rangle (\mathbf{E} + \varepsilon_i - \varepsilon_a - \varepsilon_b)^{-1} \langle ba || pi \rangle \end{aligned}$$

For electron detachment energies in which the assumptions of Koopmans's identity are qualitatively valid, neglect of off-diagonal elements of $\Sigma(\mathbf{E})$ usually introduces deviations of 0.01–0.02 eV. The resulting diagonal, or quasiparticle, approximation leads to an especially simple form of the Dyson quasiparticle equation in which

$$\mathbf{E} = \varepsilon_i + \Sigma_{ii}(\mathbf{E})$$

When the diagonal, second-order (D2) self-energy approximation is used with flexible basis sets, valence, vertical ionization energies (VIEs) of closed-shell molecules are predicted to be too small, with mean absolute deviations from reliable data of approximately 0.4 eV. Larger errors obtain for small basis sets. Predicted VIEs increase as more functions are added. Whereas

negatives of canonical Hartree–Fock orbital energies usually give VIEs that are too large, chiefly because of their neglect of final-state relaxation of orbitals, D2 results that are extrapolated with respect to basis saturation provide an informal lower bound. For every Koopmans result that is refined with D2 corrections, only a partial integral transformation to the Hartree–Fock basis is required. The latter transformation has fourth-power arithmetic scaling. Because evaluation of $\Sigma_{ii}(E)$ matrix elements has cubic scaling, it constitutes no bottleneck.

A noniterative formula in which the pole is approximated by

$$E \approx \varepsilon_i + \Sigma_{ii}^{(2)}(\varepsilon_i)$$

is identical to the second-order result of Rayleigh–Schrödinger perturbation theory in which the N -electron, Møller–Plesset fluctuation potential also is used to generate total energies for states with $N - 1$ electrons. (The same conclusion may be reached in third, but not higher orders.)¹⁷ However, iterations with respect to E commonly yield nonnegligible shifts of approximately 0.05 eV. Pole searches may be accelerated by evaluating the derivatives of $\Sigma_{ii}(E)$ with respect to E and using Newton’s method to estimate the next guess. Convergence to within 0.01 eV usually follows after the third iteration.

A perturbative analysis of the second-order self-energy^{7,18} discloses that final-state relaxation effects for electron detachment (or attachment) energies are attributable to terms in the 2hp (or 2ph) summation where i or j (a or b) equals p. The remaining terms in these summations account for final-state correlation effects. Second-order, pair correlation energies in the N -electron reference state that are destroyed (created) in final states with $N - 1$ ($N + 1$) electrons are given by the 2ph (2hp) summation.

To efficiently estimate VIEs for a set of chemically related molecules, spin-scaled D2 approximations have been introduced.^{19,20} Several scaled versions of the D2 self-energy with the general formula,

$$\begin{aligned} \Sigma_{pp}^{(2)}(E) = & \frac{1}{2} \Sigma_{aj} \langle pa | ij \rangle (E + \varepsilon_a - \varepsilon_i - \varepsilon_j)^{-1} [C_{C-2hp} \langle ij | pa \rangle + C_{E-2hp} \langle ji | pa \rangle] \\ & + \frac{1}{2} \Sigma_{iab} \langle pi | ab \rangle (E + \varepsilon_i - \varepsilon_a - \varepsilon_b)^{-1} [C_{C-2ph} \langle ab | pi \rangle + C_{E-2ph} \langle ba | pi \rangle], \end{aligned}$$

have been examined for the purpose of enabling calculations on large molecules. Coulomb (C subscript) and exchange (E subscript) contributions and the 2hp and 2ph terms have been given four separate weights. Because D2

often succeeds in identifying Koopmans defects, where the order of final states predicted with canonical orbital energies is incorrect, it is a better basis for parametrizations than the Hartree–Fock equations. When a linear fit of Hartree–Fock orbital energies to reliable data necessarily fails because of Koopmans defects, parametrized versions of the D2 quasiparticle equation may yield useful tools for interpolation.

The D2 method, without the introduction of scaling parameters, also has been used in the context of semiempirical Hamiltonians.²¹ Successful assignments of photoelectron spectra in which the Koopmans ordering of final states is incorrect have been realized for several classes of organic and inorganic compounds.

For valence electron binding energies where a frozen-orbital determinant is a reasonable description of the final state, the D2 approximation provides valuable, semiquantitative corrections to the results of Koopmans's identity. However, for core ionization energies, where final-state orbital relaxation is strong, the orbital energy provided by the transition operator method (TOM) is a superior zero-order approximation.^{22–24} Matrix elements of the transition operator read

$$F_{pq}^{\text{TOM}} = h_{pq} + \sum_r \langle pr \parallel qr \rangle n_r.$$

Occupation numbers of 0 and 1 are assigned to each spin-orbital, save for a single spin-orbital (ie, the transition orbital) assigned to an occupation number of 1/2. (This choice of occupation numbers is a special case of grand-canonical Hartree–Fock theory.)^{25,26} The eigenvalue corresponding to the transition spin-orbital, ϵ_p^{TOM} , incorporates orbital relaxation effects. For the grand-canonical Hartree–Fock density operator, a generalized form for the second-order self-energy obtains, where

$$\Sigma_{pq}^{(2)}(E) = \frac{1}{2} \sum_{rst} N_{rst} \langle qr \parallel st \rangle (E + \epsilon_r - \epsilon_s - \epsilon_t)^{-1} \langle st \parallel pr \rangle$$

$$N_{rst} = n_r(1 - n_s)(1 - n_t) + (1 - n_r)n_s n_t.$$

The second-order, transition-operator (TOEP2) method²⁴ also employs the diagonal self-energy approximation. Poles satisfy the equation

$$E = \epsilon_p^{\text{TOM}} + \Sigma_{pp}^{(2)}(E).$$

This method provides a useful, semiquantitative account of core and valence electron binding energies, with mean absolute errors of approximately 0.35 eV for valence IEs.

