One-Particle Green's Function with Multiconfiguration Reference States

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Abstract

The Green's function formalism in the superoperator notation is extended to admit a multiconfiguration reference state. The advantages of this more general reference state over the Hartree-Fock state are discussed. Hermiticity of the superoperators for the multiconfiguration reference state is analyzed. Explicit formulas and calculation procedures for the implementation of this Green's function theory are given and specialized to include terms consistent through second order.

1. Introduction

Since the early works of Linderberg and Öhrn [1], and the *ab initio* developments of Doll and Reinhardt [2], Purvis and Öhrn [3], Simons and Smith [4], Pickup and Goscinski [5], Cederbaum *et al.* [6], Schneider *et al.* [7], and others [8, 9], Green's function calculations have become quite established methods for calculating certain properties of atomic and molecular systems. The technology for the calculation of ionization energies within the Green's function formalism has become quite sophisticated due to the use of correlated ground states and extended operator manifolds to describe the corresponding ionic states [4, 6-9]. In the approach employed here, one expresses the one-electron Green's function (G) in the superoperator form of Goscinski and Lukman [10]. This technique allows the formulation of approximations in a coherent manner via choices of the reference wave function and the operators which comprise the inner projection [11] manifold. It has been shown by one of us [12] that, if one employs a complete operator space within the inner projection, the use of an approximate reference state affects only the residues of the Green's function (the so-called Feynman-Dyson amplitudes [7] $\langle \Psi_\alpha^{N-1} | a_j | \Psi_\beta^N \rangle$, $\langle \Psi_\alpha^{N+1} | a_i^+ | \Psi_\beta^N \rangle$); the exact nature of the pole structure is still preserved. The poles of G are the ionization potentials and electron affinities of the system. Of course, truncation of the operator space, which is inevitable for most calculations, does lead to a dependence of the poles of the Green's function on the choice of the reference state. The choices of reference states have so far been restricted to (i) the Hartree-Fock state [3] (HF), (ii) HF plus doubly excited [4] configurations whose coefficients are determined by Rayleigh-Schrödinger perturbation theory (RSPT), (iii) HF plus doubly and singly excited configurations [8, 9] with RSPT coefficients. Though the second and third possibilities attempt to introduce correlation, the ground-state description remains inadequate whenever

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the zeroth-order state of the perturbation exapnsion (HF) is a poor description of the system. These conditions arise, for example, in circumstances where more than one major configuration must be included to obtain a physically reasonable description of the system. Such is the case in the description of F_2 (Ref. 13) and for H_2 (Ref. 14) at large bond lengths. Another important example is provided by the CO_2, CO_2^- system [15, 16] for which the equilibrium geometries of the neutral ground state ($^1A_1$) and of the ion ($^2A_1$) are significantly different (the OCO angle is 180° for $^1A_1$ and 135° for $^2A_1$).

Of course, it is not only because of anion–neutral geometry differences that one might wish to employ a multiconfiguration (MC) reference state. It is equally important to have available a practical Green's function framework in terms of which one can compute molecular ionization energies given a MC function which has been employed to accurately treat correlation effects in the reference state.

In the present paper our aim is to extend the Green's function formalism to include the use of multiconfiguration reference states. This development provides a new tool which has the potential to adequately describe the properties of molecules which are represented by correlated reference states. Because of the use of an extended operator space, this development includes self-energy corrections to the ionization energies and has the advantage that the reference state can be systematically improved in order to uniformly describe the system over the enitre range of internuclear variables.

In Section 2 we introduce our notations and choice of operator manifold to be used with the multiconfiguration reference state. We give explicit expression for the Green's function and introduce the concept of order to rank the relative importance of each term. In Section 3 this ordering concept is used to simplify the expressions for the Green's function to yield results which are consistent through second order. We then discuss potential further approximations as well as computational procedures to be used in implementing our results.

2. Formal Development

A. Notation

The spectral representation of the one-particle Green's function written in the superoperator notation has the form [10]

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

where $\mathbf{a}$ is a set of electron annihilation operators $\mathbf{a} = \{a_i\}$, $\hat{I}$ and $\hat{H}$ are the superoperator identity and Hamiltonian, defined as

$$\hat{H}X_i = [H, X_i]_-, \qquad \hat{I}X_i = X_i \tag{2a}$$

where the electronic Hamiltonian is written in terms of the electron creation and annihilation operators [17] as

$$H = \sum_{ij} h_{ij} a_i^+ a_j + \frac{1}{2} \sum_{ij,kl} V_{ij,kl} a_i^+ a_j^+ a_l a_k \tag{2b}$$

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

$$h_{ij} = \langle \phi_i | h | \phi_j \rangle; \qquad V_{ij,kl} = \langle \phi_i(1)\phi_j(2) \left| \frac{1}{r_{12}} \right| \phi_k(1)\phi_l(2) \rangle \tag{2c}$$

The above set of creation and annihilation operators support the following binary product, defined in terms of the expectation value of the anticommutator

$$(X_i | X_j) \equiv \langle \Psi | [X_i^\dagger, X_j]_+ | \Psi \rangle \tag{3}$$

The superoperator resolvent $(E\hat{I} - \hat{H})^{-1}$ can be represented via the inner projection technique [11] which, for a complete set of operators **h**, allows $\mathbf{G}(E)$ to be written as

$$\mathbf{G}(E) = (\mathbf{a}|\mathbf{h})(\mathbf{h}|(E\hat{I} - \hat{H})|\mathbf{h})^{-1}(\mathbf{h}|\mathbf{a}) \tag{4}$$

This equation provides the basic starting point for the introduction of various approximations which lead to practical methods for computing $\mathbf{G}(E)$. The two essential approximations consist of making a truncation of the operator space **h** and of choosing a reference function Ψ.

B. Operator Space and Multiconfiguration Reference State

Our choice of projection manifold **h** has been facilitated by a theorem recently given by Manne [18]. This theorem essentially states that, given an N-electron Slater determinant $\Phi_0 = \prod_\alpha a_\alpha^+ |\mathrm{vac}\rangle$, and a manifold of operators

$$\begin{aligned} \mathbf{h}_1 &= \{a_\alpha\}, \{a_m\} \\ \mathbf{h}_3 &= \{a_m^+ a_\alpha a_\beta\}, \{a_\alpha^+ a_m a_n\}, \qquad \alpha < \beta,\ m < n \\ \mathbf{h}_5 &= \{a_m^+ a_n^+ a_\alpha a_\beta a_\gamma\}, \{a_\alpha^+ a_\beta^+ a_m a_n a_p\}, \qquad \alpha < \beta < \gamma,\ m < n < p \\ &\ \vdots \end{aligned} \tag{5}$$

($\alpha, \beta, \gamma, \ldots$ label the set of spin orbitals $\{\alpha\}$ that are occupied in Φ_0, $m, n, p, \ldots$ label the set of spin orbitals $\{\mathrm{m}\}$ that are unoccupied in Φ_0, and f, g, i, j, k, l label a general spin orbital), the set $\mathbf{h} = \{\mathbf{h}_i\}$ is complete when operating on any reference state Ψ provided that the overlap $\langle \Phi_0 | \Psi \rangle \neq 0$. It is important to point out that Manne's proof does not place restrictions on the determinant Φ_0 or the orbitals $\{\alpha\}$ which are occupied in Φ_0.

