

Polarization Green's Function with Multiconfiguration Self-Consistent-Field Reference States

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Abstracts

The polarization Green's-function formalism in the superoperator notation of Goscinski and Lukman is re-derived using a multiconfiguration self-consistent-field (MC-SCF) reference state to establish the superoperator metric. The potential advantages of employing this more general reference state in Green's-function theories and certain inherent weaknesses associated with the traditional Hartree-Fock or Rayleigh-Schrödinger perturbation theory reference state choices are briefly discussed. The Hermiticity of the superoperators is analyzed within the framework of the MC-SCF reference state. Using a concept of order appropriate for this reference state choice, explicit formulas and computational procedures for the implementation of this Green's-function theory are presented and specialized to include terms consistent through second order.

Le formalisme des fonctions de Green de polarisation dans la notation utilisant les superopérateurs de Goscinski et Lukman a été réétabli avec un état de référence MC-SCF pour obtenir le métrique des superopérateurs. Les avantages potentiels de cet état de référence plus général ainsi que certains points faibles inhérents associés aux états de référence utilisés traditionnellement dans les théories de perturbation Hartree-Fock ou Rayleigh-Schrödinger sont discutés brièvement. L'hermiticité des superopérateurs est analysée dans le cadre des états de référence MC-SCF. Utilisant une notion d'ordre propre à cet état de référence on présente des formules explicites et des procédés de calcul pour la réalisation de cette théorie des fonctions de Green, qui sont spécialisés pour inclure des termes constants jusqu'au second ordre.

Der Formalismus für Green'sche Funktionen von Polarisierungstyp in der Superoperatorbezeichnung von Goscinski und Lukman wird mittels eines MC-SCF-Referenzzustands hergeleitet. Die möglichen Vorteile mit diesem allgemeineren Referenzzustand und gewisse mit den in den traditionellen Hartree-Fock- oder Rayleigh-Schrödinger-Störungstheorien verwendeten Referenzzuständen verbundene eigene Schwächen werden kurz diskutiert. Die Hermitizität der Superoperatoren wird im Rahmen des MC-SCF-Referenzzustands analysiert. Mittels eines für diesen Referenzzustand geeigneten Ordnungsbegriffs werden explizite Formeln und Rechnungsverfahren für die Implementierung dieser Theorie von Green'schen Funktionen vorgelegt und spezialisiert um Glieder bis zur zweiten Ordnung einzuschließen.

I. Introduction

In the last decade, Green's-function approaches to the direct calculation of electronic excitation energies and other spectral properties have been employed with considerable success to many atomic and molecular systems [1-18]. Electron attachment and detachment processes (i.e., ionization processes) also have been studied extensively with Green's-function methods [9-11, 19-27]. This paper focuses on the development of a new Green's-function approach in which the

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polarization Green's-function (i.e., two-electron Green's-function) equations describing excitation processes are re-derived with respect to a MC-SCF reference state. Two of us (A.B. and J.S.) recently completed an analogous development for the one-electron Green's function, which describes ionization processes [28].

The numerous Green's-function studies reported in the recent literature employ either equations-of-motion [1-10, 19, 20] or propagator [11-18, 21-28] formulations of the electronic excitation (or ionization) problem. Equations-of-motion methods, originally applied to problems in nuclear theory [29] and subsequently developed for atomic and molecular excitation and ionization calculations by McKoy and co-workers [5, 6] and others [1-4, 7-10, 19, 20], recover the results of Green's-function theories by casting the excitation or ionization problem in terms of equations of motion for the excitation or ionization operators of the system. The random phase approximation and the time dependent Hartree-Fock theory are the lowest-order formulations of the equations of motion [6]. Higher random-phase approximations employing extended excitation (or ionization) operator represents and correlated references states are required to achieve accurate results in most molecular applications [5-8, 19, 20]. Solutions to the equations of motion are usually established by means of an operator matrix eigenvalue problem [5-8, 19] or an operator perturbation theory [9, 10]. Simons [10, 30] and Harris [31] have discussed ambiguities in equations-of-motion formulations that take as their starting point a function-level equation. These ambiguities can be avoided either by deriving the equations-of-motion formalism with respect to an operator-level equation, as shown by Simons and Dalgaard [10], or by working directly with the well-defined propagator equations describing excitation processes.

In the works of Linderberg [11], Öhrn [11, 24, 27], Purvis [24], Jørgensen [14, 16-18, 21], Oddershede [14, 17, 18], Cederbaum [25], and others [12, 13, 15, 22, 23, 26], the Green's-function equations are decoupled by perturbation methods, geometrical approximations, or Löwdin's technique of inner projection and partitioning on an operator manifold [32]. When applied to the polarization Green's function, these procedures give excitation energies as poles and transition amplitudes as residues.

Green's-function method for excitations owe their attractiveness to their ability to provide access to excited state properties by expressing them as differences from ground state properties, which are easily approximated. Formal and computational simplicity arising from cancellation of correlation terms common to both the ground state and the excited state of interest [15, 33], together with a relative insensitivity of the operator-level equations to reference state approximations [15, 29], have also been advanced as reasons for preferring the Green's-function approach to the more-traditional methods for calculating excited-state properties, configuration interaction, and perturbation theory. In addition, propagator decoupling procedures have the advantage of giving transition amplitudes directly as residues of the Green's function.

However, recent work by Oddershede and Jørgensen [17] and others [5-8, 12-16] has emphasized the importance of extended operator manifolds and

correlated reference state choices in obtaining accurate excited state properties from Green's-function methods. Theoretical arguments supporting these requirements, originally advanced by Simons [34] for the one-electron Green's function, are equally applicable to approximations involving the polarization Green's function. Simons shows that if a complete operator manifold is employed within the inner projection, the use of an approximate reference state affects only the residues; the exact nature of the pole structure, which for the polarization Green's function is characterized by poles at (\pm) the exact excitation energies, is still preserved. However, operator manifold truncation, an inevitable practical necessity in the computational implementation of a Green's-function theory, does lead to a dependence of the pole structure on the quality of the reference-state approximation. Balanced descriptions of the polarization Green's function, in which both the operator manifold and the reference state are well approximated, are therefore necessary to ensure accuracy; an extended-operator manifold cannot fully compensate for a poor reference state choice and vice versa [17, 34]. Simons and Dalgaard [10] have also pointed out that caution must be exercised in defining and interpreting the operator metrics used in these Green's-function procedures, which has prompted them to introduce a new metric form, well defined mathematically, that recovers the results of the traditional metric forms such as employed by Goscinski and Lukman [35].

While most of the errors associated with Green's-function methods arise from approximations introduced to make the problem computationally tractable (e.g., operator manifold truncation), the necessity of choosing an approximate reference state in terms of which the operator metric is to be defined represents a fundamental weakness in the method [28]. Even those reference states for which correlation has been introduced by augmenting a Hartree-Fock (HF) state with Rayleigh-Schrödinger perturbation theory (RSPT) double-excitation configurations (first order) or both single- and double-excitation configurations (second order), cannot describe well the situation where the zeroth-order HF state poorly represents the system. For example, such a situation occurs in the lowest singlet states of carbenes, where more than one major configuration must be included to yield an adequate state description, even at a zeroth-order level of approximation [36-38]. Ground states of numerous other systems (e.g., Be, F₂, O₂) [39-41] are not well represented by single-configuration approximations. Also, a molecule severely distorted from its equilibrium geometry often requires the flexibility of additional configurations to characterize correctly its electronic structure (e.g., H₂ at large internuclear separations) [42].

In the interest of extending the polarization Green's-function formalism to the chemically interesting class of systems with highly correlated ground states, we re-derive the polarization Green's-function equations through second order using a multiconfiguration self-consistent-field (MC-SCF) reference state [43, 44] within the Goscinski-Lukman superoperator metric [35]. Of course, adequate description of a ground-state correlation is not the only advantage to be gained with the use of a MC-SCF reference state. By admitting this reference state, which dissociates correctly, unlike HF or RSPT reference states, detailed investigation of

excited-state potential surfaces becomes possible within the Green's-function framework. The main points of difference between using RSPT and MC-SCF reference states occur in (i) assessing orders of magnitude of the various terms that arise in the matrix elements of the Green's function; configuration coefficients in the MC-SCF case are determined by optimization of the MC-SCF reference function for minimum energy as opposed to ordering in the electron interaction strength with an RSPT function, and (ii) in the nature of the non-Hermitian components induced in the matrix elements of the Green's function.

The development presented in the following sections will draw upon our recently completed MC-SCF derivation for the one-electron Green's function [28]. In particular, the concept of order introduced in this earlier study will be carried over without modification to the polarization Green's function case. Our notations and choice of operator manifold to be used with the MC-SCF reference state are introduced in Sec. II. We also give explicit expressions for the polarization Green's function in this section and we introduce a concept of order to assess the relative importance of each term. In Sec. III, this ordering concept is used to produce a consistent second-order approximation to the polarization Green's-function equations. We then discuss other possible approximations, as well as computational procedures to be used in implementing our results.

II. Formal Development

A. Notation

The spectral representation of the polarization Green's function in the superoperator notation is [17, 35]

$$\tilde{\mathbf{P}}(E) = (\mathbf{b}^\dagger | (E\hat{I} - \hat{H})^{-1} | \mathbf{b}^\dagger), \quad (1a)$$

where \mathbf{b}^\dagger is a tensor product set of complete sets of fermion creation $\{a_i^\dagger\}$ and annihilation $\{a_i\}$ operators

$$\mathbf{b}^\dagger = \{a_i^\dagger\} \times \{a_j\} = \{a_i^\dagger a_j\}, \quad (1b)$$

and \hat{I} and \hat{H} are the superoperator identity and Hamiltonian, respectively. These superoperators are defined with respect to an arbitrary operator X_i of the projection manifold \mathbf{h} as [35]

$$\hat{I}X_i = X_i, \quad (2a)$$

and

$$\hat{H}X_i = [H, X_i]_{-}. \quad (2b)$$

The electronic Hamiltonian in Eq. (2b) is assumed to be in the second-quantized form [45]

$$H = \sum_{ij} h_{ij} a_i^\dagger a_j + \frac{1}{2} \sum_{ijkl} V_{ijkl} a_i^\dagger a_j^\dagger a_l a_k, \quad (2c)$$

where h_{ij} and V_{ijkl} are one- and two-electron integrals in the spin-orbital basis $\{\phi_i\}$ of the chosen MC-SCF reference state Ψ ;

$$h_{ij} = \int \phi_i^*(1) \left(-\frac{1}{2} \nabla_1^2 - \sum_k \frac{Z_k}{|\mathbf{r}_1 - \mathbf{R}_k|} \right) \phi_j(1) d1, \quad (2d)$$

$$V_{ijkl} = \iint \phi_i^*(1) \phi_j^*(2) \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \phi_k(1) \phi_l(2) d1 d2 \quad (2e)$$

For the subsequent development, we also find it convenient to define a two-electron integral difference

$$\bar{V}_{ijkl} = V_{ijkl} - V_{ijlk}. \quad (2f)$$

The operators of a particle-conserving projection manifold \mathbf{h} appropriate for use with the polarization Green's function support the following binary commutator product average with respect to the MC-SCF reference state [34]:

$$\langle X_i | X_j \rangle = \langle \Psi | [X_i^\dagger, X_j] | \Psi \rangle \quad \forall X_i, X_j \in \mathbf{h}. \quad (3)$$

Using Löwdin's technique of inner projection [32] on the operator manifold \mathbf{h} , here assumed to be complete, the superoperator resolvent $(E\hat{I} - \hat{H})^{-1}$ may be reexpressed in the form

$$(E\hat{I} - \hat{H})^{-1} = |\mathbf{h}\rangle (\mathbf{h} | E\hat{I} - \hat{H} | \mathbf{h})^{-1} \langle \mathbf{h}|, \quad (4)$$

which, upon substitution in the polarization Green's-function expression given in Eq. (1a) yields

$$\tilde{\mathbf{P}}(E) = (\mathbf{b}^\dagger | \mathbf{h}) (\mathbf{h} | E\hat{I} - \hat{H} | \mathbf{h})^{-1} \langle \mathbf{h} | \mathbf{b}^\dagger, \quad (5)$$

This equation provides the basic starting point for the introduction of various approximations leading to practical methods for computing $\tilde{\mathbf{P}}(E)$. The two essential approximations consist of selecting a point at which to truncate the operator manifold \mathbf{h} and picking a reference function Ψ .