Despite its retention of nondiagonal elements of the self-energy operator and its inclusion of ring, ladder, and mixed ring-ladder terms beyond second-order, the 2ph-TDA yields larger average errors for valence VIEs than the less computationally demanding D2 method. The chief advantage of 2ph-TDA is its ability to produce a first-order account of correlation states in which 2hp or 2ph configurations dominate over the h and p configurations assumed in Koopmans's identity. In the inner-valence region of a photoelectron spectrum, numerous poles with low strengths obliterate the Koopmans picture of one-hole final states.²⁷ Canonical Hartree-Fock orbital energies in the inner-valence region therefore have little physical meaning with respect to specific transitions. For typical molecules, the He II photoelectron spectrum (ie, up to approximately 40 eV) may be qualitatively assigned with 2ph-TDA calculations.

To generate all third-order terms in $\mathbf{F} + \boldsymbol{\sigma}(\mathbf{E})$ or $\boldsymbol{\Sigma}(\mathbf{E})$ with Hartree-Fock orbitals, the following approximation suffices:

$$\boldsymbol{\Sigma}^{3+}(\mathbf{E}) = \boldsymbol{\Sigma}^{(3)}(\infty) + (\mathbf{a}|\hat{\mathbf{H}}\mathbf{f}_3)_1 (\mathbf{f}_3|(\mathbf{E}\hat{\mathbf{I}} - \hat{\mathbf{H}})\mathbf{f}_3)_0^{-1} (\mathbf{f}_3|\hat{\mathbf{H}}\mathbf{a})_1.$$

Third-order, energy-independent terms are added to an expression for $\boldsymbol{\sigma}(\mathbf{E})$ in which the primary-secondary couplings are correct through second-order (because of first-order terms in the density operator) and the inverse, first-order matrix of secondary-secondary couplings generates terms in all orders. Whereas all third-order terms in $\boldsymbol{\Sigma}(\mathbf{E})$ are present, there are many higher-order terms as well. Therefore, this approximation may be denominated 3+. Expressions for the primary-secondary couplings with real orbitals read

$$\begin{aligned} (a_a^\dagger a_i a_j | \hat{\mathbf{H}} a_p)_1 &= (a_a^\dagger a_i a_j | \hat{\mathbf{H}} a_p)_0 + \frac{1}{2} \sum_{bc} t_{jibc} \langle pa || bc \rangle + (1 - P_{ij}) \sum_{bk} t_{k_jba} \langle pk || bi \rangle \\ &= \hat{\mathbf{H}}_{aj,p}^{(1)} + \hat{\mathbf{H}}_{aj,p}^{(2)} \\ (a_1^\dagger a_a a_b | \hat{\mathbf{H}} a_p)_1 &= (a_1^\dagger a_a a_b | \hat{\mathbf{H}} a_p)_0 + \frac{1}{2} \sum_{jk} t_{j_kba} \langle pi || jk \rangle + (1 - P_{ab}) \sum_{jc} t_{ijbc} \langle pc || ja \rangle \\ &= \hat{\mathbf{H}}_{iab,p}^{(1)} + \hat{\mathbf{H}}_{iab,p}^{(2)} \end{aligned}$$

For each value of p, there are fifth-power contractions. Determination of all primary-secondary couplings therefore is a sixth-power process and constitutes the chief noniterative bottleneck in 3+ calculations. (In practice, iterative processes with fifth-power scaling may require more arithmetic

operations.) This additional effort is rewarded with superior accuracy in calculations on valence ionization energies and electron affinities.²⁸

One may extend the 3+ self-energy by adding more energy-independent terms.²⁹ One such approach is based on a relationship between the electron propagator matrix and the one-electron density matrix that reads

$$\mathbf{P} = (2\pi i)^{-1} \int_C \mathbf{G}(E) dE,$$

where C denotes a contour in the complex plane that includes all electron detachment poles and where electron propagator matrix elements with a complex argument are given by

$$G_{rs}(E) = \lim_{\eta \rightarrow 0} \left[\sum_m V_{rm} V_{sm}^* (E - A_m + i\eta)^{-1} + \sum_n U_{rm}^* U_{sn} (E - D_n - i\eta)^{-1} \right].$$

By truncating the expansion of the Dyson equation,

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

after the second term, the approximation

$$\mathbf{P} \approx (2\pi i)^{-1} \int_C [\mathbf{G}_0(E) + \mathbf{G}_0(E) \mathbf{\Sigma}(E) \mathbf{G}_0(E)] dE$$

is obtained. An approximate density matrix defined in this way yields a new $\mathbf{\Sigma}(\infty)$ and therefore a new $\mathbf{\Sigma}(E)$. By setting

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

where

$$\mathbf{\sigma}^{3+}(E) = (\mathbf{a} | \hat{\mathbf{H}} \mathbf{f}_3)_1 (\mathbf{f}_3 | (E \hat{\mathbf{I}} - \hat{\mathbf{H}}) \mathbf{f}_3)_0^{-1} (\mathbf{f}_3 | \hat{\mathbf{H}} \mathbf{a})_1,$$

one may obtain \mathbf{P} and $\mathbf{\Sigma}(\infty)$ self-consistently. This extension of the 3+ self-energy is the most common version of the third-order algebraic diagrammatic construction, or ADC(3).² It suffices to recover all fourth order terms and many higher-order terms in $\mathbf{\Sigma}(\infty)$. In the ADC(3) method, sixth-power contractions that scale as $\sigma^2 v^4$ are performed iteratively in the determination of $\mathbf{\Sigma}(\infty)$. Whereas the correlation contribution to \mathbf{P} has a vanishing trace for the 3+ self-energy and for the exact case, its ADC(3) counterpart does not have this property. This deviation stems from the retention of only some

$\Sigma(\infty)$ terms in fifth and higher orders of the fluctuation potential and may become problematic for large molecules.