In this particular development we choose Ψ to be a multiconfiguration N-electron state

$$\Psi(\mathbf{C}, \phi) = \sum_{K=0} \Phi_K(\phi) C_K \tag{6}$$

where the $\Phi_K(\phi)$ are configurations constructed from the set of multiconfigurational orbitals $\{\phi_i\}$. The configurations Φ_K, $K \geq 1$ are assumed to have been obtained as excitations from Φ_0. The configuration Φ_0 is the determinant discussed above, which is chosen to define the operator manifold **h**. With this choice for Φ_0 the overlap criterion $\langle \Phi_0 | \Psi \rangle \neq 0$ is automatically satisfied. Usually Φ_0 would be chosen to be the dominant configuration, or one of the dominant configurations, for the given molecular geometry. As is seen later, this stipulation simplifies accounting for the order of magnitudes of various terms appearing in the calculation of the Green's function matrix elements. The specific MC wave function used here is taken to be an expansion of the type shown in Eq. (6) for which the set of orbitals $\{\phi_i\}$ and mixing coefficients $\{C_k\}$ are variationally optimized for minimum energy. The variational principle when applied to such multiconfiguration self-consistent-field (MCSCF) wave functions leads to the generalized Brillouin theorem [19] (GBT), which may be expressed as

$$\langle \Psi | \hat{H}(a_i^+ a_j) | \Psi \rangle \equiv \langle \hat{H}(a_i^+ a_j) \rangle = 0 \qquad (7)$$

The expectation value is hereafter taken with respect to the MCSCF reference state. It is this GBT which is actually employed to compute the MC wave function [20, 21]. In what follows, we assume that the optimal orbitals and mixing coefficients have already been so obtained.

It has been demonstrated that if a HF reference state is used with a truncated projection manifold consisting of the $\mathbf{h}_1$ and $\mathbf{h}_3$ subspaces (defined with respect to the HF determinant) then all "second-order" terms are included [2, 3, 5]. The term "second order" in the above context refers to the terms appearing in the Green's function expressions containing products of two or fewer two-electron integrals in their numerators and are hence of second or lower order in RSPT. Because of the fact that a MCSCF wave function is more general, and thus closer to the true eigenstate of the Hamiltonian than the HF wave function, we expect that the use of this same truncated manifold (consisting of $\mathbf{h}_1$, $\mathbf{h}_3$ defined with respect to Φ_0) includes at least the equivalent of the "second-order RSPT" terms. In what follows, we develop a different concept of order that arises naturally for the MCSCF reference wave function and we provide further justification for our use of the $\mathbf{h}_1$, $\mathbf{h}_3$ subspace. To facilitate further progress we orthogonalize the $\mathbf{h}_1$ and $\mathbf{h}_3$ subspaces. It becomes obvious shortly that this is sufficient for our case; it is not necessary to orthogonalize the $\mathbf{h}_3$ operators to one another. The Schmidt procedure then gives

$$\mathbf{h}_3 = \{a_m^+ a_\alpha a_\beta + \langle a_m^+ a_\beta \rangle a_\alpha - \langle a_m^+ a_\alpha \rangle a_\beta\}, \quad \{a_\alpha^+ a_m a_n + \langle a_\alpha^+ a_n \rangle a_m - \langle a_\alpha^+ a_m \rangle a_n\} \qquad (8)$$

Thus we have

$$(\mathbf{h}_1 | \mathbf{h}_1) = \mathbf{1}, \quad (\mathbf{h}_1 | \mathbf{h}_3) = \mathbf{0}, \quad \text{and} \quad (\mathbf{h}_3 | \mathbf{h}_3) = \mathbf{S} \qquad (9)$$

Using Eqs. (9), Eq. (4) can be partitioned to express $G^{-1}(E)$ as follows*:

$$G^{-1}(E) = (\mathbf{h}_1 | E\hat{I} - \hat{H} | \mathbf{h}_1) - (\mathbf{h}_1 | \hat{H} | \mathbf{h}_3)(\mathbf{h}_3 | E\hat{I} - \hat{H} | \mathbf{h}_3)^{-1}(\mathbf{h}_3 | \hat{H} | \mathbf{h}_1) \equiv \mathbf{A}(E) - \mathbf{B}\mathbf{M}(E)^{-1}\mathbf{C}, \qquad (10)$$

where the matrices **A**, **B**, **C**, and **M** are defined as

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* It is possible to show that for Eq. (10) to hold it is sufficient to have $(\mathbf{h}_1 | \mathbf{h}_i) = 0$, $i = 3, 5, \ldots$ With the resolution of the identity expressed as $\hat{1} = |\mathbf{h})(\mathbf{h}|\mathbf{h})^{-1}(\mathbf{h}|$ the representation of the inverse of a superoperator $\hat{A}$ becomes $(\mathbf{h}|\hat{A}^{-1}|\mathbf{h}) = (\mathbf{h}|\mathbf{h})(\mathbf{h}|\hat{A}|\mathbf{h})^{-1}(\mathbf{h}|\mathbf{h})$. From this and $(\mathbf{h}_1|\mathbf{h}_i) = 0$, one immediately has Eq. (10).

$$\mathbf{A}(E) = (\mathbf{h}_1|E\hat{I} - \hat{H}|\mathbf{h}_1)$$
$$\mathbf{B} = (\mathbf{h}_1|\hat{H}|\mathbf{h}_3)$$
$$\mathbf{C} = (\mathbf{h}_3|\hat{H}|\mathbf{h}_1)$$

and

$$\mathbf{M}(E) = (\mathbf{h}_3|E\hat{I} - \hat{H}|\mathbf{h}_3) \tag{11}$$

C. *Hermiticity of $\hat{H}$*

The superoperator Hamiltonian $\hat{H}$ is Hermitian if and only if the following relation is true for its matrix elements:

$$(X_i|\hat{H}X_j) - (X_j|\hat{H}X_i)^* = 0 \tag{12}$$

If the reference state Ψ is an exact eigenstate of H, Eq. (12) is satisfied identically so that $\hat{H}$ is Hermitian. However, in calculations involving approximate reference states, the matrix elements of $\hat{H}$ do not in general satisfy Eq. (12). This leads to artificial complications such as having to work with non-Hermitian matrices and having to stipulate the order of operations in the scalar product. This Hermiticity problem must be addressed for our chosen MCSCF reference state because it can potentially lead to extraneous non-Hermitian contributions to $\mathbf{G}(E)$. It is relatively straightforward to show that Eq. (12) can, in general, be rewritten as $\langle \hat{H}[X_i^+,X_j]_+ \rangle = 0$. This fact can now be exploited in our analysis of the matrices which occur in Eq. (10). First we consider the $\mathbf{A}$ matrix for which $X_i, X_j \in \mathbf{h}_1$. Then it immediately follows that

$$\langle \hat{H}[a_i^+,a_j]_+ \rangle = 0 \tag{13}$$

since $[a_i^+,a_j]_+ = \delta_{ij}$ which obviously commutes with H. Hence $\mathbf{A}$ is Hermitian for any choice of reference state. In considering the elements of $\mathbf{B}$ for which $X_i \in \mathbf{h}_1$; $\mathbf{X}_j \in \mathbf{h}_3$, we find

$$\begin{aligned}\langle \hat{H}[a_i^+,a_m^+a_\alpha a_\beta + \langle a_m^+a_\beta\rangle a_\alpha - \langle a_m^+a_\alpha\rangle a_\beta]_+\rangle \\ = -\delta_{\alpha i}\langle \hat{H}(a_m^+a_\beta)\rangle + \delta_{\beta i}\langle \hat{H}(a_m^+a_\alpha)\rangle = 0\end{aligned} \tag{14a}$$

and

$$\begin{aligned}\langle \hat{H}[a_i^+,a_\alpha^+a_m a_n + \langle a_\alpha^+a_n\rangle a_m - \langle a_\alpha^+a_m\rangle a_n]_+\rangle \\ = -\delta_{im}\langle \hat{H}(a_\alpha^+a_n)\rangle + \delta_{in}\langle \hat{H}(a_\alpha^+a_m)\rangle = 0\end{aligned} \tag{14b}$$

