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# New approach to the one-particle Green's function for finite Fermi systems

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A new approach to the one-particle Green's functions $\underline{G}$ for finite electronic systems is presented. This approach is based on the diagrammatic perturbation expansions of the Green's function and of the dynamic self-energy part $\underline{M}$ related to $\underline{G}$ via the Dyson equation. The exact summation of the latter expansion is reformulated in terms of a simple algebraic form referred to as algebraic diagrammatic construction (ADC). The ADC defines in a systematical way a set of approximation schemes ($n$th-order ADC schemes) that represent infinite partial summations for $\underline{M}$ and (via the Dyson equation) for $\underline{G}$ being complete through $n$th order of perturbation theory. The corresponding mathematical procedures are essentially Hermitian eigenvalue problems in restricted configuration spaces of unperturbed ionic configurations. Explicit equations for the second-, third-, and fourth-order ADC schemes are derived and analyzed. While the second- and third-order schemes can be viewed as systematic rederivations of previous approximation schemes, the fourth-order ADC scheme represents a complete fourth-order approximation for the self-energy and the one-particle Green's function which was hitherto not available.

## I. INTRODUCTION

The one-particle Green's function[1–4] is a well-recognized means of calculating the ionization and attachment spectra of finite electronic (or nucleonic) systems. The conceptual advantage of the Green's-function method and of related many-body methods lies in the fact that the interesting physical information for the ionization and attachment process is calculated directly without resorting to separate calculations for the (initial) ground state and the (final) ionic states as is the case in more conventional approaches. The ionization energies and electron affinities are determined from the location of the poles of the (Fourier-transformed) one-particle Green's function while the spectral intensities are derived from the corresponding residues. A large number of calculations for atoms and molecules has been presented since the first applications a decade ago. For a more detailed discussion and references the reader is referred to review articles.[5–8]

As is well known, there exist perturbation expansions for the one-particle Green's function (more precisely, for the matrix of Green's functions) $\underline{G}$ and for the related self-energy $\underline{\Sigma}$ in terms of the famous Feynman diagrams[1–4] which are very useful in the construction of approximation schemes. An obvious way of obtaining an approximation for $\underline{\Sigma}$ is to employ a finite expansion for the self-energy, an example of which is the outer-valence Green's-function method (OVGF) (Refs. 6 and 9). This method is based on the third-order expansion for the self-energy and includes higher-order contributions by a renormalization procedure. The OVGF has proven to provide accurate results for the outer-valence ionic main states that are well described in the quasiparticle picture.[6,7] For energy regions where higher excited (shakeup) configurations play a role, the OVGF method does not apply. Here, the self-energy itself has poles and thus cannot properly be described by a finite expansion.

Approximation schemes which maintain the analytical properties of the exact self-energy are derived as infinite partial summations of the perturbation series for $\underline{\Sigma}$. Well-known examples for such infinite summations of special classes of diagrams are the random-phase approximation (RPA) and the ladder summations for $\underline{\Sigma}(\omega)$ (see, e.g., Mattuck[3]). However, for finite electronic systems these approximations have proven to be inadequate. Here, the third-order contributions for the ionic main states and the first-order contributions for the secondary states are already incomplete and selective and the results may be worse than in the simple second-order expansion for $\underline{\Sigma}(\omega)$. A summation of both RPA and ladder-type diagrams (restricted, however, to special "time orderings") is achieved by the so-called two-particle—one-hole Tamm-Dancoff approximation (2p-h—TDA).[6,10] The 2p-h—TDA summation is complete only up to second order and, as a consequence, the main ionic states are less accurately described than in the OVGF method. On the other hand, the secondary states are here treated consistently through first order and this allows for an at least qualitatively correct description of the entire valence ionization spectrum. In particular, the 2p-h—TDA provides access to the inner-valence regime, where generally the simple one-particle picture of ionization breaks down.[11,12] This effect has been demonstrated by 2p-h—TDA calculations for numerous molecules.[11,13]

The 2p-h—TDA scheme can readily be extended so that the resulting infinite partial summation for the self-energy (and thus for the Green's function) is complete up to third order. These extended 2p-h—TDA equations have been presented previously.[14] Applications to atoms[14] and molecules[15] show that this approach significantly improves the level of accuracy for the ionic main states matching that of the OVGF method.

Other concepts for the derivation of approximation schemes for the one-particle Green's function have been presented, alternative to the diagrammatic approach. One such concept is the equation-of-motion method (EOM) which, being originally formulated for the electronic excitation problem,[16,17] has been transferred to the treatment of ionization and electron-attachment processes.[18,19] The basic EOM equations are formulated in terms of ground-state expectation values of exact excitation operators for $N\pm1$ particles. Equations, fully equivalent to the EOM equations, also emerge from a propagator formalism.[20,21] In this formalism the so-called superoperator representation of the one-particle Green's function is expanded via inner-projection techniques in an operator space of $(N\pm1)$-particle excitation operators.

In both the EOM and the propagator approaches approximation schemes result from expansions of the (exact) excitation operators and the ground state in terms of basic operators and unperturbed configurations, respectively. Within the framework of these formalisms a complete third-order scheme has been worked out[18,22–24] which is essentially equivalent to the diagrammatically derived extended 2p-h—TDA. We mention that the simpler 2p-h—TDA scheme can also be obtained within the EOM approach.[25]

In spite of the simplicity of the basic equations, the derivation of extended approximation schemes in the EOM becomes increasingly complicated and is by no means straightforward: Besides the question of the proper expansion of the excitation operators in terms of basic operators, complications arise due to the high-order expansions required for the ground state, the nonorthogonality of the basic excitations with respect to the correlated ground state, and the non-Hermiticity of the resulting secular equations. The difficulties may be appreciated by consulting previous attempts to proceed beyond third order.[26,27]

In the diagrammatic approach, on the other hand, a well-defined prescription for constructing higher-order approximation schemes for the self-energy and the Green's function was hitherto not available at all. It is the purpose of this article to present a new diagrammatic approach which allows for a systematic construction of extended approximation schemes. This approach, which we call the algebraic diagrammatic construction (ADC), starts explicitly from the diagrammatic perturbation expansion for the self-energy. We present a simple algebraic scheme by which (in principle) this perturbation expansion can be summed up exactly. This scheme defines in a natural way a set of systematic approximations that represent infinite partial summations for the self-energy (and the Green's function) being exact up to a finite order of perturbation theory. The resulting mathematical procedures involve Hermitian eigenvalue problems within limited spaces of physical excitations of $N\pm1$ particles. We shall present the explicit construction of the "$n$th-order ADC schemes" for $n=2,3$, and 4. As will be seen, the second- and third-order ADC schemes recover the 2p-h—TDA and the extended 2p-h—TDA schemes, respectively, which thereby are rederived from a systematic point of view. The fourth-order scheme clearly goes beyond all previous approximation schemes. It gives results which are exact up to fourth order for the ionic main states and furthermore yields the secondary (satellite) states consistent through second order, which is an important step towards a quantitative description of the spectral regions where the secondary states play a role, i.e., for the inner valence and the core ionization. We mention that the ADC scheme is quite general and applies also to other Green's functions, e.g., for the polarization propagator where a similar approach has been presented recently.[28]

In Sec. II below we review briefly the theory of the one-particle Green's function as far as is needed for our purpose. The presentation of the general ADC scheme and the explicit construction of the second-, third-, and fourth-order approximations are contained in Sec. III. In Sec. IV we discuss the physical content of the resulting ADC schemes. A short summary is given in Sec. V.