B. Operator Space and Multiconfiguration Reference State

Our choice of projection manifold \mathbf{h} is based upon generalization of a completeness theorem for ionization operator manifolds, recently given by Manne [46] and elaborated upon by Dalgaard [47], to the case of a particle-conserving operator manifold. The theorem essentially states that given an N -electron independent-particle state $\Phi_0 = \prod_{i=1}^N a_{\alpha_i}^\dagger |\text{vac}\rangle$ (i.e., an N -electron Slater determinant) and a manifold of operators

$$\mathbf{h} = \bigcup_{n=1}^N \mathbf{h}_{2n} = \{\mathbf{h}_2, \mathbf{h}_4, \dots, \mathbf{h}_{2N}\}, \quad (6)$$

whose submanifolds, the \mathbf{h}_{2n} , are comprised of particle-conserving excitation and de-excitation operators of particle-hole rank n with respect to the orbital

operator manifold \mathbf{h} is defined with respect to the configuration Φ_0 , hence the overlap criterion for the completeness of \mathbf{h} , $\langle \Phi_0 | \Psi \rangle = C_0 \neq 0$ is automatically satisfied. Thus, inner projection of the Green's function on a manifold \mathbf{h} defined with respect to the Φ_0 component of a MC-SCF reference state Ψ is a formally correct procedure, provided that \mathbf{h} is not truncated. Φ_0 is typically chosen to be one of the dominant configurations of the reference state at the given molecular geometry. This stipulation on Φ_0 markedly simplifies the assignment of orders of magnitude to the various Green's-function matrix elements.

If we limit our considerations to a truncated projection manifold $\mathbf{h}^{(4)}$ comprised only of the \mathbf{h}_2 and \mathbf{h}_4 submanifolds, then, as we shall later show, all terms through second order are included in the polarization Green's function. This is also true for RSPT reference states projected on $\mathbf{h}^{(4)}$, although the concept of "order" in this case refers to two-electron integral products, i.e., orders in the electron interaction strength [17]. Since the MC-SCF reference function more closely approaches a true eigenstate of the Hamiltonian than a HF- or even a RSPT-level function, it is reasonable to expect that on $\mathbf{h}^{(4)}$, use of a MC-SCF function can lead to a new second-order theory that will recover *at least* all terms through second "order" in the sense of an RSPT electron interaction [28]. In what follows, we develop a new concept of order arising naturally from the MC-SCF reference state choice, and we provide further justification for employing the truncated manifold $\mathbf{h}^{(4)}$.

C. Basic Working Equations

Within the MC-SCF superoperator product given in Eq. (3), elements of the \mathbf{h}_2 and \mathbf{h}_4 submanifolds displayed in Eq. (7) are not orthogonal to one another. To facilitate further progress, we now orthogonalize the \mathbf{h}_2 and \mathbf{h}_4 submanifolds of $\mathbf{h}^{(4)}$. Since superoperator overlap matrices are explicitly evaluated, it is not necessary to reorthogonalize the new \mathbf{h}_4 operators to one another. Using the Schmidt orthogonalization procedure, the submanifolds \mathbf{h}_2 and \mathbf{h}_4 listed in Eq. (7) are redefined as

$$\mathbf{h}_2^S = [\mathbf{q}_2^{S\dagger}, \mathbf{q}_2^S] \equiv \mathbf{h}_2 = [\{a_m^\dagger a_\alpha\}, \{a_\beta^\dagger a_n\}] \quad (11a)$$

and

$$\begin{aligned} \mathbf{h}_4^S = [\mathbf{q}_4^{S\dagger}, \mathbf{q}_4^S] &\equiv \mathbf{h}_4 - \mathbf{h}_2(\mathbf{h}_2|\mathbf{h}_4) \\ &= \left[\left\{ a_p^\dagger a_\mu a_q^\dagger a_\nu - \sum_\alpha (1 - P_{pq}) a_q^\dagger a_\alpha \langle a_\alpha^\dagger a_p^\dagger a_\mu a_\nu \rangle \right. \right. \\ &\quad \left. \left. - \sum_m (1 - P_{\mu\nu}) a_m^\dagger a_\nu \langle a_p^\dagger a_q^\dagger a_\mu a_m \rangle \right\}, \right. \\ &\quad \left\{ a_\lambda^\dagger a_s a_\sigma^\dagger a_t - \sum_\beta (1 - P_{st}) a_\beta^\dagger a_t \langle a_\lambda^\dagger a_\sigma^\dagger a_s a_\beta \rangle \right. \\ &\quad \left. \left. - \sum_n (1 - P_{\lambda\sigma}) a_\sigma^\dagger a_n \langle a_n^\dagger a_\lambda^\dagger a_s a_t \rangle \right\} \right]; \quad (11b) \end{aligned}$$

In writing Eq. (11b), we have employed a binary index exchange operator P_{ij} . When operating on a term to the right, it converts i to j and j to i . The two-particle density averages (i.e., $\langle a_i^\dagger a_j^\dagger a_k a_l \rangle$) in Eq. (11b) are taken with respect to the MCC-SCF reference state Ψ . The usual index restrictions $p < q$, $\mu < \nu$, and $\lambda < \sigma$, $s < t$ apply to the elements $\{ \{ (q_4^S)_{p\mu q\nu}^\dagger \}, \{ (q_4^S)_{\lambda\sigma t} \} \}$ of \mathbf{h}_4^S . In what follows, we drop the superscript S and assume that the symbols $\mathbf{h}_2 = [\mathbf{q}_2^\dagger, \mathbf{q}_2]$ and $\mathbf{h}_4 = [\mathbf{q}_4^\dagger, \mathbf{q}_4]$ refer to the orthogonalized submanifolds given in Eqs. (11a) and (11b). For the orthogonalized manifold $\mathbf{h}^{(4)} = \mathbf{h}_2 \cup \mathbf{h}_4$ the superoperator overlap equations become

$$(\mathbf{h}_2|\mathbf{h}_2) = \mathbf{S}_{2,2}, \quad (12a)$$

$$(\mathbf{h}_2|\mathbf{h}_4) = \mathbf{S}_{2,4} = \mathbf{O}_{2,4}, \quad (12b)$$

$$(\mathbf{h}_4|\mathbf{h}_2) = \mathbf{S}_{4,2} = \mathbf{O}_{4,2}, \quad (12c)$$

and

$$(\mathbf{h}_4|\mathbf{h}_4) = \mathbf{S}_{4,4}, \quad (12d)$$

where

$$\mathbf{S}_{2n,2n'} = \begin{bmatrix} (\mathbf{q}_{2n}^\dagger|\mathbf{q}_{2n'}^\dagger) & (\mathbf{q}_{2n}^\dagger|\mathbf{q}_{2n'}) \\ (\mathbf{q}_{2n}|\mathbf{q}_{2n'}^\dagger) & (\mathbf{q}_{2n}|\mathbf{q}_{2n'}) \end{bmatrix} \quad n, n' \in 1, 2. \quad (12e)$$

Using Eqs. (12a)–(12e), the polarization Green's-function expression given in Eq. (5) can be partitioned on the orthogonal inner projection manifold $\mathbf{h}^{(4)}$ to yield*

$$\tilde{\mathbf{P}}(E) = (\mathbf{b}^\dagger|\mathbf{h}_2)\mathbf{P}(E)(\mathbf{h}_2|\mathbf{b}^\dagger), \quad (13a)$$

with

$$\begin{aligned} \mathbf{P}^{-1}(E) &= (\mathbf{h}_2|\hat{\mathbf{P}}^{-1}(E)|\mathbf{h}_2) \\ &= (\mathbf{h}_2|E\hat{\mathbf{I}} - \hat{\mathbf{H}}|\mathbf{h}_2) - (\mathbf{h}_2|\hat{\mathbf{H}}|\mathbf{h}_4)(\mathbf{h}_4|E\hat{\mathbf{I}} - \hat{\mathbf{H}}|\mathbf{h}_4)^{-1}(\mathbf{h}_4|\hat{\mathbf{H}}|\mathbf{h}_2) \\ &= \mathbf{A}(E) - \mathbf{B}\mathbf{M}^{-1}(E)\mathbf{C}. \end{aligned} \quad (13b)$$

The matrices \mathbf{A} , \mathbf{B} , \mathbf{M} , and \mathbf{C} in Eq. (13b) are given as

$$\mathbf{A}(E) = (\mathbf{h}_2|E\hat{\mathbf{I}} - \hat{\mathbf{H}}|\mathbf{h}_2) = E\mathbf{S}_{2,2} - \mathbf{A}', \quad (13c)$$

$$\mathbf{A}' = (\mathbf{h}_2|\hat{\mathbf{H}}|\mathbf{h}_2), \quad (13d)$$

$$\mathbf{B} = (\mathbf{h}_2|\hat{\mathbf{H}}|\mathbf{h}_4), \quad (13e)$$

$$\mathbf{C} = (\mathbf{h}_4|\hat{\mathbf{H}}|\mathbf{h}_2), \quad (13f)$$

$$\mathbf{M}(E) = (\mathbf{h}_4|E\hat{\mathbf{I}} - \hat{\mathbf{H}}|\mathbf{h}_4) = E\mathbf{S}_{4,4} - \mathbf{M}', \quad (13g)$$

* It is possible to show that for Eqs. (13a) and (13b) to hold, it is sufficient to have $(\mathbf{h}_2|\mathbf{h}_i) = 0$ for $i = 4, 6, 8, \dots$. With the superoperator resolution of the identity expressed as $\hat{\mathbf{I}} = |\mathbf{h}\rangle(\mathbf{h}|\mathbf{h})^{-1}\langle\mathbf{h}|$, the representation of the inverse of a superoperator $\hat{\mathbf{A}}$ becomes $(\mathbf{h}|\hat{\mathbf{A}}^{-1}|\mathbf{h}) = (\mathbf{h}|\mathbf{h})(\mathbf{h}|\hat{\mathbf{A}}|\mathbf{h})^{-1}(\mathbf{h}|\mathbf{h})$. This representation taken together with the condition $(\mathbf{h}_2|\mathbf{h}_i) = 0$ ensured by our use of a Schmidt-orthogonalized projection manifold [see Eqs. (12b)–(12c)] immediately gives Eqs. (13a) and (13b) from Eq. (5).

and

$$\mathbf{M}' = (\mathbf{h}_4 | \hat{H} | \mathbf{h}_4). \quad (13h)$$

The expressions displayed in Eqs. (13a)–(13h) constitute our basic working equations when defined with respect to a MC-SCF reference state. Like the overlap matrices in Eqs. (12a)–(12e), each of the constituent Green's-function matrices in Eqs. (13c)–(13h) breaks down into four blocks within $[\mathbf{q}_{2n}^\dagger, \mathbf{q}_{2n}]$ representation of the \mathbf{h}_{2n} ; e.g.,

$$\mathbf{A}(E) = \begin{bmatrix} (\mathbf{q}_2^\dagger | E\hat{I} - \hat{H} | \mathbf{q}_2^\dagger) & (\mathbf{q}_2^\dagger | E\hat{I} - \hat{H} | \mathbf{q}_2) \\ (\mathbf{q}_2 | E\hat{I} - \hat{H} | \mathbf{q}_2^\dagger) & (\mathbf{q}_2 | E\hat{I} - \hat{H} | \mathbf{q}_2) \end{bmatrix}. \quad (14a)$$

Consequently, the polarization Green's-function matrix shown in Eq. (13b) breaks down into four blocks as well

$$\mathbf{P}^{-1}(E) = \begin{bmatrix} (\mathbf{q}_2^\dagger | \hat{P}^{-1}(E) | \mathbf{q}_2^\dagger) & (\mathbf{q}_2^\dagger | \hat{P}^{-1}(E) | \mathbf{q}_2) \\ (\mathbf{q}_2 | \hat{P}^{-1}(E) | \mathbf{q}_2^\dagger) & (\mathbf{q}_2 | \hat{P}^{-1}(E) | \mathbf{q}_2) \end{bmatrix}. \quad (14b)$$

D. Hermiticity of \hat{H}

1. Hermiticity condition. The superoperator Hamiltonian \hat{H} is Hermitian if and only if

$$(X_i | \hat{H} | X_j) - (X_j | \hat{H} | X_i)^* = 0 \quad \forall X_i, X_j \in \mathbf{h}. \quad (15)$$

It is relatively easy to show that the left-hand side of Eq. (15) may be re-expressed as

$$(X_i | \hat{H} | X_j) - (X_j | \hat{H} | X_i)^* = \langle \hat{H} [X_i^\dagger, X_j]_- \rangle \quad (16)$$

for operators X_i, X_j belonging to a particle-conserving manifold. If the reference state Ψ with respect to which Eq. (15) is averaged is an exact eigenstate of H , then Eq. (15) is exactly satisfied and \hat{H} is Hermitian on \mathbf{h} . Thus, with an exact Ψ , the propagator separation theorem is valid for the poles of $\mathbf{P}(E)$, even if a truncated projection manifold is employed. However, a first-order change in the reference ground state relative to the exact ground state (i.e., $\Psi = \Psi_{\text{exact}} + \delta\Psi_{\text{exact}}$) can induce non-Hermitian components in the matrix elements of $\mathbf{P}(E)$, which in turn may give rise to artificial imaginary components in its pole structure. Since the matrix elements of $\mathbf{P}(E)$ are superoperator expectation values of \hat{H} or $E\hat{I} - \hat{H}$, extraneous non-Hermitian contributions to $\mathbf{P}(E)$ for our chosen MC-SCF reference state Ψ can be determined by computing $\langle \hat{H} [X_i^\dagger, X_j]_- \rangle$ for those operators X_i and X_j over which the \mathbf{A} , \mathbf{B} , \mathbf{C} , and \mathbf{M} matrices of $\mathbf{P}(E)$ are defined.