The final equalities of Eqs. (14) are a result of the GBT given in Eq. (7). Thus

$$(\mathbf{h}_1|\hat{H}|\mathbf{h}_3) = (\mathbf{h}_3|\hat{H}|\mathbf{h}_1)^* \tag{15}$$

and hence

$$\mathbf{B}^+ = \mathbf{C} \tag{16}$$

if one uses a MCSCF reference state obeying Eq. (7). A similar analysis of the terms of $\mathbf{M}$ for which $X_i, X_j \in \mathbf{h}_3$ gives, using the GBT of Eq. (7):

$$
\begin{aligned}
\langle \hat{H}[(\mathbf{h}_3^+)_{m\alpha\beta},(\mathbf{h}_3)_{n\mu\nu}]_+\rangle = {} & \delta_{mn}\langle \hat{H}(a_\beta^+ a_\alpha^+ a_\mu a_\nu)\rangle \\
& + \delta_{\alpha\mu}\langle \hat{H}(a_\beta^+ a_n^+ a_\nu a_m)\rangle - \delta_{\alpha\nu}\langle \hat{H}(a_\beta^+ a_n^+ a_\mu a_m)\rangle \\
& - \delta_{\beta\mu}\langle \hat{H}(a_n^+ a_\nu a_\alpha^+ a_m)\rangle + \delta_{\beta\nu}\langle \hat{H}(a_n^+ a_\mu a_\alpha^+ a_m)\rangle
\end{aligned} \tag{17a}
$$

$$
\langle \hat{H}[(\mathbf{h}_3^+)_{m\alpha\beta},(\mathbf{h}_3)_{\mu pq}]_+\rangle = 0 \tag{17b}
$$

and

$$
\begin{aligned}
& \langle \hat{H}[(\mathbf{h}_3^+)_{\alpha mn},(\mathbf{h}_3)_{\mu pq}]_+\rangle \\
& \quad = \delta_{\alpha\mu}\langle \hat{H}(a_n^+ a_m^+ a_p a_q)\rangle + \delta_{mp}\langle \hat{H}(a_n^+ a_\mu^+ a_q a_\alpha)\rangle \\
& \quad - \delta_{mq}\langle \hat{H}(a_n^+ a_\mu^+ a_p a_\alpha)\rangle - \delta_{np}\langle \hat{H}(a_\mu^+ a_q a_m^+ a_\alpha)\rangle \\
& \quad + \delta_{nq}\langle \hat{H}(a_\mu^+ a_p a_m^+ a_\alpha)\rangle
\end{aligned} \tag{17c}
$$

It is quite evident that the terms in Eqs. (17a) and (17c) do not in general vanish, except for the trivial case of the diagonal elements. A diagonal approximation to **M** is an especially relevant case because of the large dimension of the **M** matrix which needs to be inverted many times during the search for the zeros of $\mathbf{G}^{-1}(E)$. Thus it becomes computationally rather attractive to approximate **M** in diagonal or near-diagonal form. Furthermore, since the non-Hermiticity is an artifact of the choice of reference state, remedies such as averaging the off-diagonal terms or defining a symmetric commutator should be viable alternatives. We return to this aspect in a later discussion.

D. *Explicit Expressions*

To facilitate our discussion, the following more explicit representation of the terms of the $\mathbf{G}^{-1}(E)$ matrix are reproduced:

$$
\begin{aligned}
[\mathbf{G}^{-1}(E)]_{fg} &= (\mathbf{A} - \mathbf{B}\mathbf{M}^{-1}\mathbf{B}^+)_{fg} \\
&= A_{fg} - \sum_{a,b} B_{fa} M_{ab}^{-1} B_{gb}^*
\end{aligned} \tag{18a}
$$

The indices a, b are restricted by the $\mathbf{h}_3$ manifold to be of the types (i) $a = m\alpha\beta$, $b = n\mu\nu$, (ii) $a = m\alpha\beta$, $b = \mu pq$, (iii) $a = \alpha pq$, $b = n\mu\nu$, and (iv) $a = \alpha mn$, $b = \mu pq$. With these restrictions we are able to obtain the following set of expressions for the terms in the above Eq. (18a):

$$
\begin{aligned}
A_{fg} &= E\delta_{fg} + h_{gf} + \sum_{ij} \overline{V}_{ig,jf}\langle a_i^+ a_j\rangle \\
&\equiv E\delta_{fg} + h_{gf} + A'_{fg} \\
&\equiv E\delta_{fg} + A''_{fg}
\end{aligned} \tag{18b}
$$

$$
\begin{aligned}
B_{f,m\alpha\beta} = {} & \langle a_m^+ a_\alpha\rangle A'_{f\beta} - \langle a_m^+ a_\beta\rangle A'_{f\alpha} \\
& + \sum_{ij} \{\overline{V}_{i\alpha,jf}\langle a_i^+ a_m^+ a_\beta a_j\rangle + \overline{V}_{i\beta,fj}\langle a_m^+ a_\alpha a_i^+ a_j\rangle + {}^1\!/_2\overline{V}_{ij,mf}\langle a_i^+ a_j^+ a_\alpha a_\beta\rangle\}
\end{aligned} \tag{18c}
$$

$$
B_{f,\alpha mn} = \langle a_\alpha^+ a_m\rangle A'_{fn} - \langle a_\alpha^+ a_n\rangle A'_{fm} + \sum_{ij} \{\overline{V}_{im,jf}\langle a_i^+ a_\alpha^+ a_n a_j\rangle
$$

$$+ \overline{V}_{in.fj}\langle a_\alpha^+ a_m a_i^+ a_j\rangle + {}^1\!/\!_2\overline{V}_{ij.\alpha f}\langle a_i^+ a_j^+ a_m a_n\rangle\} \tag{18d}$$

$$M_{ab} = E(\mathbf{h}_3|\mathbf{h}_3)_{ab} - (\mathbf{h}_3|\hat{H}|\mathbf{h}_3)_{ab} \equiv ES_{ab} - M'_{ab} \tag{18c}$$

$$\begin{aligned} S_{m\alpha\beta.n\mu\nu} = {} & \langle a_\beta^+ a_\alpha^+ a_\mu a_\nu\rangle\delta_{mn} + \langle a_\beta^+ a_n^+ a_\nu a_m\rangle\delta_{\alpha\mu} \\ & - \langle a_\beta^+ a_n^+ a_\mu a_m\rangle\delta_{\alpha\nu} - \langle a_n^+ a_\nu a_\alpha^+ a_m\rangle\delta_{\mu\beta} + \langle a_n^+ a_\mu a_\alpha^+ a_m\rangle\delta_{\nu\beta} \\ & - \langle a_\beta^+ a_m\rangle\langle a_n^+ a_j\rangle\delta_{\mu\alpha} + \langle a_n^+ a_\nu\rangle\langle a_\alpha^+ a_m\rangle\delta_{\mu\beta} - \langle a_n^+ a_\mu\rangle\langle a_\alpha^+ a_m\rangle\delta_{\nu\beta} \\ & + \langle a_n^+ a_\mu\rangle\langle a_\beta^+ a_m\rangle\delta_{\nu\alpha} \end{aligned} \tag{18f}$$

$$S_{m\alpha\beta.\mu pq} = 0 \tag{18g}$$

$$S_{\alpha pq.n\mu\nu} = 0 \tag{18h}$$

$$\begin{aligned} S_{\alpha mn.\mu pq} = {} & \langle a_n^+ a_m^+ a_p a_q\rangle\delta_{\alpha\mu} + \langle a_n^+ a_\mu^+ a_q a_\alpha\rangle\delta_{mp} \\ & - \langle a_n^+ a_\mu^+ a_p a_\alpha\rangle\delta_{mq} - \langle a_\mu^+ a_q a_m^+ a_\alpha\rangle\delta_{np} + \langle a_\mu^+ a_p a_m^+ a_\alpha\rangle\delta_{nq} \\ & + \langle a_m^+ a_\alpha\rangle\langle a_\mu^+ a_q\rangle\delta_{pn} - \langle a_n^+ a_\alpha\rangle\langle a_\mu^+ a_q\rangle\delta_{pm} \\ & - \langle a_m^+ a_\alpha\rangle\langle a_\mu^+ a_p\rangle\delta_{qn} + \langle a_n^+ a_\alpha\rangle\langle a_\mu^+ a_p\rangle\delta_{qm} \end{aligned} \tag{18i}$$

