

A non-Dyson third-order approximation scheme for the electron propagator

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An efficient third-order propagator method to compute ionization potentials and electron affinities of atoms and molecules is presented. The development is based on the algebraic diagrammatic construction (ADC) representing a specific reformulation of the diagrammatic perturbation series of the electron propagator $\mathbf{G}(\omega)$. In contrast with previous approximation schemes, relying on the Dyson equation and approximations for the self-energy part, the ADC procedure here is applied directly to the $(N \mp 1)$ -electron parts $\mathbf{G}^-(\omega)$ and $\mathbf{G}^+(\omega)$, respectively, of the electron propagator. This leads to decoupled secular equations for the ionization energies ($(N-1)$ -electron part) and electron affinities ($(N+1)$ -electron part), respectively. In comparison with the Dyson-type approach, there is a substantial reduction of the secular matrix dimension opposed by a small additional expense in computing some second- and third-order contributions to the secular matrix elements. The relationship of the non-Dyson ADC(3) method to coupled cluster methods is outlined.

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I. INTRODUCTION

Computational schemes based on the one-particle Green's function or the electron propagator^{1,2} have been widely used in the study of ionization and electron attachment processes of atoms and molecules. For an overview and references the reader is referred to review articles³⁻⁹ and text books.^{10,11} As is well known, these methods allow for a direct access to the ionization (attachment) energies and spectral intensities. Another advantage over conventional methods is the intrinsic size-consistency (here, more specifically, size-extensivity) of the results, which is a crucial requirement in the application to larger systems (for example, see Ref. 11).

Most electron propagator methods rely in one form or another of the Dyson equation, which relates the one-particle Green's function \mathbf{G} to the so-called (proper) self-energy part $\mathbf{\Sigma}$. The latter quantity itself is subject to a diagrammatic perturbation expansion, being simpler than that of \mathbf{G} . Several approximation schemes, for example the OVGf method^{3,12} and the partial third-order (P3) approximation,⁹ are based on finite perturbation expansions of $\mathbf{\Sigma}$ in the Dyson equation. Systematic third- and fourth-order approximations to the self-energy have been obtained by a procedure referred to as algebraic-diagrammatic construction (ADC).^{13,14} This approach is based on the comparison of the original diagrammatic perturbation expansion with a so-called intermediate representation of the self-energy part, or more generally, of any propagator under consideration. By performing this comparison successively through higher order n of perturbation theory, one can obtain approximation schemes [ADC(n) schemes] that represent a complete summation of the diagrammatic series through order n and an infinite, though partial summation of higher-order terms. At the third-order

level, essentially equivalent approximation schemes have been developed in the framework of the equation-of-motion method (EOM) (Refs. 15, 16) and the superoperator formalism.¹⁷⁻¹⁹ In practice, the latter methods take on the form of (in general Hermitian) secular equations, where the ionization (attachment) energies are determined as the eigenvalues of a secular matrix, while the eigenvectors are related to spectral intensities. As a characteristic feature of the Dyson-type approximation schemes, the configuration spaces here comprise both $(N-1)$ - and $(N+1)$ -electron configurations.

The ADC procedure is quite general and may as well be applied directly to the one-particle Green's function \mathbf{G} , or more specifically, to its $(N \pm 1)$ -particle parts \mathbf{G}^+ and \mathbf{G}^- , respectively, as has been demonstrated (through second order) in Ref. 20. This leads to a decoupling of the Dyson-type secular equations into two separate sets of equations, one for the ionization energies and the other for the electron affinities. The price for this splitting of the secular problem into two parts is more complicated perturbation-theoretical expressions for the secular matrix elements. The latter complication makes the direct ADC schemes impractical at higher order, say for $n \geq 4$. At the third-order level, however, the additional expense required to determine the matrix elements is rather small and is far outweighed by the savings in the secular problem. The purpose of this paper is to derive the direct (or non-Dyson) third-order ADC equations for \mathbf{G}^\pm and to discuss the potential of this method as a practical means for computing ionization potentials and electron affinities of larger molecules.

The method to be considered here has to be seen in the context of related non-Dyson approaches, such as the coupled-cluster Green's function (CCGF) method,^{21,22} the equation-of-motion coupled-cluster (EOMCC) variants for ionization potentials (IP) and electron affinities (EA),^{23,24} and the consistent operator expansions of the electron propagator.^{25,26} For a general comparison of these methods,

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based on the concept of so-called intermediate state representations, we may refer the reader to Ref. 27. Some special aspects will be addressed in Sec. V below.

II. ALGEBRAIC-DIAGRAMMATIC CONSTRUCTION (ADC) FOR THE ONE-PARTICLE GREEN'S FUNCTION

The formulation of ADC propagator schemes has been given previously at some detail for the case of the polarization propagator,¹³ the self-energy part of the one-particle Green's function (electron propagator),¹⁴ and the p - p propagator.^{28,29} In the following we will apply the ADC procedure directly to the $(N-1)$ -particle part \mathbf{G}^- of the one-particle Green's function through third order. The treatment of the $(N+1)$ -particle case is analogous (see Appendix B).

A. Review of the one-particle Green's function

In the following we consider an N -electron system with a (nondegenerate) ground state $|\Psi_0^N\rangle$ and energy E_0^N . Moreover, we will assume a single-particle representation based on the ground state Hartree-Fock (HF) orbitals $|\varphi_p\rangle$. Corresponding to the occupation numbers $n_p = 1 - \bar{n}_p = 1$ and 0 in the HF ground state $|\Phi_0^N\rangle$, the orbitals $|\varphi_p\rangle$ are denoted as hole states (occupied orbitals) or particle states (unoccupied or virtual orbitals), respectively. In energy representation the one-particle Green's function (electron propagator) is a matrix of functions¹

$$G_{pq}(\omega) = G_{pq}^+(\omega) + G_{pq}^-(\omega), \quad (1)$$

where

$$G_{pq}^+(\omega) = \langle \Psi_0^N | c_p(\omega - \hat{H} + E_0^N + i\eta)^{-1} c_q^\dagger | \Psi_0^N \rangle, \quad (2)$$

$$G_{pq}^-(\omega) = \langle \Psi_0^N | c_q^\dagger(\omega + \hat{H} - E_0^N - i\eta)^{-1} c_p | \Psi_0^N \rangle. \quad (3)$$

Here $c_p^\dagger(c_p)$ denote creation (destruction) operators associated with the HF orbitals $|\varphi_p\rangle$; \hat{H} is the Hamiltonian of the system, and η is a positive infinitesimal required to define the Fourier transformation between time and energy representations. The parts $\mathbf{G}^+(\omega)$ and $\mathbf{G}^-(\omega)$ contain physical information on the $(N+1)$ -particle and $(N-1)$ -particle systems, respectively. This becomes explicit in the spectral representation¹ obtained by inserting complete sets of $(N\pm 1)$ -particle (energy) eigenstates $|\Psi_n^{N\pm 1}\rangle$ on the right-hand side of Eq. (2) and Eq. (3), respectively. For the $(N-1)$ -particle part, on which we will specialize our considerations in the following, the result reads

$$G_{pq}^-(\omega) = \sum_{n \in \{N-1\}} \frac{x_{nq}^* x_{np}}{\omega - \omega_n - i\eta}. \quad (4)$$

Here the (negative) pole positions

$$-\omega_n = E_n^{N-1} - E_0^N \quad (5)$$

are identified as the ionizations energies of the system, while the residue amplitudes

$$x_{np} = \langle \Psi_n^{N-1} | c_p | \Psi_0^N \rangle \quad (6)$$

referred to as spectroscopic amplitudes, are related to spectral intensities. The spectral representation Eq. (4) may be written in a compact matrix notation as

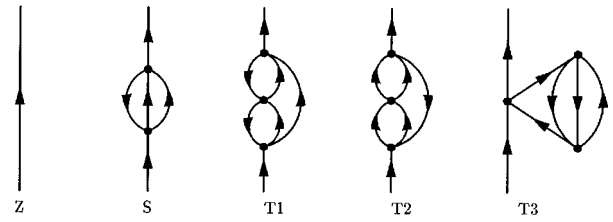


FIG. 1. Feynman diagrams (in Abrikosov form) for the one-particle Green's function (electron propagator) through third order.

$$\tilde{\mathbf{G}}(\omega) = \mathbf{x}^\dagger (\omega - \mathbf{\Omega})^{-1} \mathbf{x}, \quad (7)$$

where $\mathbf{\Omega}$ is the diagonal matrix of (negative) ionization energies, $\Omega_{nm} = \omega_n \delta_{nm}$. The matrix elements x_{np} of \mathbf{x} are defined in Eq. (6). For notational convenience we have introduced in Eq. (7) the transposed matrix $\tilde{\mathbf{G}}(\omega) = \mathbf{G}^-(\omega)^t$, that is, $\tilde{G}_{pq}(\omega) = G_{qp}^-(\omega)$. The infinitesimal $i\eta$ is dropped whenever it is not essential.

In Fig. 1 the Feynman diagrams (in Abrikosov form) for \mathbf{G} are shown through third order. In both zeroth and second order there is a single diagram (Z and S, respectively), while the third order comprises three diagrams (T1-T3). Note that there is no first-order contribution, as we suppose a HF one-particle representation here. In n th order each Feynman diagram gives rise to $(n+2)!$ time ordered (or Goldstone) diagrams, which can readily be evaluated using the diagrammatic rules as specified, for example, in Ref. 3 or Ref. 12. The set of time ordered diagrams decomposes into two distinct classes I and II corresponding to the two possible time orderings of the external vertices t and t' . Class I ($t > t'$) and class II ($t < t'$) contribute exclusively to \mathbf{G}^+ and \mathbf{G}^- , respectively. Figure 2 shows the 12 time ordered diagrams contributing to \mathbf{G}^- in second order. In third order there are already 60 Goldstone diagrams for \mathbf{G}^- per Feynman diagram (see Fig. 3 displaying the diagrams associated with T1).