## II. THEORETICAL FOUNDATIONS

### A. One-particle Green's function

The matrix of one-particle Green's functions $\underline{G}$ is defined with respect to a suitably chosen basis of one-particle states $|q\rangle$ (in general, a discrete set of Hartree-Fock orbitals) by[1]

$$G_{pq}(t,t')=-i\langle\Psi_0|\hat{T}c_p(t)c_q^\dagger(t')|\Psi_0\rangle\ . \tag{1}$$

Here, $|\Psi_0\rangle$ is the exact (closed-shell) ground state of the considered $N$-particle system, $c_q^\dagger(t)$ $[c_q(t)]$ denote creation (destruction) operators for the one-particle states $|q\rangle$ in the Heisenberg representation, and $\hat{T}$ is Wick's time-ordering operator which introduces generalized step functions

$$\Theta(\tau)=\begin{cases}0, & \tau<0\\ e^{-\eta\tau}, & \tau\geq 0\end{cases} \tag{2}$$

of the time differences $\tau=\pm(t-t')$. The positive infinitesimal $\eta$ guarantees the convergence of the Fourier transform

$$\underline{G}(\omega)=\int d(t-t')e^{i\omega(t-t')}\underline{G}(t,t')\ . \tag{3}$$

Here a time-independent Hamiltonian is assumed. The components of $\underline{G}(\omega)$ can be expressed by the well-known spectral representation[1]

$$G_{pq}(\omega)=\sum_n\frac{\langle\Psi_0|c_p|\Psi_n^{N+1}\rangle\langle\Psi_n^{N+1}|c_q^\dagger|\Psi_0\rangle}{\omega+E_0^N-E_n^{N+1}+i\eta}+\sum_m\frac{\langle\Psi_0|c_q^\dagger|\Psi_m^{N-1}\rangle\langle\Psi_m^{N-1}|c_p|\Psi_0\rangle}{\omega+E_m^{N-1}-E_0^N-i\eta}\ . \tag{4}$$

Here, $E_n^{N\pm1}$ and $|\Psi_n^{N\pm1}\rangle$ denote the energies and states of the $(N\pm1)$-particle systems, $E_0^N$ is the ground-state energy. The physical significance of the one-particle Green's function is evident from Eq. (4). The ionization energies

$$I_n=E_n^{N-1}-E_0^N \tag{5}$$

and electron affinities

$$A_n=E_0^N-E_n^{N+1} \tag{6}$$

are derived from the pole positions of $\underline{G}(\omega)$. The residues are products of the transition amplitudes

$$x_p^{(n)}=\langle\Psi_n^{N-1}|c_p|\Psi_0\rangle\ , \tag{7a}$$

$$y_p^{(n)}=\langle\Psi_n^{N+1}|c_p^\dagger|\Psi_0\rangle\ . \tag{7b}$$

These quantities are related to the spectral intensities of the ionization and the electron-attachment experiment, respectively. In the case of a photoelectron experiment (with a photon energy $\omega_0$ sufficiently above the respective threshold), the spectral electron intensity associated with the final ionic state $|\Psi_n^{N-1}\rangle$ is given by the expression

$$P_n\sim\sum_k\left|\sum_p\tau_{kp}x_p^{(n)}\right|^2\delta(E_k+I_n-\omega_0)\ . \tag{8}$$

Here, the $\tau_{kp}$ denotes the matrix element of the dipole operator taken with the one-particle state $|p\rangle$ and the continuum state $|k\rangle$ with kinetic energy $E_k$. For a thorough discussion of the spectral intensities the reader is referred to the review article by Cederbaum and Domcke.[6]

### B. Self-energy

In the following we shall make use of the usual decomposition of the full Hamiltonian,

$$\begin{aligned}\hat{H}&=\hat{H}_0+\hat{H}_I\ ,\\ \hat{H}_0&=\sum\epsilon_i c_i^\dagger c_i\ ,\\ \hat{H}_I&=\hat{W}+\hat{V}=\sum W_{ij}c_i^\dagger c_j+\tfrac{1}{2}\sum V_{ijkl}c_i^\dagger c_j^\dagger c_l c_k\ ,\end{aligned} \tag{9}$$

into a diagonal one-particle part $\hat{H}_0$ and a perturbation part $\hat{H}_I$, which consists of the two-particle (Coulomb) interaction and a nondiagonal one-particle part $\hat{W}$. For simplicity we shall assume a representation in terms of Hartree-Fock (HF) one-particle states $|j\rangle$. Then, the $\epsilon_i$ are the HF orbital energies. The matrix elements of the two-particle (Coulomb) interaction are defined according to

$$V_{ijkl}=\langle\phi_i(1)\phi_j(2)|V(1,2)|\phi_k(1)\phi_l(2)\rangle\ . \tag{10}$$

In the HF case the nondiagonal one-particle part $\hat{W}$ is determined by the matrix elements

$$W_{ij}=-\sum_k V_{ik[jk]}n_k\ . \tag{11}$$

Here and in the following we use the notation $V_{ij[kl]}=V_{ijkl}-V_{ijlk}$ for the antisymmetrized two-particle matrix element, and $n_k=1-\bar{n}_k$ for the HF occupation numbers, i.e., $n_k=1$ $(n_k=0)$ for $|k\rangle$ occupied (unoccupied) in the HF ground state $|\Phi_0\rangle$. We stress that the choice $\hat{H}_0=\hat{H}_{\text{HF}}$ does not restrict the generality of our approach. The formulation for an arbitrary $\hat{H}_0$ is, though more lengthy, a straightforward extension of the HF case.

The one-particle Green's function $\underline{G}$ is related to the so-called self-energy $\underline{\Sigma}$ by the Dyson equation[1] which in the $\omega$ representation reads

$$\underline{G}(\omega)=\underline{G}^0(\omega)+\underline{G}^0(\omega)\underline{\Sigma}(\omega)\underline{G}(\omega) \tag{12}$$

and allows for the (formal) solution

$$\underline{G}(\omega)=\{[\underline{G}^0(\omega)]^{-1}-\underline{\Sigma}(\omega)\}^{-1}\ . \tag{13}$$

The "free" Green's function

$$G_{pq}^0(\omega)=\delta_{pq}\left[\frac{n_p}{\omega-\epsilon_p-i\eta}+\frac{\bar{n}_p}{\omega-\epsilon_p+i\eta}\right] \tag{14}$$

introduced here follows from Eq. (1) for the free

Hamiltonian $\hat{H}_0$.

The self-energy $\underline{\Sigma}(\omega)$ can be written as the sum

$$\underline{\Sigma}(\omega)=\underline{\Sigma}(\infty)+\underline{M}(\omega) \tag{15}$$

of a static ($\omega$-independent) part $\underline{\Sigma}(\infty)$ and a dynamic ($\omega$-dependent) part $\underline{M}(\omega)$. Let us first consider the latter part. Following Ethofer and Schuck[29] and Winter,[30] $\underline{M}(\omega)$ can be expressed in a symmetric way in terms of the so-called two-particle-hole (2p-h) response function $\underline{R}$ which is defined according to

$$R_{123,1'2'2'}=G_{123,1',2'3'}-G_{23,3'4}G^{-1}_{45}G_{51,1'2'} \; . \tag{16}$$

In this short-hand notation, summation and time integration over doubly occurring indices are implied. The two- and three-particle Green's functions in Eq. (16) are defined according to the general definition[31]

$$G_{1\cdots n,1'\cdots n'}(t_1,\ldots,t_{n'})=(-i)^n\langle\Psi_0\,|\,\hat{T}c_1(t_1)\cdots c_n(t_n)c^\dagger_{n'}(t_{n'})\cdots c^\dagger_{1'}(t_{1'})\,|\,\Psi_0\rangle \; . \tag{17}$$

The 2p-h—response function is a complicated function of six time arguments (or five time differences). We mention that, as in the case of the p-h and p-p response functions, one can formulate a Bethe-Salpeter equation for the 2p-h—response function.[29] For the purpose of representing the $\omega$-dependent self-energy it is sufficient to employ the simpler 2p-h propagator

$$\Pi_{jkl,j'k'l'}(t,t')=\lim_{\substack{t_j,t_k,t_l\to t\\ t_{j'},t_{k'},t_{l'}\to t'}} R_{j'kl,k'l'j}(t_{j'},t_k,t_l,t_{k'},t_{l'},t_j) \tag{18}$$

which depends on the time difference $t-t'$ only. The limit on the right-hand side of Eq. (18) is independent of the ordering of the time arguments.[30] Introducing the Fourier transform

$$\Pi_{jkl,j'k'l'}(\omega)=\int d(t-t')e^{i\omega(t-t')}\Pi_{jkl,j'k'l'}(t,t') \tag{19}$$

the final result for the $\omega$-dependent self-energy part reads

$$M_{pq}(\omega)=\frac{1}{4}\sum_{\substack{j,k,l,\\ j',k',l'}} V_{pj[kl]}\Pi_{jkl,j'k'l'}(\omega)V^*_{qj[kl]} \; . \tag{20}$$