$$\begin{aligned} M'_{m\alpha\beta.n\mu\nu} = {} & (a_m^+ a_\alpha a_\beta|\hat{H}|a_n^+ a_\mu a_\nu) \\ & + \langle a_n^+ a_\nu\rangle\{B^{\bullet}_{\mu.m\alpha\beta} - \langle a_m^+ a_\beta\rangle A''_{\alpha\mu} + \langle a_m^+ a_\alpha\rangle A''_{\beta\mu}\} \\ & + \langle a_n^+ a_\mu\rangle\{B^{\bullet}_{\nu.m\alpha\beta} - \langle a_m^+ a_\beta\rangle A''_{\alpha\nu} + \langle a_m^+ a_\alpha\rangle A''_{\beta\nu}\} \\ & + \langle a_m^+ a_\beta\rangle B_{\alpha.n\mu\nu} - \langle a_m^+ a_\alpha\rangle B_{\beta.n\mu\nu} \end{aligned} \tag{18j}$$

where

$$\begin{aligned} (a_m^+ a_\alpha a_\beta|\hat{H}|a_n^+ a_\mu a_\nu) = {} & h_{mn}\langle a_\beta^+ a_\alpha^+ a_\mu a_\nu\rangle - h_{\mu\alpha}\langle a_\beta^+ a_n^+ a_\nu a_m\rangle \\ & + h_{\mu\beta}\langle a_n^+ a_\nu a_\alpha^+ a_m\rangle + h_{\nu\alpha}\langle a_\beta^+ a_n^+ a_\mu a_m\rangle - h_{\nu\beta}\langle a_n^+ a_\mu a_\alpha^+ a_m\rangle \\ & + \sum_i \{h_{in}(\langle a_\beta^+ a_i^+ a_\nu a_m\rangle\delta_{\alpha\mu} - \langle a_\beta^+ a_i^+ a_\mu a_m\rangle\delta_{\alpha\nu} \\ & - \langle a_i^+ a_\nu a_\alpha^+ a_m\rangle\delta_{\beta\mu} + \langle a_i^+ a_\mu a_\alpha^+ a_m\rangle\delta_{\beta\nu}) + h_{\mu i}(\langle a_\beta^+ a_\alpha^+ a_\nu a_i\rangle\delta_{mn} \\ & + \langle a_\beta^+ a_n^+ a_i a_m\rangle\delta_{\alpha\nu} - \langle a_n^+ a_i a_\alpha^+ a_m\rangle\delta_{\beta\nu}) + h_{\nu i}(-\langle a_\beta^+ a_\alpha^+ a_\mu a_i\rangle\delta_{mn} \\ & - \langle a_\beta^+ a_n^+ a_i a_m\rangle\delta_{\alpha\mu} + \langle a_n^+ a_i a_\alpha^+ a_m\rangle\delta_{\beta\mu})\} + {}^1\!/\!_2 \sum_{ij} \{2\overline{V}_{im.jn}\langle a_\beta^+ a_\alpha^+ a_i^+ a_\mu a_\nu a_j\rangle \\ & + \overline{V}_{ij.\alpha n}\langle a_\beta^+ a_i^+ a_j^+ a_\mu a_\nu a_m\rangle + \overline{V}_{ij.n\beta}\langle a_i^+ a_j^+ a_\mu a_\nu a_\alpha^+ a_m\rangle \\ & + \overline{V}_{m\mu.ij}\langle a_\beta^+ a_\alpha^+ a_\nu a_i a_j\rangle + 2\overline{V}_{i\mu.\alpha j}\langle a_\beta^+ a_i^+ a_n^+ a_\nu a_j a_m\rangle \\ & + 2\overline{V}_{i\mu.j\beta}\langle a_n^+ a_\nu a_i^+ a_j a_\alpha^+ a_m\rangle + \overline{V}_{ij.m\nu}\langle a_\beta^+ a_\alpha^+ a_n^+ a_\mu a_j a_i\rangle \\ & + 2\overline{V}_{i\nu.j\alpha}\langle a_\beta^+ a_n^+ a_\mu a_i^+ a_j a_m\rangle + 2\overline{V}_{i\nu.\beta j}\langle a_i^+ a_n^+ a_\mu a_j a_\alpha^+ a_m\rangle \\ & + {}^1\!/\!_2 \sum_{ijk} \overline{V}_{ij.nk}\{\langle a_\beta^+ a_i^+ a_j^+ a_k a_\nu a_m\rangle\delta_{\alpha\mu} + \langle a_\beta^+ a_i^+ a_j^+ a_\mu a_k a_m\rangle\delta_{\alpha\nu} \\ & + \langle a_i^+ a_j^+ a_\nu a_k a_\alpha^+ a_m\rangle\delta_{\beta\mu} + \langle a_i^+ a_j^+ a_k a_\mu a_\alpha^+ a_m\rangle\delta_{\beta\nu}\} \\ & + \overline{V}_{i\mu.jk}\{\langle a_\beta^+ a_\alpha^+ a_i^+ a_\nu a_k a_j\rangle\delta_{mn} + \langle a_\beta^+ a_i^+ a_n^+ a_k a_j a_m\rangle\delta_{\alpha\nu} \\ & + \langle a_n^+ a_i^+ a_k a_j a_\alpha^+ a_m\rangle\delta_{\beta\nu}\} + \overline{V}_{i\nu.jk}\{\langle a_\beta^+ a_\alpha^+ a_\mu a_i^+ a_k a_j\rangle\delta_{mn} \\ & + \langle a_\beta^+ a_n^+ a_i^+ a_k a_j a_m\rangle\delta_{\alpha\mu} + \langle a_i^+ a_n^+ a_k a_j a_\alpha^+ a_m\rangle\delta_{\beta\mu}\} \end{aligned} \tag{18k}$$

$$\begin{aligned} M'_{\alpha mn.\mu pq} = {} & (a_\alpha^+ a_m a_n|\hat{H}|a_\mu^+ a_p a_q) \\ & + \langle a_\mu^+ a_q\rangle\{B^{\bullet}_p\alpha mn - \langle a_\alpha^+ a_n\rangle A^{\bullet}_{mp} + \langle a_\alpha^+ a_m\rangle A^{\bullet}_{np}\} \end{aligned}$$

$$\begin{aligned}
&- \langle a_\mu^+ a_p \rangle \{ B^*_{q,\alpha mn} - \langle a_\alpha^+ a_n \rangle A^*_{mq} + \langle a_\alpha^+ a_m \rangle A^*_{nq} \} \\
&\qquad + \langle a_\alpha^+ a_n \rangle B_{m,\mu pq} - \langle a_\alpha^+ a_m \rangle B_{n,\mu pq}
\end{aligned} \tag{18l}$$