The design of the 3+ and ADC(3) methods assumes the need to include all third-order terms in $\Sigma(E)$ and embraces the inclusion of higher-order terms. An alternative approach is based on examination of improvements to the second-order self-energy and retention of terms that suffice to provide reliable predictions of electron binding energies.³⁰ For the calculation of electron detachment energies, an asymmetric superoperator metric is adopted, where

$$\langle X|Y \rangle_D = \langle \text{HF} | [X^\dagger, Y]_+ (1 + T_2^{(1)}) | \text{HF} \rangle,$$

and where the reference Hartree–Fock determinantal wave function, $|\text{HF}\rangle$, and the first-order Møller–Plesset wave function define the double excitation amplitudes of $T_2^{(1)}$. The operator manifold comprises the \mathbf{a} and \mathbf{f}_3 spaces. Second-order terms appear only when Y is a 2ph operator or X is a 2hp operator. For electron detachment energies, all of these second-order terms except those occurring in the 2hp-h block of $\hat{\mathbf{H}}$ may be neglected. First-order terms in the 2ph–2ph block of $\hat{\mathbf{H}}$ also may be omitted. After Hermitizing $\hat{\mathbf{H}}$, the resulting self-energy matrix elements are expressed as

$$\begin{aligned} \Sigma_{ij}^{\text{NR2-D}}(E) &= \left[\hat{\mathbf{H}}_{i,2hp}^{(1)} + \frac{1}{2} \hat{\mathbf{H}}_{i,2hp}^{(2)} \right] (\mathbf{f}_{2hp} | (E\hat{I} - \hat{H}) \mathbf{f}_{2hp})_0^{-1} \left[\hat{\mathbf{H}}_{2hp,j}^{(1)} + \frac{1}{2} \hat{\mathbf{H}}_{2hp,j}^{(2)} \right] \\ &\quad + \hat{\mathbf{H}}_{i,2ph}^{(1)} (\mathbf{f}_{2ph} | (E\hat{I} - \hat{H}_0) \mathbf{f}_{2ph})_0^{-1} \hat{\mathbf{H}}_{2ph,j}^{(1)} \\ \Sigma_{ia}^{\text{NR2-D}}(E) &= \left[\hat{\mathbf{H}}_{i,2hp}^{(1)} + \frac{1}{2} \hat{\mathbf{H}}_{i,2hp}^{(2)} \right] (\mathbf{f}_{2hp} | (E\hat{I} - \hat{H}) \mathbf{f}_{2hp})_0^{-1} \hat{\mathbf{H}}_{2hp,a}^{(1)} \\ &\quad + \hat{\mathbf{H}}_{i,2ph}^{(1)} (\mathbf{f}_{2ph} | (E\hat{I} - \hat{H}_0) \mathbf{f}_{2ph})_0^{-1} \hat{\mathbf{H}}_{2ph,a}^{(1)} \\ \Sigma_{ai}^{\text{NR2-D}}(E) &= [\Sigma_{ia}^{\text{NR2-D}}(E)]^* \\ \Sigma_{ab}^{\text{NR2-D}}(E) &= \hat{\mathbf{H}}_{a,2hp}^{(1)} (\mathbf{f}_{2hp} | (E\hat{I} - \hat{H}) \mathbf{f}_{2hp})_0^{-1} \hat{\mathbf{H}}_{2hp,b}^{(1)} \\ &\quad + \hat{\mathbf{H}}_{a,2ph}^{(1)} (\mathbf{f}_{2ph} | (E\hat{I} - \hat{H}_0) \mathbf{f}_{2ph})_0^{-1} \hat{\mathbf{H}}_{2ph,b}^{(1)} \end{aligned}$$

The designation NR2 was chosen because this self-energy approximation is nondiagonal, renormalized, and complete through second order. Ring and ladder renormalizations are generated by the first-order terms that occur in

$(\mathbf{f}_{2hp} | (\hat{E}\hat{I} - \hat{H}) \mathbf{f}_{2hp})_0^{-1}$. There are no energy-independent terms. Because 2ph rings and ladders and second-order p-2hp terms are neglected, the need for electron repulsion integrals with four virtual indices is eliminated in NR2 calculations of electron detachment energies. The most arithmetically intensive contraction has o^3v^3 scaling and is the only step that requires electron repulsion integrals with three virtual indices.

For the calculation of electron attachment energies, the metric is chosen according to

$$(\mathbf{X}|\mathbf{Y})_A = \left\langle \text{HF} | \left(1 + T_2^{(1)} \right)^\dagger [\mathbf{X}^\dagger, \mathbf{Y}]_+ | \text{HF} \right\rangle$$

and the roles of particles and holes are reversed in the selection of self-energy terms. For electron attachment energies,

$$\begin{aligned} \Sigma_{ab}^{\text{NR2-A}}(E) &= \left[\hat{\mathbf{H}}_{a,2ph}^{(1)} + \frac{1}{2} \hat{\mathbf{H}}_{a,2ph}^{(2)} \right] (\mathbf{f}_{2ph} | (\hat{E}\hat{I} - \hat{H}) \mathbf{f}_{2ph})_0^{-1} \left[\hat{\mathbf{H}}_{2ph,b}^{(1)} + \frac{1}{2} \hat{\mathbf{H}}_{2ph,b}^{(2)} \right] \\ &\quad + \hat{\mathbf{H}}_{a,2hp}^{(1)} (\mathbf{f}_{2hp} | (\hat{E}\hat{I} - \hat{H}_0) \mathbf{f}_{2hp})_0^{-1} \hat{\mathbf{H}}_{2hp,b}^{(1)} \end{aligned}$$

$$\begin{aligned} \Sigma_{ai}^{\text{NR2-A}}(E) &= \left[\hat{\mathbf{H}}_{a,2ph}^{(1)} + \frac{1}{2} \hat{\mathbf{H}}_{a,2ph}^{(2)} \right] (\mathbf{f}_{2ph} | (\hat{E}\hat{I} - \hat{H}) \mathbf{f}_{2ph})_0^{-1} \hat{\mathbf{H}}_{2ph,i}^{(1)} \\ &\quad + \hat{\mathbf{H}}_{a,2hp}^{(1)} (\mathbf{f}_{2hp} | (\hat{E}\hat{I} - \hat{H}_0) \mathbf{f}_{2hp})_0^{-1} \hat{\mathbf{H}}_{2hp,i}^{(1)} \end{aligned}$$

$$\Sigma_{ia}^{\text{NR2-A}}(E) = [\Sigma_{ai}^{\text{NR2-A}}(E)]^*$$

$$\begin{aligned} \Sigma_{ij}^{\text{NR2-A}}(E) &= \hat{\mathbf{H}}_{i,2ph}^{(1)} (\mathbf{f}_{2ph} | (\hat{E}\hat{I} - \hat{H}) \mathbf{f}_{2ph})_0^{-1} \hat{\mathbf{H}}_{2ph,j}^{(1)} \\ &\quad + \hat{\mathbf{H}}_{i,2hp}^{(1)} (\mathbf{f}_{2hp} | (\hat{E}\hat{I} - \hat{H}_0) \mathbf{f}_{2hp})_0^{-1} \hat{\mathbf{H}}_{2hp,j}^{(1)}. \end{aligned}$$