We note that $\underline{\Pi}(\omega)$ has a spectral representation of the form

$$\Pi_{jkl,j'k'l'}(\omega)=\sum_\mu \frac{g^{(\mu)}_{jkl}g^{(\mu)*}_{j'k'l'}}{\omega-\omega_\mu+i\eta\sigma_\mu} \; , \tag{21}$$

where according to $\sigma_\mu=\pm 1$ the poles are located below or above the real $\omega$ axis, respectively. As a consequence of Eq. (20), one obtains the spectral representation for the $\omega$-dependent self-energy part,

$$M_{pq}(\omega)=\sum_n \frac{m^{(n)}_p m^{(n)*}_q}{\omega-\omega_n+i\eta\sigma_n} \; , \tag{22}$$

where the coupling (Dyson) amplitudes are given by

$$m^{(n)}_p=\frac{1}{2}\sum_{j,k,l} V_{pj[kl]}g^{(n)}_{jkl} \; . \tag{23}$$

We mention that Eq. (22) can be derived directly from the spectral representation (4) for $\underline{G}(\omega)$ and the Dyson equation.[32]

As is the case for the one-particle Green's function $\underline{G}(\omega)$ the poles of $\underline{\Pi}(\omega)$ and $\underline{M}(\omega)$ are located either in the upper ($\sigma_n=+1$) or in the lower complex $\omega$ plane ($\sigma_n=-1$). Thus, the 2p-h propagator $\underline{\Pi}(\omega)$ and the $\omega$-dependent self-energy part $\underline{M}(\omega)$ can be written as sums

$$\underline{\Pi}(\omega)=\underline{\Pi}^{\mathrm{I}}(\omega)+\underline{\Pi}^{\mathrm{II}}(\omega) \; , \tag{24a}$$

$$\underline{M}(\omega)=\underline{M}^{\mathrm{I}}(\omega)+\underline{M}^{\mathrm{II}}(\omega) \; , \tag{24b}$$

of two parts I and II, being analytic in the upper and the lower complex $\omega$ plane, respectively. Physically, the parts I and II are associated with excitations of $N+1$ and $N-1$ particles, respectively. One should keep in mind that the energies $\omega_n$ appearing in the spectral representations for $\underline{M}$ do not yet correspond to energies of physical states. The latter result only upon the coupling to the one-particle (1p) and one-hole (1h) configurations via the Dyson equation. It should also be noticed that $\underline{\Pi}(\omega)$ is more general than $\underline{M}(\omega)$ in that it contains additional poles corresponding to those ionic states, which, for example, due to symmetry restrictions, do not couple with the 1p or 1h configurations.

We finally consider the static part $\underline{\Sigma}(\infty)$ of the self-energy part. As is well known,[6,29,30] $\underline{\Sigma}(\infty)$ can be expressed by the one-particle Green's function according to

$$\Sigma_{pq}(\infty)=W_{pq}+\sum_{k,l}V_{pk[ql]}\frac{1}{2\pi i}\oint G_{lk}(\omega)d\omega \; . \tag{25}$$

Here, the contour integration closes in the upper complex $\omega$ plane. Replacing $\underline{G}(\omega)$ by the right-hand side of Eq. (13) one obtains an equation, by which the static part $\underline{\Sigma}(\infty)$ can be determined self-consistently if $\underline{M}(\omega)$ (or an approximation for it) is given. This means that the problem of determining the full self-energy and the one-particle Green's function can be reduced to the problem of calculating the dynamic self-energy part $\underline{M}(\omega)$. Of course, one can also make use of the direct (diagrammatic) perturbation expansion for $\underline{\Sigma}(\infty)$.

The representation of the self-energy according to Eqs. (15), (22), and (24) allows us to reformulate the Dyson equation (13) as a diagonalization problem:

$$\underline{A}\underline{X}=\underline{X}\underline{E},\ \underline{X}^{\dagger}\underline{X}=\underline{\mathbb{1}}\ , \tag{26}$$

$$\underline{A}=\begin{bmatrix} \underline{\epsilon}+\underline{\Sigma}(\infty) & \underline{m}^{\rm I} & \underline{m}^{\rm II} \\ (\underline{m}^{\rm I})^{\dagger} & \underline{\Omega}^{\rm I} & 0 \\ (\underline{m}^{\rm II})^{\dagger} & 0 & \underline{\Omega}^{\rm II} \end{bmatrix} . \tag{27}$$

Here, $\underline{\epsilon}$ denotes the diagonal matrix of the one-particle energies, $\underline{\Omega}^{\rm I,II}$ are the diagonal matrices of the spectral energies $\omega_n$ of the self-energy parts $\underline{M}^{\rm I,II}(\omega)$, and $\underline{m}^{\rm I,II}$ are the corresponding matrices of the coupling (Dyson) amplitudes $m_p^{(n)}$. The one-particle Green's function is then obtained as

$$G_{pq}(\omega)=\sum_n \frac{x_p^{(n)}x_q^{(n)*}}{\omega-e_n} \tag{28}$$

in terms of the eigenvalues $e_n$ and the corresponding eigenvector components $x_p^{(n)}=X_{pn}$. For these algebraic equations the infinitesimal $\pm i\eta$ is nonessential and has been dropped. With respect to numerical applications it is often more advantageous to resort to the original form (13) of the Dyson equation, where an efficient graphical algorithm for determining the poles and amplitudes of $\underline{G}(\omega)$ is available.[33]

### C. Diagrammatic perturbation theory

As is well known, the self-energy $\underline{\Sigma}$ can be expanded in a diagrammatically formulated perturbation series. For the rules of drawing and evaluating these diagrams the reader is referred to textbooks[3,4] and review articles.[6] The Feynman diagrams (in Abrikosov notation) for the static and the dynamic self-energy part $\underline{\Sigma}(\infty)$ and $\underline{M}(\omega)$ up to fourth order have been presented elsewhere.[6] We would draw attention to the fact that each $n$th-order Feynman diagram gives rise to $n!$ time orderings or Goldstone diagrams by which the result of the $n-2$ internal integrations required for the evaluation of this Feynman diagram can be formulated. For the following discussion it is important to note that the $n!$ Goldstone diagrams for a given $n$th-order Feynman diagram can be divided into two distinct classes according to the ordering of the external vertices ($t>t'$ and $t<t'$). The first class ($t>t'$) contributes exclusively to $\underline{M}^{\rm I}(\omega)$ while the second class ($t<t'$) contributes to $\underline{M}^{\rm II}(\omega)$ only; there are no mixed terms and $\underline{M}^{\rm I}(\omega)$ and $\underline{M}^{\rm II}(\omega)$ may be calculated separately from their respective diagrammatic expansions. All second-, third-, and fourth-order Goldstone diagrams for $\underline{M}^{\rm I}(\omega)$ are shown in Figs. 2, 3, and 4, respectively.

## III. ALGEBRAIC DIAGRAMMATIC CONSTRUCTION FOR THE DYNAMIC SELF-ENERGY PART

In this section we present a new approximation scheme for the $\omega$-dependent self-energy part $\underline{M}(\omega)$. In accordance with a similar approach for the polarization propagator[28] we shall refer to this scheme as the algebraic diagrammatic construction (ADC). The general ADC concept is introduced in Sec. III A. In Sec. III B we demonstrate the usefulness of this approach by the explicit construction of the second-, third-, and fourth-order ADC schemes, which represent infinite partial summations for $\underline{M}(\omega)$ being complete through second, third, and fourth order in the perturbation, respectively. The question of the existence and uniqueness of the ADC approach is addressed in Sec. III C.

### A. General formulation of the ADC concept

The central quantities considered in the following are the two parts $\underline{M}^{\rm I}(\omega)$ and $\underline{M}^{\rm II}(\omega)$ of the dynamic self-energy. Since the treatment of both parts is essentially identical, we may concentrate our discussion on the part I. For the sake of notational brevity we shall omit the superscripts I,II whenever they are nonessential.