For further use we recall the Dyson equation,¹

$$\mathbf{G}(\omega) = \mathbf{G}^{(0)}(\omega) + \mathbf{G}^{(0)}(\omega) \mathbf{\Sigma}(\omega) \mathbf{G}(\omega) \quad (8)$$

which relates $\mathbf{G}(\omega)$ to the self-energy part

$$\mathbf{\Sigma}(\omega) = \mathbf{\Sigma}(\infty) + \mathbf{M}(\omega). \quad (9)$$

Here $\mathbf{\Sigma}(\infty)$ is the static (ω -independent) part and $\mathbf{M}(\omega)$ is the dynamic (ω -dependent) part of $\mathbf{\Sigma}(\omega)$. In a similar way as for the one-particle Green's function, there is a decomposition¹⁴

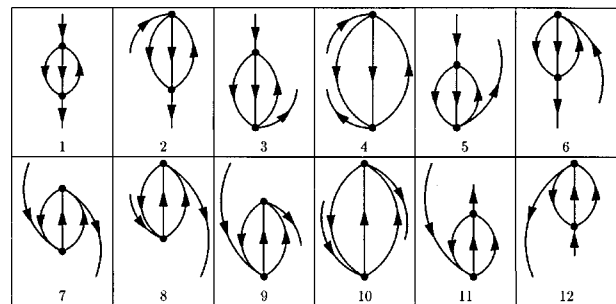


FIG. 2. Second-order Goldstone diagrams (in Abrikosov form) contributing to \mathbf{G}^- .

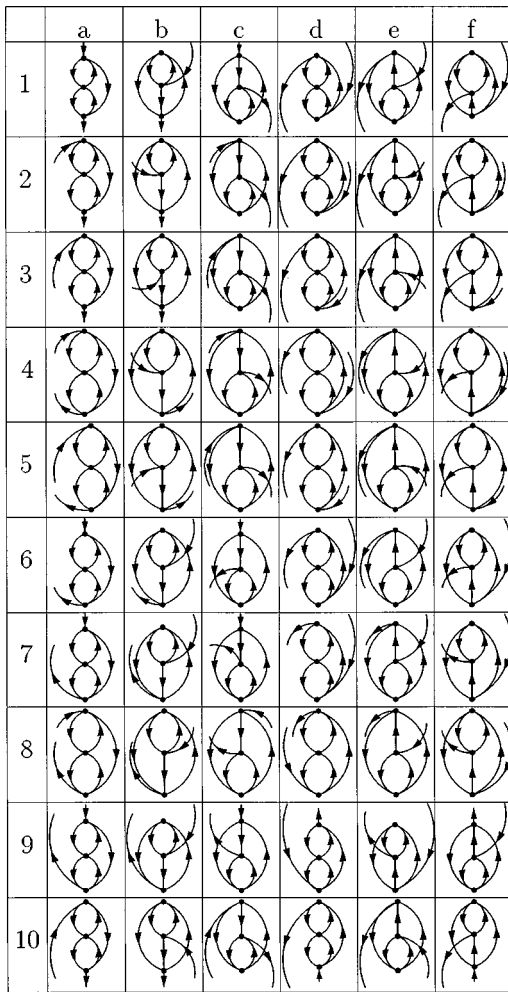


FIG. 3. Goldstone diagrams (in Abrikosov form) associated with the third-order Feynman diagram $T1$; only diagrams contributing to \mathbf{G}^- are shown.

$$\mathbf{M}(\omega) = \mathbf{M}^+(\omega) + \mathbf{M}^-(\omega) \quad (10)$$

of the dynamic self-energy part.

B. General ADC equations

The ADC approach sets out from the following non-diagonal representation:

$$\tilde{\mathbf{G}}(\omega) = \mathbf{f}^\dagger (\omega - \mathbf{K} - \mathbf{C})^{-1} \mathbf{f}. \quad (11)$$

This form may be considered as arising from inserting a complete set of so-called intermediate states^{20,27} $|\tilde{\Psi}_J^{N-1}\rangle$ on the right-hand side of Eq. (3). The intermediate states $|\tilde{\Psi}_J^{N-1}\rangle$ are related to the so-called correlated excited states $\hat{C}_J |\Psi_0^N\rangle$ where \hat{C}_J denote excitation operators of the manifold

$$\{\hat{C}_J\} \equiv \{c_k; c_a^\dagger c_k c_l, k < l; c_a^\dagger c_b^\dagger c_j c_k c_l, a < b, j < k < l; \dots\}, \quad (12)$$

that is, physical excitation operators of $N-1$ particles. Here the subscripts a, b, c, \dots and i, j, k, l, \dots refer to unoccupied (virtual) and occupied orbitals, respectively; the letters p, q, r, \dots will be used to label both occupied and unoccupied orbitals. Capital Latin subscripts denote strings of single-particle in-

dices, $J = (a, b, \dots; i, j, k, \dots)$. The configurations J may be distinguished as one-hole ($1h$), two-hole-one-particle ($2h-1p$), $3h-2p, \dots$ -excitations, or, more generally, as $\mu h - (\mu - 1)p$ -excitations, $\mu = 1, 2, \dots, N$. In the intermediate state representation (ISR), the secular matrix $\mathbf{K} + \mathbf{C}$ is given by

$$(\mathbf{K} + \mathbf{C})_{IJ} = \langle \tilde{\Psi}_I^{N-1} | E_0^N - \hat{H} | \tilde{\Psi}_J^{N-1} \rangle, \quad (13)$$

while the so-called effective transition moments are defined as

$$f_{Iq} = \langle \tilde{\Psi}_I^{N-1} | c_q | \Psi_0^N \rangle \quad (14)$$

in analogy to the spectroscopic amplitudes Eq. (6). For a given intermediate state representation the ionization energies Ω are obtained from the solution of the secular equations

$$(\mathbf{K} + \mathbf{C})\mathbf{Y} = \mathbf{Y}\Omega, \quad \mathbf{Y}^\dagger \mathbf{Y} = \mathbf{1}, \quad (15)$$

where \mathbf{Y} denotes the matrix of eigenvectors. Its components relate intermediate states and energy eigenstates according to

$$Y_{Jn} = \langle \tilde{\Psi}_J^{N-1} | \Psi_n^{N-1} \rangle; \quad (16)$$

and the relation

$$\mathbf{x} = \mathbf{Y}^\dagger \mathbf{f} \quad (17)$$

allows one to determine the spectroscopic amplitudes. In the ADC procedure the quantities $\mathbf{K} + \mathbf{C}$ and \mathbf{f} are constructed by using perturbation theory. Both \mathbf{C} and \mathbf{f} are subject to perturbation expansions,

$$\mathbf{C} = \mathbf{C}^{(1)} + \mathbf{C}^{(2)} + \mathbf{C}^{(3)} \dots \quad (18)$$

$$\mathbf{f} = \mathbf{f}^{(0)} + \mathbf{f}^{(1)} + \mathbf{f}^{(2)} \dots \quad (19)$$

Here the usual Møller-Plesset partitioning $\hat{H} = \hat{H}_0 + \hat{H}_I$ of the Hamiltonian is supposed. The zeroth-order or HF part of the secular matrix is given by the diagonal matrix \mathbf{K} of HF energies, that is,

$$K_{II} = \epsilon_I, \quad n_I = 1, \quad (20)$$

$$K_{akl,akl} = \epsilon_k + \epsilon_l - \epsilon_a, \quad \bar{n}_a n_k n_l = 1,$$

and so forth. Inserting these expansions [Eqs. (18)–(20)] in the ADC form [Eq. (11)], one arrives at a well defined perturbation expansion of $\tilde{\mathbf{G}}$, which now may be compared through successive order n with the original diagrammatic series for \mathbf{G}^- .