In the evaluation of $\hat{\mathbf{H}}_{a,2ph}^{(2)}$, there is a contraction with o^2v^4 arithmetic scaling that involves electron repulsion integrals with three virtual indices. Inclusion of the first-order 2ph-2ph elements of $\hat{\mathbf{H}}$ entails a need for electron repulsion integrals with four virtual indices. NR2 calculations of electron attachment energies may be expected to require more arithmetic operations and memory than their counterparts for electron detachment energies.

Arithmetic bottlenecks encountered in 3+ and NR2 calculations may be reduced by introducing two additional approximations. To evaluate products of $(\mathbf{f}_3 | (\hat{E}\hat{I} - \hat{H}) \mathbf{f}_3)_0^{-1}$ with other matrices, repeated multiplications are

required. As a result, self-energy terms in all orders are retained. However, if the inverse matrix is approximated according to

$$\begin{aligned} (\mathbf{f}_3 | (\hat{E}\hat{I} - \hat{H}) \mathbf{f}_3)_0^{-1} &\approx (\mathbf{f}_3 | (\hat{E}\hat{I} - \hat{H}_0) \mathbf{f}_3)_0^{-1} + (\mathbf{f}_3 | (\hat{E}\hat{I} - \hat{H}_0) \mathbf{f}_3)_0^{-1} \\ &\quad (\mathbf{f}_3 | (\hat{H} - \hat{H}_0) \mathbf{f}_3)_0 (\mathbf{f}_3 | (\hat{E}\hat{I} - \hat{H}_0) \mathbf{f}_3)_0^{-1}, \end{aligned}$$

only terms up to fourth order remain and all third-order terms are conserved. By applying these arguments to the 3+ self-energy, the third-order self-energy's structure is shown:

$$\begin{aligned} \Sigma^{(3)}(E) = &\Sigma^{(2)}(E) + \Sigma^{(3)}(\infty) + \hat{\mathbf{H}}_{13}^{(2)} (\mathbf{f}_3 | (\hat{E}\hat{I} - \hat{H}_0) \mathbf{f}_3)_0^{-1} \hat{\mathbf{H}}_{31}^{(1)} \\ &+ \hat{\mathbf{H}}_{13}^{(1)} (\mathbf{f}_3 | (\hat{E}\hat{I} - \hat{H}_0) \mathbf{f}_3)_0^{-1} \hat{\mathbf{H}}_{31}^{(2)} \\ &+ \hat{\mathbf{H}}_{13}^{(1)} (\mathbf{f}_3 | (\hat{E}\hat{I} - \hat{H}_0) \mathbf{f}_3)_0^{-1} (\mathbf{f}_3 | (\hat{H} - \hat{H}_0) \mathbf{f}_3)_0 (\mathbf{f}_3 | (\hat{E}\hat{I} - \hat{H}_0) \mathbf{f}_3)_0^{-1} \hat{\mathbf{H}}_{31}^{(1)} \end{aligned}$$

The last term is responsible for the ring and ladder diagrams that appear in third order. Applying similar truncations to the NR2 self-energy formulae defines nondiagonal, partial third-order (NP3) approximations. For example, whereas the occupied–occupied block of the NP3 self-energy matrix for electron detachment energies reads

$$\begin{aligned} \Sigma_{ij}^{\text{NP3-D}}(E) = &\Sigma_{ij}^{(2)}(E) + \frac{1}{2} \hat{\mathbf{H}}_{i,2\text{hp}}^{(1)} (\mathbf{f}_{2\text{hp}} | (\hat{E}\hat{I} - \hat{H}_0) \mathbf{f}_{2\text{hp}})_0^{-1} \hat{\mathbf{H}}_{2\text{hp},j}^{(2)} \\ &+ \frac{1}{2} \hat{\mathbf{H}}_{i,2\text{hp}}^{(2)} (\mathbf{f}_{2\text{hp}} | (\hat{E}\hat{I} - \hat{H}_0) \mathbf{f}_{2\text{hp}})_0^{-1} \hat{\mathbf{H}}_{2\text{hp},j}^{(1)} \\ &+ \hat{\mathbf{H}}_{i,2\text{hp}}^{(1)} (\mathbf{f}_{2\text{hp}} | (\hat{E}\hat{I} - \hat{H}_0) \mathbf{f}_{2\text{hp}})_0^{-1} (\mathbf{f}_{2\text{hp}} | (\hat{H} - \hat{H}_0) \mathbf{f}_{2\text{hp}})_0 \\ &\quad (\mathbf{f}_{2\text{hp}} | (\hat{E}\hat{I} - \hat{H}_0) \mathbf{f}_{2\text{hp}})_0^{-1} \hat{\mathbf{H}}_{2\text{hp},j}^{(1)}, \end{aligned}$$

the virtual–virtual block of its counterpart for electron attachments reads

$$\begin{aligned} \Sigma_{ab}^{\text{NP3-A}}(E) = &\Sigma_{ab}^{(2)}(E) + \frac{1}{2} \hat{\mathbf{H}}_{a,2\text{ph}}^{(1)} (\mathbf{f}_{2\text{ph}} | (\hat{E}\hat{I} - \hat{H}_0) \mathbf{f}_{2\text{ph}})_0^{-1} \hat{\mathbf{H}}_{2\text{ph},b}^{(2)} \\ &+ \frac{1}{2} \hat{\mathbf{H}}_{a,2\text{ph}}^{(2)} (\mathbf{f}_{2\text{ph}} | (\hat{E}\hat{I} - \hat{H}_0) \mathbf{f}_{2\text{ph}})_0^{-1} \hat{\mathbf{H}}_{2\text{ph},b}^{(1)} \\ &+ \hat{\mathbf{H}}_{a,2\text{ph}}^{(1)} (\mathbf{f}_{2\text{ph}} | (\hat{E}\hat{I} - \hat{H}_0) \mathbf{f}_{2\text{ph}})_0^{-1} (\mathbf{f}_{2\text{ph}} | (\hat{H} - \hat{H}_0) \mathbf{f}_{2\text{ph}})_0 \\ &\quad (\mathbf{f}_{2\text{ph}} | (\hat{E}\hat{I} - \hat{H}_0) \mathbf{f}_{2\text{ph}})_0^{-1} \hat{\mathbf{H}}_{2\text{ph},b}^{(1)} \end{aligned}$$