As we have seen [Eq. (20)], the self-energy part $\underline{M}^{\rm I}(\omega)$ is related to the part I of the 2p-h propagator according to

$$M^{\rm I}_{pq}(\omega)=\underline{V}_p^{\dagger}\underline{\Pi}^{\rm I}(\omega)\underline{V}_q\ . \tag{29}$$

Here, a matrix notation has been adopted where $\underline{V}_p$ denotes the vector of the components

$$(\underline{V}_p)_{jkl}=V^{*}_{pj[kl]},\ \ j,k<l\ . \tag{30}$$

Note, that due to the index restriction $k<l$ introduced here, the factor $\frac{1}{4}$ of Eq. (20) is absent.

Now the basic points of the ADC may be stated as follows.

(1) The exact self-energy parts $\underline{M}^{\rm I}(\omega)$ and $\underline{M}^{\rm II}(\omega)$ can be obtained by the simple algebraic form

$$M_{pq}(\omega)=\underline{U}_p^{\dagger}(\omega\underline{\mathbb{1}}-K-\underline{C})^{-1}\underline{U}_q\ , \tag{31}$$

where $\underline{U}_p$ is a constant ($\omega$-independent) vector of "modified coupling amplitudes" for the orbital $p$ and $\underline{K}$ and $\underline{C}$ are constant Hermitian matrices, the latter being referred to as the "modified interaction matrix." These quantities are defined with respect to the space of physical $(N\pm1)$-particle excitations excluding the 1h and 1p configurations. More specifically, the configuration space for the $(N+1)$-particle case $\underline{M}^{\mathrm{I}}(\omega)$ is given by the 2p-1h, 3p-2h,. . ., excitations, while the $(N-1)$-particle case $\underline{M}^{\mathrm{II}}(\omega)$ requires the 2h-1p, 3h-2p,. . ., excitations.

(2) Both the (column) vectors $\underline{U}_p$ and the matrix $\underline{C}$ are determined by perturbation expansions

$$\underline{U}_p=\underline{U}_p^{(1)}+\underline{U}_p^{(2)}+\cdots \;, \tag{32a}$$

$$\underline{C}=\underline{C}^{(1)}+\underline{C}^{(2)}+\cdots \;, \tag{32b}$$

each series starting with a first-order contribution $\underline{U}_p^{(1)}$ and $\underline{C}^{(1)}$, respectively. The matrix $\underline{K}$ is given as the diagonal matrix of zeroth-order (HF) excitation energies, e.g.,

$$K_{jkl,jkl}=-\epsilon_j+\epsilon_k+\epsilon_l, \quad n_n\bar{n}_k\bar{n}_l=1$$

$$K_{ijklm,ijklm}=-\epsilon_i-\epsilon_j+\epsilon_k+\epsilon_l+\epsilon_m \;, \qquad n_in_j\bar{n}_k\bar{n}_l\bar{n}_m=1 \tag{33}$$

for the 2p-1h and the 3p-2h space, respectively.

(3) A set of systematic approximations $\underline{M}(\omega;n)$, $n=2,3,\ldots$, for $\underline{M}^{\mathrm{I,II}}(\omega)$ is obtained by requiring that the form

$$M_{pq}(\omega;n)=\underline{U}_p^{\dagger}(n)[\omega\mathbb{1}-\underline{K}-\underline{C}(n)]^{-1}\underline{U}_q(n) \tag{34}$$

is exact up to $n$th order in the perturbation, that is,

$$M_{pq}(\omega;n)=\sum_{\nu=2}^{n}M_{pq}^{(\nu)}(\omega)+O(n+1)\;. \tag{35}$$

Here, $M_{pq}^{(\nu)}(\omega)$ denotes the $\nu$th-order contribution for the self-energy parts $\underline{M}^{\mathrm{I,II}}(\omega)$ in the diagrammatic perturbation expansion. We shall see, by the explicit construction for $n=2$, 3, and 4, how this comparison enables one to make a unique evaluation of the quantities involved, $\underline{U}_p(n)$ and $\underline{C}(n)$.

(4) The configuration space for the $n$th-order approximation is restricted to the lowest $(m+1)$p-$m$h excitations [$(m+1)$h-$m$p excitations in case II], $m=1,\ldots,[\frac{1}{2}n]$.

We would like to stress that the $n$th-order ADC schemes [ADC ($n$)] defined by Eqs. (34) and (35) represent infinite partial summations for $\underline{M}^{\mathrm{I,II}}(\omega)$ which, by construction, are exact up to $n$th order. The most important point with respect to actual applications is that the configuration space required for the $n$th-order scheme is restricted. For example, the second- and third-order schemes for $\underline{M}^{\mathrm{I}}(\omega)$ and $\underline{M}^{\mathrm{II}}(\omega)$ are formulated within the space of 2p-1h and 2h-1p excitations, respectively. For the fourth-order scheme the 3p-2h excitations (for I), and the 3h-2p excitations (for II) are additionally required.

We finally establish the connection with the calculation of the Green's function via the Dyson equation. For given ADC expressions $\underline{U}_p$ and $\underline{C}$, the matrix inversion problem of Eq. (31) or Eq. (34) is equivalent to the eigenvalue problem

$$(\underline{K}+\underline{C})\underline{Y}=\underline{Y}\underline{\Omega}\;, \tag{36}$$

where $\underline{\Omega}$ and $\underline{Y}$ denote the diagonal matrix of eigenvalues and the matrix of eigenvectors, respectively. The eigenvalues determine the poles of the self-energy parts $\underline{M}^{\mathrm{I,II}}(\omega)$ and the Dyson amplitudes are obtained according to

$$m_p^{(n)}=\underline{U}_p^{\dagger}\underline{Y}^{(n)}\;, \tag{37}$$

where $\underline{Y}^{(n)}$ denotes the $n$th eigenvector. In a second step the Dyson equation can be solved either by resorting to the original form (13) or by the diagonalization according to Eqs. (26) and (27). Obviously, the latter is equivalent to the following diagonalization problem:

$$\underline{B}\underline{X}=\underline{X}\underline{E},\quad \underline{X}^{\dagger}\underline{X}=\mathbb{1}\;, \tag{38a}$$

$$\underline{B}=\begin{bmatrix} \underline{\epsilon}+\underline{\Sigma}^{(\infty)} & (\underline{U}^{\mathrm{I}})^{\dagger} & (\underline{U}^{\mathrm{II}})^{\dagger} \\ \underline{U}^{\mathrm{I}} & \underline{K}^{\mathrm{I}}+\underline{C}^{\mathrm{I}} & 0 \\ \underline{U}^{\mathrm{II}} & 0 & \underline{K}^{\mathrm{II}}+\underline{C}^{\mathrm{II}} \end{bmatrix}. \tag{38b}$$

By arranging the submatrices corresponding to the ionic configurations in the order 1p, 1h, 2p-1h, 2h-1p, 3p-2h, . . . , one arrives at the structure displayed in Fig. 1. It should be observed that in the ADC approach the only coupling between the $(N+1)$- and $(N-1)$-particle configurations occurs via the static self-energy part $\underline{\Sigma}(\infty)$ and the modified coupling amplitudes $\underline{U}_p$; there is no direct coupling between a $(m+1)$p-$m$h block, $m\geq1$, of $N+1$ particles and a $(m'+1)$h-$m'$p block, $m'\geq1$, of $N-1$ particles.

### B. Explicit construction of the ADC schemes

Following the general principles presented in Sec. III A, we shall now explicitly construct the modified coupling amplitudes $\underline{U}_p$ and the modified interaction matrices $\underline{C}$ for the second-, third- and fourth-order ADC schemes.