2. A matrix hermiticity. $\langle \hat{H} [X_j^\dagger, X_i]_- \rangle$ [Eq. (16)] must be computed for X_i, X_j belonging to each of the four blocks of \mathbf{A} shown in Eq. (14a). For the block with $X_i = a_m^\dagger a_\alpha$, $X_j = a_n^\dagger a_\beta$, $\in \mathbf{q}_2^\dagger$ evaluation of Eq. (16) using the generalized Brillouin

theorem [Eq. (10)] gives

$$\begin{aligned}\langle \hat{H}[(q_2)_{\alpha m}, (q_2^\dagger)_{n\beta}]_- \rangle &= \langle \hat{H}[a_\alpha^\dagger a_m, a_n^\dagger a_\beta]_- \rangle \\ &= \delta_{nm} \langle \hat{H}(a_\alpha^\dagger a_\beta) \rangle - \delta_{\beta\alpha} \langle \hat{H}(a_n^\dagger a_m) \rangle \\ &= 0.\end{aligned}\quad (17a)$$

Similar application of Eq. (10) to Eq. (16) for the block of **A** with $X_i = \alpha^\dagger a_m$, $X_j = a_\beta^\dagger a_n \in \mathbf{q}_2$ yields

$$\begin{aligned}\langle \hat{H}[(q_2^\dagger)_{m\alpha}, (q_2)_{\beta n}]_- \rangle &= \langle \hat{H}[a_m^\dagger a_\alpha, a_\beta^\dagger a_n]_- \rangle \\ &= \delta_{\alpha\beta} \langle \hat{H}(a_m^\dagger a_n) \rangle - \delta_{nm} \langle \hat{H}(a_\beta^\dagger a_\alpha) \rangle \\ &= 0.\end{aligned}\quad (17b)$$

The operators X_i^\dagger and X_j commute in the two remaining blocks of **A**, where $X_i = a_m^\dagger a_\alpha \in \mathbf{q}_2^\dagger$, $X_j = a_\beta^\dagger a_n \in \mathbf{q}_2$, and $X_i = a_\alpha^\dagger a_m \in \mathbf{q}_s$, $X_j = a_n^\dagger a_\beta \in \mathbf{q}_2^\dagger$. Thus, the **A** matrix is Hermitian within the MC-SCF reference state choice used to establish the generalized Brillouin theorem.

3. Relationship between B and C. **B** and **C** are "nonsquare" matrices, so considerations of Hermiticity do not apply directly. However, the matrix product $\mathbf{B}\mathbf{M}^{-1}\mathbf{C}$ appearing in $\mathbf{P}^{-1}(E)$ cannot be Hermitian for Hermitian \mathbf{M}^{-1} unless **B** and **C** are adjoints of each other. To address the problem of non-Hermiticity in $\mathbf{B}\mathbf{M}^{-1}\mathbf{C}$, we can consider **B** and **C** as a couple and investigate deviations from the perfect adjoint relationship

$$\mathbf{B} = \mathbf{C}^\dagger. \quad (18a)$$

In this case, Eq. (16) becomes a tool to investigate the value of

$$\Delta = \mathbf{B} - \mathbf{C}^\dagger, \quad (18b)$$

where

$$\Delta_{i,j} = \Delta(X_i, X_j) = B_{i,j} - C_{j,i}^* = \langle \hat{H}[X_i^\dagger, X_j]_- \rangle \quad (18c)$$

for $X_i \in \mathbf{h}_2$ and $X_j \in \mathbf{h}_4$. Equation (18c) follows directly from the defining Eqs. (13e)–(13f) for **B** and **C**. For the block of Δ with $X_i \in \mathbf{q}_2^\dagger$, $X_j \in \mathbf{q}_4$, we have

$$\begin{aligned}\Delta_{m\alpha, p\mu q\nu} &= \langle \hat{H}[(q_2)_{\alpha m}, (q_4^\dagger)_{p\mu q\nu}]_- \rangle \\ &= (1 - P_{pq}) \delta_{mq} \langle \hat{H}(a_\alpha^\dagger a_p^\dagger a_\mu a_\nu) \rangle + (1 - P_{\mu\nu}) \delta_{\nu\alpha} \langle \hat{H}(a_p^\dagger a_q^\dagger a_\mu a_m) \rangle\end{aligned}\quad (18d)$$

and for the block characterized by $X_i \in \mathbf{q}_2$, $X_j \in \mathbf{q}_4$, Eq. (16) yields

$$\begin{aligned}\Delta_{\beta n, \lambda\sigma t} &= \langle \hat{H}[(q_2^\dagger)_{n\beta}, (q_4)_{\lambda\sigma t}]_- \rangle \\ &= (1 - P_{st}) \delta_{tn} \langle \hat{H}(a_\lambda^\dagger a_\sigma^\dagger a_\beta a_t) \rangle + (1 - P_{\lambda\sigma}) \delta_{\beta\sigma} \langle \hat{H}(a_n^\dagger a_\lambda^\dagger a_\beta a_t) \rangle.\end{aligned}\quad (18e)$$

Equations (18d) and (18e) are evaluated explicitly in Appendix A. In the other two blocks of Δ , where $X_i \in \mathbf{q}_2^\dagger$, $X_j \in \mathbf{q}_4$ and $X_i \in \mathbf{q}_2$, $X_j \in \mathbf{q}_4^\dagger$, it is easy to verify that

$[X_i^\dagger, X_j]_- = 0$. From Eqs. (18d) and (18e), it is seen that $\Delta \neq 0$, hence **B** and **C** are not adjoints of each another. However, if **B** and **C** are redefined as the symmetrized matrices

$$\tilde{\mathbf{B}} = \frac{1}{2}(\mathbf{B} + \mathbf{C}^\dagger) = \mathbf{B} - \frac{1}{2}\Delta = \mathbf{C}^\dagger + \frac{1}{2}\Delta \quad (18f)$$

and

$$\tilde{\mathbf{C}} = \frac{1}{2}(\mathbf{B}^\dagger + \mathbf{C}) = \mathbf{B}^\dagger - \frac{1}{2}\Delta^\dagger = \mathbf{C} + \frac{1}{2}\Delta^\dagger, \quad (18g)$$

then obviously

$$\tilde{\mathbf{B}} = \tilde{\mathbf{C}}^\dagger. \quad (18h)$$

In the limit of an exact reference state, $\Delta = 0$, and Eqs. (18f)–(18g) collapse to

$$\tilde{\mathbf{B}} = \mathbf{B} \quad (18i)$$

and

$$\tilde{\mathbf{C}} = \mathbf{C}. \quad (18j)$$

The symmetrized matrices $\tilde{\mathbf{B}}$ and $\tilde{\mathbf{B}}^\dagger = \tilde{\mathbf{C}}$ will be used in deriving more explicit representations for the Green's-function equations. With a high-quality MC-SCF reference state Ψ , the matrix elements of Δ are small and Eqs. (18f) and (18g) are well approximated.

4. Hermiticity of \mathbf{M} . Analysis of the blocks of **M** by means of Eq. (16) and the generalized Brillouin theorem [Eq. (10)] yields

$$\langle \hat{H}[X_i^\dagger, X_j]_- \rangle \begin{cases} \neq 0 & X_i, X_j \in \mathbf{q}_4^\dagger \text{ and } X_i, X_j \in \mathbf{q}_4 \ (i \neq j), \\ = 0 & X_i \in \mathbf{q}_4^\dagger, X_j \in \mathbf{q}_4 \text{ and } X_i \in \mathbf{q}_4, X_j \in \mathbf{q}_4^\dagger. \end{cases} \quad (19)$$

Owing to the complexity of the matrix elements in Eq. (19), explicit expressions for these non-Hermiticity factors are not reproduced in the text, but are available from the authors upon request. Except for the trivial case of the diagonal elements, the non-Hermiticity factors in Eq. (19) do not vanish, hence **M** is non-Hermitian. Since **M**, the matrix of largest dimension in $\mathbf{P}^{-1}(E)$, must be inverted many times during the $\mathbf{P}(E)$ pole search, a Hermitian diagonal approximation to its matrix elements becomes computationally attractive. Diagonal **M** approximations have been used with success in computational implementations of other Green's-function theories employing correlated reference states [17–20, 24]. Since the non-Hermiticity of **M** is an artifact that disappears in the limit of an exact reference state, nondiagonal Hermitian approximations such as averaging off-diagonal matrix elements or defining **M** with respect to a symmetric commutator should also be viable. Given the high quality of the MC-SCF reference state used to calculate **M**, the off-diagonal **M** matrix elements will be small and approximations involving truncation or modification of these elements will provide reasonable descriptions of **M**. We elaborate upon this point in Sec. III.

E. Explicit Expressions

1. Notation. In order to simplify our discussion, an indexed representation of $\mathbf{P}^{-1}(E)$, Eq. (13b), is reproduced below:

$$\begin{aligned} [\mathbf{P}^{-1}(E)]_{ab,fg} &= [\mathbf{A}(E) - \tilde{\mathbf{B}}\mathbf{M}^{-1}(E)\tilde{\mathbf{B}}^{\dagger}]_{ab,fg} \\ &= A_{ab,fg} - \sum_{\Lambda, \Omega} \tilde{B}_{ab, \Lambda} M_{\Lambda \Omega}^{-1} \tilde{B}_{fg, \Omega}^*. \end{aligned} \quad (20a)$$

The combined indices Λ and Ω in Eq. (20a) stand for groups of spin-orbital indices running over the elements of the $\mathbf{h}_4 = [\mathbf{q}_4^{\dagger}, \mathbf{q}_4]$ submanifold:

$$\begin{aligned} \Lambda &= \begin{cases} (p\mu q\nu) & \mathbf{q}_4^{\dagger}, \\ (\mu p \nu q) & \mathbf{q}_4, \end{cases} \\ \Omega &= \begin{cases} (s\lambda t\sigma) & \mathbf{q}_4^{\dagger}, \\ (\lambda s \sigma t) & \mathbf{q}_4. \end{cases} \end{aligned} \quad (20b)$$

The spin-orbital indices ab and fg are restricted to run over the elements of the $\mathbf{h}_2 = [\mathbf{q}_2^{\dagger}, \mathbf{q}_2]$ submanifold:

$$\begin{aligned} ab &= \begin{cases} m\alpha & \mathbf{q}_2^{\dagger}, \\ \alpha m & \mathbf{q}_2, \end{cases} \\ fg &= \begin{cases} n\beta & \mathbf{q}_2^{\dagger}, \\ \beta n & \mathbf{q}_2. \end{cases} \end{aligned} \quad (20c)$$

By using these unspecified spin orbital labels (i.e., ab and fg) to denote the element of $\mathbf{P}^{-1}(E)$, explicit expressions applicable to each of the four blocks of $\mathbf{P}^{-1}(E)$ displayed in Eq. (14b) can be derived. Using the generalized Brillouin theorem of Eq. (10) to discard null-valued terms, we are able to obtain the following explicit representations for the various matrix elements appearing in Eq. (20a).