The second approximation is neglect of the off-diagonal elements of $\Sigma(\mathbf{E})$ in the canonical, Hartree–Fock orbital basis. For a given electron binding energy corresponding to spin-orbital \mathbf{r} , only the elements of $\hat{\mathbf{H}}_{\mathbf{r},2\text{hp}}^{(2)}$ or $\hat{\mathbf{H}}_{\mathbf{r},2\text{ph}}^{(2)}$ must be evaluated and the corresponding sixth-power contractions are reduced to fifth power. Arithmetic operations are similarly reduced when $(\mathbf{f}_3 | (\mathbf{E}\hat{\mathbf{I}} - \hat{\mathbf{H}})\mathbf{f}_3)_0^{-1} \hat{\mathbf{H}}_{31}$ products are formed. The resulting diagonal third-order (D3) and P3^{31,32} self-energies therefore have fifth-power arithmetic scaling. For real spin-orbitals, the D3 self-energy matrix elements may be written as

$$\begin{aligned} \Sigma_{\mathbf{r}\mathbf{r}}^{(3)}(\mathbf{E}) = & \frac{1}{2} \sum_{\text{aij}} \langle \mathbf{ra} \| \mathbf{ij} \rangle (\mathbf{E} + \varepsilon_a - \varepsilon_i - \varepsilon_j)^{-1} \left[\langle \mathbf{ra} \| \mathbf{ij} \rangle + 2\hat{\mathbf{H}}_{\text{raij}}^{(2)} + \mathbf{U}_{\text{raij}}(\mathbf{E}) \right] \\ & + \frac{1}{2} \sum_{\text{iab}} \langle \mathbf{ri} \| \mathbf{ab} \rangle (\mathbf{E} + \varepsilon_i - \varepsilon_a - \varepsilon_b)^{-1} \left[\langle \mathbf{ri} \| \mathbf{ab} \rangle + 2\hat{\mathbf{H}}_{\text{riab}}^{(2)} + \mathbf{U}_{\text{riab}}(\mathbf{E}) \right] \\ & + \Sigma_{\mathbf{r}\mathbf{r}}^{(3)}(\infty), \end{aligned}$$

where

$$\begin{aligned} \mathbf{U}_{\text{raij}}(\mathbf{E}) = & -\frac{1}{2} \sum_{\text{kl}} \langle \mathbf{ra} \| \mathbf{kl} \rangle (\mathbf{E} + \varepsilon_a - \varepsilon_k - \varepsilon_l)^{-1} \langle \mathbf{kl} \| \mathbf{ij} \rangle \\ & - (1 - \mathbf{P}_{\text{ij}}) \sum_{\text{bkc}} \langle \mathbf{rb} \| \mathbf{jk} \rangle (\mathbf{E} + \varepsilon_b - \varepsilon_j - \varepsilon_k)^{-1} \langle \mathbf{ak} \| \mathbf{bi} \rangle \\ \mathbf{U}_{\text{riab}}(\mathbf{E}) = & \frac{1}{2} \sum_{\text{cde}} \langle \mathbf{ri} \| \mathbf{cd} \rangle (\mathbf{E} + \varepsilon_i - \varepsilon_c - \varepsilon_d)^{-1} \langle \mathbf{cd} \| \mathbf{ab} \rangle \\ & + (1 - \mathbf{P}_{\text{ab}}) \sum_{\text{jce}} \langle \mathbf{rj} \| \mathbf{bc} \rangle (\mathbf{E} + \varepsilon_j - \varepsilon_b - \varepsilon_c)^{-1} \langle \mathbf{ic} \| \mathbf{ja} \rangle. \end{aligned}$$

The usual computational bottleneck occurs in the $\mathbf{U}_{\text{riab}}(\mathbf{E})$ expression, where a contraction with ov^4 scaling must be repeated for various values of \mathbf{E} . For P3 electron detachment energies,

$$\begin{aligned} \Sigma_{\text{kk}}^{\text{P3-D}}(\mathbf{E}) = & \frac{1}{2} \sum_{\text{aij}} \langle \mathbf{ka} \| \mathbf{ij} \rangle (\mathbf{E} + \varepsilon_a - \varepsilon_i - \varepsilon_j)^{-1} \left[\langle \mathbf{ka} \| \mathbf{ij} \rangle + \hat{\mathbf{H}}_{\text{kaij}}^{(2)} + \mathbf{U}_{\text{kaij}}(\mathbf{E}) \right] \\ & + \frac{1}{2} \sum_{\text{iab}} |\langle \mathbf{ki} \| \mathbf{ab} \rangle|^2 (\mathbf{E} + \varepsilon_i - \varepsilon_a - \varepsilon_b)^{-1}, \end{aligned}$$

and for P3 electron attachment energies,

$$\begin{aligned} \Sigma_{\text{cc}}^{\text{P3-A}}(\mathbf{E}) = & \frac{1}{2} \sum_{\text{iab}} \langle \mathbf{ci} \| \mathbf{ab} \rangle (\mathbf{E} + \varepsilon_i - \varepsilon_a - \varepsilon_b)^{-1} \left[\langle \mathbf{ci} \| \mathbf{ab} \rangle + \hat{\mathbf{H}}_{\text{ciab}}^{(2)} + \mathbf{U}_{\text{ciab}}(\mathbf{E}) \right] \\ & + \frac{1}{2} \sum_{\text{aij}} |\langle \mathbf{ca} \| \mathbf{ij} \rangle|^2 (\mathbf{E} + \varepsilon_a - \varepsilon_i - \varepsilon_j)^{-1}. \end{aligned}$$

In the former case, the evaluation of $\hat{\mathbf{H}}_{\text{kaij}}^{(2)}$ intermediates requires a contraction that scales as o^2v^3 ; iterations with respect to E require o^3v^2 contractions. For electron attachment energies, P3's noniterative, and iterative bottlenecks have o^2v^3 and ov^4 scaling factors.