#### *1. Second and third order*

The second-order contribution to the self-energy part $\underline{M}^{\mathrm{I}}(\omega)$ arising from the diagram of Fig. 2 is given by

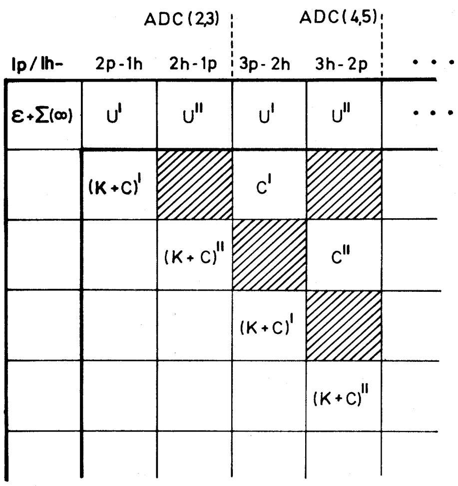


FIG. 1. Structure of the eigenvalue problem [Eq. (38)] for the one-particle Green's function in the ADC approach. Note that there is no direct coupling between $(n+1)$p-$n$h excitations of the $(N+1)$-particle system and $(m+1)$h-$m$h excitations of the $(N-1)$-particle system for $m,n\geq 1$.

$$M_{pq}^{\mathrm{I}(2)}(\omega)=\sum_{j,k<l}\frac{V_{pj[kl]}V_{qj[kl]}^{*}}{\omega+\epsilon_j-\epsilon_k-\epsilon_l}n_j\bar{n}_k\bar{n}_l\ . \tag{39}$$

This expression fits trivially into the algebraic form of Eq. (34) yielding

$$U_{p,jkl}=U_{p,jkl}^{(1)}=V_{pj[kl]}^{*}\ , \tag{40a}$$

$$K_{jkl,jkl}=-\epsilon_j+\epsilon_k+\epsilon_l\ , \tag{40b}$$

$$C_{jkl,j'k'l'}=0\ . \tag{40c}$$

The configuration space is spanned by the 2p-1h excitations

$$(j,k,l),\ \text{with}\ n_j\bar{n}_k\bar{n}_l=1\ \text{and}\ k<l\ . \tag{41a}$$

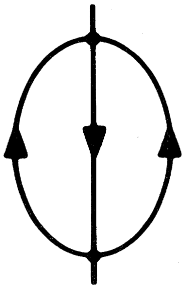


FIG. 2. Second-order time-ordered (Goldstone) diagram for the self-energy part $\underline{M}^{\mathrm{I}}(\omega)$.

For case II the resulting expressions for $\underline{K}$, $\underline{U}_p$, and $\underline{C}$ are formally given also by Eqs. (40a)—(40c). The configuration space, however, is defined by all 2h-1p excitations

$$(j,k,l),\ \text{with}\ \bar{n}_j n_k n_l=1\ \text{and}\ k<l\ . \tag{41b}$$

We note that in the strict second-order scheme the modified interaction matrix $\underline{C}$ vanishes. A straightforward extension can be obtained by employing the first-order expressions for $\underline{C}$ which, strictly speaking, are derived within the third-order scheme discussed below:

$$C_{jkl,j'k'l'}=C_{jkl,j'k'l'}^{(1)}\quad\text{for I}\ , \tag{42a}$$

$$C_{jkl,j'k'l'}=-C_{jkl,j'k'l'}^{(1)}\quad\text{for II}\ , \tag{42b}$$

where

$$\begin{aligned}C_{jkl,j'k'l'}^{(1)}=&\ \delta_{jj'}V_{kl[k'l']}-(\delta_{kk'}V_{j'l[jl']}+\delta_{ll'}V_{j'k[jk']})\\&+(k\leftrightarrow l)\ .\end{aligned} \tag{42c}$$

The resulting approximation scheme for the self-energy part $\underline{M}(\omega)$ is identical with the two-particle-hole Tamm-Dancoff approximation (2p-h—TDA) mentioned in Sec. I.

So that we may construct the third-order ADC equations, we expand the algebraic form of Eq. (34) to third order:

$$\begin{aligned}M_{pq}(\omega;3)&=\underline{U}_p^{\dagger}(3)[\omega\underline{\mathbb{1}}-\underline{K}-\underline{C}(3)]^{-1}\underline{U}_q(3)\\&=\underline{U}_p^{(1)\dagger}[\omega\underline{\mathbb{1}}-\underline{K}]^{-1}\underline{U}_q^{(1)}+\underline{U}_p^{(2)\dagger}[\omega\underline{\mathbb{1}}-\underline{K}]^{-1}\underline{U}_q^{(1)}+\underline{U}_p^{(1)\dagger}[\omega\underline{\mathbb{1}}-\underline{K}]^{-1}\underline{U}_q^{(2)}\\&\quad+\underline{U}_p^{(1)\dagger}[\omega\underline{\mathbb{1}}-\underline{K}]^{-1}\underline{C}^{(1)}[\omega\underline{\mathbb{1}}-\underline{K}]^{-1}\underline{U}_q^{(1)}+O(4)\ .\end{aligned} \tag{43}$$

This expansion starts with the second-order contribution which has already been considered. Since $\underline{U}_p$ is at least of first order, the three third-order contributions on the right-hand side of Eq. (43) involve the second-order terms $\underline{U}_p^{(2)}$ and the first-order term $\underline{C}^{(1)}$. These quantities have to be determined by comparison with the third-order contribution in the diagrammatic perturbation expansion for $\underline{M}^{\mathrm{I}}(\omega)$ or $\underline{M}^{\mathrm{II}}(\omega)$, respectively. In Fig. 3 the third-order diagrams contributing to $\underline{M}^{\mathrm{I}}(\omega)$ are shown. The corresponding analytical expressions have been given elsewhere.[6] The diagrams C1,D1 are easily identified with the last third-order term of Eq. (43). This determines $\underline{C}^{(1)}$. The diagrams C3,D3 and C2,D2

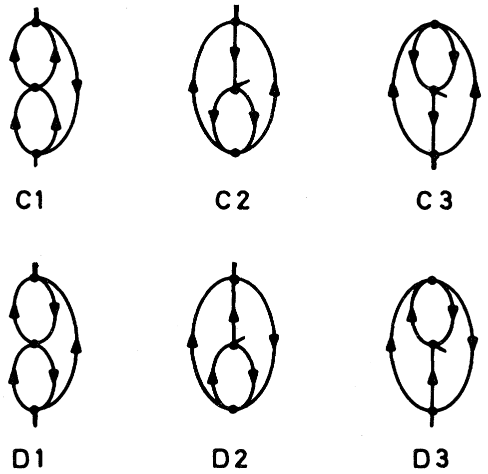


FIG. 3. Time-ordered (Goldstone) diagrams for the self-energy part $\underline{M}^{\mathrm{I}}(\omega)$ in third order.

correspond to the first and the second term of third order, respectively. They allow us to evaluate $\underline{U}_p^{(2)}$. The expressions resulting for the case of $\underline{M}^{\mathrm{I}}(\omega)$ read as follows:

$$U_{p,jkl} = U^{(1)}_{p,jkl} + U^{(2)}_{p,jkl} \,, \tag{44a}$$

$$U^{(2)}_{p,jkl} = -\tfrac{1}{2}\sum_{u,v}\gamma_{kluv}V^*_{pj[uv]}n_u n_v + \left[\sum_{r,v}\gamma_{krvj}V^*_{pr[vl]}\bar{n}_r n_v\right] - (k\leftrightarrow l) \,, \tag{44b}$$

where

$$\gamma_{rsuv} = \frac{V_{rs[uv]}}{\epsilon_r + \epsilon_s - \epsilon_u - \epsilon_v} \,, \tag{44c}$$

$$C_{jkl,j'k'l'} = C^{(1)}_{jkl,j'k'l'} \,. \tag{44d}$$

Here, $U^{(1)}_{p,jkl}$ and $C^{(1)}_{jkl,j'k'l'}$ are given by Eqs. (40a) and (42c), respectively. The configuration space is specified by the definition (41a).

For the case of $\underline{M}^{\mathrm{II}}(\omega)$ the configuration space is defined by (41b), and the results are

$$U_{p,jkl} = U^{(1)}_{p,jkl} - \bar{U}^{(2)}_{p,jkl} \,, \tag{45a}$$

$$C_{jkl,j'k'l'} = -C^{(1)}_{jkl,j'k'l'} \,. \tag{45b}$$

Here, $U^{(1)}_{p,jkl}$ and $C^{(1)}_{jkl,j'k'l'}$ are (formally) given by Eqs. (40a) and (42c), respectively. $\bar{U}_{p,jkl}$ is obtained from the expression (44b) for $\underline{U}^{(2)}_{p,jkl}$ by exchanging the occupation numbers according to $n_s \leftrightarrow \bar{n}_s$:

$$\bar{U}^{(2)}_{p,jkl} \equiv U^{(2)}_{p,jkl}\,(n_i \leftrightarrow \bar{n}_i) \,. \tag{45c}$$

The algebraic form of Eq. (31) implemented with the modified coupling amplitudes $\underline{U}_p$ and the modified interaction matrix $\underline{C}$ as given by Eqs. (44) and (45) constitutes the third-order ADC scheme [ADC(3)] for the self-energy part $\underline{M}(\omega)$. Clearly, this approximation represents an infinite partial summation being exact up to third order in the perturbation. Via the Dyson equation and Eq. (25) one obtains a complete third-order approximation for the one-particle Green's function. As has been mentioned in Sec. I the ADC(3) equations for $\underline{G}$ are essentially equivalent to the third-order EOM equations and to the extended 2p-h—TDA equations. A discussion of the ADC(3) scheme is given in Sec. IV B.