where

$$\begin{aligned}
(a_\alpha^+ a_m a_n | \hat{H} | a_\mu^+ a_p a_q) &= h_{\alpha\mu} \langle a_n^+ a_m^+ a_p a_q \rangle - h_{pm} \langle a_n^+ a_\mu^+ a_q a_\alpha \rangle \\
&+ h_{pn} \langle a_\mu^+ a_q a_m^+ a_\alpha \rangle + h_{qm} \langle a_n^+ a_\mu^+ a_p a_\alpha \rangle - h_{qn} \langle a_\mu^+ a_p a_m^+ a_\alpha \rangle \\
&+ \sum_i \{ h_{i\mu} [\langle a_n^+ a_i^+ a_q a_\alpha \rangle \delta_{mp} - \langle a_n^+ a_i^+ a_p a_\alpha \rangle \delta_{mq} \\
&- \langle a_i^+ a_q a_m^+ a_\alpha \rangle \delta_{np} + \langle \alpha_i^+ a_p a_m^+ a_\alpha \rangle \delta_{nq}] \\
&+ h_{pi} [\langle a_n^+ a_m^+ a_q a_i \rangle \delta_{\alpha\mu} + \langle a_n^+ a_\mu^+ a_i a_\alpha \rangle \delta_{mq} - \langle a_\mu^+ a_i a_m^+ a_\alpha \rangle \delta_{nq}] \\
&+ h_{qi} [- \langle a_n^+ a_m^+ a_p a_i \rangle \delta_{\alpha\mu} - \langle a_n^+ a_\mu^+ a_i a_\alpha \rangle \delta_{mp} + \langle a_\mu^+ a_i a_m^+ a_\alpha \rangle \delta_{np}] \} \\
&+ \tfrac{1}{2} \sum_{ij} \{ 2\overline{V}_{i\alpha,j\mu} \langle a_n^+ a_m^+ a_i^+ a_p a_q a_j \rangle + \overline{V}_{ij,m\mu} \langle a_n^+ a_i^+ a_j^+ a_p a_q a_\alpha \rangle \\
&+ \overline{V}_{ij,\mu n} \langle a_i^+ a_j^+ a_p a_q a_m^+ a_\alpha \rangle + \overline{V}_{\alpha p,ij} \langle a_n^+ a_m^+ a_\mu^+ a_q a_i a_j \rangle \\
&+ 2\overline{V}_{ip,mj} \langle a_n^+ a_i^+ a_\mu^+ a_q a_j a_\alpha \rangle + 2\overline{V}_{ip,jn} \langle a_\mu^+ a_q a_i^+ a_j a_m^+ a_\alpha \rangle \\
&+ \overline{V}_{ij,\alpha q} \langle a_n^+ a_m^+ a_\mu^+ a_p a_j a_i \rangle + 2\overline{V}_{iq,jm} \langle a_n^+ a_\mu^+ a_p a_i^+ a_j a_\alpha \rangle \\
&+ 2\overline{V}_{iq,nj} \langle a_i^+ a_\mu^+ a_p a_j a_m^+ a_\alpha \rangle \} + \tfrac{1}{2} \sum_{ijk} \overline{V}_{ij,\mu k} \{ \langle a_n^+ a_i^+ a_j^+ a_k a_q a_\alpha \rangle \delta_{mp} \\
&+ \langle a_n^+ a_i^+ a_j^+ a_p a_k a_\alpha \rangle \delta_{mq} + \langle a_i^+ a_j^+ a_q a_k a_m^+ a_\alpha \rangle \delta_{np} + \langle a_i^+ a_j^+ a_k a_p a_m^+ a_\alpha \rangle \delta_{nq} \} \\
&+ \overline{V}_{ip,jk} [\langle a_n^+ a_m^+ a_i^+ a_q a_k a_j \rangle \delta_{\alpha\mu} + \langle a_n^+ a_i^+ a_\mu^+ a_k a_j a_\alpha \rangle \delta_{mq} \\
&+ \langle a_\mu^+ a_i^+ a_k a_j a_m^+ a_\alpha \rangle \delta_{nq}] + \overline{V}_{iq,jk} [\langle a_n^+ a_m^+ a_p a_i^+ a_k a_j \rangle \delta_{\alpha\mu} \\
&+ \langle a_n^+ a_\mu^+ a_i^+ a_k a_j a_\alpha \rangle \delta_{mp} + \langle a_i^+ a_\mu^+ a_k a_j a_m^+ a_\alpha \rangle \delta_{np}]
\end{aligned} \tag{18m}$$

and

$$\begin{aligned}
M'_{m\alpha\beta,\mu pq} &= (a_m^+ a_\alpha a_\beta | \hat{H} | a_\mu^+ a_p a_q) \\
&+ \langle a_\mu^+ a_q \rangle \{ B^*_{pm\alpha\beta} - \langle a_m^+ a_\beta \rangle A^*_{\alpha p} + \langle a_m^+ a_\alpha \rangle A^*_{\beta p} \} \\
&- \langle a_\mu^+ a_p \rangle \{ B^*_q m\alpha\beta \\
&- \langle a_m^+ a_\beta \rangle A^*_{\alpha q} + \langle a_m^+ a_\alpha \rangle A^*_{\beta q} \} \\
&+ \langle a_m^+ a_\beta \rangle \, B_{\alpha,\mu pq} - \langle a_m^+ a_\alpha \rangle \, B_{\beta,\mu pq}
\end{aligned}$$

where

$$\begin{aligned}
(a_m^+ a_\alpha a_\beta | \hat{H} | a_\mu^+ a_p a_q) &= h_{m\mu} \langle a_\beta^+ a_\alpha^+ a_p a_q \rangle - h_{p\alpha} \langle a_\beta^+ a_\mu^+ a_q a_m \rangle \\
&+ h_{p\beta} \langle a_\mu^+ a_q a_\alpha^+ a_m \rangle + h_{q\alpha} \langle a_\beta^+ a_\mu^+ a_p a_m \rangle - h_{q\beta} \langle a_\mu^+ a_p a_\alpha^+ a_m \rangle \\
&+ \tfrac{1}{2} \sum_{ij} \{ 2\overline{V}_{im,j\mu} \langle a_\beta^+ a_\alpha^+ a_i^+ a_p a_q a_j \rangle + \overline{V}_{ij,\alpha\mu} \langle a_\beta^+ a_i^+ a_j^+ a_p a_q a_m \rangle \\
&+ \overline{V}_{ij,\mu\beta} \langle a_i^+ a_j^+ a_p a_q a_\alpha^+ a_m \rangle + \overline{V}_{mp,ij} \langle a_\beta^+ a_\alpha^+ a_\mu^+ a_q a_i a_j \rangle \\
&+ 2\overline{V}_{ip,\alpha j} \langle a_\beta^+ a_i^+ a_\mu^+ a_q a_j a_m \rangle + 2\overline{V}_{ip,j\beta} \langle a_\mu^+ a_q a_i^+ a_j a_\alpha^+ a_m \rangle \\
&+ \overline{V}_{ij,mq} \langle a_\beta^+ a_\alpha^+ a_\mu^+ a_p a_j a_i \rangle + 2\overline{V}_{iq,j\alpha} \langle a_\beta^+ a_\mu^+ a_p a_i^+ a_j a_m \rangle \\
&+ 2\overline{V}_{iq,\beta j} \langle a_i^+ a_\mu a_p a_j a_\alpha^+ a_m \rangle \}
\end{aligned} \tag{18n}$$

In the above expressions, $\overline{V}_{ij,kl} \equiv V_{ij,kl} - V_{ij,lk}$ and Eq. (18b) defines the matrix elements A'_{fg} and A''_{fg}. We note that the calculation of the matrix elements of the **A**, **B**, and **M** matrices require the one- and two-electron integrals (h_{ij} and $V_{ij,kl}$) in terms of the MCSCF orbital basis, as well as the elements of the one-, two-, and three-particle density matrix elements ($\langle a_i^+ a_j \rangle$, $\langle a_i^+ a_j^+ a_k a_l \rangle$, $\langle a_i^+ a_j^+ a_k^+ a_l a_f a_g \rangle$) calculated with respect to the MCSCF reference state.

E. Order Analysis

Our next job is to assign orders of magnitude to the various terms appearing in Eqs. (18) with the intention of locating and deleting small (third-order and higher) terms. We note, for example, that the elements of the **A**, **B**, and **M** matrices contain terms of the type, $\overline{V} \langle a^+ \cdots a \rangle$, where $\langle a^+ \cdots a \rangle$ contains a small number of creation and annihilation operator pairs. The terms $\langle a_i^+ a_j \rangle$, $\langle a_i^+ a_j^+ a_l a_k \rangle$, and $\langle a_i^+ a_j^+ a_k^+ a_l a_f a_g \rangle$ are the elements of one- and two- and three-particle reduced density matrices corresponding to our MCSCF reference state. We assume that these elements are already available. We also assume that for the systems of interest a distinct boundary exists between the set of spin orbitals with large (near-unit) occupation numbers $\langle a_i^+ a_i \rangle$ and the set of orbitals with small (near-zero) occupation numbers[*] (denoted L and S, respectively). We note that since these diagonal terms $\langle a_i^+ a_i \rangle$ are sums of squares of the mixing coefficients of the MCSCF wave function, this assumption is equivalent to a similar partition among these coefficients. With this assumption, we assign zeroth order to the large occupation numbers and second order to the small occupation numbers:

$$\begin{aligned} \langle a_i^+ a_i \rangle &= O(0), \quad \text{if } i \in L \\ &= O(2), \quad \text{if } i \in S \end{aligned} \tag{19a}$$

where $O(n)$ means a term of nth order. Furthermore, it is possible to assign an upper bound to the magnitude of the off-diagonal density matrix elements appearing in Eqs. (18) by using the Schwarz inequality

$$|\langle a_i^+ a_j \rangle|^2 \le \langle a_i^+ a_i \rangle \langle a_j^+ a_j \rangle \tag{19b}$$

which, in a straightforward manner, results in the following order statements:

$$\begin{aligned} \langle a_i^+ a_j \rangle &= O(1), \quad \text{if } i \in S, j \in L, \text{ or } i \in L, j \in S \\ \langle a_i^+ a_j \rangle &= O(2), \quad \text{if } i, j \in S \end{aligned} \tag{19c}$$