2. A matrix. Evaluation of Eqs. (13c) and (13d) yields

$$A_{ab,fg} = ((h_2)_{ab} | E\hat{I} - \hat{H} | (h_2)_{fg}) = ES_{ab,fg} - A'_{ab,fg}, \quad (21a)$$

where

$$S_{ab,fg} = \delta_{af} \langle a_b^{\dagger} a_g \rangle - \delta_{bg} \langle a_f^{\dagger} a_a \rangle \quad (21b)$$

and

$$\begin{aligned} A'_{ab,fg} &= h_{af} \langle a_b^{\dagger} a_g \rangle + h_{gb} \langle a_f^{\dagger} a_a \rangle - \sum_i \{ \delta_{bg} h_{if} \langle a_i^{\dagger} a_a \rangle + \delta_{af} h_{gi} \langle a_b^{\dagger} a_i \rangle \} \\ &+ \frac{1}{2} \sum_{ij} \{ \bar{V}_{gajj} \langle a_b^{\dagger} a_f^{\dagger} a_j a_i \rangle + \bar{V}_{ijfb} \langle a_i^{\dagger} a_j^{\dagger} a_g a_a \rangle \\ &+ 2 \bar{V}_{igjb} \langle a_f^{\dagger} a_i^{\dagger} a_j a_a \rangle + 2 \bar{V}_{aiff} \langle a_b^{\dagger} a_i^{\dagger} a_j \bar{a}_g \rangle \} \\ &+ \frac{1}{2} \sum_{ijk} \{ \delta_{af} \bar{V}_{igjk} \langle a_b^{\dagger} a_i^{\dagger} a_k a_j \rangle + \delta_{bg} \bar{V}_{ijkf} \langle a_i^{\dagger} a_j^{\dagger} a_k a_a \rangle \}. \end{aligned} \quad (21c)$$

3. Conjugate $\tilde{\mathbf{B}}$ and $\tilde{\mathbf{C}}$ Matrices. Using the explicit expressions given in Eq. (11b) for the $\Lambda = (p\mu q\nu)$ component of \mathbf{h}_4 , Eqs. (13e) and (13f) for the nonconjugate \mathbf{B} and \mathbf{C} matrices become

$$\begin{aligned} B_{ab,p\mu q\nu} &= ((h_2)_{ab} | \hat{H} | (q_4^\dagger)_{p\mu q\nu}) \\ &= B'_{ab,p\mu q\nu} - \sum_{\alpha} (1 - P_{pq}) \langle a_{\alpha}^\dagger a_p^\dagger a_{\mu} a_{\nu} \rangle A'_{ab,q\alpha} \\ &\quad - \sum_m (1 - P_{\mu\nu}) \langle a_p^\dagger a_q^\dagger a_{\mu} a_m \rangle A'_{ab,m\nu} \end{aligned} \quad (22a)$$

and

$$\begin{aligned} C_{p\mu q\nu,ab} &= ((q_4^\dagger)_{p\mu q\nu} | \hat{H} | (h_2)_{ab}) \\ &= C'_{p\mu q\nu,ab} - \sum_{\alpha} (1 - P_{pq}) \langle a_{\alpha}^\dagger a_p^\dagger a_{\mu} a_{\nu} \rangle^* A'_{q\alpha,ab} \\ &\quad - \sum_m (1 - P_{\mu\nu}) \langle a_p^\dagger a_q^\dagger a_{\mu} a_m \rangle^* A'_{m\nu,ab}, \end{aligned} \quad (22b)$$

where

$$B'_{ab,p\mu q\nu} = (a_b^\dagger a_b | \hat{H} | a_p^\dagger a_{\mu} a_q^\dagger a_{\nu}), \quad (22c)$$

and

$$C'_{p\mu q\nu,ab} = (a_p^\dagger a_{\mu} a_q^\dagger a_{\nu} | \hat{H} | a_a^\dagger a_b). \quad (22d)$$

The elements of the Hermitian \mathbf{A}' matrix appearing in the Schmidt components of Eqs. (22a) and (22b) are written out with general indices in Eq. (21c). Substitution of Eqs. (22a) and (22b) into the expression for $\tilde{\mathbf{B}}$, Eq. (18f), yields

$$\begin{aligned} \tilde{B}_{ab,p\mu q\nu} &= \tilde{B}'_{ab,p\mu q\nu} - \sum_{\alpha} (1 - P_{pq}) \langle a_{\alpha}^\dagger a_p^\dagger a_{\mu} a_{\nu} \rangle A'_{ab,q\alpha} \\ &\quad - \sum_m (1 - P_{\mu\nu}) \langle a_p^\dagger a_q^\dagger a_{\mu} a_m \rangle A'_{ab,m\nu} = \tilde{C}_{p\mu q\nu,ab}^* \end{aligned} \quad (22e)$$

with

$$\tilde{B}'_{ab,p\mu q\nu} = \frac{1}{2} [B'_{ab,p\mu q\nu} + C_{p\mu q\nu,ab}^*]. \quad (22f)$$

In deriving Eq. (22e), we have used the obvious fact that Schmidt components of \mathbf{B} and \mathbf{C} are conjugate to one another. Since the matrix elements of $\tilde{\mathbf{B}}'$ are quite lengthy, they are not shown here, but are available upon request from the authors. Order-truncated expressions for $\tilde{\mathbf{B}}'$ are displayed in Appendix A however. The elements $\tilde{B}_{ab,\mu p \nu q}$ can be obtained from the $\tilde{B}_{ab,p\mu q\nu}$ elements of Eq. (22e) by the simple index transformation $\Lambda(\mathbf{q}_4^\dagger \rightarrow \mathbf{q}_4) = (p \rightarrow \mu, \mu \rightarrow p, \nu \rightarrow q, q \rightarrow \nu)$.

4. \mathbf{M} matrix. With the combined index labels for \mathbf{h}_4 defined in Eq. (20b), the expressions given in Eqs. (13g) and (13h) for the \mathbf{M} matrix become

$$M_{\Lambda\Omega} = ((h_4)_{\Lambda} | E\hat{I} - \hat{H} | (h_4)_{\Omega}) = ES_{\Lambda\Omega} - M'_{\Lambda\Omega}. \quad (23a)$$

Since it is necessary to introduce a diagonal approximation to the \mathbf{M} matrix to bring it into a computationally manageable form, the complicated explicit

expressions for its off-diagonal elements are not reproduced. For the diagonal elements of the $\mathbf{q}_4^\dagger, \mathbf{q}_4$ block of \mathbf{M} with $\Lambda = \Omega = (p\mu q\nu)$, we have

$$S_{p\mu q\nu, p\mu q\nu} = ((q_4^\dagger)_{p\mu q\nu} | (q_4^\dagger)_{p\mu q\nu}) \quad (23b)$$

and

$$M'_{p\mu q\nu, p\mu q\nu} = ((q_4^\dagger)_{p\mu q\nu} | \hat{H} | (q_4^\dagger)_{p\mu q\nu}). \quad (23c)$$

\mathbf{M} is evaluated by substituting into Eqs. (23b) and (23c) the explicit form for $(q_4^\dagger)_{p\mu q\nu}$ given in Eq. (11b) and employing the generalized Brillouin theorem [Eq. (10)] to simplify the resulting expressions. Matrix elements for the $\mathbf{q}_4, \mathbf{q}_4$ block of \mathbf{M} can be recovered from Eqs. (23b) and (23c) by the index transformation $\Lambda(\mathbf{q}_4^\dagger \rightarrow \mathbf{q}_4) = \Omega(\mathbf{q}_4^\dagger \rightarrow \mathbf{q}_4) = (p \rightarrow \mu, \mu \rightarrow p, \nu \rightarrow q, q \rightarrow \nu)$. The complexity of Eqs. (23b) and (23c) precludes their explicit publication, except in an abridged order-truncated form, as shown in Appendix A. Explicit expressions for the complete diagonal and off-diagonal matrix elements of \mathbf{M} are also available from the authors upon request.

F. Order Analysis

To calculate the \mathbf{A} , \mathbf{B} , and \mathbf{M} matrix elements presented in Sec. II E, it is necessary to know the values of certain one- and two-electron integrals (i.e., h_{ij} , \bar{V}_{ijkl}) and certain components of the one-, two-, three-, and four-particle density matrices [i.e., $\langle (\prod_{i=1}^n a_i^\dagger) (\prod_{j=1}^n a_j) \rangle$, $n \in 1, 2, 3, 4$], where both the integrals and density-matrix components are defined with respect to the MC-SCF orbital basis $\{\phi_i\}$. It is important to keep in mind that for a specific choice of the MC-SCF reference state Ψ , many of the complicated terms appearing in \mathbf{A} , $\tilde{\mathbf{B}}$, and \mathbf{M} will be zero. In particular, only a few of the three- and four-particle density matrices will contribute. By restricting the Green's-function theory to second order, it is possible to eliminate many of the smaller higher-order terms as well.

In this section, we assign orders to the various components of \mathbf{A} , $\tilde{\mathbf{B}}$, and \mathbf{M} then discard terms higher than second order. The order concept we employ was developed earlier for the analogous MC-SCF one-electron Green's-function problem [28]. For completeness, we summarize this earlier development before implementing it to simplify the various terms in \mathbf{A} , $\tilde{\mathbf{B}}$, and \mathbf{M} . This new concept of order is based upon the physically reasonable assumption that for most systems of interest, the MC-SCF spin-orbital set $\{\phi_i\}$ can be partitioned into two disjoint subsets L and S , whose elements have either large (near unit) or small (near zero) occupation numbers with respect to the MC-SCF reference state Ψ :

$$\langle \eta_i^\dagger \rangle = \langle a_i^\dagger a_i \rangle \approx \begin{cases} 1 \rightarrow i \in L \\ 0 \rightarrow i \in S \end{cases} \quad (24a)$$

(i.e., we are assuming that ϕ_i will either be occupied or unoccupied in most of the dominant configurations of Ψ).^{*} This assumption lets us assign orders of magnitude to the diagonal density matrix elements (i.e., $\langle a_i^\dagger a_i \rangle$, $\langle a_i^\dagger a_j^\dagger a_j a_i \rangle$, $\langle a_i^\dagger a_j^\dagger a_k^\dagger a_k a_j a_i \rangle$, $\langle a_i^\dagger a_j^\dagger a_k^\dagger a_l^\dagger a_l a_k a_j a_i \rangle$). Using the Schwartz inequality, upper bounds to the orders of the off-diagonal density matrix elements can be found by relating them to products of diagonal elements, whose orders are known:

$$\begin{aligned} |\langle a_i^\dagger a_j \rangle|^2 &\leq \langle a_i^\dagger a_i \rangle \langle a_j^\dagger a_j \rangle, \\ |\langle a_i^\dagger a_j^\dagger a_k a_l \rangle|^2 &\leq \langle a_i^\dagger a_j^\dagger a_j a_i \rangle \langle a_l^\dagger a_k^\dagger a_k a_l \rangle. \end{aligned} \quad (24b)$$

For example, in the case of the one-particle density matrix whose diagonal elements are ordered as

$$\langle a_i^\dagger a_i \rangle = \begin{cases} O(0) & i \in L \\ O(2) & i \in S \end{cases} \quad (24c)$$

application of Eqs. (24a) and (24b) enables us to write

$$\langle a_i^\dagger a_j \rangle = \begin{cases} O(0) & i, j \in L \\ O(1) & i \in S, j \in L \text{ and } i \in L, j \in S, \\ O(2) & i, j \in S. \end{cases} \quad (24d)$$

Similar concepts are easily extended to the higher-order density matrix elements. The overall result is quite simple: to determine the order of a term containing an n -particle density matrix element $\langle (\prod_{i=1}^n a_i^\dagger) (\prod_{j=1}^n a_j) \rangle$, one counts the number of spin-orbital indices belonging to S ; the total count is equal to the order of this element. Representative examples of this occupation number ordering concept are presented in Table I.

Before we can apply this concept of order to the terms of $\mathbf{P}^{-1}(E)$, it is necessary to develop rules for ordering products of density-matrix elements with one- and two-electron integrals and with other density-matrix elements. Since a one-electron integral h_{ij} can be quite large (e.g., h_{ii} is of the order of the orbital energy ϵ_i), we do not truncate any terms of the type $h_{ij} \langle (\prod_{i'=1}^n a_{i'}^\dagger) (\prod_{j'=1}^n a_{j'}) \rangle$, even if the density element by itself is higher than the desired order. With only a few exceptions, the magnitude of a two-electron integral lies between 0 and 1, thus a

^{*} For a MC-SCF wave function of the type given in Eq. (8), $\Psi = \sum_{K=0}^M C_K \Phi_K$, this assumption implies that the set of mixing coefficients $\{C_K | K=0, M\}$ can be partitioned as $\{C_L | L=0, m\}$ and $\{C_S | S=m+1, M\}$ such that $|C_L|^2 \gg |C_S|^2$ for all L and S . This is generally true for nonextended systems; an example can be seen in Ref. 44 where for $b^{-1} \sum^+ NH$ at $R_e = 1.95$ bohr, the C_L set has valence configurations $3\sigma^2 1\pi^2$ and $3\sigma 4\sigma 1\pi^2$ with coefficients 0.92 and -0.37 , respectively. In contrast, the coefficient of largest magnitude from the C_S set is 0.09. While the assumption of a distinct L/S boundary may not be strictly valid for delocalized systems such as metals, an L/S partition can still be constructed by including in the L -orbital subset those orbitals with occupation number averages of intermediate magnitude.