We note that the (third-order) ADC equations reflect the symmetry properties of the underlying Hamiltonian. For a spin-independent Hamiltonian one easily arrives at a spin-free formulation of the ADC equations. For applications to atoms extended 2p-h—TDA [or ADC(3)] working equations have been presented which make use of the full rotation symmetry.[14]

### 2. *Fourth order*

Our construction of the second- and third-order ADC schemes has recovered systematically previous approximation schemes. The particular benefit of this approach, however, will become apparent from the construction of the fourth-order scheme. Certainly, this represents a formidable task: In fourth order, there occur (in Abrikosov notation) 10 Feynman diagrams for $\underline{M}(\omega)$, each generating 24 time orderings (Goldstone diagrams), leading to a total of 240 diagrams—the 120 diagrams contributing to $\underline{M}^{\mathrm{I}}(\omega)$ are shown in Fig. 4. In spite of this at-first-sight intimidating situation, the problem of identifying and evaluating the algebraic entities is surprisingly simple and straightforward, once the diagrams are drawn.

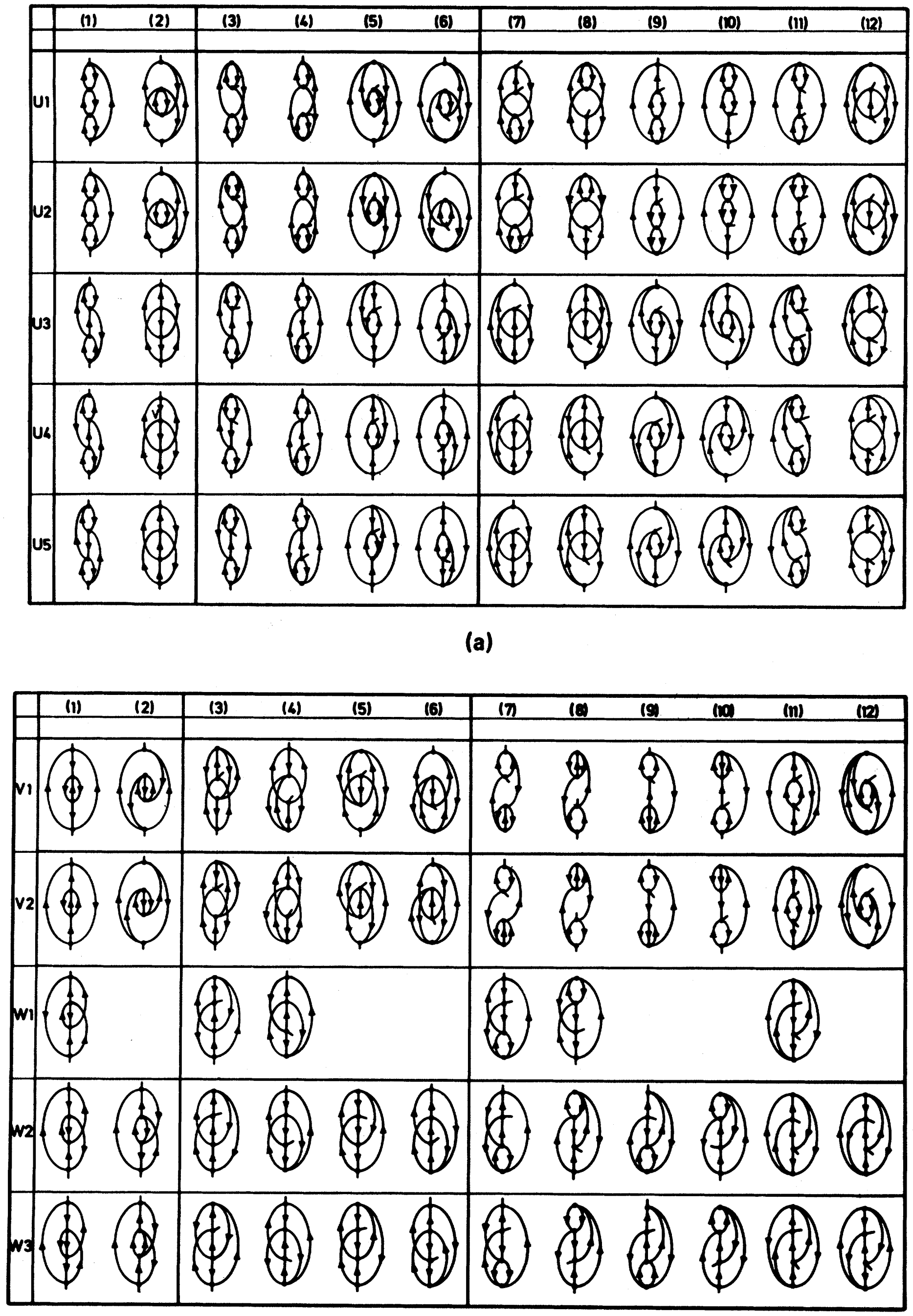
As a new feature of the fourth-order case the configuration space now has to be enlarged by the 3p-2h excitations for $\underline{M}^{\mathrm{I}}(\omega)$ and the 3h-2p excitations for $\underline{M}^{\mathrm{II}}(\omega)$. Consider, for example, the diagram V1(1): According to the diagrammatic rules, each cut between successive vertices introduces an energy denominator of the form

$$(\omega + \epsilon_i + \epsilon_j + \cdots - \epsilon_k - \epsilon_l - \cdots)^{-1} \,,$$

where $i,j,\ldots,$ represent hole and $k,l,\ldots,$ particle lines intersected by the cut. The diagram V1(1) starts with a 2p-1h denominator

$$(\omega + \epsilon_i - \epsilon_k - \epsilon_l)^{-1} \,,$$

proceeds with a 3p-2h denominator



(a)

(b)

FIG. 4. The 120 time-ordered (Goldstone) diagrams for the self-energy part $\underline{M}^{\rm I}(\omega)$ in fourth order. The diagrams contributing to $\underline{M}^{\rm II}(\omega)$ are obtained by turning upside down each diagram in this figure. For the diagram type W1 only six time orderings are shown, since in the Abrikosov notation employed here each two time orderings of the diagram W1 are identical: When all time orderings are counted, one has to introduce a factor $\frac{1}{2}$.

$$(\omega+\epsilon_i+\epsilon_j-\epsilon_k-\epsilon_l-\epsilon_m)^{-1} ,$$

and ends again with a 2p-1h denominator. Obviously, this diagram corresponds to the coupling between 2p-1h and 3p-2h excitations.