The resulting n th order ADC approximation schemes (ADC(n) schemes) combine the secular equations [Eqs. (15) and (17)] (matrix diagonalization) with finite perturbation expansions for the elements of the secular matrix $\mathbf{K} + \mathbf{C}$ and the effective transition moments \mathbf{f} . The explicit configuration space of the ADC(n) secular equations for $n=2$ and 3 is spanned by the $1h$ and $2h-1p$ excitations and grows in each even order n by one excitation class. This property of the explicit ADC configuration spaces has been referred to as *compactness*.^{20,27} The perturbation expansions for the secular matrix elements are *regular*, that is, they behave essentially as the perturbation expansions of the ground state energy and wave function, respectively.²⁰ Finally, the ADC method is

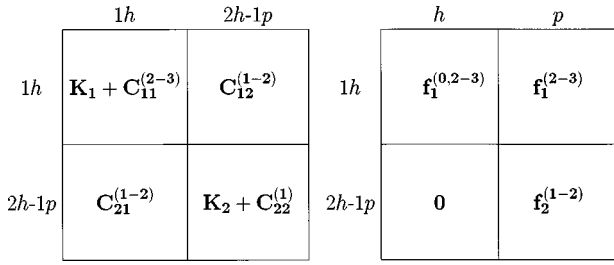


FIG. 4. Block structure of the secular matrix $\mathbf{K} + \mathbf{C}$ and of the effective transition moment matrix \mathbf{f} of the non-Dyson third-order ADC scheme.

size-consistent (size-extensive) which means that for a system of separate fragments the results do not depend on whether the method is applied to the whole system or to one of the fragments.^{27,30}

The perturbation theoretical approach to the ISR has been augmented by a direct construction procedure^{20,27} for the intermediate states $|\tilde{\Psi}_J\rangle$, yielding nonperturbational closed-form expressions for the blocks of $\mathbf{K} + \mathbf{C}$ and \mathbf{f} in terms of (generalized) ground state density matrices

$$\rho_{IJ} = \langle \Psi_0^N | \hat{C}_I^\dagger \hat{C}_J | \Psi_0^N \rangle \quad (21)$$

and ground state expectation values of the type $\langle \Psi_0^N | [\hat{C}_I^\dagger, \hat{H}] \hat{C}_J | \Psi_0^N \rangle$, where \hat{C}_J denote the excitation operators of $(N-1)$ particles as defined in Eq. (12). For example, the equations

$$\mathbf{f}_{hh} = \boldsymbol{\rho}_{hh}^{1/2}, \quad (22)$$

$$\mathbf{f}_{hp} = \boldsymbol{\rho}_{hh}^{-1/2} \boldsymbol{\rho}_{hp}, \quad (23)$$

relate the blocks of \mathbf{f} to the one-particle density matrix $\boldsymbol{\rho}$ [as defined in Eq. (21)]. Here the subscripts h and p are used to designate the subblocks of $\boldsymbol{\rho}$ and of \mathbf{f} corresponding to the distinction of occupied (hole) and unoccupied (particle) entries. For the definition of $\boldsymbol{\rho}_{hp}$ see Eq. (39).

III. EXPLICIT ADC EXPRESSIONS THROUGH THIRD ORDER

In this section we perform the comparison of the ADC form and the diagrammatic perturbation series for \mathbf{G}^- explicitly through third order. In the first two subsections our analysis will be based on the use of Goldstone diagrams which allow one to write up directly analytical expressions for a given Feynman diagram. An alternative way to evaluate Feynman diagrams is used in Sec. III C. The partitioning of the configurations J into $1h$ ($\mu=1$) and $2h-1p$ ($\mu=2$) states imposes an obvious block structure of $\mathbf{K} + \mathbf{C} = (\mathbf{K}_\mu \delta_{\mu\mu'} + \mathbf{C}_{\mu\mu'})$ and of $\mathbf{f} = (\mathbf{f}_\mu)$, $\mu, \mu' = 1, 2$ (see Fig. 4), which will be used in the following.

A. Second-order ADC

In zeroth order the comparison between \mathbf{G}^- and the ADC form

$$\tilde{\mathbf{G}}^{(0)}(\omega) = \mathbf{f}_1^{(0)\dagger} (\omega - \mathbf{K}_1)^{-1} \mathbf{f}_1^{(0)}, \quad (24)$$

is trivial and allows us to specify the zeroth-order contribution to the block \mathbf{f}_1 of \mathbf{f} ,

$$f_{kq}^{(0)} = \delta_{kq} n_k. \quad (25)$$

Supposing a HF representation, the first-order contribution to \mathbf{G} vanishes, and in particular $\tilde{\mathbf{G}}^{(1)}(\omega) = \mathbf{0}$. This means for the ADC expression that

$$\mathbf{C}_{11}^{(1)} = \mathbf{0} \quad (26)$$

and

$$\mathbf{f}_1^{(1)} = \mathbf{0}. \quad (27)$$

The lowest nontrivial order is $n=2$. Here the $2h-1p$ configurations ($\mu=2$) come explicitly into play. The second-order Goldstone diagrams of Fig. 2 are to be compared to the second-order ADC form reading

$$\tilde{\mathbf{G}}^{(2)}(\omega) = \mathbf{f}_1^{(2)\dagger} (\omega - \mathbf{K}_1)^{-1} \mathbf{f}_1^{(0)} + \text{h.c.} \quad (28a)$$

$$+ \mathbf{f}_2^{(1)\dagger} (\omega - \mathbf{K}_2)^{-1} \mathbf{f}_2^{(1)} \quad (28b)$$

$$+ \mathbf{f}_1^{(0)\dagger} (\omega - \mathbf{K}_1)^{-1} \mathbf{C}_{12}^{(1)} (\omega - \mathbf{K}_2)^{-1} \\ \times \mathbf{C}_{21}^{(1)} (\omega - \mathbf{K}_1)^{-1} \mathbf{f}_1^{(0)} \quad (28c)$$

$$+ \mathbf{f}_1^{(0)\dagger} (\omega - \mathbf{K}_1)^{-1} \mathbf{C}_{11}^{(2)} (\omega - \mathbf{K}_1)^{-1} \mathbf{f}_1^{(0)} \quad (28d)$$

$$+ \mathbf{f}_2^{(1)\dagger} (\omega - \mathbf{K}_2)^{-1} \mathbf{C}_{21}^{(1)} (\omega - \mathbf{K}_1)^{-1} \mathbf{f}_1^{(0)} + \text{h.c.} \quad (28e)$$

The quantities to be determined at this stage are $\mathbf{C}_{11}^{(2)}$, $\mathbf{C}_{21}^{(1)}$, $\mathbf{f}_1^{(2)}$, and $\mathbf{f}_2^{(1)}$. A closer inspection of Fig. 2 shows that most of the diagrams (1–12) can be readily assigned to distinct terms on the right-hand side of Eq. (28). For example, one may readily identify (1) and (28c), (2,3) and (28e), (4) and (28b), yielding explicit expressions for $\mathbf{C}_{12}^{(1)}$ and $\mathbf{f}_2^{(1)}$. Moreover, (5,6,11,12) are of the form of (28a), thus giving contributions to $\mathbf{f}_1^{(2)}$. By contrast, the diagrams (7–10) do not fit individually to any of the terms (28a)–(28e). However, as a straightforward calculation shows, the sum $S = (7) + (8) + (9) + (10)$ of those diagrams contributes both to (28a) and (28d), thereby specifying $\mathbf{C}_{11}^{(2)}$ and the hole block $\mathbf{f}_{1h}^{(2)}$ of $\mathbf{f}_1^{(2)}$. The decomposition of S can be made unique by requiring that the $\mathbf{f}_{1h}^{(2)}$ block is Hermitian, leading to a “maximally nondiagonal” part $\mathbf{C}_{11}^{(2)}$. The resulting expressions for the ADC quantities are given in Appendix A. It should be mentioned that the ADC(2) equations for \mathbf{G}^- have been given earlier in Ref. 20 [note that $\mathbf{C}_{11}^{(2)}$ in Eq. (A2a) of Ref. 20 has a wrong sign].

B. Third order ADC: Goldstone analysis of diagrams

The terms of the ADC form in third order, $\tilde{\mathbf{G}}^{(3)}$, are compiled in Table I. At this level the quantities $\mathbf{C}_{11}^{(3)}$, $\mathbf{C}_{12}^{(2)}$, $\mathbf{C}_{22}^{(1)}$, $\mathbf{f}_1^{(3)}$, and $\mathbf{f}_2^{(2)}$ have to be determined by comparison with the third-order diagrams $T1$ – $T3$ of Fig. 1. We will now describe briefly how the contributions arising from $T1$ and $T2$ can be specified by inspecting their Goldstone diagrams. Here the treatment of $T2$ is analogous to that of $T1$, as the two Feynman diagrams are topologically similar. The sixty Goldstone diagrams for $T1$ in Fig. 3 are divided into 10 groups of each 6 diagrams, where each group (1,2,...,10) is associated with a specific position of the two outer vertices (i, j), $i < j = 1, \dots, 5$. The six diagrams (a, b, \dots, f) within each

TABLE I. Third order contributions in the ADC representation [Eq. (11)] of $\tilde{\mathbf{G}}^-(\omega)$.

(A)	$\mathbf{f}_1^{(0)\dagger}(\omega - \mathbf{K}_1)^{-1} \mathbf{C}_{12}^{(1)}(\omega - \mathbf{K}_2)^{-1} \mathbf{C}_{22}^{(1)}(\omega - \mathbf{K}_2)^{-1} \mathbf{C}_{21}^{(1)}(\omega - \mathbf{K}_1)^{-1} \mathbf{f}_1^{(0)}$
(B)	$\mathbf{f}_1^{(0)\dagger}(\omega - \mathbf{K}_1)^{-1} \mathbf{C}_{12}^{(2)}(\omega - \mathbf{K}_2)^{-1} \mathbf{C}_{21}^{(1)}(\omega - \mathbf{K}_1)^{-1} \mathbf{f}_1^{(0)} + \text{h.c.}$
(C)	$\mathbf{f}_1^{(0)\dagger}(\omega - \mathbf{K}_1)^{-1} \mathbf{C}_{11}^{(3)}(\omega - \mathbf{K}_1)^{-1} \mathbf{f}_1^{(0)}$
(D)	$\mathbf{f}_1^{(3)\dagger}(\omega - \mathbf{K}_1)^{-1} \mathbf{f}_1^{(0)} + \text{h.c.}$
(E)	$\mathbf{f}_2^{(1)\dagger}(\omega - \mathbf{K}_2)^{-1} \mathbf{C}_{22}^{(1)}(\omega - \mathbf{K}_2)^{-1} \mathbf{C}_{21}^{(1)}(\omega - \mathbf{K}_1)^{-1} \mathbf{f}_1^{(0)} + \text{h.c.}$
(F)	$\mathbf{f}_2^{(1)\dagger}(\omega - \mathbf{K}_2)^{-1} \mathbf{C}_{22}^{(1)}(\omega - \mathbf{K}_2)^{-1} \mathbf{f}_2^{(1)}$
(G)	$\mathbf{f}_2^{(1)\dagger}(\omega - \mathbf{K}_2)^{-1} \mathbf{C}_{21}^{(2)}(\omega - \mathbf{K}_1)^{-1} \mathbf{f}_1^{(0)} + \text{h.c.}$
(H)	$\mathbf{f}_2^{(2)\dagger}(\omega - \mathbf{K}_2)^{-1} \mathbf{C}_{21}^{(1)}(\omega - \mathbf{K}_1)^{-1} \mathbf{f}_1^{(0)} + \text{h.c.}$
(I)	$\mathbf{f}_2^{(2)\dagger}(\omega - \mathbf{K}_2)^{-1} \mathbf{f}_2^{(1)} + \text{h.c.}$