D2 tends to overestimate corrections to canonical Hartree–Fock orbital energies and therefore to produce underestimates of electron detachment energies. However, D3 displays the opposite trend, especially as basis sets approach completeness. Estimates of higher-order terms usually are necessary to obtain results of predictive quality. For this purpose, the outer valence Green's function (OVGF) methods^{2,33} contain two multiplicative factors for third-order terms in which ratios of third-order and second-order terms are formed. These factors read

$$\begin{aligned} X_r &= -2 \left[\hat{\mathbf{H}}_{r,2hp}^{(1)} (\mathbf{f}_{2hp} | (\hat{E}\hat{I} - \hat{H}_0) \mathbf{f}_{2hp})_0^{-1} \hat{\mathbf{H}}_{2hp,r}^{(2)} \right. \\ &\quad \left. + \hat{\mathbf{H}}_{r,2ph}^{(1)} (\mathbf{f}_{2ph} | (\hat{E}\hat{I} - \hat{H}_0) \mathbf{f}_{2ph})_0^{-1} \hat{\mathbf{H}}_{2ph,r}^{(2)} \right] \left[\Sigma_{rr}^{(2)}(E) \right]^{-1} \\ X_r^{2hp} &= -2 \left[\hat{\mathbf{H}}_{r,2hp}^{(1)} (\mathbf{f}_{2hp} | (\hat{E}\hat{I} - \hat{H}_0) \mathbf{f}_{2hp})_0^{-1} \hat{\mathbf{H}}_{2hp,r}^{(2)} \right] \\ &\quad \times \left[\hat{\mathbf{H}}_{r,2hp}^{(1)} (\mathbf{f}_{2hp} | (\hat{E}\hat{I} - \hat{H}_0) \mathbf{f}_{2hp})_0^{-1} \hat{\mathbf{H}}_{2ph,r}^{(1)} \right]^{-1} \\ X_r^{2ph} &= -2 \left[\hat{\mathbf{H}}_{r,2ph}^{(1)} (\mathbf{f}_{2ph} | (\hat{E}\hat{I} - \hat{H}_0) \mathbf{f}_{2ph})_0^{-1} \hat{\mathbf{H}}_{2ph,r}^{(2)} \right] \\ &\quad \times \left[\hat{\mathbf{H}}_{r,2ph}^{(1)} (\mathbf{f}_{2ph} | (\hat{E}\hat{I} - \hat{H}_0) \mathbf{f}_{2ph})_0^{-1} \hat{\mathbf{H}}_{2ph,r}^{(1)} \right]^{-1}. \end{aligned}$$

In the A version, energy-independent and energy-dependent terms in third order are scaled as follows:

$$\Sigma_{rr}^{\text{OVGF-A}}(E) = \Sigma_{rr}^{(2)}(E) + (1 + X_r)^{-1} \left[\Sigma_{rr}^{(3)}(E) - \Sigma_{rr}^{(2)}(E) \right].$$

Two scaling factors are applied to the energy-dependent, third-order terms in the B version, so that

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

In the C version, a more complicated formula is introduced for cases where second-order terms are small:

$$\begin{aligned}\Sigma_{\text{rr}}^{\text{OVGF-C}}(E) &= \Sigma_{\text{rr}}^{(2)}(E) + (1 + X_{\text{r}}^{\text{C}})^{-1} \left[\Sigma_{\text{rr}}^{(3)}(E) - \Sigma_{\text{rr}}^{(2)}(E) \right] \\ X_{\text{r}}^{\text{C}} &= \left[X_{\text{r}}^{2\text{hp}} \Sigma_{\text{rr}}^{3-2\text{hp}}(E) + X_{\text{r}}^{2\text{ph}} \Sigma_{\text{rr}}^{3-2\text{ph}}(E) \right] \\ &\quad \left[\Sigma_{\text{rr}}^{3-2\text{hp}}(E) + \Sigma_{\text{rr}}^{3-2\text{ph}}(E) \right]^{-1}.\end{aligned}$$

The scaling factors and self-energy matrix elements generally are evaluated at the D3 pole energy. Results of the A, B, and C versions are usually within 0.1 eV of each other. A recommended value which is reported typically as the recommended OVGf result emerges from the selection criteria of von Niessen³³:

1. If $E^{\text{OVGF-A}} \leq 15 \text{ eV}$, the $E^{\text{OVGF-B}}$ value is chosen when $\Sigma_{\text{rr}}^{(2)}(E) \geq 0.6 \text{ eV}$.
2. If $E^{\text{OVGF-A}} \leq 15 \text{ eV}$, the $E^{\text{OVGF-C}}$ value is chosen when $\Sigma_{\text{rr}}^{(2)}(E) < 0.6 \text{ eV}$.
3. If $E^{\text{OVGF-A}} \leq 15 \text{ eV}$ and $|X_{\text{r}}| \leq 0.85$, the $E^{\text{OVGF-A}}$ value is chosen unless $\Sigma_{\text{rr}}^{(2)}(E) < 0.6 \text{ eV}$ and $|X_{\text{r}}^{\text{C}}| \leq 0.85$. In the latter case, the $E^{\text{OVGF-C}}$ value is chosen.
4. If $E^{\text{OVGF-A}} > 15 \text{ eV}$, $|X_{\text{r}}| > 0.85$ and $\Sigma_{\text{rr}}^{(2)}(E) < 0.6 \text{ eV}$, the $E^{\text{OVGF-C}}$ value is chosen.
5. If $E^{\text{OVGF-A}} > 15 \text{ eV}$, $|X_{\text{r}}| > 0.85$ and $\Sigma_{\text{rr}}^{(2)}(E) \leq 0.6 \text{ eV}$, the $E^{\text{OVGF-B}}$ value is chosen unless $|X_{\text{r}}^{2\text{hp}}| > 0.85$, $|X_{\text{r}}^{2\text{ph}}| > 0.85$, $E^{\text{OVGF-C}} < 15 \text{ eV}$, or $|X_{\text{r}}^{\text{C}}| > 0.85$. In the latter cases, the $E^{\text{OVGF-C}}$ value is chosen.