The fourth-order terms of the ADC(4) form

$$M^{\rm I}_{pq}(\omega;4)=\underline{U}_p^{\dagger}(4)[\omega\underline{1}-\underline{K}-\underline{C}(4)]^{-1}\underline{U}_q(4) \quad (46)$$

are listed in Table I. Since the modified coupling amplitudes for the 3p-2h (3h-2p) space are at least of

TABLE I. Fourth-order terms of the ADC representation for $M^{\mathrm{I}}_{pq}(\omega)$. The designation by a, b, and c refers to the occurrence of exclusively 2p-1h excitations, of both 2p-1h and 3p-2h excitations, and of exclusively 3p-2h excitations, respectively.

| | Fourth-order terms of $M^{\mathrm{I}}_{pq}(\omega)$ |
|---|---|
| 1a | $\underline{U}_p^{(3)\dagger}(\omega\underline{\mathbb{1}}-\underline{K})^{-1}\underline{U}_q^{(1)}$ |
| | $\underline{U}_p^{(1)\dagger}(\omega\underline{\mathbb{1}}-\underline{K})^{-1}\underline{U}_q^{(3)}$ |
| 2a,2c | $\underline{U}_p^{(2)\dagger}(\omega\underline{\mathbb{1}}-\underline{K})^{-1}\underline{U}_q^{(2)}$ |
| 3a,3b | $\underline{U}_p^{(2)\dagger}(\omega\underline{\mathbb{1}}-\underline{K})^{-1}\underline{C}^{(1)}(\omega\underline{\mathbb{1}}-\underline{K})^{-1}\underline{U}_q^{(1)}$ |
| | $\underline{U}_p^{(1)\dagger}(\omega\underline{\mathbb{1}}-\underline{K})^{-1}\underline{C}^{(1)}(\omega\underline{\mathbb{1}}-\underline{K})^{-1}\underline{U}_q^{(2)}$ |
| 4a,4b | $\underline{U}_p^{(1)\dagger}(\omega\underline{\mathbb{1}}-\underline{K})^{-1}\underline{C}^{(1)}(\omega\underline{\mathbb{1}}-\underline{K})^{-1} \times\underline{C}^{(1)}(\omega\underline{\mathbb{1}}-\underline{K})^{-1}\underline{U}_q^{(1)}$ |
| 5a | $\underline{U}_p^{(1)\dagger}(\omega\underline{\mathbb{1}}-\underline{K})^{-1}\underline{C}^{(2)}(\omega\underline{\mathbb{1}}-\underline{K})^{-1}\underline{U}_q^{(1)}$ |

second order, the following terms are explicitly involved in the fourth-order expansion.

(1) The modified coupling amplitudes for the 2p-1h (2h-1p) space

$$U_{p,jkl}=U^{(1)}_{p,jkl}+U^{(2)}_{p,jkl}+U^{(3)}_{p,jkl} \tag{47}$$

are needed through third order. Here, the first- and second-order contributions have already been obtained and only the third-order term has to be determined from the diagrammatic fourth-order contribution.

(2) The modified coupling amplitudes for the 3p-2h (3h-2p) space,

$$U_{p,ijklm}=U^{(2)}_{p,ijklm}\ , \tag{48}$$

are at least of second order.

(3) The modified interaction matrix $\underline{C}$ can be divided into a 2p-1h (2h-1p) part

$$C_{jkl,j'k'l'}=C^{(1)}_{jkl,j'k'l'}+C^{(2)}_{jkl,j'k'l'} \tag{49}$$

required through second order,

(4) a 2p-1h—3p-2h (2h-1p—3h-2p) interaction part

$$C_{jkl,i'j'k'l'm'}=C^{(1)}_{jkl,i'j'k'l'm'} \tag{50}$$

required in first order.

(5) The 3p-2h (3h-2p) part

$$C_{ijklm,i'j'k'l'm'}=0 \tag{51}$$

vanishes in the strict fourth-order case.

In order to determine the newly occurring terms in the expansions (47)—(51) (and to verify the previous terms) it is necessary to identify the fourth-order contributions listed in Table I with the diagrammatic fourth-order contribution. For most diagrams this identification is quite obvious and the result can be taken from Table II, where the corresponding term of Table I is assigned to each diagram of Fig. 4. As a further specification the symbols (a), (b), and (c) indicate pure 2p-1h, mixed 2p-1h—3p-2h, and pure 3p-2h terms, respectively. Conversely, with the help of Table II one can easily trace all diagrams that contribute to a given algebraic term of the fourth-order contribution for $M^{\mathrm{I}}_{pq}(\omega)$.

Table II shows that most diagrams are assigned to a single algebraic term. However, there is a group of diagrams that do not fit as straightforwardly into the algebraic scheme, namely, the time orderings (2), (5), (6), and (12) of U1, U2, V1, and V2. We consider the diagram U1(2) as an appropriate example. Apparently, this diagram introduces a 4p-3h demoninator

$$(\omega+\epsilon_h+\epsilon_i+\epsilon_j-\epsilon_k-\epsilon_l-\epsilon_m-\epsilon_n)^{-1}$$

and one might conclude that this requires the explicit consideration of the 4p-3h (4h-3p) configurations for the fourth-order ADC scheme. However, as is shown in Appendix A these denominators exactly cancel out if all four time orderings (2), (5), (6), and (12) of the diagram U1 are taken into account. The sum of these diagrams gives contributions to the algebraic terms (1a) and (5a) of Table I, and, as a consequence, introduces third-order contributions

TABLE II. Assignment of the fourth-order diagrams for $M^{\mathrm{I}}_{pq}(\omega)$ to the fourth-order terms of the ADC representations of Table I.

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| U1 | 4a | 1a,5a | 3a | 3a | 1a,5a | 1a,5a | 1a | 1a | 1a | 1a | 2a | 1a,5a |
| U2 | 4a | 1a,5a | 3a | 3a | 1a,5a | 1a,5a | 1a | 1a | 1a | 1a | 2a | 1a,5a |
| U3 | 4a | 4b | 3a | 3a | 3b | 3b | 1a | 1a | 1a | 1a | 2a | 2c |
| U4 | 4a | 4b | 3a | 3a | 3b | 3b | 1a | 1a | 1a | 1a | 2a | 2c |
| U5 | 4a | 4b | 3a | 3a | 3b | 3b | 1a | 1a | 1a | 1a | 2a | 2c |
| V1 | 4b | 1a,5a | 3b | 3b | 1a,5a | 1a | 1a | 1a | 1a | 1a | 2c | 1a,5a |
| V2 | 4b | 1a,5a | 3b | 3b | 1a,5a | 1a | 1a | 1a | 1a | 1a | 2c | 1a,5a |
| W1 | 4b | 4b | 3b | 3b | 3b | 3b | 1a | 1a | 1a | 1a | 2c | 2c |
| W2 | 4b | 4b | 3b | 3b | 3b | 3b | 1a | 1a | 1a | 1a | 2c | 2c |
| W3 | 4b | 4b | 3b | 3b | 3b | 3b | 1a | 1a | 1a | 1a | 2c | 2c |

for $U_{p,jkl}$ and second-order contributions for $C_{jkl,j'k'l'}$.

Now it is a straightforward task to evaluate the essential algebraic terms of Table I that are needed to determine the new terms of $\underline{U}_p$ and $\underline{C}$. For this purpose not all diagrams of fourth order have to be evaluated, although for a verification of the fourth-order scheme one has to carry out the comparison for all diagrams. The resulting expressions for $\underline{U}_p(4)$ and $\underline{C}(4)$, in part somewhat lengthy, are explicitly given by the Eqs. (B1)—(B16) of Appendix B. A discussion of the ADC(4) equations is given in Sec. IV C.

### C. Existence and uniqueness of the ADC

By explicit construction we have shown that the ADC assertions of Sec. III A are valid up to fourth order. We shall now shortly discuss the general justification. Let us consider the spectral representation for the self-energy part $\underline{M}^{\mathrm{I}}(\omega)$, which according to Eqs. (22) and (24) may be written in the form

$$M^{\mathrm{I}}_{pq}(\omega)=\underline{m}_p^{\dagger}(\omega\underline{\mathbb{1}}-\underline{\Omega})^{-1}\underline{m}_q \;, \tag{52}$$

where $\underline{\Omega}$ denotes the diagonal matrix of the energies $\omega_n$ and $\underline{m}_p$ is the (column) vector of the amplitudes $m_p^{(n)*}$. Obviously, this representation is a special form of the ADC representation (31), namely, a form where the modified interaction matrix

$$\underline{C}'=\underline{\Omega}-\underline{K} \tag{53}$$

is diagonal. The general nondiagonal ADC representation follows from Eq. (52) by introducing the "transformed" quantities

$$\underline{U}_p=\underline{Y}\,\underline{m}_p \;, \tag{54a}$$

$$\underline{K}+\underline{C}=\underline{Y}\,\underline{\Omega}\,\underline{Y}^{\dagger} \;, \tag{54b}$$

where $\underline{Y}$ is a unitary matrix

$$\underline{Y}^{\dagger}\underline{Y}=\underline{\mathbb{1}} \;. \tag{54c}$$

Thus, the existence of the ADC representation is readily established. On the other hand, the (column) vectors $\underline{U}_p$ and the matrix $\underline{C}$ are not uniquely determined by Eqs. (54) since the unitary matrix $\underline{Y}$ is not specified and the question arises, whether the ADC approach leads to a unique construction of its basic quantities $\underline{U}_p$ and $\underline{C}$.