group correspond to the six-possible time orderings of the three inner vertices. In Table II, we have specified how the Goldstone diagrams contribute to the third-order ADC terms of Table I. Obviously, a given term may get contributions from more than one diagram. In some cases it is necessary to combine several diagrams before an assignment can be made. This concerns diagrams with so called five-line cuts [five $G^{(0)}$ -lines between adjacent vertices], for example diagrams $d1-d8$. Actually not all diagrams need to be considered as they give no further information with respect to the ADC quantities (of course, they may be used for checks). The diagram $a1$ (both for $T1$ and $T2$) specifies entirely the first-order interaction matrix elements of the $2h-1p$ -block, $\mathbf{C}_{22}^{(1)}$. Comparing $a3$ and $b3$ with the term (H) of Table I yields $\mathbf{f}_2^{(2)}$. The second-order $1h/2h-1p$ -coupling matrix elements $\mathbf{C}_{12}^{(2)}$ are derived from $b1$ and $b2$. The largest effort is required in evaluating $\mathbf{C}_{11}^{(3)}$ and $\mathbf{f}_1^{(3)}$. Contributions to $\mathbf{C}_{11}^{(3)}$ arise from the diagrams 1, 2, 4, and 6 (having two 5-line cuts) of type d , e , and f . The four diagrams 1, 2, 4, and 6 of each type must be summed up in order to yield the form of term (C) in Table I. Diagrams with one five line cut contributing to $\mathbf{f}_1^{(3)}$ are $b7, b8, c3, c5$ and, furthermore, diagrams 3, 5, 7, 8 of type $d-f$. Here each two diagrams must be summed to yield the form of term (D). For each pair of diagrams contributing to $\mathbf{f}_1^{(3)}$ there is a Hermitian conjugate contribution: such Hermitian conjugate pairs are ($b7, b8$) and ($c3, c5$); ($d3, d5$) and ($d7, d8$); ($e3, e5$) and ($f7, f8$); ($e7, e8$) and ($f3, f5$). Finally, the six diagrams $a9-f9$ re-

TABLE II. Assignment of third order Goldstone diagrams ($a1-f10$) of Fig. 3 to the third order terms in the ADC representation of $\tilde{\mathbf{G}}^-(\omega)$ as denoted in Table I.

	a	b	c	d	e	f
1	A	B	B	C	C	C
2	E	B	G	C	C	C
3	H	H	D	D	D	D
4	F	G	G	C	C	C
5	I	I	D	D	D	D
6	E	G	B	C	C	C
7	H	D	H	D	D	D
8	I	D	I	D	D	D
9	D	D	D	D	D	D
10	D	D	D	D	D	D

main to be considered each of which gives a contribution to $\mathbf{f}_1^{(3)}$; the diagrams $a10-f10$ are Hermitian conjugates of $a9-f9$. When the three diagrams $b7-b9$ are combined appropriately, one gets rid of the six-line cuts and the associated denominators in the analytical expressions. As a consequence, one may identify now the $\mathbf{f}_{1p}^{(3)}$ block as arising according to

$$f_{ka}^{(3)} = \frac{1}{\epsilon_k - \epsilon_a} (M_{ak}^{(3)+}(\epsilon_k) + M_{ak}^{(3)-}(\epsilon_a)) \quad (29)$$

from the (ω -dependent) third-order self-energy part $\mathbf{M}^{(3)}(\omega)$. The latter result is derived in a general way in Sec. IV. The final expressions for $\mathbf{C}_{11}^{(3)}$, $\mathbf{C}_{12}^{(2)}$, $\mathbf{C}_{22}^{(1)}$, $\mathbf{f}_1^{(3)}$, and $\mathbf{f}_2^{(2)}$ are listed in Appendix A.

C. Third order ADC: A projection method

In the following we consider an alternative method to evaluate the diagrams for $\tilde{\mathbf{G}}^-(\omega)$, which in the case of the $T3$ diagram is much simpler than the Goldstone analysis. The method is based on the observation that the $(N-1)$ -particle part $\tilde{\mathbf{G}}^-(\omega)$ can be obtained from the full one-particle Green's function $\mathbf{G}(\omega)$ by the following projection integral:

$$\tilde{\mathbf{G}}^-(\omega) = \frac{1}{2\pi i} \oint \frac{\mathbf{G}(\omega')}{\omega - \omega' - i\eta} d\omega'. \quad (30)$$

Here the integration path has to be closed in the upper ω' -plane. Obviously, the same projection procedure may be applied to the n th order contribution $\tilde{\mathbf{G}}^{(n)}(\omega)$ and to each individual Feynman diagram. Let us recall that in second and third order the Dyson equation [Eq. (8)] allows one to relate $\tilde{\mathbf{G}}^{(2)}(\omega)$ and $\tilde{\mathbf{G}}^{(3)}(\omega)$ to the corresponding self-energy contributions according to

$$\tilde{\mathbf{G}}^{(2)}(\omega) = \mathbf{G}^{(0)}(\omega) \mathbf{M}^{(2)}(\omega) \mathbf{G}^{(0)}(\omega), \quad (31)$$

$$\tilde{\mathbf{G}}^{(3)}(\omega) = \mathbf{G}^{(0)}(\omega) (\mathbf{\Sigma}^{(3)}(\infty) + \mathbf{M}^{(3)}(\omega)) \mathbf{G}^{(0)}(\omega). \quad (32)$$

In particular, one may retrieve the third-order Feynman diagram $T3$ as arising from the static self-energy part $\mathbf{\Sigma}(\infty)$ in third order,

$$(T3)_{pq} = (\mathbf{G}^{(0)}(\omega) \mathbf{\Sigma}^{(3)}(\infty) \mathbf{G}^{(0)}(\omega))_{pq}. \quad (33)$$

Here the projection procedure [Eq. (30)] can readily be performed, yielding one contribution of the form (C) in Table I and two Hermitian conjugate contributions of the form (D). This shows that $T3$ gives rise to direct contributions to $\mathbf{C}_{11}^{(3)}$ and to $\mathbf{f}_{1p}^{(3)}$,

$$\tilde{\mathbf{C}}_{kk'}^{(3)} = \mathbf{\Sigma}_{k'k}^{(3)}(\infty), \quad (34)$$

$$\tilde{f}_{ka}^{(3)} = \frac{1}{\epsilon_k - \epsilon_a} \mathbf{\Sigma}_{ak}^{(3)}(\infty), \quad n_k \bar{n}_a = 1. \quad (35)$$

For the other two third-order Feynman diagrams $T1$ and $T2$ the projection method is less practical as here the ω -dependent contributions $\mathbf{M}^{(3)}(\omega)$ come into play.

IV. THE ADC METHOD AND THE ONE-PARTICLE DENSITY MATRIX

A. Spectral moments and ground state expectation values in the ADC formulation

In the ADC formulation a part of the physical information contained in the one-particle Green's function can be obtained without the need to diagonalize the secular matrix $\mathbf{K} + \mathbf{C}$. Let us, for example, consider the spectral moments of the ionization spectrum,

$$S_{pq}^{(m)} = \langle \Psi_0^N | c_p^\dagger (E_0^N - \hat{H})^m c_q | \Psi_0^N \rangle \quad (36)$$

$$= \sum_n (E_0^N - E_n^{N-1})^m x_{np}^* x_{nq}. \quad (37)$$

As can readily be seen, these quantities can be calculated directly from the ADC secular matrix and the effective transition moments according to

$$\mathbf{S}^{(m)} = \mathbf{f}^\dagger (\mathbf{K} + \mathbf{C})^m \mathbf{f}. \quad (38)$$

As special case of Eq. (36) ($m=0$) one may consider the matrix elements,

$$\rho_{pq} = \langle \Psi_0^N | c_p^\dagger c_q | \Psi_0^N \rangle \quad (39)$$

of the one-particle density matrix $\boldsymbol{\rho}$, for which Eq. (38) becomes

$$\boldsymbol{\rho} = \mathbf{f}^\dagger \mathbf{f}. \quad (40)$$

In a similar way, one may write the ground state expectation value of a one-particle operator

$$\hat{A} = \sum_{r,s} A_{rs} c_r^\dagger c_s \quad (41)$$

in the form

$$\langle \Psi_0^N | \hat{A} | \Psi_0^N \rangle = \text{Tr}(\mathbf{A}^t \boldsymbol{\rho}) = \text{Tr}(\mathbf{A}^t \mathbf{f}^\dagger \mathbf{f}), \quad (42)$$

where Tr denotes the trace of a matrix, and \mathbf{A}^t is the transpose of \mathbf{A} . Applying this relation to the particle-number operator

$$\hat{N} = \sum_r c_r^\dagger c_r \quad (43)$$

one finds the sum rule

$$\text{Tr}(\mathbf{f}^\dagger \mathbf{f}) = N \quad (44)$$

which can be used as a test for the quality of the respective ADC approximation.