---

[*] This assumption for an MCSCF wave function of the type given in Eq. (6) implies that the set of mixing coefficients can be separated as $\{C_L, L = 1, m\}$ and $\{C_S, S = m, M\}$ 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. 20 (p. 1059) where for NH($b\,^1\Sigma^+$) at R_e (= 1.95 bohr) the C_L set has configurations $3\sigma^2 1\pi^2$ and $3\sigma 4\sigma 1\pi^2$ with coefficients 0.91 and −0.37, respectively, and the coefficient of largest magnitude from the C_S set is 0.08. Another example can be seen in Ref. 24 where orbital occupation numbers for Purine are calculated as 1.997, 1.990, 1.984, 1.966, 1.953, 0.079, 0.056, 0.55, 0.030. The assumption may not strictly hold for delocalized systems such as metals.

The analysis for the case of the two- and three-particle reduced density matrices, which also occur in Eqs. (18), can be carried through in analogous fashion. For example,

$$|\langle a_i^\dagger a_j^\dagger a_k a_l\rangle|^2 \le \langle a_i^\dagger a_j^\dagger a_j a_i\rangle \langle a_l^\dagger a_k^\dagger a_k a_l\rangle \tag{20a}$$

$$|\langle a_i^\dagger a_j^\dagger a_k^\dagger a_l a_f a_g\rangle|^2 \le \langle a_i^\dagger a_j^\dagger a_k^\dagger a_k a_j a_i\rangle \langle a_g^\dagger a_f^\dagger a_l^\dagger a_l a_f a_g\rangle \tag{20b}$$

the right-hand sides of these equations being products of diagonal terms of the appropriate reduced density matrices. For these diagonal terms, the following order assignments can be made:

$$\begin{aligned} \langle a_i^\dagger a_j^\dagger a_j a_i\rangle &= O(0), \quad \text{if } i, j \in L \\ &= O(2), \quad \text{if } i \in L, j \in S, \text{ or } i \in S, j \in L \\ &= O(4), \quad \text{if } i, j \in S \end{aligned} \tag{20c}$$

from which follows the orders of the off-diagonal terms

$$\begin{aligned} \langle a_i^\dagger a_j^\dagger a_k a_l\rangle &= O(0), \quad \text{if } i, j, kl \in L \\ &= O(1), \quad \text{if one of the orbitals } i, j, k, l \in S \\ &= O(2), \quad \text{if two of the orbitals} \in S \\ &= O(3), \quad \text{if three of the orbitals} \in S \\ &= O(4), \quad \text{if } i, j, k, l \in S \end{aligned} \tag{20d}$$

It should be noted that for the special case when $j = k$ is a "core" orbital which is occupied in all configurations, then $\langle a_i^\dagger a_j^\dagger a_k a_l\rangle = \langle a_i^\dagger a_l\rangle$ and the order assignments of Eq. (20d) are consistent with those of Eq. (19c).

The ordering of the diagonal and off-diagonal terms in the three-body density matrix elements can be assigned in an analogous manner. Thus, to determine the order of a term which consists of the average value of a product of an equal number of creation and annihilation operators arranged so that all creation operators are to the left of all of the annihilation operators, one simply counts the number of spin-orbital indices that belong to S. In the following, the word "order" refers to the above-introduced occupation number "size." We do not use the RSPT concept of order at all in the present work because the entire RSPT concept fails under the physical conditions (e.g., distorted geometries) in which we are interested.

3. Operational Considerations

A. *Implementation of the Order Concept*

To utilize this concept of ordering, one further partitions the sets of spin orbitals $\{\alpha\}$, $\{\mathrm{m}\}$, defined with respect to occupation in Φ_0 into disjoint subsets of spin orbitals, $\{\alpha_L\}$, $\{\alpha_S\}$, $\{\mathrm{m}_L\}$, $\{\mathrm{m}_S\}$, with large and small occupation numbers defined with respect to the diagonal elements of the one-particle density matrix, where

$$\{\alpha_L\} \cup \{\alpha_S\} = \{\alpha\}, \quad \{\mathbf{m}_L\} \cup \{\mathbf{m}_S\} = \{\mathbf{m}\}, \quad \{\alpha_L\} \cup \{\mathbf{m}_L\} = L, \quad \{\alpha_S\} \cup \{\mathbf{m}_S\} = S$$

As mentioned before, if Φ_0 is chosen as the dominant configuration at some geometry then, without loss of generality, it can be assumed that there are no spin orbitals with small occupation numbers which are occupied in Φ_0, i.e., $\{\alpha\} = \{\alpha_L\}$. It is to be expected that in calculations involving small-to-medium-sized molecules the set $\{\mathbf{m}_S\}$ will contain many more spin orbitals than the set $\{\mathbf{m}_L\}$. The spin orbitals can then be arranged within the sets $\{\alpha\}$ and $\{\mathbf{m}\}$ so that blocks of the **A**, **B**, and **M** matrices, partitioned by the operator indices, can be further partitioned by using the $\{\mathbf{m}_L\}$ and $\{\mathbf{m}_S\}$ classification. These observations allow one to calculate different blocks of the matrices that contribute to the $\mathbf{G}^{-1}(E)$ matrix using different computational formulas and thus, while maintaining order consistency, to substantially reduce the computational effort. This is achieved simply by truncating the summation indices in such a way that terms contributing past a certain order (past second order in our case) are not included. For example the **B** matrix can be blocked into ten partitions of the type

$$\begin{array}{rl}
B_{f,m\alpha\beta}\text{: (i)} & f, m, \alpha, \beta \in L \\
\text{(ii)} & f, \alpha, \beta \in L, \quad m \in S \\
B_{f,\alpha mn}\text{: (iii)} & f, \alpha, m, n \in L \\
\text{(iv)} & f, \alpha, n \in L, \quad m \in S \\
\text{(v)} & f, \alpha \in L, \quad m, n \in S \\
B_{f,m\alpha\beta}\text{: (vi)} & m, \alpha, \beta \in L, \quad f \in S \\
\text{(vii)} & \alpha, n \in L, \quad f, m \in S \\
B_{f,\alpha nm}\text{: (viii)} & \alpha, m, n \in L, \quad f \in S \\
\text{(ix)} & \alpha, n \in L, \quad f, m \in S \\
\text{(x)} & \alpha \in L, \quad f, m, n \in S
\end{array} \tag{21}$$

where the blocks of largest dimension usually are those labeled (ix) and (x) since the number of spin orbitals in S will be considerably larger than the number of spin orbitals in L for most calculations that exceed minimal-basis quality. Because the **A** matrix has, at most, second-order terms [see Eqs. (18b), (19a), and (19c)], no truncation of the summation indices is used in the calculation of its elements. As is shown below, the **B** matrix contains terms which are zeroth, first, and second order, and the **M** matrix has zeroth- and higher-order contributions. Thus, to obtain all second-order contributions to $\mathbf{BM}^{-1}\mathbf{B}^{+}$, one needs to compute **B** and $\mathbf{M}^{-1}$ both through second order. Because the **M** matrix is to be further approximated, its detailed discussion is deferred until the next section.