TABLE I. Examples of the occupation number ordering concept. It is assumed in these examples that L consists of all orbitals occupied in Φ_0 , the dominant configuration of the MC-SCF reference state, and S consists of those orbitals unoccupied in Φ_0 . Orbitals belonging to L or S are thus denoted by Greek indices or the Roman indices m, n, o, \dots, z , respectively.

Density Matrix element	L/S Classification	Order (#S)
$\langle a_m^\dagger a_m \rangle$	$\langle S^\dagger L \rangle$	1
$\langle a_\alpha^\dagger a_\rho^\dagger a_\mu a_\nu \rangle$	$\langle L^\dagger S^\dagger LL \rangle$	1
$\langle a_p^\dagger a_q^\dagger a_\nu a_m \rangle$	$\langle S^\dagger S^\dagger LS \rangle$	3
$\langle a_\nu^\dagger a_\mu^\dagger a_\rho^\dagger a_q^\dagger a_\mu a_\nu a_i \rangle$	$\langle L^\dagger L^\dagger S^\dagger LLL \rangle$ $i \in L$	1
	$\langle L^\dagger L^\dagger S^\dagger LLS \rangle$ $i \in S$	2
$\langle a_\nu^\dagger a_\mu^\dagger a_i^\dagger a_q^\dagger a_\rho a_\mu a_\nu a_j \rangle$	$\langle L^\dagger L^\dagger L^\dagger S^\dagger SLLL \rangle$ $i, j \in L$	2
	$\langle L^\dagger L^\dagger S^\dagger S^\dagger SLLL \rangle$ $i \in S, j \in L$	3
	$\langle L^\dagger L^\dagger L^\dagger S^\dagger SLLS \rangle$ $i \in L, j \in S$	3
	$\langle L^\dagger L^\dagger S^\dagger S^\dagger SLLS \rangle$ $i, j \in S$	4

lower bound to the order of the product $\bar{V}_{ijkl} \langle (\prod_{i'=1}^n a_i^\dagger) (\prod_{j'=1}^n a_j) \rangle$ will be given by the order of its density-matrix component. An integral V_{ijij} can be greater than unity if ϕ_i and ϕ_j are radially contracted orbitals whose electron densities $|\phi_i|^2$ and $|\phi_j|^2$ overlap significantly within a small region of space. Typically there exist only one or two such orbitals in a basis $\{\phi_j\}$ that can give a two-electron integral not bounded by unity. Thus, for almost every integral V_{ijkl} , the order of $V_{ijkl} \langle (\prod_{i'=1}^n a_i^\dagger) (\prod_{j'=1}^n a_j) \rangle$ is either the same as or higher than the order of the density-matrix element alone. For products of density matrix elements, each element in the product is ordered separately and product terms higher than the desired order are then truncated. More refined order approximations that consider the magnitudes of the individual one- and two-electron integrals are also possible. We use the occupation number concept of order in Sec. II to bring the expression for \mathbf{A} , $\tilde{\mathbf{B}}$, and \mathbf{M} and hence $\mathbf{P}^{-1}(E)$ into a consistent, computationally tractable second order form. Unlike RSPT ordering in the electron interaction, this occupation number ordering scheme preserves itself even when applied to systems with highly correlated reference states or severely distorted geometries.

III. Operational Considerations

A. L/S Orbital Partition

As discussed in Sec. II F, the occupation number ordering concept assumes a partition of the MC-SCF spin-orbital set $\{\phi_i\}$ into two disjoint subsets $\{\phi_i | i \in L\}$ and $\{\phi_j | j \in S\}$ based upon orbital occupation number magnitude in the MC-SCF reference state Ψ . Accordingly, we repartition our occupied and unoccupied spin-orbital subsets $\{\phi_\alpha\}$ and $\{\phi_m\}$, which are defined with respect to the Φ_0

component of Ψ , into L and S subsets:

$$\begin{aligned}\{\phi_i\} &= \{\phi_i | i \in L\} \cup \{\phi_i | i \in S\} = \{\phi_\alpha\} \cup \{\phi_m\}, \\ \{\phi_\alpha\} &= \{\phi_\alpha | \alpha \in L\} \cup \{\phi_\alpha | \alpha \in S\}, \\ \{\phi_m\} &= \{\phi_m | m \in L\} \cup \{\phi_m | m \in S\}, \\ \{\phi_i | i \in L\} &= \{\phi_\alpha | \alpha \in L\} \cup \{\phi_m | m \in L\}, \\ \{\phi_j | j \in S\} &= \{\phi_\alpha | \alpha \in S\} \cup \{\phi_m | m \in S\}.\end{aligned}\tag{25a}$$

Since Φ_0 is chosen to be the dominant configuration in Ψ , it can be assumed without loss of generality that $\{\phi_\alpha | \alpha \in S\} = \emptyset$ and thus

$$\{\phi_i | i \in L\} = \{\phi_\alpha\} \cup \{\phi_m | m \in L\},\tag{25b}$$

and

$$\{\phi_j | j \in S\} = \{\phi_m | m \in S\}.\tag{25c}$$

Furthermore, in basis sets of even moderate size, $\{\phi_m | m \in S\}$ will contain many more elements than $\{\phi_m | m \in L\}$.

B. Implementation of the Occupation Number Ordering Concept

The L/S classification of the MC-SCF orbital set enables us to partition each of the four main blocks of $\mathbf{P}^{-1}(E)$ shown in Eq. (14b) into four sub-blocks, giving a total partition of 16 blocks. For example, the $(q_2^\dagger)_{m\alpha}; (q_2^\dagger)_{n\beta}$ block of $\mathbf{P}^{-1}(E)$ can be further partitioned as

$$\begin{array}{l} P_{m\alpha, n\beta}^{-1}: \\ \qquad m\alpha, n\beta \\ \begin{array}{l} 1. \quad LL, LL \\ 2. \quad LL, SL \\ 3. \quad SL, LL \\ 4. \quad SL, SL. \end{array} \end{array}\tag{26a}$$

In deriving this partition, we have assumed that Eq. (25c) holds; orbitals occupied in the dominant MC-SCF configuration Φ_0 (i.e., orbitals designated by Greek indices) belong exclusively to L , while the unoccupied orbitals in Φ_0 (i.e., orbitals designated by Roman indices m, n, \dots, z) can belong to either L or S . The sub-blocks in Eq. (26a) are listed in order of increasing size. Since only a few of the orbitals m, n, o, \dots, z unoccupied in Φ_0 belong to L , sub-block 1 of Eq. (26a) contains far fewer matrix elements than any of the other sub-blocks. Sub-blocks 2 and 3 contain the same number of matrix elements, which is in turn less than the number of matrix elements found in sub-block 4. Similar considerations allow us to partition the other three main blocks of $\mathbf{P}^{-1}(E)$. Within each of the 16 sub-blocks of $\mathbf{P}^{-1}(E)$, the order concept introduced in Sec. II F can be applied to systematically truncate higher order terms. This brings about a substantial

reduction in computational effort while preserving the order consistency of the approximation.

To carry out this truncation process, it is necessary to establish an L/S partition of the \mathbf{A} , $\tilde{\mathbf{B}}$, and \mathbf{M} matrices comprising $\mathbf{P}^{-1}(E)$. The \mathbf{A} matrix constituent has the same indices and main blocks as $\mathbf{P}^{-1}(E)$, so the L/S partition of Eq. (26a) can be applied directly, giving with truncation the contribution of \mathbf{A} to each of the 16 sub-blocks of $\mathbf{P}^{-1}(E)$. Thus for the $(q_2^\dagger)_{m\alpha}; (q_2^\dagger)_{n\beta}$ block of \mathbf{A} , we have the four sub-blocks

$$\begin{aligned} &A_{m\alpha, n\beta}: \\ &\quad m\alpha, n\beta \\ &\quad 1. \quad LL, LL \\ &\quad 2. \quad LL, SL \\ &\quad 3. \quad SL, LL \\ &\quad 4. \quad SL, SL \end{aligned} \quad (26b)$$

The $\tilde{\mathbf{B}}$ and \mathbf{M} matrices contribute to $\mathbf{P}^{-1}(E)$ as the product $\tilde{\mathbf{B}}\mathbf{M}^{-1}\tilde{\mathbf{B}}^\dagger$. With L/S partitioning, each of the four main blocks of $\tilde{\mathbf{B}}$ (and hence $\tilde{\mathbf{B}}^\dagger$) breaks down into eight sub-blocks. For example, in the $(q_2^\dagger)_{m\alpha}, (q_4^\dagger)_{\rho\mu q\nu}$ block, we have

$$\begin{aligned} &\tilde{B}_{m\alpha, \rho\mu q\nu}: \\ &\quad m\alpha, \rho\mu q\nu \\ &\quad 1. \quad LL, LLLL \\ &\quad 2. \quad LL, LLSL \\ &\quad 3. \quad LL, SLLL \\ &\quad 4. \quad LL, SL SL \\ &\quad 5. \quad SL, LLLL \\ &\quad 6. \quad SL, LLSL \\ &\quad 7. \quad SL, SLLL \\ &\quad 8. \quad SL, SL SL. \end{aligned} \quad (26c)$$

Each of the two diagonal blocks of the \mathbf{M} matrix can be partitioned into four sub-blocks. Within the $(q_4^\dagger)_{\rho\mu q\nu}; (q_4^\dagger)_{\rho\mu q\nu}$ block, we get the partition

$$\begin{aligned} &M_{\rho\mu q\nu, \rho\mu q\nu}: \\ &\quad \rho\mu q\nu, \rho\mu q\nu \\ &\quad 1. \quad LLLL, LLLL \\ &\quad 2. \quad LL SL, LL SL \\ &\quad 3. \quad SLLL, SLLL \\ &\quad 4. \quad SL SL, SL SL. \end{aligned} \quad (26d)$$

The number of matrix elements in a given sub-block of $\tilde{\mathbf{B}}$ or \mathbf{M} depends upon the number of Roman indices belonging to L (i.e., the more Roman indices belonging to L the smaller the block). By truncating each of the sub-blocks of $\tilde{\mathbf{B}}$ and \mathbf{M} to within a given order, $\tilde{\mathbf{B}}\mathbf{M}^{-1}\tilde{\mathbf{B}}^\dagger$ can be approximated through that order. For example, if all zeroth-, first-, and second-order terms in \mathbf{A} , $\tilde{\mathbf{B}}$, and \mathbf{M} are retained, then $\tilde{\mathbf{B}}\mathbf{M}^{-1}\tilde{\mathbf{B}}^\dagger$ contains all terms to second order plus certain terms of higher order. We speak of $\tilde{\mathbf{B}}\mathbf{M}^{-1}\tilde{\mathbf{B}}^\dagger$ as being approximated through second order. Since

\mathbf{M} appears in this product as an inverse of its diagonal elements, the concept of an approximation exact to second order is difficult to apply. Other Green's-function methods have also employed approximations through a given order with good success [18–20, 27, 28].

As a specific example of the ordering process, we investigate components of \mathbf{A} , $\tilde{\mathbf{B}}$, and \mathbf{M} contributing through second order to sub-block 4 of the $(q_2^\dagger)_{m\alpha}; (q_2^\dagger)_{n\beta}$ main block of $\mathbf{P}^{-1}(E)$. Since \mathbf{A} has the same block structure as $\mathbf{P}^{-1}(E)$, we will thus order sub-block 4 of Eq. (26b). While many of the sub-blocks of $\tilde{\mathbf{B}}$ and \mathbf{M} contribute to sub-block 4 of $\mathbf{P}^{-1}(E)$, we choose to order sub-block 8 of $\tilde{\mathbf{B}}$ in Eq. (26c) and sub-block 4 of \mathbf{M} in Eq. (26d) so that all of the Greek indices we consider in this example will belong to L and all of the Roman indices m, n, o, \dots, z will belong to S .^{*} However, Roman summation indices in these matrix blocks can still run over both L and S .

In carrying out the order truncations for \mathbf{A} , $\tilde{\mathbf{B}}$ and \mathbf{M} , it is also necessary in some cases to restrict summations over the general orbital indices $i, j, k, l \in L \cup S$ that appear in these matrices (i.e., without restrictions, terms higher than second order would be included). To express these restrictions in a simple form, we enclose the set of summation indices in parentheses and denote with a subscript the maximum number of indices that can belong to S . For example, the notation $\sum_{(i)_0}$ implies that the i index cannot run over any S -type orbitals, hence this summation is equivalent to the restricted summation $\sum_{i \in L}$. A restricted double summation $\sum_{(ij)_0}$ implies $\sum_{i \in L, j \in L}$, but a more modest restriction $\sum_{(ij)_1}$ would permit $\sum_{i \in L, j \in L}$, $\sum_{i \in L, j \in S}$, and $\sum_{i \in S, j \in L}$ summations. Similar restrictions can be written out for the three-index summations $\sum_{(ijk)_n}$. With this convention, a summation over m indices $\sum_{(ijk) \dots}_n$ is completely unrestricted if $n = m$, partially restricted if $0 < n < m$, and completely restricted if $n = 0$.