Furthermore, the ground state energy E_0^N can be obtained directly from the ADC quantities according to

$$E_0^N = \frac{1}{2} \text{Tr}(\mathbf{f}^\dagger (\mathbf{K} + \mathbf{C}) \mathbf{f} + \mathbf{T} \mathbf{f}^\dagger \mathbf{f}). \quad (45)$$

Here \mathbf{T} denotes the matrix of the one-particle integrals T_{rs} of the one-particle part of the Hamiltonian. This result follows readily from the well-known expression¹

$$E_0^N = \frac{1}{4\pi i} \oint \text{Tr}((\boldsymbol{\omega} \mathbf{1} + \mathbf{T}) \mathbf{G}(\boldsymbol{\omega})) d\boldsymbol{\omega}, \quad (46)$$

where again the integration path has to be closed in the upper complex $\boldsymbol{\omega}$ -plane; note that only the \mathbf{G}^- part contributes

here. At a specific ADC(n) level of approximation the expressions for the respective ground state expectation values [Eqs. (40), (42), (44), and (45)] lead to finite perturbation theoretical expansions, being complete through order n .

Finally let us consider the static self-energy part $\boldsymbol{\Sigma}(\infty)$ which is needed both to generate the \mathbf{C}_{11} block of the ADC secular matrix and the hp block of \mathbf{f} (see Sec. III C). As is well known the matrix elements are given by^{3,31,32}

$$\Sigma_{pq}(\infty) = \sum_{r,s} V_{pr[qs]} (\rho_{rs} - \rho_{rs}^{(0)}). \quad (47)$$

As shown by this relation, $\boldsymbol{\Sigma}(\infty)$ can be calculated consistently through third or fourth order by expanding the density matrix through second or third order, respectively.

B. Relations between the one-particle density matrix and the effective transition amplitudes

The one-particle density matrix $\boldsymbol{\rho}$ is related to the ADC quantity \mathbf{f} according to Eq. (40) derived in the preceding subsection. Now we will consider the reverse relations [Eqs. (22) and (23)], by which the $1h$ -block of \mathbf{f} can be expressed in terms of $\boldsymbol{\rho}$. A perturbation expansion of $\boldsymbol{\rho}$ through third order can be readily obtained by combining the well-known projection formula¹

$$\boldsymbol{\rho}^t = \frac{1}{2\pi i} \oint \mathbf{G}(\boldsymbol{\omega}) d\boldsymbol{\omega} = \frac{1}{2\pi i} \oint (\mathbf{G}^{(0)}(\boldsymbol{\omega}) + \mathbf{G}^{(0)}(\boldsymbol{\omega}) \boldsymbol{\Sigma}(\boldsymbol{\omega}) \times \mathbf{G}^{(0)}(\boldsymbol{\omega})) d\boldsymbol{\omega} + O(4) \quad (48)$$

with the Dyson series for $\mathbf{G}(\boldsymbol{\omega})$. As above the contour integration is to be closed in the upper complex $\boldsymbol{\omega}$ -plane. The error introduced by truncating this series after the second term is of fourth order, so that Eq. (48) may be used to generate the perturbation series

$$\boldsymbol{\rho} = \boldsymbol{\rho}^{(0)} + \boldsymbol{\rho}^{(2)} + \boldsymbol{\rho}^{(3)} + \dots \quad (49)$$

through third order. Let us note that

$$\rho_{rs}^{(0)} = \delta_{rs} n_r \quad (50)$$

and that there is (supposing a HF representation) no first-order contribution. The result of the projection procedure becomes particularly simple for the hp (and the ph) block of $\boldsymbol{\rho}$,

$$\rho_{ka} = \frac{1}{\epsilon_k - \epsilon_a} (\Sigma_{ak}(\infty) + M_{ak}^+(\epsilon_k) + M_{ak}^-(\epsilon_a)) + O(4). \quad (51)$$

This result can readily be split up into second and third-order contributions $\boldsymbol{\rho}_{hp}^{(2)}$ and $\boldsymbol{\rho}_{hp}^{(3)}$. The explicit expressions for the hh and pp parts cannot be written in such a compact way; they are given in Appendix A. It should be noted that the static self-energy part on the right-hand side of Eq. (48) does not contribute to $\boldsymbol{\rho}_{hh}$ and $\boldsymbol{\rho}_{pp}$. The combination of Eq. (47) and Eq. (51) may be used to define a self-consistency procedure for $\boldsymbol{\Sigma}(\infty)$.

The relations Eq. (22) and Eq. (23) can be exploited according to

$$\mathbf{f}_{1h} = \mathbf{1} + \frac{1}{2} \boldsymbol{\rho}_{hh}^{(2)} + \frac{1}{2} \boldsymbol{\rho}_{hh}^{(3)} + O(4), \quad (52)$$

$$\mathbf{f}_{1p} = \boldsymbol{\rho}_{hp}^{(2)} + \boldsymbol{\rho}_{hp}^{(3)} + O(4), \quad (53)$$

in a perturbation-theoretical way. Here we have used the properties $\boldsymbol{\rho}_{hh} = \mathbf{1} + O(2)$ and $\boldsymbol{\rho}_{hp} = O(2)$.

It is interesting to note that a diagrammatic perturbation expansion for the density matrix can be obtained by selecting a subset of Goldstone diagrams for \mathbf{G}^- . In performing the projection procedure [Eq. (48)] to the Goldstone terms of \mathbf{G}^- one observes that terms with more than one ω -dependent denominators vanish, for example,

$$\oint \frac{d\omega}{(\omega - a - i\eta)(\omega - b - i\eta)} = 0,$$

where a, b are real numbers. Thus one needs to consider only those diagrams where the two outer vertices are in consecutive order (i.e., having only a single ω -dependent denominator). After replacing the single ω -denominator in these diagrams by the factor 1 (as a result of the contour integration) the resulting analytical expressions apply directly to the matrix elements of $\boldsymbol{\rho}$. In second order, for example, the diagrams (4–6) and (10–12) in Fig. 2 are associated with $\boldsymbol{\rho}^{(2)}$. Obviously, (10) and (6) contribute to hh - and pp -block, respectively while the hp -block is given by (5) and (11); note that the terms (6) and (12) are the Hermitian conjugate to (5) and (11), respectively. In a similar way the third-order diagrams ($a-f$) 5,8,9,10 (see Fig. 3) are readily assigned to the blocks of $\boldsymbol{\rho}^{(3)}$.

V. DISCUSSION AND CONCLUDING REMARKS

The third-order ADC procedure applied here to the $(N-1)$ -particle part of the one-particle Green's function has led to a practical approximation scheme for computing ionization potentials and the associated spectroscopic amplitudes. The structure of the Hermitian secular matrix $\mathbf{K} + \mathbf{C}$ is shown schematically in Fig. 4. The explicit ADC(3) configuration space is spanned by the $1h$ and $2h-1p$ configurations. The secular matrix elements are given by finite perturbation-theoretical expressions extending at most through third order (in the $1h$ block \mathbf{C}_{11}). The ionization potentials are directly determined as the eigenvalues of $\mathbf{K} + \mathbf{C}$. The secular matrix $\mathbf{K} + \mathbf{C}$ is augmented by a matrix \mathbf{f} of effective transition moments. The latter quantity is needed to calculate the spectroscopic amplitudes (as scalar products of the eigenvectors of $\mathbf{K} + \mathbf{C}$ and the columns of \mathbf{f}) and also allows one to compute N -electron ground state properties including the total energy. It should be mentioned that the present ADC(3) equations reflect the symmetry properties of the underlying Hamiltonian. This means that these equations decouple with respect to different irreducible representations of the symmetry group. For a spin-independent Hamiltonian spin-free working equations can be derived in a straightforward way (for example, see Ref. 8).