As particular examples of the application of the above ordering process, an element of block (x) of **B** can be calculated to second order as [see Eq. (18d)]:

$$\begin{aligned}
B_{f,\alpha mn} = {} & \langle a_\alpha^+ a_m \rangle A'_{fn} - \langle a_\alpha^+ a_n \rangle A'_{fm} \\
& + \tfrac{1}{2} \sum_{(ij)_0} V_{ij,\alpha f} \langle a_i^+ a_j^+ a_m a_n \rangle + \sum_{(ij)_1} \overline{V}_{im,jf} \langle a_i^+ a_\alpha^+ a_n a_j \rangle \\
& + \sum_{(i)_1} \overline{V}_{mn,fi} \langle a_\alpha^+ a_i \rangle - \sum_{(ij)_1} \overline{V}_{in,fj} \langle a_\alpha^+ a_i^+ a_m a_j \rangle
\end{aligned} \tag{22a}$$

and a diagonal element of the **M**′ matrix of the form $M'_{\alpha mn,\mu pq}$, with $m, n, p, q, \in s; \alpha, \mu \in L$ may be calculated to second order as

$$
\begin{aligned}
M'_{\alpha nm,\alpha mn} = {} & 2\langle a_\alpha^+ a_n\rangle B_{m,\alpha mn} - 2\langle a_\alpha^+ a_m\rangle B_{n,\alpha mn} \\
& - \langle a_\alpha^+ a_n\rangle^2 A''_{mm} - \langle a_\alpha^+ a_m\rangle^2 A''_{nn} + 2\langle a_\alpha^+ a_n\rangle\langle a_\alpha^+ a_m\rangle A''_{nm} \\
& - (h_{mm} + h_{nn})\langle a_\alpha^+ a_\alpha\rangle + h_{\alpha\alpha}\langle a_n^+ a_m^+ a_m a_n\rangle \\
& + h_{mm}\langle a_n^+ a_\alpha^+ a_\alpha a_n\rangle + h_{nn}\langle a_m^+ a_\alpha^+ a_\alpha a_m\rangle - 2h_{mn}\langle a_\alpha^+ a_m^+ a_n a_\alpha\rangle \\
& + \sum_{(i)_0} h_{i\alpha}\{\langle a_n^+ a_i^+ a_n a_\alpha\rangle + \langle a_m^+ a_i^+ a_m a_\alpha\rangle\} \\
& + \sum_{(i)_1} \{h_{i\alpha}\langle a_i^+ a_\alpha\rangle - h_{mi}\langle a_m^+ a_\alpha^+ a_i a_\alpha\rangle - h_{ni}\langle a_n^+ a_\alpha^+ a_i a_\alpha\rangle\} \\
& + \overline{V}_{nm,mn}\langle a_\alpha^+ a_\alpha\rangle + \sum_{(i)_1} \{2\overline{V}_{in,nm}\langle a_i^+ a_\alpha^+ a_m a_\alpha\rangle + 2\overline{V}_{im,mn}\langle a_i^+ a_\alpha^+ a_n a_\alpha\rangle\} \\
& + \sum_{(i,j)_2} (\overline{V}_{im,nj} + V_{in,nj})\langle a_\alpha^+ a_i^+ a_j a_\alpha\rangle \\
& + \sum_{(ij)_0} \{\overline{V}_{im,mj}\langle a_n^+ a_i^+ a_\alpha^+ a_n a_j a_\alpha\rangle + \overline{V}_{in,nj}\langle a_m^+ a_i^+ a_\alpha^+ a_m a_j a_\alpha\rangle \\
& - 2\overline{V}_{im,jn}\langle a_\alpha^+ a_i^+ a_m^+ a_n a_j a_\alpha\rangle + \tfrac{1}{2}\overline{V}_{mn,ij}\langle a_n^+ a_m^+ a_j a_i\rangle\} \\
& - \tfrac{1}{2}\sum_{(ij)_1} \{\overline{V}_{ij,\alpha n}\langle a_i^+ a_j^+ a_n a_\alpha\rangle + \overline{V}_{ij,\alpha m}\langle a_i^+ a_j^+ a_m a_\alpha\rangle \\
& + \tfrac{1}{2}\sum_{(ijk)_0} \overline{V}_{ij,\alpha k}\{\langle a_n^+ a_i^+ a_j^+ a_k a_n a_\alpha\rangle + \langle a_m^+ a_i^+ a_j^+ a_k a_m a_\alpha\rangle\} \\
& + \tfrac{1}{2}\sum_{(ijk)_1} \{\overline{V}_{im,jk}\langle a_\alpha^+ a_i^+ a_m^+ a_k a_j a_\alpha\rangle + \overline{V}_{in,jk}\langle a_\alpha^+ a_i^+ a_n^+ a_k a_j a\rangle\} \\
& + \tfrac{1}{2}\sum_{(ijk)_2} \overline{V}_{ij,\alpha k} \\
& \langle a_i^+ a_j^+ a_k a_\alpha\rangle \qquad (22b)
\end{aligned}
$$

The summation indices $(i)_n$, $(ij)_n$, $(ijk)_n$ imply that of the group of indices in parentheses, at most n are allowed to be in S [e.g., $(ij)_1$ is equivalent to $ij \in L; i \in L, j \in S; i \in S, j \in L$]. The total number of terms to be computed in evaluating $B_{f,m\alpha\beta}$ via Eq. (18d) is $\sim 3N^2$, whereas the total number of terms in the example of Eq. (22a) is $\sim(4lN - l^2)$, where N is the number of spin orbitals in $\{\phi\}$ and l is the number of orbitals in L. Since the A' terms included in Eq. (22a) contain some third-order factors, order consistency has been somewhat compromised for computational efficiency in this expression. Direct calculation of the particular M' diagonal element from Eq. (18) requires $\sim 6N^3$ terms where the second-order expressions in Eq. (22b) requires $\sim(3lN^2 - 4l^2N + 5l^3)$ terms. Further reduction of the number of terms in the **A**, **B**, and **M** matrix elements can, of course, be effected by considerations of symmetry and by considerations of the types of configurations involved in the reference state.

In considering the off-diagonal terms of the **M** matrix, whose elements are not analyzed in Eq. (22b), one notes [see Eqs. (18j)-(18n)] that there are zeroth-order terms which occur. On first sight, this severely limits the kind of approximations which can be justified regarding such off-diagonal terms. However, the same off-diagonal terms appear in the expressions for the non-Hermiticity factors which arise in the matrix elements of **M** given in Eqs. (17). For example $\Sigma_i h_{in} \langle a_\beta^+ a_i^+ a_\nu a_m \rangle \delta_{\alpha\mu}$ is included in the term $\delta_{\alpha\mu} \langle \hat{H}(a_\beta^+ a_n^+ a_\nu a_m) \rangle$ of Eq. (17a). Thus, with the use of better quality reference states, all zeroth-order terms in the off-diagonal components of **M** will tend to zero. This fact may be used as a basis for making Hermitian approximations to the **M** matrix. In the following subsection we discuss some approximations which are consistent with the point of view in which these artificial non-Hermitian off-diagonal elements of **M** are neglected.

Thus far in this section, we have demonstrated how the order idea introduced earlier can be exploited to evaluate the **A**, **B**, and **M** matrix elements through second order, thereby reducing the computational effort involved. However, we have not yet fully justified our truncation of the **h** operator manifold at $\mathbf{h}_1$, $\mathbf{h}_3$. It is possible to show that the extension of the operator manifold to include $\mathbf{h}_5$ leads to corrections to the self-energy which are higher than second order. This is shown,* in analogous fashion to the order analysis for the elements of **M**, by noting that $(\mathbf{h}_5|\hat{H}|\mathbf{h}_1) = O(2)$ in the limit in which $\langle \overline{H}[\mathbf{h}_5^+;\mathbf{h}_1]_+ \rangle = 0$ and $\mathbf{M}^{-1}$ is diagonal with respect to zeroth-order terms. Hence, in the present development in which only $\mathbf{h}_1$ and $\mathbf{h}_3$ are used, we have included all terms correct to second order for $\mathbf{G}^{-1}(E)$.