In the P3+ method,³⁴ the self-energy reads

$$\begin{aligned}\Sigma_{\text{kk}}^{\text{P3+D}}(E) &= \left(1 + Y_{\text{k}}^{2\text{hp}} \right)^{-1} \frac{1}{2} \Sigma_{\text{aij}} \langle \text{ka} \parallel \text{ij} \rangle (E + \varepsilon_{\text{a}} - \varepsilon_{\text{i}} - \varepsilon_{\text{j}})^{-1} \\ &\quad \left[\langle \text{ka} \parallel \text{ij} \rangle + \hat{H}_{\text{kaij}}^{(2)} + U_{\text{kaij}}(E) \right] \\ &\quad + \frac{1}{2} \Sigma_{\text{iab}} |\langle \text{ki} \parallel \text{ab} \rangle|^2 (E + \varepsilon_{\text{i}} - \varepsilon_{\text{a}} - \varepsilon_{\text{b}})^{-1},\end{aligned}$$

where

$$Y_{\text{k}}^{2\text{hp}} = \left[-\frac{1}{2} \Sigma_{\text{aij}} \langle \text{ka} \parallel \text{ij} \rangle (E + \varepsilon_{\text{a}} - \varepsilon_{\text{i}} - \varepsilon_{\text{j}})^{-1} \hat{H}_{\text{kaij}}^{(2)} \right] \left[\Sigma_{\text{kk}}^{(2-2\text{hp})}(E) \right]^{-1}.$$

For P3+ electron attachment energies,

$$\begin{aligned} \Sigma_{cc}^{P3+A}(E) &= (1 + Y_c^{2ph})^{-1} \frac{1}{2} \sum_{iab} \langle ci || ab \rangle (E + \epsilon_i - \epsilon_a - \epsilon_b)^{-1} \\ &\quad \left[\langle ci || ab \rangle + \hat{H}_{ciab}^{(2)} + U_{ciab}(E) \right] \\ &\quad + \frac{1}{2} \sum_{aij} |\langle ca || ij \rangle|^2 (E + \epsilon_a - \epsilon_i - \epsilon_j)^{-1}. \end{aligned}$$

where

$$Y_c^{2ph} = \left[-\frac{1}{2} \sum_{iab} \langle ci || ab \rangle (E + \epsilon_i - \epsilon_a - \epsilon_b)^{-1} \hat{H}_{ciab}^{(2)} \right] \left[\Sigma_{cc}^{(2-2ph)}(E) \right]^{-1}.$$

P3+ self-energy terms and Y factors are evaluated at the P3 pole energy. The OVGf and P3+ methods entail only trivial calculations beyond D3 and P3, respectively.



5. TEST CALCULATIONS

The predictive capabilities of the presently considered self-energy approximations for valence, VIEs have been examined recently.³⁵ In this study, coupled-cluster singles and doubles plus perturbative triples, ie, CCSD(T),³⁶ calculations have been performed with correlation-consistent double, triple, and quadruple ζ basis sets^{37–39} on 21 molecules and on 52 cationic states. Basis-set extrapolations of these total energies provide standards of comparison. In Table 2, results obtained with the correlation-consistent quadruple ζ basis at the same molecular geometries are compared to these standards. In addition to the statistical measures of error (ie, mean signed error, mean absolute error, and root-mean-square error), the most taxing arithmetic bottlenecks and storage requirements are listed.

Diagonal self-energy approximations are in widest use. The most efficient of these methods, D2, consistently underestimates VIEs, but these errors decrease as the basis-set approaches completeness. D3 results tend to overestimate VIEs when large basis sets are used. OVGf produces more reliable data than D3 with the same effort. P3 is competitive with OVGf, for, with fewer arithmetic operations and smaller memory requirements, it is only slightly less accurate, despite having no selection criteria with numerical parameters. The P3+ method reduces the tendency of P3 to overestimate VIEs with almost no additional effort and is an efficient alternative to OVGf that involves no selection procedure.

Table 2 Errors of Calculated Vertical Ionization Energies^a vs Extrapolated CCSD(T) Results

Electron Propagator Method	Mean Signed Error ^b	Mean Absolute Error ^b	Root-Mean-Square Error ^b	Iterative Arithmetic Bottleneck ^c	Noniterative Arithmetic Bottleneck ^c	Largest Intermediate Matrix ^c
Koopmans	-0.75	0.83	1.01			
D2	0.50	0.52	0.61	ov ²	NA ^d	ov ²
D3	-0.28	0.39	0.55	ov ⁴	o ² v ³	v ⁴
OVSF	-0.01	0.11	0.13	ov ⁴	o ² v ³	v ⁴
P3	-0.10	0.18	0.24	o ³ v ²	o ² v ³	ov ³
P3+	0.01	0.13	0.16	o ³ v ²	o ² v ³	ov ³
2ph-TDA	0.66	0.66	0.71	ov ⁴	NA ^d	v ⁴
3+	-0.08	0.17	0.23	ov ⁴	o ² v ⁴	v ⁴
ADC(3)	-0.12	0.16	0.23	o ² v ⁴	o ² v ⁴	v ⁴
NR2	0.11	0.16	0.19	o ² v ³	o ³ v ³	ov ³

^a52 Vertical ionization energies (eV) for 21 molecules calculated with the cc-pvqz basis.

^bPositive signs correspond to underestimates of vertical ionization energies vs basis-set extrapolated CCSD(T) standards, ie, Error = VIE_{CCSD(T)} - VIE_{EP}.

^co = number of valence occupied orbitals; v = number of valence virtual orbitals.

^dNot applicable: no energy-independent intermediates are necessary.