It is interesting to compare the present approximation scheme with the common Dyson approach. A schematic view of the resulting secular matrix \mathbf{A} as needed at the third-order level is given in Fig. 5. For a specification of the various matrix elements the reader is referred to Ref. 14. The

	$1h$	$2h-1p$	$1p$	$2p-1h$
$1h$	$\mathbf{K}_1 + \Sigma_{11}^{(3)}(\infty)$	$\mathbf{C}_{12}^{(1-2)}$	$\Sigma_{11}^{(3)}(\infty)$	$\mathbf{U}_{12}^{(1-2)}$
$2h-1p$	$\mathbf{C}_{21}^{(1-2)}$	$\mathbf{K}_2 + \mathbf{C}_{22}^{(1)}$	$\mathbf{U}_{21}^{(1-2)}$	$\mathbf{0}$
$1p$	$\Sigma_{11}^{(3)}(\infty)$	$\mathbf{U}_{12}^{(1-2)}$	$\mathbf{K}_1 + \Sigma_{11}^{(3)}(\infty)$	$\mathbf{C}_{12}^{(1-2)}$
$2p-1h$	$\mathbf{U}_{21}^{(1-2)}$	$\mathbf{0}$	$\mathbf{C}_{21}^{(1-2)}$	$\mathbf{K}_2 + \mathbf{C}_{22}^{(1)}$

FIG. 5. Block structure of the secular matrix arising in the third-order Dyson method. The subscripts $1(\bar{1})$ and $2(\bar{2})$ are referring to $1h(1p)$ and $2h-1p(2p-1h)$ configurations.

ionization potentials (and electron affinities) are determined as the eigenvalues of \mathbf{A} and the spectroscopic amplitudes are directly identified as the components of the corresponding eigenvectors. As a characteristic feature of the Dyson approach, the secular equations couple $1h$ and $2h-1p$ configurations of $(N-1)$ electrons with the $1p$ and $2p-1h$ configurations of $(N+1)$ electrons. The secular matrix $\mathbf{K} + \mathbf{C}$ of the (non-Dyson) ADC(3) scheme is largely identical with the $(N-1)$ -particle block of \mathbf{A} . The only differences arise in the $1h$ -subblocks, where \mathbf{A}_{11} is lacking the second-order contribution $\mathbf{C}_{11}^{(2)}$ and part of the third-order contribution $\mathbf{C}_{11}^{(3)}$. Obviously, the matrix $\mathbf{K} + \mathbf{C}$ may be viewed as arising from the larger secular matrix \mathbf{A} by a procedure familiar from quasi-degenerate perturbation-theory (QDPT).³³ \mathbf{A} corresponds to a representation in terms of $(N \pm 1)$ -electron ‘‘model’’ states, which can be transformed into a ‘‘target state’’ representation where the $(N+1)$ - and $(N-1)$ -electron spaces are no longer coupled. The second- and third-order contributions to \mathbf{C}_{11} of the $(N-1)$ -electron target representation may thus be derived by using the familiar QDPT formulas. For example, through ‘‘second-order’’ of QDPT, one finds

$$(\mathbf{K} + \mathbf{C})_{IJ} = A_{IJ} + \sum_Q A_{IQ} A_{QJ} \frac{\frac{1}{2}(K_I + K_J) + K_Q}{(K_I - K_Q)(K_J - K_Q)} + O(3).$$

Here I and J label $(N-1)$ -electron states, whereas Q stands for $(N+1)$ -electron states. In using such formulas one must not forget that the matrix elements of \mathbf{A} are given as finite perturbation series.

Concerning the computational cost of the two secular problems, the preceding comparison makes it quite obvious that the direct ADC method is more advantageous than the Dyson approach. There is a substantial reduction of the secular matrix dimension in the non-Dyson scheme being opposed by a modest expense required in computing the additional second- and third-order contributions in the small \mathbf{C}_{11}

block. If one is interested only in the $(N-1)$ -particle part (ionization energies) the secular dimension is reduced by the factor m/n where n and m denote the number of occupied and virtual orbitals, respectively. Typically this ratio is of the order 5–10. As a preliminary analysis of the third-order contributions to the matrix elements of \mathbf{C}_{11} has shown, the five-fold summations over orbital indices arising here can be performed quite efficiently by splitting the summations into subsequent passes through segments of the Coulomb-integral list. The evaluation of the spectroscopic amplitudes in the non-Dyson approach requires one to compute the effective transition moments \mathbf{f} , which at the third order level may be somewhat costly. Usually, however, one will not be interested in determining these quantities, or the related relative spectral intensities, to utmost accuracy. This suggests a major computational saving by using the effective transition moments of the second-order ADC scheme in conjunction with the eigenvectors of the ADC(3) secular matrix; such a variant will be referred to as the ADC(3/2) scheme.

The present method combines matrix diagonalization (of a secular matrix) and perturbation theory (for the secular matrix elements and the effective transition moments). The advantages of this combination, that is *regular* perturbation expansions, *compact* configuration spaces, and *size-consistent* results, have been briefly addressed in Sec. II B. However, the use of perturbation theory introduces obvious limitations for the applicability of the method, e.g., in cases where the perturbation theory for the N -electron ground state breaks down. Related nonperturbative methods for treating ionization (electron attachment) or general electronic excitations have been developed within the framework of the coupled cluster linear response (CCLR) theory,^{34–38} the EOM-CC approach,^{39–41} the CCGF method,^{21,22} and the SAC-CI (Refs. 42, 43) method. Let us consider briefly the specific case of the IP-EOMCC method.^{21–23} The IP-EOMCC secular matrix can be viewed as a mixed representation of the Hamiltonian \hat{H} (or the shifted Hamiltonian $\hat{H} - E_0^N$) with respect to two sets of states, one set being formed by the correlated excited states $\hat{C}_J \exp(\hat{T})|\Phi_0^N\rangle$ (see Sec. II), the other set being biorthogonal to the first one (see Ref. 27). Here $\exp(\hat{T})|\Phi_0^N\rangle$ is the familiar coupled cluster representation of the N -electron ground state. In the previous applications of this biorthogonal coupled cluster (bCC) method the configuration space has been restricted to the $1h$ and $2h-1p$ configurations which is consistent with the usual coupled cluster singles and doubles (CCSD) treatment of the ground state. While the nonperturbative nature of the IP-EOMCC scheme is a very desirable feature, one should recall that the perturbation-theoretical consistency of its results (compactness property) is somewhat restricted as compared to the ADC approximations (see Ref. 27 for a general discussion). For the IP-EOMCC variant considered here this means that the (single-hole) main ionic states are described consistently through second order only, whereas a consistent third-order description would presuppose the inclusion of the next higher class of configurations, i.e., $3h-2p$ configurations. The latter remark should be particularly relevant for recent developments advocating the replacement of the ground state CC amplitudes in the correlated excited states

by perturbation theoretical expressions.^{44,45} As the ADC schemes, the resulting perturbative bCC representations combine matrix diagonalization and perturbation theory. However, one may wonder whether there remain any advantages over the simpler ADC approach if one abandons the iterative CC treatment of the \hat{T} amplitudes. In any case, consistent third-order bCC equations are not yet available and would be considerably more complex than the present ADC(3) scheme, which, moreover, has the advantage of being Hermitian.

The actual potential of the direct ADC(3) or ADC(3/2) method as a both accurate and efficient means for computing ionization energies (or electron affinities) of larger molecules has still to be tested in applications. Presently, the coding is on the way, and we hope to be able to report on the computational performance in the foreseeable future.

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APPENDIX A: ADC(3) EQUATIONS FOR THE $(N-1)$ -ELECTRON CASE

In the following we collect the expressions for the secular matrix $\mathbf{K} + \mathbf{C}$ (effective interaction) and the effective transition moments \mathbf{f} of the third-order ADC scheme for \mathbf{G}^- . The explicit ADC(3) configuration space comprises the $1h$ and $2h-1p$ configurations. For the sake of compactness we will use the short-hand notation

$$v_{abij} = \frac{V_{ab[ij]}}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}, \quad (\text{A1})$$

where $V_{ab[ij]} = V_{abij} - V_{abji}$ and ϵ_r denote the antisymmetrized Coulomb integrals in “1212” notation and HF orbital energies, respectively. The letters i, j, k, l, \dots and a, b, c, \dots refer to occupied and unoccupied orbitals, respectively. The subscripts p, q, r, \dots label both occupied and unoccupied orbitals.

(i) Effective interaction

$1h/1h$ block:

$$K_{kk'} = \epsilon_k \delta_{kk'}, \quad (\text{A2})$$

$$C_{kk'}^{(1)} = 0, \quad (\text{A3})$$

$$C_{kk'}^{(2)} = -\frac{1}{2} \sum_{a,b,l} v_{abkl} v_{abk'l}^* \left(\epsilon_a + \epsilon_b - \epsilon_l - \frac{1}{2} \epsilon_k - \frac{1}{2} \epsilon_{k'} \right), \quad (\text{A4})$$

$$C_{kk'}^{(3)} = C_{kk'}^{(A)} + C_{kk'}^{(B)} + C_{kk'}^{(C)} + C_{kk'}^{(D)} + \sum_{k'k}^{(3)}(\infty), \quad (\text{A5})$$

where

$$C_{kk'}^{(A)} = \frac{1}{4} \sum_{a,b,c,d} v_{abkl} v_{cdk'l}^* V_{cd[ab]}, \quad (\text{A6})$$

$$C_{kk'}^{(B)} = \sum_{\substack{a,b,c \\ l,m}} v_{abkl} v_{ack'm}^* V_{lc[bm]}, \quad (\text{A7})$$

$$C_{kk'}^{(C)} = \frac{1}{4} \sum_{\substack{a,b \\ l,m,j}} v_{ablm} v_{abjk'}^* V_{lm[jk]} + \text{h.c.} \quad (\text{A8})$$

$$C_{kk'}^{(D)} = \sum_{\substack{a,b,c \\ l,m}} v_{ablm} v_{bck'm}^* V_{lc[ka]} + \text{h.c.} \quad (\text{A9})$$

The constant self-energy part $\Sigma_{kk'}^{(3)}(\infty)$ can be obtained using Eq. (A25) below.

1h/2h-1p block:

$$C_{j,akl}^{(1)} = V_{kl[aj]}, \quad (\text{A10})$$

$$C_{j,akl}^{(2)} = \frac{1}{2} \sum_{b,c} v_{bckl}^* V_{bc[ja]} + \left(\sum_{b,i} v_{abli}^* V_{kb[ji]} \right) - (k \leftrightarrow l). \quad (\text{A11})$$

Here ($k \leftrightarrow l$) means repeating the preceding term, but with k and l interchanged.