B. Computational Aspects

Because of its huge dimension and because it must be inverted several times during a search for the zeros of $\det(\mathbf{G}^{-1}(E))$, the **M** matrix must be drastically approximated to make calculations computationally feasible. The simplest way of approximating the **M** matrix so that its inverse may be easily calculated is to neglect the off-diagonal elements. Other approximations may involve the deletion of selected off-diagonal blocks of the **M** matrix. This latter procedure would result in the calculation of either the inverses of several smaller matrices or an inverse of a nearly diagonal matrix. One systematic way of doing this is to construct the diagonal blocks of **M** where in each block the spin-orbital indices of the matrix elements differ by fewer than some small integer [37]. Because the off-diagonal elements of **M** contain first-order factors and because **B** contains zeroth-order terms, any scheme which neglects any or all of the off-diagonal **M** matrix destroys the completeness of our second-order treatment. However, it is probable that such approximations will have to be made.

* Order analysis of the matrix elements of $(\mathbf{h}_5|\hat{H}|\mathbf{h}_1)$ reveals that it has no real zeroth-order terms, although it does have terms, for example, [illegible] as the elements of the expansion for $\mathbf{h}_5|\hat{H}|\mathbf{h}_1)_{iq\mu\nu\lambda,\gamma}$ with $i, k, q, t \in L$ which are of zeroth order. However, the same terms also appear in the expressions for the non-Hermiticity factors $\langle \hat{H}[\mathbf{h}_5^+,\mathbf{h}_1]_+ \rangle$ which vanish in the limit of an exact reference state, and are, therefore, neglected here.

Assuming that a diagonal approximation to **M** is used, further efficiency may be realized by observing that the matrix multiplication $(\mathbf{BM}^{-1}\mathbf{B}^{+})_{fg}$ can be written as $\Sigma_k B_{fk}B_{gk}/M_{kk}$ where **B** is assumed to be real. Then depending on the dimension of the **B** matrix there are several computational procedures which may be employed. If the dimension of **B** is small enough to permit storage of the **B** matrix and the diagonal terms of the **S** and **M′** matrices in primary memory (core), then the straightforward calculation of the $\mathbf{G}^{-1}(E)$ matrix is possible. In cases where the dimension of the **B** matrix is such that only a few rows can be held in core at a time, then construction of blocks of the $\mathbf{G}^{-1}(E)$ matrix can be effected with one transfer from a secondary storage device (I/O operation from tape, disk, etc.) per block. When the dimension is so large that one or less than one row of the **B** matrix can be held in core at any time, then some flexibility can be gained by performing intermediate calculations to compute the results of $\overline{B}_{fg,k} = B_{fk} * B_{gk}, f \leq g$ and storing the lists of $\overline{B}_{fg,k}$, S_{kk}, and M'_{kk} in records of an appropriate size to perform simultaneous secondary storage transfer and intermediate calculations of the terms. The relative efficiency of these and other possible techniques depends on the dimensions of the matrices in the particular calculation and on the particular I/O procedures available. Since the construction of the $\mathbf{G}^{-1}(E)$ matrix occurs many times during a calculation of the ionization energies, the efficiency of this step becomes crucial to the overall efficiency of the entire calculation.

In carrying out a Green's function calculation using the above results, one must first compute the elements of the $\mathbf{G}^{-1}(E)$ matrix for a given value of E. The next step is to calculate $\det(\mathbf{G}^{-1}(E))$, or some approximation to it, and to perform the search for its zeros as functions of E. Since the calculation of a determinant requires $\sim N^3/3$ operations, it would be desirable to find a reliable approximation to this step. Possibilities include monitoring the eigenvalue of smallest magnitude of $\mathbf{G}^{-1}(E)$ as a function of E, or observing the convergence of a sequence of determinants calculated from successively larger submatrices of the $\mathbf{G}^{-1}(E)$ matrix. The former possibility is subject to error from the singular nature of the determinant when combined with iterative schemes for finding the smallest eigenvalue of a matrix. The latter possibility has the advantage that the construction of the submatrices may parallel the evaluation of the sequence of determinants but may be subject to slow convergence because of the nature of the MCSCF reference state as compared to other reference states where this method has been applied. One indication of this is that the off-diagonal terms of the **A** matrix will be larger with a MCSCF reference state than with a near-HF reference state. This may result [22] in the calculation of many successive determinants before an approximate value for $\det(\mathbf{G}^{-1}(E))$ can be obtained. After evaluating $\det(\mathbf{G}^{-1}(E))$, the search for its zeros can then be accomplished by standard techniques [23] such as bisection, accelerated false position, Newton-secant, or any other analytic fitting-interpolation procedure such as [3] interpolation of the function $F(E) = a + b/(c - E)$ whose form is suggested by the simple pole structure of $\mathbf{G}^{-1}(E)$.

Purvis and Öhrn [3] have made use of an alternative method for finding the poles and residues of $\mathbf{G}(E)$. Their method employs the fact that poles of $\mathbf{G}$ correspond to values of E for which eigenvalues of $\mathbf{L}(E) \equiv E\mathbf{1} - \mathbf{G}^{-1}(E)$; $\mathbf{L}\Phi_n = W_n(E)\Phi_n(E)$ obey $E = W_n(E)$. The residues Γ_n are given by $\Gamma_n = [1 - dW_n/dE]^{-1}_{E=E_n}$. To implement this technique, one must find the eigenvalues $W_n(E)$ for various values of E and then (graphically) locate that value of E for which $W_n(E) = E$.

4. Discussion and Summary

In this paper we have obtained results which permit $\mathbf{G}^{-1}(E)$ to be expressed in terms of the $\mathbf{A}$ matrix, the $\mathbf{B}$ matrix correct to second order, and some approximation to the $\mathbf{M}^{-1}$ matrix. The resultant expression will be correct to second order provided that $\mathbf{M}^{-1}$ is correct to second order, as can be seen from our expression for $\mathbf{B}\mathbf{M}^{-1}\mathbf{B}^{+}$. In actual practice, the calculated poles of $\mathbf{G}^{-1}(E)$ will be correct to second order only in those cases where the number of spin-orbital indices in the **h** operator manifold is small enough to permit the entire $\mathbf{M}$ matrix to be inverted exactly (or at least to second order) at each step in the iterative search for the zeros of $\det(\mathbf{G}^{-1}(E))$. This will happen only for very small molecules or in situations where additional approximations have been made. These additional approximations might include the use of a pseudopotential for which only the valence-orbital indices are included in the **h** operator manifold or the introduction of a "frozen-core" approximation for which only the valence orbitals are variationally optimized in the MCSCF calculation and only certain valence orbital indices are included in the **h** operator space. The use of these types of approximations may allow the calculation of chemically significant results which cannot be obtained from formalisms restricted to HF-type reference states.

Another important aspect of the results presented here is that the non-Hermiticity of the $\mathbf{M}$ matrix can be traced explicitly to certain terms. Because this non-Hermiticity vanishes as the reference state approaches the true eigenstate of the Hamiltonian, the magnitude of these terms allows an estimate to be made of the quality of the reference state and thus an estimate of the accuracy of the final results. Of course, only experience can establish the reliability and usefulness of these estimates.

In summary, the explicit expression for $\mathbf{G}^{-1}(E)$ was given in Eqs. (18) in terms of **A**, **B**, and **M** matrices. To simplify the calculation of the expressions in Eqs. (18), a concept of order of magnitude was introduced. This order concept was combined with certain assumptions about the relative sizes of terms in blocks of the appropriate reduced matrices. The expressions in Eqs. (18) were then specialized to retain up to second-order terms in Eqs. (18b), (22a), and (22b) for representative blocks of the **A**, **B**, and **M** matrices, respectively. Various procedures which simplify the computation of these expressions for ionization energies were given in Sec. 3.