In ordering through second order sub-block 4 of the $A_{m\alpha, n\beta}$ main block (i.e., $m\alpha, n\beta = SL, SL$), we find that the overlap terms $S_{m\alpha, n\beta}$ shown in Eq. (21b) are already of second or lower order, but the general expression for $A'_{m\alpha, n\beta}$ given in Eq. (21c) reduces with truncation of terms higher than second order to

$$\begin{aligned}
 A'_{m\alpha, n\beta} = & h_{mn} \langle a_\alpha^\dagger a_\beta \rangle + h_{\beta\alpha} \langle a_n^\dagger a_m \rangle \\
 & - \sum_i \{ \delta_{\alpha\beta} h_{in} \langle a_i^\dagger a_m \rangle + \delta_{mn} h_{\beta i} \langle a_\alpha^\dagger a_i \rangle \} \\
 & + \frac{1}{2} \sum_{(ij)_1} \{ \bar{V}_{\beta mij} \langle a_\alpha^\dagger a_n^\dagger a_j a_i \rangle + \bar{V}_{ijn\alpha} \langle a_i^\dagger a_j^\dagger a_\beta a_m \rangle \} \\
 & + \sum_{(ij)_0} \bar{V}_{i\beta j\alpha} \langle a_n^\dagger a_i^\dagger a_j a_m \rangle + \sum_{ij} \bar{V}_{minj} \langle a_\alpha^\dagger a_i^\dagger a_j a_\beta \rangle \\
 & + \frac{1}{2} \delta_{mn} \sum_{(ijk)_2} \bar{V}_{i\beta jk} \langle a_\alpha^\dagger a_i^\dagger a_k a_j \rangle + \frac{1}{2} \delta_{\alpha\beta} \sum_{(ijk)_1} \bar{V}_{ijkn} \langle a_i^\dagger a_j^\dagger a_k a_m \rangle.
 \end{aligned} \tag{26e}$$

^{*} Note that we have chosen to order the largest sub-blocks of \mathbf{A} , $\tilde{\mathbf{B}}$, and \mathbf{M} since all Roman indices in our example belong to the S -orbital subset. Sub-blocks of \mathbf{A} , $\tilde{\mathbf{B}}$, and \mathbf{M} having some L -type Roman indices will contain fewer matrix elements, since $\{\phi_m | m \in L\}$ contains far fewer orbitals than $\{\phi_m | m \in S\}$ in a high-quality basis set.

Within sub-block 8 of $\tilde{B}_{m\alpha, p\mu q\nu}$ (i.e., $m\alpha, p\mu q\nu = SL, SL, SL$), ordering Eq. (22e) through second order gives

$$\begin{aligned}\tilde{B}_{m\alpha, p\mu q\nu} = \tilde{B}'_{m\alpha, p\mu q\nu} - \sum_{\alpha'} (1 - P_{pq}) \langle a_{\alpha'}^{\dagger} a_p^{\dagger} a_{\mu} a_{\nu} \rangle A'_{m\alpha, q\alpha'} \\ - \sum_{(m')_0} (1 - P_{\mu\nu}) \langle a_p^{\dagger} a_q^{\dagger} a_{\mu} a_{m'} \rangle A'_{m\alpha, m'\nu}\end{aligned}\quad (26f)$$

Since the density-matrix elements in the α' summation term are first order, only the zeroth- and first-order terms of $A'_{m\alpha, q\alpha'}$ need to be retained to give the α' summation to second order:

$$\begin{aligned}A'_{m\alpha, q\alpha'} = h_{mq} \langle a_{\alpha'}^{\dagger} a_{\alpha'} \rangle + h_{\alpha'\alpha} \langle a_q^{\dagger} a_m \rangle \\ - \sum_i \{ \delta_{\alpha\alpha'} h_{iq} \langle a_i^{\dagger} a_m \rangle - \delta_{mq} h_{\alpha'i} \langle a_{\alpha'}^{\dagger} a_i \rangle \} \\ + \frac{1}{2} \sum_{(ij)_0} \{ \bar{V}_{\alpha'mij} \langle a_{\alpha'}^{\dagger} a_q^{\dagger} a_j a_i \rangle + \bar{V}_{ijq\alpha} \langle a_i^{\dagger} a_j^{\dagger} a_{\alpha'} a_m \rangle \} \\ + \sum_{(ij)_1} \bar{V}_{miqj} \langle a_{\alpha'}^{\dagger} a_i^{\dagger} a_j a_{\alpha'} \rangle \\ + \frac{1}{2} \delta_{mq} \sum_{(ijk)_1} \bar{V}_{ia'jk} \langle a_{\alpha'}^{\dagger} a_i^{\dagger} a_k a_j \rangle \\ + \frac{1}{2} \delta_{\alpha\alpha'} \sum_{(ijk)_0} \bar{V}_{ijkq} \langle a_i^{\dagger} a_j^{\dagger} a_k a_m \rangle.\end{aligned}\quad (26g)$$

The $\langle a_p^{\dagger} a_q^{\dagger} a_{\mu} a_m \rangle$ matrix elements in the m' summation are already second order, so only the zeroth-order component of $A'_{m\alpha, m'\nu}$ is needed:

$$\begin{aligned}A'_{m\alpha, m'\nu} = h_{mm'} \langle a_{\alpha'}^{\dagger} a_{\nu} \rangle + h_{\nu\alpha} \langle a_{m'}^{\dagger} a_m \rangle \\ - \sum_i \{ \delta_{\alpha\nu} h_{im'} \langle a_i^{\dagger} a_m \rangle - \delta_{mm'} h_{\nu i} \langle a_{\alpha'}^{\dagger} a_i \rangle \} \\ + \frac{1}{2} \sum_{(ij)_0} \bar{V}_{\alpha'mij} \langle a_{\alpha'}^{\dagger} a_m^{\dagger} a_j a_i \rangle \\ + \sum_{(ij)_0} \bar{V}_{mim'j} \langle a_{\alpha'}^{\dagger} a_i^{\dagger} a_j a_{\nu} \rangle \\ + \frac{1}{2} \delta_{mm'} \sum_{(ijk)_0} \bar{V}_{ivjk} \langle a_{\alpha'}^{\dagger} a_i^{\dagger} a_k a_j \rangle.\end{aligned}\quad (26h)$$

The lengthy second-order expression for $\tilde{B}'_{m\alpha, p\mu q\nu}$ is displayed in Appendix A. The order analysis of block 4 of $M_{p\mu q\nu, p\mu q\nu}$ (i.e., $p\mu q\nu = SL, SL, SL$) is also presented in Appendix A.

To assess quantitatively the extent to which $\mathbf{P}(E)$ is simplified by truncation of its matrix elements through second order, we count before and after truncation the number of distinct density matrix elements that must be summed over to compute given elements of the \mathbf{A}' , $\tilde{\mathbf{B}}'$, and \mathbf{M}''' matrices (we choose to investigate these matrices because they are the principal components of \mathbf{A} , $\tilde{\mathbf{B}}$, and \mathbf{M}).

Keeping in mind that an unrestricted summation index runs over the N elements of the MC-SCF orbital basis $\{\phi_i\}$, while a restricted index runs over only the l orbitals belonging to the large occupation number subset $\{\phi_i|i \in L\}$, we can determine exactly how many density matrix elements must be summed over to produce an element of \mathbf{A}' , $\tilde{\mathbf{B}}'$, or \mathbf{M}''' . For example, calculation of the term

$$\delta_{\alpha\beta} \sum_{ijk} \bar{V}_{ijkn} \langle a_i^\dagger a_j^\dagger a_k a_m \rangle$$

appearing in the unordered $A'_{m\alpha, n\beta}$ matrix requires summation over N^3 density matrix elements. In the second order $A'_{m\alpha, n\beta}$ matrix, however, the summation is restricted to $\sum_{(ijk)_1}$. Taking all possible permutations of the index restrictions into account, we find that only $l^3 + 3l^2s$ density-matrix elements are summed over (the s parameter is used to denote the number of MC-SCF orbitals belonging to the small occupation number subset $\{\phi_i|i \in S\}$; recall that $N = l + s$). To facilitate comparison between ordered and unordered matrix elements, we find it convenient to define a parameter $\lambda = l/N$, the fraction of MC-SCF orbitals belonging to the large occupation number subset. The range of λ is $0 < \lambda < 1$. With the appropriate substitutions in the ordered summation count of our chosen \mathbf{A}' -matrix component, we find that $l^3 + l^2s = (3\lambda^2 - 2\lambda^3)N^3$, which is less than the unordered count for N^3 for $0 < \lambda < 1$. Summation counts before and after truncation for the complete \mathbf{A}' , $\tilde{\mathbf{B}}'$, and \mathbf{M}''' matrix elements are listed in Table II.

TABLE II. Number of terms containing distinct matrix elements that must be summed over to produce single complete elements of the \mathbf{A}' , \mathbf{B}' , and \mathbf{M}''' matrices. N is the total number of elements in the MC-SCF orbital basis $\{\phi_i\}$ and $\lambda = l/N$ represents the fraction of MC-SCF orbitals belonging to the large occupation number subset $\{\phi_i|i \in L\}$, where $0 < \lambda < 1$.

matrix element	# terms before ordering		# terms after ordering (2nd order)	
$A'_{m\alpha, n\beta}$	$2N + 4N^2 + 2N^3$	Eq. (21c)	$> 2N + [1 + 4\lambda - \lambda^2]N^2 + [3\lambda - \lambda^3]N^3$	Eq. (26d)
$\tilde{B}'_{m\alpha, p\nu q\nu}$	$16N + 14N^2 + 14N^3$	*	$> 15N + [1 + 12\lambda - 5\lambda^2]N^2 + [3\lambda + 15\lambda^2 - 5\lambda^3]N^3$	Eq. (A4)
$M'''_{p\nu q\nu, p\nu q\nu}$	$24N + 30N^2 + 16N^3$	*	$> 20N + [2 + 8\lambda + 5\lambda^2]N^2 + [6\lambda + 3\lambda^2 + 2\lambda^3]N^3$	Eq. (A10)

* Owing to their excessive length and complexity, explicit expressions for the complete $\tilde{\mathbf{B}}'$ and \mathbf{M}''' matrix elements are not reproduced in the text. However, they are available from the authors upon request.

It is easily seen from the expressions in this table that the simplification in $\mathbf{P}(E)$ effected by truncation of its matrix elements through second order is dramatic. This is especially true for high-quality basis sets where N is much larger than l , making λ much smaller than unity.

C. Approximations to the \mathbf{M} Matrix and Operator Manifold

Some justification is called for making a diagonal approximation to the \mathbf{M} matrix, since many of its off-diagonal elements contain zeroth-order terms. The existence of such low order off-diagonal terms would seem to place severe limits on the kinds of approximations that can be justified. Fortunately, however, many of the same off-diagonal terms appear in the non-Hermiticity factors for \mathbf{M} displayed in Appendix A. For example, the zeroth-order term $\sum_i h_{\mu i} \langle a_{\mu}^{\dagger} a_{\nu} a_i \rangle$ appearing in Eq. (A10) for the diagonal $M'''_{\rho\mu q\nu, \rho\mu q\nu}$ matrix can be traced back to several related zeroth-order terms of the more general off-diagonal $M'''_{\rho\mu q\nu, s\lambda i\sigma}$ matrix, such as the term $\delta_{\rho i} \delta_{q s} \sum_i h_{\sigma i} \langle a_{\mu}^{\dagger} a_{\nu} a_{\lambda} a_i \rangle$. However, it can be shown that this term is contained in the non-Hermiticity factor $\delta_{\rho i} \delta_{q s} \langle \hat{H} (a_{\mu}^{\dagger} a_{\nu} a_{\lambda} a_{\sigma}) \rangle$ of $M'''_{\rho\mu q\nu, s\lambda i\sigma}$. This indicates that such terms, artifacts of the reference-state approximation, will tend to zero when a high-quality reference state (e.g., the MC-SCF reference state Ψ) is employed.* We use these facts as a basis for making a Hermitian diagonal approximation to \mathbf{M} . As we have noted, other Green's-function theories employing the more traditional RSPT reference states have utilized diagonal approximations to \mathbf{M} with good computational success. Since the magnitude of the spurious off-diagonal contributions to \mathbf{M} diminishes as the quality of the reference state increases, using a MC-SCF reference state will further enhance the viability of the diagonal \mathbf{M} approximation. Finally, it should be noted that the lower-order off-diagonal terms of \mathbf{M} cluster around the diagonal elements (e.g., the lower-order terms of $M_{\rho\mu q\nu, s\lambda i\sigma}$ contain delta functions of the types $\delta_{\rho s}$, $\delta_{\rho i}$, $\delta_{\mu \lambda}$, $\delta_{\mu \sigma}$, $\delta_{q s}$, $\delta_{q i}$, $\delta_{\nu \lambda}$), which suggests the use of a near-diagonal approximation as a computationally accessible means of overcoming the inherent deficiencies of the diagonal approximation.