2h-1p/2h-1p block:

$$\begin{aligned} K_{akl,a'k'l'} &= (-\epsilon_a + \epsilon_k + \epsilon_l) \delta_{aa'} \delta_{kk'} \delta_{ll'}, \\ C_{akl,a'k'l'}^{(1)} &= -\delta_{aa'} V_{k'l'[kl]} + (\delta_{kk'} V_{al'[a'l]} \\ &\quad + \delta_{ll'} V_{ak'[a'k]}) - (k \leftrightarrow l). \end{aligned} \quad (\text{A12})$$

It should be noted that the relative signs have been chosen in such a way that the first-order contributions to \mathbf{C} agree with

$$C_{IJ}^{(1)} = \langle \Phi_I | E_0^{(1)} - \hat{H}_I | \Phi_J \rangle,$$

where $\{|\Phi_J\rangle\} \equiv \{c_k |\Phi_0^N\rangle, c_a^\dagger c_k c_l |\Phi_0^N\rangle, \dots\}$ are the usual $(N-1)$ -electron HF configurations.

(ii) Effective transition moments

1h part:

$$f_{kq}^{(0)} = \delta_{kq}, \quad (\text{A13})$$

$$f_{kq}^{(1)} = 0, \quad (\text{A14})$$

$$f_{kk'}^{(2)} = -\frac{1}{4} \sum_{a,b,l} v_{abkl} v_{abk'l'}^*. \quad (\text{A15})$$

Note that $f_{kk'}^{(2)}$ is a Hermitian matrix. According to Eqs. (51), (53) the particle part, $f_{ka}^{(2)}$, may be written as

$$f_{ka}^{(2)} = \frac{1}{\epsilon_k - \epsilon_a} (M_{ak}^{(2)+}(\epsilon_k) + M_{ak}^{(2)-}(\epsilon_a)), \quad (\text{A16})$$

where

$$M_{ak}^{(2)+}(\epsilon_k) = -\frac{1}{2} \sum_{b,c,j} V_{aj[bc]} v_{bckj}, \quad (\text{A17})$$

$$M_{ak}^{(2)-}(\epsilon_a) = \frac{1}{2} \sum_{b,i,j} V_{ij[kb]} v_{abij}. \quad (\text{A18})$$

In third order, the hole part, $f_{kk'}$, consists of four contributions

$$f_{kk'}^{(3)} = f_{kk'}^{(A)} + f_{kk'}^{(B)} + f_{kk'}^{(C)} + f_{kk'}^{(D)}, \quad (\text{A19})$$

where

$$f_{kk'}^{(A)} = \frac{1}{4} \sum_{\substack{a,b,c,d \\ l}} v_{abkl} v_{cdk'l}^* \frac{V_{cd[ab]}}{\epsilon_c + \epsilon_d - \epsilon_k - \epsilon_l}, \quad (\text{A20})$$

$$f_{kk'}^{(B)} = \sum_{\substack{a,b,c \\ l,m}} v_{abkl} v_{ack'm}^* \frac{V_{lc[bm]}}{\epsilon_a + \epsilon_c - \epsilon_k - \epsilon_m}, \quad (\text{A21})$$

$$f_{kk'}^{(C)} = \frac{1}{4} \sum_{\substack{a,b \\ l,m,j}} v_{ablm} v_{abjk'}^* \frac{V_{lm[jk]}}{\epsilon_a + \epsilon_b - \epsilon_k - \epsilon_j}, \quad (\text{A22})$$

$$f_{kk'}^{(D)} = \sum_{\substack{a,b,c \\ l,m}} v_{ablm} v_{bck'm}^* \frac{V_{lc[ka]}}{\epsilon_b + \epsilon_c - \epsilon_k - \epsilon_m}. \quad (\text{A23})$$

Obviously, the present form of $f_{kk'}^{(3)}$ is not Hermitian. One may proceed to a Hermitian expression according to

$$f_{kk'}^{(h)} = \frac{1}{2} (f_{kk'}^{(3)} + f_{kk'}^{(3)\dagger}).$$

This choice would introduce additional contributions to $C_{kk'}^{(3)}$ of the form

$$\tilde{C}_{kk'}^{(3)} = (\epsilon_k - \epsilon_{k'}) f_{kk'}^{(a)},$$

where

$$f_{kk'}^{(a)} = \frac{1}{2} (f_{kk'}^{(3)} - f_{kk'}^{(3)\dagger})$$

is the anti-Hermitian contribution of $f_{kk'}^{(3)}$.

For the particle part, $f_{ka}^{(3)}$, a compact representation follows from Eqs. (51) and (53),

$$f_{ka}^{(3)} = \frac{1}{\epsilon_k - \epsilon_a} (\Sigma_{ak}^{(3)}(\infty) + M_{ak}^{(3)+}(\epsilon_k) + M_{ak}^{(3)-}(\epsilon_a)). \quad (\text{A24})$$

The third-order static and dynamic self-energy contributions $\Sigma^{(3)}(\infty)$, $\mathbf{M}^{(3)+}(\omega)$, and $\mathbf{M}^{(3)-}(\omega)$ have been specified, for example, in Ref. 3 or Ref. 8. Alternatively, as a consequence of Eq. (47), $\Sigma^{(3)}(\infty)$ can be obtained according to

$$\Sigma_{pq}^{(3)}(\infty) = \sum_{r,s} V_{pr[qs]} (\rho_{rs}^{(2)} - \rho_{rs}^{(0)}) \quad (\text{A25})$$

using the second-order density matrix elements as given below.

2h-1p part:

$$f_{akl,j} = 0, \quad (\text{A26})$$

$$f_{akl,b}^{(1)} = -v_{abkl}, \quad (\text{A27})$$

$$f_{akl,b}^{(2)} = (g_{akl,b}^{(A)} + g_{akl,b}^{(B)} + g_{akl,b}^{(C)} + g_{akl,b}^{(D)}) \frac{1}{\epsilon_a + \epsilon_b - \epsilon_k - \epsilon_l}, \quad (\text{A28})$$

where

$$g_{akl,b}^{(A)} = \frac{1}{2} \sum_{i,j} v_{abij} V_{ij[kl]}, \quad (\text{A29})$$

$$g_{akl,b}^{(B)} = \frac{1}{2} \sum_{c,d} v_{cdkl} V_{ab[cd]}, \quad (\text{A30})$$

$$g_{akl,b}^{(C)} = \sum_{j,c} v_{bcjl} V_{aj[ck]} - (k \leftrightarrow l), \quad (\text{A31})$$

$$g_{akl,b}^{(D)} = \sum_{j,c} v_{acjk} V_{bj[cl]} - (k \leftrightarrow l). \quad (\text{A32})$$

The expressions given for the blocks of \mathbf{f} can be used together with Eqs. (40), (52), and (53) to specify the perturbation expansion of the one-particle density matrix ρ through third order. Following Eq. (52) one finds for the h -block of ρ ,

$$\rho_{kk'} = \delta_{kk'} + 2f_{kk'}^{(2)} + (f_{kk'}^{(3)} + f_{kk'}^{(3)\dagger}) + O(4). \quad (\text{A33})$$

Note that the Hermitian part, $f_{kk'}^{(h)(3)}$, has to be used here. For the hp -block, Eq. (53) shows that through third order the perturbation expansions of ρ_{ka} and f_{ka} are identical,

$$\rho_{ka} = f_{ka}^{(2)} + f_{ka}^{(3)} + O(4). \quad (\text{A34})$$

Finally, for the p -block $\rho_{aa'}$ one has to resort to Eq. (40) implying

$$\rho_{aa'} = \sum_k f_{ka}^\dagger f_{ka'} + \sum_{b,k,l} f_{bkl,a}^\dagger f_{bkl,a'} + O(4). \quad (\text{A35})$$

As f_{ka} is (at least) of second order the simpler result

$$\rho_{aa'} = \sum_{b,k,l} f_{bkl,a}^\dagger f_{bkl,a'} + O(4), \quad (\text{A36})$$

applies for expanding $\rho_{aa'}$ through third order.

Note that the static-self energy part $\Sigma(\infty)$ can be calculated through fourth order by using the above third-order expansions for ρ in Eq. (47).

APPENDIX B: ADC(3) EQUATIONS FOR THE $(N+1)$ -ELECTRON CASE

The ADC equations for the $(N+1)$ -particle case part $\mathbf{G}^+(\omega)$ can be derived in a essentially analogous way as described for $\mathbf{G}^-(\omega)$.

The ADC representation of $\mathbf{G}^+(\omega)$ reads

$$\mathbf{G}^+(\omega) = \mathbf{f}^\dagger (\omega - \mathbf{K} - \mathbf{C})^{-1} \mathbf{f}, \quad (\text{B1})$$

where the secular matrix $\mathbf{K} + \mathbf{C}$ can be viewed as an $(N+1)$ -electron intermediate state representation

$$(\mathbf{K} + \mathbf{C})_{IJ} = \langle \tilde{\Psi}_I^{N+1} | \hat{H} - E_0^N | \tilde{\Psi}_J^{N+1} \rangle \quad (\text{B2})$$

of $\hat{H} - E_0^N$, while the effective transition amplitudes f_{Iq} are given by

$$f_{Iq} = \langle \tilde{\Psi}_I^{N+1} | c_q^\dagger | \Psi_0^N \rangle. \quad (\text{B3})$$

The $(N+1)$ -electron intermediate states $|\tilde{\Psi}_I^{N+1}\rangle$ are related to the ‘‘physical’’ operators

$$\{\hat{C}_J\} \equiv \{c_a^\dagger; c_j c_a^\dagger c_b^\dagger, a < b; \dots\},$$

which, when acting on the N -electron ground state, give rise to a complete set of $(N+1)$ -electron states.