Nondiagonal self-energy methods also are compared in Table 2. For calculating valence VIEs, 2ph-TDA produces worse results than D2 with much higher effort. Unlike D2, 2ph-TDA is capable of giving a qualitatively meaningful description of shake-up (ie, chiefly 2hp) final states in photoelectron spectra and of core-excited (ie, chiefly 2ph) electron attachments. The 3+ method is a considerable improvement over 2ph-TDA for valence VIEs that retains the ability of the latter approximation to account for correlation final states. The iterative, sixth-power contractions that distinguish ADC(3) from 3+ do not appear to procure any advantage for this test set. 3+ and ADC(3) tend to overestimate VIEs; error criteria will increase slightly as larger basis sets are employed. For the nondiagonal methods, NR2 has the smallest error measures, arithmetic scaling factors, and memory requirements. Improvements in basis sets will reduce errors in the majority of cases where NR2 underestimates VIEs.



6. RECENT APPLICATIONS AND EXTENSIONS

Electron propagator methods have been applied to the calculation of ionization energies of common amino acids in the gas phase and, with the benefit of polarizable continuum models, in aqueous solution.⁴⁰ Applications to the photoelectron spectra of fullerenes, macrocyclic molecules, and nucleotide fragments have been reviewed.⁴¹ Electron binding energies of compounds that are effective scavengers of free radicals have been determined.^{42,43} Electron propagator methods have been used to predict bound, excited states of anionic fullerenes.⁴⁴ They have facilitated assignments of the photoelectron spectra of tetrazoles.^{45,46} The nature of diffuse electronic structure in substituted aza-uracil and thio-uracil anions has been elucidated.⁴⁷⁻⁴⁹ A systematic study of electron-accepting molecules that may be useful in photovoltaic devices showed the predictive power of electron propagator methods.²⁸ Electron binding energies of confined atoms, crucial quantities for understanding their electronic structure, have been determined with electron propagator methods.⁵⁰ Calculations on electron affinities of cations provided essential information for the determination of photoionization cross sections in the molecular quantum defect model.⁵¹ The electronic structure of metallocenes and their Penning ionization spectra have been interpreted.⁵² Electron propagator calculations provided an explanation for the remarkable changes in anion electronic structure that depend on coordination to noble-gas atoms.⁵³ They also demonstrated how Dyson orbitals may be localized or delocalized in halide-water

complexes and in aqueous solution.^{54–56} Anion photoelectron spectra of superalkalides were interpreted with electron propagator methods.^{57,58}

A comparison of various approaches to calculating ionization energies of molecules reported superior performance for electron propagator methods.⁵⁹ Automated derivations of improved electron propagator methods have been incorporated into a general electronic structure package named for Löwdin.⁶⁰ An approach to self-energy expressions of any order and the convergence of perturbative expansions have been examined.¹⁷



7. CONCLUSIONS AND PROSPECTS

The Dyson quasiparticle equation provides a framework for accurate and efficient calculation of molecular electron binding energies. The simplest self-energy approximation, D2, often suffices to correct qualitative errors obtained with canonical Hartree–Fock orbital energies, eg, incorrect orderings of final states caused by neglect of final-state orbital relaxation or differential correlation effects. A restricted need for transformed electron repulsion integrals and low arithmetic demands indicate that D2 results should be obtained routinely after self-consistent-field iterations are complete. D2 provides a suitable foundation for parametrized interpolation schemes or semiempirical approaches that pertain to selected classes of molecules. Because the largest corrections to Koopmans results generally occur at the D2 level, this approximation can provide reliable diagnostics of basis-set effects and a means of estimating the results of higher-order calculations that are infeasible with large basis sets.

For predictions of valence, VIEs with mean, unsigned errors between 0.1 and 0.2 eV, the OVGf methods and their selection procedure constitute an efficient alternative to methods based on many-electron state functions or density functionals. This tool can be especially powerful when several final states of a given irreducible representation are needed. More computationally efficient alternatives of similar accuracy are provided by the partial third-order (P3) approximation and its renormalized extension (P3+). The quasiparticle, or diagonal self-energy, methods (ie, D2, OVGf, P3, and P3+) are most useful when the Koopmans description of an electron binding energy is qualitatively valid. In these cases, the Dyson orbital is a canonical Hartree–Fock orbital times the square root of the pole strength. The success of these methods implies that the chief flaw in the Koopmans description often pertains not to the quality of the occupied orbitals, but to the potential that determines their energies. In such cases, the addition

of easily calculated, nonlocal, energy-dependent corrections to canonical Hartree–Fock orbital energies suffices for a prediction of electron binding energies that verifies the presence of gas-phase molecular species in experimental samples and enables assignments of photoelectron spectral peaks. For core ionization energies, where orbital relaxation effects are large, the TOM produces an orbital energy that may be improved with low-order, self-energy corrections, such as D2 generalized to grand-canonical Hartree–Fock reference ensembles.

More general (nonquasiparticle) approximations include all elements of the self-energy matrix. When correlation states in photoelectron spectra are under consideration, the collapse of the Koopmans picture can be diagnosed with 2ph-TDA calculations, although a quantitatively accurate description generally demands a self-energy with higher-order terms. Whereas the two-particle-one-hole Tamm–Dancoff approximation (2ph-TDA) fails to generate reliable results for valence, VIEs, other nondiagonal alternatives, such as renormalized third-order (3+), the third-order algebraic diagrammatic construction (ADC(3)) and the nondiagonal, renormalized, second-order (NR2) methods yield mean absolute errors between 0.1 and 0.2 eV. The NR2 method achieves competitive accuracy with smaller demands for arithmetic operations and memory. All of these nondiagonal methods are capable of describing 2hp correlation final states qualitatively. Their Dyson orbitals are linear combinations of canonical Hartree–Fock orbitals. Dyson orbitals for electron affinities are likely to require such flexibility. Recent studies of vertical electron affinities of electron-accepting molecules indicate that the NR2 method may be a promising approach.²⁸

Higher accuracy for valence electron binding energies, quantitatively accurate calculations for correlation final states such as shakeups in photoelectron spectra or core-excited anions, descriptions of strong orbital relaxation effects for inner-shell ionization energies, and descriptions of more complex correlation effects that involve several open shells may be treated by introducing higher operator manifolds and more correlated reference states. Descriptions of low-spin, open-shell states that conserve exact spin quantum numbers may be accommodated with more flexible Ansätze for reference density matrices. Research along these lines is in progress.

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