Our choice of a truncated operator manifold $\mathbf{h}^{(4)} = \mathbf{h}_2 \cup \mathbf{h}_4$ for MC-SCF Green's-function theories employing the occupation number ordering concept is based upon the success of similar manifold truncations in RSPT ordering schemes. However, we have implicitly assumed that with our truncated manifold $\mathbf{h}^{(4)}$, all contributions through second order to the \mathbf{A} , $\tilde{\mathbf{B}}$, and \mathbf{M} matrices are recovered. The validity of this assumption can be demonstrated by showing that extension of the operator manifold to include \mathbf{h}_6 leads to self-energy corrections that are higher than second order. This is accomplished, in analogy with the order analysis for the elements of \mathbf{M} , by noting that $(\mathbf{h}_6 | \hat{H} | \mathbf{h}_2) = O(2)$ in the limit $\langle \hat{H} | \mathbf{h}_6, \mathbf{h}_2 \rangle \rightarrow 0$, where \mathbf{M}^{-1} is diagonal with respect to zeroth-order terms.† Extension of the operator

* There also exist some zeroth-order Hermitian terms in the off-diagonal matrix elements of \mathbf{M} that cannot be traced to artificial non-Hermiticity (i.e., they make no contribution to $\langle \hat{H} [X_i^{\dagger}, X_j] \rangle$). However, it can be reasonably argued that these are not true zeroth-order terms, since from the Schwartz inequality expressions given in Eq. (24b), formal justification is provided for the computationally verified density matrix result that such off-diagonal terms are smaller in magnitude than their diagonal counterparts (e.g., $|\langle a_i^{\dagger} a_j \rangle| < |\langle a_i^{\dagger} a_i \rangle|$). In the interest of simplicity, our order analysis scheme does not discriminate between diagonal and off-diagonal density matrix elements containing equal numbers of S-type orbitals.

† Order analysis of the $(\mathbf{h}_6 | \hat{H} | \mathbf{h}_2)$ matrix reveals that it has no real zeroth-order terms, although it does have some spurious zeroth-order non-Hermitian terms that vanish in the limit of an exact reference state.

manifold to include \mathbf{h}_6 is therefore not required to obtain all terms for $\mathbf{P}^{-1}(E)$ through second order within the MC-SCF reference state choice.

D. Computational Aspects

Although the formal expressions for \mathbf{A} , $\tilde{\mathbf{B}}$, and \mathbf{M} look quite complicated and unamenable to computation, only a few terms survive for a specific MC-SCF reference state choice. For example, a four-particle density matrix element $\langle a_i^\dagger a_j^\dagger a_q^\dagger a_r^\dagger a_\nu a_\mu a_p a_q \rangle$ is nonzero only if there exist configurations Φ_K and Φ_L in the MC-SCF state $\Psi = \sum_K C_K \Phi_K$ such that $|\Phi_K\rangle = a_i^\dagger a_j^\dagger a_q^\dagger a_r^\dagger a_\nu a_\mu a_p a_q |\Phi_L\rangle$ (i.e., the operator $a_i^\dagger a_j^\dagger a_q^\dagger a_r^\dagger a_\nu a_\mu a_p a_q$ must "connect" the two configurations Φ_K and Φ_L). For a typical MC-SCF reference function (ca. 20 configurations), it is obvious that only a few nonzero four-particle density-matrix elements exist. There will be proportionately higher numbers of nonzero three-, two-, and one-particle density-matrix elements, but these too must connect elements of the configuration set $\{\Phi_K\}$ contained in the MC-SCF reference state Ψ . These "connectivity restrictions" can be utilized to simplify the calculation of $\mathbf{P}^{-1}(E)$. Instead of calculating all density-matrix elements within the multiple summations and then deciding which ones are nonzero, a time-consuming process owing to the lengthy decision processes involved, we calculate all nonzero one-, two-, three-, and four-particle density matrix elements with respect to a given MC-SCF state (e.g., $\langle a_i^\dagger a_j^\dagger a_q^\dagger a_r^\dagger a_\nu a_\mu a_p a_q \rangle$, $\langle a_i^\dagger a_j^\dagger a_q^\dagger a_k a_p a_q \rangle$, $\langle a_i^\dagger a_j^\dagger a_p a_q \rangle$, $\langle a_i^\dagger a_p \rangle$, etc.) and store them together with their associated two-electron integrals (e.g., $\bar{V}_{ijp\mu}$, \bar{V}_{ijkp} , \bar{V}_{ijpq}). This is easily accomplished by comparing each configuration Φ_K in Ψ to the other configurations in Ψ and finding the one-, two-, three-, and four-particle connecting operators between them. Only those density matrix elements that are expectation values of the connecting operators for the MC-SCF configuration set $\{\Phi_K\}$ will contribute to the summations comprising the \mathbf{A} , $\tilde{\mathbf{B}}$, and \mathbf{M} matrix elements.

Because the off-diagonal elements of \mathbf{M} contain first-order factors and $\tilde{\mathbf{B}}$ has zeroth-order terms, neglecting any or all off-diagonal terms of \mathbf{M} destroys the completeness of our second-order treatment. However, owing to the huge dimension of the \mathbf{M} matrix, which needs to be inverted many times during a search for the zeros of $\text{Det}[\mathbf{P}^{-1}(E)]$, approximations such as neglecting all or most of the off-diagonal terms of \mathbf{M} are necessary. Techniques for efficiently evaluating $\mathbf{P}(E)$ given a diagonal approximation to \mathbf{M} follow directly from procedures discussed for the one-electron MC-SCF Green's-function problem [28].

Since the calculation of a determinant $\text{Det}[\mathbf{P}^{-1}(E)]$ requires many operations, it is desirable to find a reliable approximation to this step. Calculating a sequence of determinants from successively larger submatrices of the $\mathbf{P}^{-1}(E)$ matrix and observing the convergence of this sequence may be a viable procedure. After the $\text{Det}[\mathbf{P}^{-1}(E)]$ has been obtained, the search for its zeros can be accomplished by standard techniques such as bisection, accelerated false position, Newton-secant, etc.

The poles and residues of $\mathbf{P}(E)$ can alternatively be found following the method suggested by Layzer [49] and employed by Purvis and Öhrn [24] to the

case of the one-particle Green's function. The method is based upon the fact that poles of $\mathbf{P}(E)$ correspond to values of E for which eigenvalues of $\mathbf{L}(E) \equiv E\hat{\mathbf{I}} - \mathbf{P}^{-1}(E)$; $\mathbf{L}\phi_n = W_n(E)\phi_n(E)$ obey $E = W_n(E)$. The residues Γ_n are given by $\Gamma_n = (1 - dW_n/dE)_{E=E_n}^{-1}$. To implement this technique, one must find eigenvalues $W_n(E)$ for various values of E and then (graphically) locate that value of E for which $W_n(E) = E$.

IV. Conclusion

In this paper we have obtained working equations that permit $\mathbf{P}^{-1}(E)$ to be expressed in terms of the \mathbf{A} , $\tilde{\mathbf{B}}$, and \mathbf{M} matrices correct through second order within the MC-SCF reference state choice. A new concept of order based upon occupation number size is employed to carry out the order analysis. Incorporating the considerable advantages of a MC-SCF reference state in a polarization Green's-function gives rise to intricate formal expressions, which, however, simplify dramatically into a computationally manageable form once a specific choice for the MC-SCF state is established.

Appendix A: Evaluation of $\tilde{\mathbf{B}}$, Δ , and \mathbf{M}

From Eqs. (18b) and (22f) we have the definitions

$$\Delta = \mathbf{B} - \mathbf{C}^\dagger, \quad (\text{A1})$$

$$\tilde{\mathbf{B}}' = \frac{1}{2}[\mathbf{B}' + \mathbf{C}'^\dagger]. \quad (\text{A2})$$

Since \mathbf{B} and \mathbf{C} have Schmidt components that are adjoints of one another [see Eqs. (22a) and (22b)], it is also correct to write

$$\Delta = \mathbf{B}' - \mathbf{C}'^\dagger. \quad (\text{A3})$$

Explicit expressions for Δ and $\tilde{\mathbf{B}}'$ can be found by evaluating the \mathbf{B}' and \mathbf{C}' matrices defined in Eqs. (22c) and (22d), taking the adjoint of \mathbf{C}' , and substituting the resulting expressions into Eqs. (A2) and (A3). In writing out the matrix elements of $\tilde{\mathbf{B}}'$, we employ the convention that only conjugate Hermitian terms common to \mathbf{B}' and \mathbf{C}'^\dagger appear outside of the double brackets $[[\]]$. The corresponding Δ matrix element is automatically recovered by removing all Hermitian terms, changing the sign of each term within the double brackets arising from \mathbf{C}'^\dagger (i.e., each term with a conjugated density-matrix element

$$\left\langle \left(\prod_{i=1}^n a_i^\dagger \right) \left(\prod_{j=1}^n a_j \right) \right\rangle^*$$

and multiplying the final expression by 2. It is important to keep in mind that all density matrix elements are real; the conjugated density matrix elements appearing in the expressions for $\tilde{\mathbf{B}}'$ and Δ serve only to identify which terms arise from \mathbf{C}'^\dagger . We evaluate $\tilde{\mathbf{B}}'$ (and thus Δ) for the particular choice of indices $(q_2^\dagger)_{m\alpha}$, $(q_1^\dagger)_{p\mu q\nu}$. By assuming $m\alpha$, $p\mu q\nu = SL, SL$ and truncating terms higher than second order according to the procedures developed in Sec. III, we recover the

ordered expression for sub-block 8 or $\tilde{B}_{m\alpha, p\mu q\nu}$;