At the ADC(3) level the explicit configuration space is restricted to the class of $1p$ - and $(2p-1h)$ -configurations. The (diagonal) zeroth order part of the secular matrix reads

$$K_{aa'} = \delta_{aa'} \epsilon_a,$$

$$K_{jab,j'a'b'} = \delta_{jj'} \delta_{aa'} \delta_{bb'} (-\epsilon_j + \epsilon_a + \epsilon_b). \quad (\text{B4})$$

In the following, we specify the resulting expressions for \mathbf{C} and \mathbf{f} . This can be done in a compact form by establishing the formal relations to the $(N-1)$ -case considered in Appendix A. For example, the first-order contribution to the coupling block $C_{a,jbc}$ is given by

$$C_{a,jbc}^{(1)}(N+1) = -C_{a,jbc}^{(1)*}(N-1). \quad (\text{B5})$$

This means to take the formal expression of the $(N-1)$ -particle case as given by Eq. (A10), to replace particle by hole and hole by particle indices as indicated on the right-hand side, then to take the complex conjugate, and finally to change the sign. The following expressions have to be interpreted in a similar way,

$$C_{a,jbc}^{(2)}(N+1) = \overline{C_{a,jbc}^{(2)*}}(N-1). \quad (\text{B6})$$

Here the overbar indicates that in addition to the $(p \leftrightarrow h)$ exchange also the internal summation indices must be exchanged accordingly,

$$C_{jab,j'a'b'}^{(1)}(N+1) = -C_{jab,j'a'b'}^{(1)*}(N-1), \quad (\text{B7})$$

$$C_{aa'}^{(2)}(N+1) = \overline{C_{a'a}^{(2)*}}(N-1), \quad (\text{B8})$$

$$C_{aa'}^{(3)}(N+1) = -\overline{C_{a'a}^{(3)*}}(N-1). \quad (\text{B9})$$

Note that in Eqs. (B8) and (B9) the indices on the left- and the right-hand side are transposed.

$$f_{aa'}^{(2)}(N+1) = \overline{f_{a'a}^{(2)*}}(N-1), \quad (\text{B10})$$

$$f_{aa'}^{(3)}(N+1) = -\overline{f_{a'a}^{(3)*}}(N-1). \quad (\text{B11})$$

Analogously to Eqs. (A16) and (A24), the hole-part, f_{qk} can be evaluated consistently through third order by using the relation

$$f_{ak} = \frac{1}{\epsilon_a - \epsilon_k} (\Sigma_{ak}(\infty) + M_{ak}^+(\epsilon_k) + M_{ak}^-(\epsilon_a)) + O(4), \quad (\text{B12})$$

$$f_{jab,l}^{(1)}(N+1) = -f_{jab,l}^{(1)*}(N-1), \quad (\text{B13})$$

$$f_{jab,l}^{(2)}(N+1) = \overline{f_{jab,l}^{(2)*}}(N-1). \quad (\text{B14})$$

As an analogon to the one-particle density matrix ρ [Eq. (39)] one may consider the matrix $\tilde{\rho}$ of elements

$$\tilde{\rho}_{rs} = \langle \Psi_0^N | c_r c_s^\dagger | \Psi_0^N \rangle = -\frac{1}{2\pi i} \oint G_{rs}(\omega) d\omega. \quad (\text{B15})$$

Here the contour integration closes in the lower complex ω -plane. The discussion in Sec. IV and the expressions Eqs. (A33)–(A36) can be easily transferred to the case of $\tilde{\rho}$. It should be noted that the obvious relationship

$$\rho_{rs} + \tilde{\rho}_{rs} = \delta_{rs} \quad (\text{B16})$$

allows one to evaluate the pp -block of ρ according to

$$\rho_{aa'} = \delta_{aa'} - \tilde{\rho}_{aa'} \quad (\text{B17})$$

from $\tilde{\rho}_{aa'}$ instead of using Eq. (A36).

- ¹A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, New York, 1971).
- ²A. A. Abrikosov, L. P. Gorkov, and I. E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, Englewood Cliffs, 1963).
- ³L. S. Cederbaum and W. Domcke, *Adv. Chem. Phys.* **36**, 205 (1977).
- ⁴J. Simons, *Annu. Rev. Phys. Chem.* **28**, 1 (1977).
- ⁵J. Oddershede, *Adv. Quantum Chem.* **11**, 275 (1978).
- ⁶M. F. Herman, K. F. Freed, and D. L. Yeager, *Adv. Chem. Phys.* **48**, 1 (1981).
- ⁷Y. Öhrn and G. Born, *Adv. Quantum Chem.* **13**, 1 (1981).
- ⁸W. von Niessen, J. Schirmer, and L. S. Cederbaum, *Comput. Phys. Rep.* **1**, 59 (1984).
- ⁹J. V. Ortiz, V. G. Zakrzewski, and O. Dolgounitcheva, in *Conceptual Trends in Quantum Chemistry*, edited by E. Kryachko (Kluwer, Dordrecht, 1997), Vol. 3; J. V. Ortiz, *J. Chem. Phys.* **104**, 7599 (1996); **108**, 1008 (1998).
- ¹⁰P. Jørgensen and J. Simons, *Second Quantization-Based Methods in Quantum Chemistry* (Academic, New York, 1981).
- ¹¹R. McWeeny, *Methods of Molecular Quantum Mechanics* (Academic, London, 1989).
- ¹²L. S. Cederbaum, *J. Phys. B* **8**, 290 (1975).
- ¹³J. Schirmer, *Phys. Rev. A* **26**, 2395 (1982).
- ¹⁴J. Schirmer, L. S. Cederbaum, and O. Walter, *Phys. Rev. A* **28**, 1237 (1983).
- ¹⁵D. J. Rowe, *Rev. Mod. Phys.* **40**, 153 (1968).
- ¹⁶C. W. McCurdy, T. N. Rescigno, D. L. Yeager, and V. McKoy, in *Methods of Electronic Structure Theory*, edited by H. F. Schaefer (Plenum, New York, 1977).
- ¹⁷D. Gosinski and B. Lukman, *Chem. Phys. Lett.* **7**, 573 (1970).
- ¹⁸B. T. Pickup and O. Gosinski, *Mol. Phys.* **26**, 19 (1973).
- ¹⁹P. Jørgensen, *Annu. Rev. Phys. Chem.* **26**, 359 (1975).
- ²⁰J. Schirmer, *Phys. Rev. A* **43**, 4647 (1991).
- ²¹M. Nooijen and J. G. Snijders, *Int. J. Quantum Chem., Symp.* **26**, 55 (1992).
- ²²M. Nooijen and J. G. Snijders, *Int. J. Quantum Chem.* **47**, 3 (1993); **48**, 15 (1993).
- ²³J. F. Stanton and J. Gauss, *J. Chem. Phys.* **101**, 8938 (1994).
- ²⁴M. Nooijen and R. J. Bartlett, *J. Chem. Phys.* **102**, 3629 (1995).
- ²⁵M. D. Prasad, S. Pal, and D. Mukherjee, *Phys. Rev. A* **31**, 1287 (1985).
- ²⁶D. Mukherjee and W. Kutzelnigg, in *Many-Body Methods in Quantum Chemistry*, edited by U. Kaldor (Springer, Berlin, 1989).
- ²⁷F. Mertins and J. Schirmer, *Phys. Rev. A* **53**, 2140 (1996).
- ²⁸J. Schirmer and A. Barth, *Z. Phys. A* **317**, 267 (1984).
- ²⁹A. Tarantelli and L. S. Cederbaum, *Phys. Rev. A* **39**, 1656 (1989).
- ³⁰J. Schirmer and F. Mertins, *Int. J. Quantum Chem.* **58**, 329 (1996).
- ³¹J. Winter, *Nucl. Phys. A* **194**, 535 (1972).
- ³²S. Ethofer and P. Schuck, *Z. Phys.* **228**, 264 (1969).
- ³³P. Durand and J.-P. Malrieu, *Adv. Chem. Phys.* **67**, 321 (1987).
- ³⁴H. J. Monkhorst, *Int. J. Quantum Chem., Symp.* **11**, 421 (1977).
- ³⁵D. Mukherjee and P. K. Mukherjee, *Chem. Phys.* **39**, 325 (1979).
- ³⁶S. Gosh, D. Mukherjee, and D. Bhattacheryya, *Chem. Phys.* **72**, 161 (1982).
- ³⁷E. Dalgaard and H. J. Monkhorst, *Phys. Rev. A* **28**, 1217 (1983).
- ³⁸H. Koch and P. Jørgensen, *J. Chem. Phys.* **93**, 3333 (1990).
- ³⁹H. Sekino and R. J. Bartlett, *Int. J. Quantum Chem., Symp.* **18**, 255 (1984).
- ⁴⁰J. Geertsen, M. Rittby, and R. J. Bartlett, *Chem. Phys. Lett.* **164**, 57 (1989).
- ⁴¹J. F. Stanton and R. J. Bartlett, *J. Chem. Phys.* **98**, 7029 (1993).
- ⁴²H. Nakatsuji and K. Hirao, *Chem. Phys. Lett.* **47**, 569 (1977).
- ⁴³K. Hirao and Y. Hatano, *Chem. Phys. Lett.* **111**, 533 (1984).
- ⁴⁴M. Nooijen and J. G. Snijders, *J. Chem. Phys.* **102**, 1681 (1995).
- ⁴⁵J. F. Stanton and J. Gauss, *J. Chem. Phys.* **103**, 1064 (1995).