$$\begin{aligned}
 \tilde{B}'_{m\alpha, p\mu q\nu} = & \frac{1}{2}[B'_{m\alpha, p\mu q\nu} + C'^*_{p\mu q\nu, m\alpha}] \\
 = & (1 - P_{pq})h_{mq}\langle a_\alpha^\dagger a_p^\dagger a_\mu a_\nu \rangle + (1 - P_{\mu\nu})h_{\mu\alpha}\langle a_p^\dagger a_q^\dagger a_\nu a_m \rangle + \sum_i \bar{V}_{miqp}\langle a_\alpha^\dagger a_i^\dagger a_\mu a_\nu \rangle \\
 & + \frac{1}{2} \sum_{(ij)_0} \{(1 - P_{pq})\bar{V}_{ijq\alpha}\langle a_i^\dagger a_j^\dagger a_p^\dagger a_\mu a_\nu a_m \rangle + (1 - P_{\mu\nu})\bar{V}_{\mu mij}\langle a_\alpha^\dagger a_p^\dagger a_q^\dagger a_\nu a_j a_i \rangle\} \\
 & + \sum_{(ij)_1} (1 - P_{pq})\bar{V}_{mipj}\langle a_\alpha^\dagger a_i^\dagger a_q^\dagger a_j a_\mu a_\nu \rangle \\
 & + \left[\left[\frac{1}{2} \sum_i \{ \langle a_\alpha^\dagger a_i^\dagger a_\mu a_\nu \rangle (1 - P_{pq})\delta_{mq}h_{ip} \right. \right. \\
 & \quad + (1 - P_{pq})(1 - P_{\mu\nu})\delta_{\alpha\nu}h_{ip}\langle a_i^\dagger a_q^\dagger a_\mu a_m \rangle \\
 & \quad + \langle a_p^\dagger a_q^\dagger a_i a_m \rangle (1 - P_{\mu\nu})\delta_{\nu i}h_{\alpha\mu} \\
 & \quad + (1 - P_{pq})(1 - P_{\mu\nu})\delta_{mp}h_{\nu i}\langle a_\alpha^\dagger a_q^\dagger a_\mu a_i \rangle \\
 & \quad \left. \left. + h_{\alpha i}(1 - P_{pq})\delta_{mp}\langle a_\nu^\dagger a_\mu^\dagger a_q a_i \rangle^* + h_{im}(1 - P_{\mu\nu})\delta_{\alpha\nu}\langle a_i^\dagger a_\mu^\dagger a_q a_p \rangle^* \right\} \right. \\
 & + \frac{1}{4} \sum_{(ij)_1} \{ \bar{V}_{\mu vij}(1 - P_{pq})\delta_{mq}\langle a_\alpha^\dagger a_p^\dagger a_j a_i \rangle \\
 & \quad \left. + \bar{V}_{ijpq}(1 - P_{\mu\nu})\delta_{\alpha\nu}\langle a_i^\dagger a_j^\dagger a_\mu a_m \rangle \right\} \\
 & - \frac{1}{4}(1 - P_{pq})\delta_{qm} \sum_{ij} \bar{V}_{\alpha pij}\langle a_\nu^\dagger a_\mu^\dagger a_j a_i \rangle^* \\
 & - \frac{1}{4}(1 - P_{\mu\nu})\delta_{\alpha\mu} \sum_{(ij)_0} \bar{V}_{ijm\nu}\langle a_i^\dagger a_j^\dagger a_q a_p \rangle^* \\
 & + \frac{1}{4}(1 - P_{pq}) \left\{ \delta_{mp} \sum_{(ijk)_2} \bar{V}_{ijkq}\langle a_\alpha^\dagger a_i^\dagger a_j^\dagger a_k a_\mu a_\nu \rangle \right. \\
 & \quad \left. + (1 - P_{\mu\nu})\delta_{b\nu} \sum_{(ijk)_0} \bar{V}_{ijkq}\langle a_i^\dagger a_j^\dagger a_p^\dagger a_\mu a_k a_m \rangle \right\} \\
 & + \frac{1}{4}(1 - P_{pq}) \sum_{(ijk)_1} \{ \delta_{mp}(1 - P_{\mu\nu})\bar{V}_{iujk}\langle a_\alpha^\dagger a_i^\dagger a_q^\dagger a_\nu a_k a_j \rangle \\
 & \quad + \delta_{qm}V_{i\alpha jk}\langle a_\nu^\dagger a_\mu^\dagger a_i^\dagger a_q a_k a_j \rangle^* \} \\
 & \left. + \frac{1}{4}(1 - P_{\mu\nu})\delta_{\mu\alpha} \sum_{(ijk)_0} \bar{V}_{ijk\alpha}\langle a_\nu^\dagger a_i^\dagger a_j^\dagger a_q a_k a_p \rangle^* \right] \Bigg]. \quad (A4)
 \end{aligned}$$

In order to express matrix elements compactly, we make use of a binary exchange operator P_{ij} which when operating on a term to the right-hand side, converts i to j and j to i .

Approximating Eq. (23a) for the diagonal \mathbf{M} matrix to second order effects a dramatic simplification of its matrix elements. In sub-block 4 of the $M_{p\mu q\nu, p\mu q\nu} = ES_{p\mu q\nu, p\mu q\nu} - M'_{p\mu q\nu, p\mu q\nu}$ main block, where $p\mu q\nu = (SLSL)$, the ordered overlap

matrix expression given in Eq. (23b) becomes

$$\begin{aligned}
 S_{p\mu q\nu, p\mu q\nu} &= ((q_4^\dagger)_{p\mu q\nu} | (q_4^\dagger)_{p\mu q\nu}) \\
 &= \langle a_\nu^\dagger a_\mu^\dagger a_\mu a_\nu \rangle + (1 + P_{pq}) \langle a_\nu^\dagger a_p^\dagger a_\mu^\dagger a_\mu a_\nu a_p \rangle \\
 &\quad + 2 \sum_\alpha (1 + P_{pq}) |\langle a_p^\dagger a_\alpha^\dagger a_\mu a_\nu \rangle|^2 \\
 &\quad + \sum_{\alpha\beta} (1 + P_{pq}) \langle a_\nu^\dagger a_\mu^\dagger a_q a_\alpha \rangle \langle a_\beta^\dagger a_q^\dagger a_\mu a_\nu \rangle \langle a_\alpha^\dagger a_\beta \rangle. \quad (A5)
 \end{aligned}$$

In approximating Eq. (23c) for M' to second order, it proves convenient to divide the matrix up as

$$\begin{aligned}
 M'_{p\mu q\nu, p\mu q\nu} &= ((q_4^\dagger)_{p\mu q\nu} | \hat{H} | (q_4^\dagger)_{p\mu q\nu}) \\
 &= M''_{p\mu q\nu, p\mu q\nu} + M'''_{p\mu q\nu, p\mu q\nu} \quad (A6)
 \end{aligned}$$

where

$$\begin{aligned}
 M''_{p\mu q\nu, p\mu q\nu} &= (a_p^\dagger a_\mu a_q^\dagger a_\nu | \hat{H} | (q_4^\dagger)_{p\mu q\nu} - a_p^\dagger a_\mu a_q^\dagger a_\nu) \\
 &\quad + ((q_4^\dagger)_{p\mu q\nu} - a_p^\dagger a_\mu a_q^\dagger a_\nu | \hat{H} | (q_4^\dagger)_{p\mu q\nu}), \quad (A7)
 \end{aligned}$$

and

$$M'''_{p\mu q\nu, p\mu q\nu} = (a_p^\dagger a_\mu a_q^\dagger a_\nu | \hat{H} | a_p^\dagger a_\mu a_q^\dagger a_\nu). \quad (A8)$$

Evaluation of the M'' Schmidt matrix elements given in Eq. (A7) followed by truncation of the resulting expressions to second order yields

$$\begin{aligned}
 M''_{p\mu q\nu, p\mu q\nu} &= \sum_\alpha \{ \langle a_\alpha^\dagger a_q^\dagger a_\mu a_\nu \rangle (B_{p\alpha, p\mu q\nu} + C'_{p\mu q\nu, p\alpha}) \\
 &\quad - \langle a_\alpha^\dagger a_p^\dagger a_\mu a_\nu \rangle (B_{q\alpha, p\mu q\nu} + C'_{p\mu q\nu, q\alpha}) \} \\
 &\quad + \sum_{(m)_0} \{ \langle a_p^\dagger a_q^\dagger a_\nu a_m \rangle (B_{m\mu, p\mu q\nu} + C'_{p\mu q\nu, m\mu}) \\
 &\quad - \langle a_p^\dagger a_q^\dagger a_\mu a_m \rangle (B_{m\nu, p\mu q\nu} + C'_{p\mu q\nu, m\nu}) \} \quad (A9)
 \end{aligned}$$

Since the density-matrix elements in the α summation of Eq. (A9) are first order, only the zeroth- and first-order terms in the \mathbf{B} and \mathbf{C}' matrix elements are kept. In the m summation however, the density matrix elements are already second order; only the zeroth-order components of its \mathbf{B} and \mathbf{C}' matrix elements need to be retained. The most complicated component of M' , the M''' matrix given in Eq. (A8), is approximated to second order as

$$\begin{aligned}
 M'''_{p\mu q\nu, p\mu q\nu} &= (a_p^\dagger a_\mu a_q^\dagger a_\nu | \hat{H} | a_p^\dagger a_\mu a_q^\dagger a_\nu) \\
 &= (h_{pp} + h_{qq}) \langle a_\nu^\dagger a_\mu^\dagger a_\mu a_\nu \rangle + (h_{\mu\mu} + h_{\nu\nu}) \langle a_p^\dagger a_q^\dagger a_q a_p \rangle \\
 &\quad - \sum_i \{ (1 + P_{pq}) h_{ip} \langle a_i^\dagger a_q^\dagger a_q a_p \rangle + (1 + P_{\mu\nu}) h_{\mu i} \langle a_\mu^\dagger a_\nu^\dagger a_\nu a_i \rangle \} \\
 &\quad - (1 + P_{pq}) h_{pp} \langle a_\nu^\dagger a_\mu^\dagger a_q^\dagger a_q a_\mu a_\nu \rangle - (1 + P_{\mu\nu}) h_{\mu\mu} \langle a_\nu^\dagger a_p^\dagger a_q^\dagger a_q a_p a_\nu \rangle \\
 &\quad + (1 + P_{pq}) h_{pq} \langle a_\nu^\dagger a_\mu^\dagger a_p^\dagger a_q a_q a_\mu a_\nu \rangle + (1 + P_{\mu\nu}) h_{\mu\nu} \langle a_\mu^\dagger a_p^\dagger a_q^\dagger a_q a_p a_\nu \rangle
 \end{aligned}$$

$$\begin{aligned}
& + (1 + P_{pq}) \sum_i h_{ip} \{ (1 + P_{\mu\nu}) \langle a_\nu^\dagger a_i^\dagger a_q^\dagger a_p a_\nu \rangle + \langle a_\nu^\dagger a_i^\dagger a_\mu^\dagger a_\mu a_\nu a_p \rangle \} \\
& + (1 + P_{\mu\nu}) \sum_i h_{\mu i} \{ (1 + P_{pq}) \langle a_\mu^\dagger a_\nu^\dagger a_p^\dagger a_p a_\nu a_i \rangle + \langle a_\mu^\dagger a_p^\dagger a_q^\dagger a_p a_q a_i \rangle \} \\
& + \frac{1}{2} \left[2 \bar{V}_{pqpq} \langle a_\nu^\dagger a_\mu^\dagger a_\mu a_\nu \rangle + \sum_{(ij)_0} \bar{V}_{ijpq} \langle a_i^\dagger a_j^\dagger a_p a_q \rangle + \sum_{ij} \bar{V}_{\mu\nu ij} \langle a_\nu^\dagger a_\mu^\dagger a_j a_i \rangle \right. \\
& \quad + 2 \sum_i (1 + P_{pq}) \{ \bar{V}_{piqp} \langle a_\nu^\dagger a_\mu^\dagger a_i^\dagger a_q a_\mu a_\nu \rangle \\
& \quad \quad \quad + \bar{V}_{pqip} \langle a_\nu^\dagger a_\mu^\dagger a_q^\dagger a_\mu a_\nu a_i \rangle \} \\
& \quad + \sum_{(ij)_0} \{ \bar{V}_{\mu\nu ij} (1 + P_{pq}) \langle a_\mu^\dagger a_\nu^\dagger a_p^\dagger a_p a_j a_i \rangle \\
& \quad \quad \quad + \bar{V}_{ijpq} (1 + P_{\mu\nu}) \langle a_i^\dagger a_j^\dagger a_\mu^\dagger a_\mu a_q a_p \rangle \} \\
& \quad + (1 + P_{\mu\nu})(1 - P_{pq}) \sum_{(ij)_1} \bar{V}_{\mu p ij} \langle a_\nu^\dagger a_\mu^\dagger a_p^\dagger a_\nu a_j a_i \rangle \\
& \quad + 2 \sum_{ij} \langle a_\nu^\dagger a_\mu^\dagger a_i^\dagger a_\mu a_\nu a_j \rangle (1 + P_{pq}) \bar{V}_{ipjp} \\
& \quad + (1 + P_{\mu\nu}) \sum_{(ijk)_2} \bar{V}_{i\mu jk} \langle a_\nu^\dagger a_\mu^\dagger a_i^\dagger a_\nu a_k a_j \rangle \\
& \quad + 2(1 + P_{pq}) \sum_{(ij)_0} \{ \bar{V}_{pijp} \langle a_\nu^\dagger a_\mu^\dagger a_i^\dagger a_q^\dagger a_q a_\mu a_\nu a_j \rangle \\
& \quad \quad \quad + \bar{V}_{qijp} \langle a_\mu^\dagger a_\nu^\dagger a_i^\dagger a_q^\dagger a_p a_\mu a_\nu a_j \rangle \} \\
& \quad + \sum_{(ijk)_1} (1 + P_{pq}) \bar{V}_{ijkp} \langle a_\nu^\dagger a_i^\dagger a_j^\dagger a_\mu^\dagger a_k a_\mu a_\nu a_p \rangle \\
& \quad + (1 + P_{\mu\nu}) \sum_{(ijk)_0} \bar{V}_{i\mu jk} \{ \langle a_\mu^\dagger a_\nu^\dagger a_i^\dagger a_q^\dagger a_q a_\nu a_k a_j \rangle \\
& \quad \quad \quad + \langle a_\nu^\dagger a_i^\dagger a_p^\dagger a_\mu^\dagger a_k a_j a_p \rangle \} \Big]. \quad (A10)
\end{aligned}$$

In actual computations where a specific MC-SCF reference state is chosen, many of the terms appearing in Eqs. (A4)–(A10), in particular, most of the terms containing three- and four-particle density matrix elements, will be zero. These computational simplifications are discussed further in Sec. III D.

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