In order to clarify the problem of uniqueness it is worthwhile to return to the diagonal representation of Eqs. (52) and (53). The diagonal representation obviously is a distinct mathematical form which leads to a unique construction of the amplitudes $\underline{m}_p$ and the matrix $\underline{C}$. It is interesting to repeat the explicit derivation of the second- and third-order scheme in the diagonal version. In second order the ADC and the diagonal representation are identical since the modified interaction matrices vanish. The diagrammatic third-order contribution contains a "nondiagonal" term, namely, the last term of the right-hand side of Eq. (43),

$$X(1)=\underline{U}_p^{(1)\dagger}(\omega\underline{\mathbb{1}}-\underline{K})^{-1}\underline{C}^{(1)}(\omega\underline{\mathbb{1}}-\underline{K})^{-1}\underline{U}_q^{(1)} \tag{55}$$

which is associated with the diagrams C(1) and D(1) of Fig. 3. In order to arrive at the diagonal representation we write the matrix $\underline{C}^{(1)}$ [given by Eq. (42c) for the case I] as the sum of its diagonal part $\underline{C}'$ and the nondiagonal remainder $\underline{C}''$,

$$\underline{C}^{(1)}=\underline{C}'+\underline{C}'' \;. \tag{56}$$

Thus, the right-hand side of Eq. (55) decomposes into a part containing only genuine quadratic poles $(\omega+\epsilon_j-\epsilon_k-\epsilon_l)^{-2}$ and a part containing mixed products

$$(\omega+\epsilon_j-\epsilon_k-\epsilon_l)^{-1}(\omega+\epsilon_{j'}-\epsilon_{k'}-\epsilon_{l'})^{-1} \;,$$

where

$$(j,k,l)\neq(j',k',l') \;.$$

performing a partial-fraction decomposition for the latter part, one finally arrives at the expression

$$\begin{aligned}X(1)=&\ \underline{U}_p^{(1)\dagger}(\omega\underline{\mathbb{1}}-\underline{K})^{-2}\underline{C}'\underline{U}_q^{(1)}\\&+\underline{\widetilde{U}}_p^{(2)\dagger}(\omega\underline{\mathbb{1}}-\underline{K})^{-1}\underline{U}_q^{(1)}\\&+\underline{U}_p^{(1)\dagger}(\omega\underline{\mathbb{1}}-\underline{K})^{-1}\underline{\widetilde{U}}_q^{(2)} \;,\end{aligned} \tag{57a}$$

where

$$\widetilde{U}^{(2)}_{p,jkl}=\frac{1}{2}\sum_{\substack{j',k',l'\\(j',k',l')\neq(j,k,l)}}\frac{C^{(1)}_{jkl,j'k'l'}V^{*}_{pj'[k'l']}}{\epsilon_j-\epsilon_k-\epsilon_l-\epsilon_{j'}+\epsilon_{k'}+\epsilon_{l'}} \;. \tag{57b}$$

Obviously, the right-hand side of Eq. (57a) now fits into the diagonal representation. Together with the remaining two third-order terms of Eq. (43) corresponding to the diagrams C2, C3, D2, and D3 this leads to the coupling amplitudes

$$m_p^{(jkl)*}=U^{(1)}_{p,jkl}+U^{(2)}_{p,jkl}+\widetilde{U}^{(2)}_{p,jkl} \tag{58a}$$

and matrix elements

$$C'_{jkl,j'k',l'}=\delta_{jj'}\delta_{kk'}\delta_{ll'}C^{(1)}_{jkl,jkl} \tag{58b}$$

of the diagonal third-order representation.

Here (for the case I) $U^{(1)}_{p,jkl}$, $U^{(2)}_{p,jkl}$, $\widetilde{U}^{(2)}_{p,jkl}$, and $C^{(1)}_{jkl,jkl}$ are given by Eqs. (40a), (44b), (57b), and (42c), respectively. Proceeding in this way one may generate direct Rayleigh-Schrödinger perturbation expansions for the poles $\omega_n$ and the Dyson amplitudes $m_p^{(n)}$ of the self-energy part $\underline{M}(\omega)$. As can be seen by inspection of the term $\tilde{U}^{(2)}_{p,jkl}$ of Eq. (57b), these Rayleigh-Schrödinger—type expansions contain terms with "dangerous" denominators, i.e., demoninators which are given as the differences of (zeroth-order) excitation energies for excitations within the same class, e.g., 2p-1h excitations. Such dangerous denominators do not occur in the ADC expansions.

As the construction of the diagonal representation in third order has shown, it is possible to transfer nondiagonal contributions of the ADC matrix $\underline{C}$ into the modified coupling amplitudes $\underline{U}_p$. Conversely, it is easily established (for the orders considered so far) that it is not possible to transfer contributions of the ADC amplitudes $\underline{U}_p$ into the matrix $\underline{C}$. In this sense the matrix $\underline{C}$ constructed by the ADC is "maximally nondiagonal" and thus represents a distinct mathematical form as opposed to the other form, namely, the diagonal representation. One may also say the ADC representation is obtained from the diagonal representation by transferring all terms with dangerous denominators in the expansion of the amplitudes $m_p^{(n)}$ into the interaction matrix $\underline{C}$, which in the ADC approach is subject to a full diagonalization. In this sense the ADC may be regarded as an advantageous combination of a diagonalization problem and perturbation theory.

Finally we would like to draw attention to an obvious generalization of the scope of the ADC scheme. The modified coupling amplitudes $\underline{U}_p$ are obtained as linear forms in the "outer" Coulomb matrix elements $V_{pj[kl]}$. By replacing the outer Coulomb matrix elements in $\underline{U}_p$ and $\underline{U}_q$ by (arbitrary) matrix elements $Z_{jkl} \leftarrow V_{pj[kl]}$ and $Z'_{jkl} \leftarrow V_{qj[kl]}$ the ADC form (31) can provide the general transition function $T(\omega)=\underline{Z}^{\dagger}\underline{\Pi}(\omega)\underline{Z}'$ and, in particular, the components of the 2p-h propagator $\underline{\Pi}(\omega)$ itself.

## IV. DISCUSSION OF THE ADC SCHEMES FOR THE ONE-PARTICLE GREEN'S FUNCTION

In order to obtain a better understanding of the ADC approximations for $\underline{M}(\omega)$ and $\underline{G}(\omega)$ presented in the preceding section it is useful to compare the results of the ADC approach with those of the familiar wave-function description for the $N$-particle ground state and the $(N\pm 1)$-particle ionic states. As a tool for this analysis we shall consider the lowest-order expressions for the ionization energies and for the transition amplitudes resulting from the Green's function approach as well as the expressions derived by the conventional Rayleigh-Schrödinger perturbation expansions.[34–36]

### A. Second-order approximation

We start our discussion by considering the simple second-order approximation for the self-energy [ADC(2)]; although $\underline{M}^{(2)}(\omega)$ represents only a finite summation for the self-energy one obtains an infinite partial summation for $\underline{G}(\omega)$ by the Dyson equation, whereby the peculiar coupling between $(N+1)$- and $(N-1)$-particle configurations also comes into play: It is interesting to clarify the effect of this mathematical device, which is specific to the Green's-function approach.

#### 1. *Ionization energies*

Let us consider the ionic main state $|\Psi_q^{N-1}\rangle$ of the $(N-1)$-particle system which derives (in the sense of the adiabatic theorem) from the unperturbed hole configuration

$$|\Phi_q^{N-1}\rangle = c_q\,|\Phi_0\rangle \;. \tag{59}$$

Here, $|\Phi_0\rangle$ denotes the Hartree-Fock ground state. The energy up to second order $E_0^N(2)$ of the exact $N$-particle ground state is given by the Rayleigh-Schrödinger expression

$$E_0^N(2)=E_0^N(1)-\sum_{\substack{i<j\\ k<l}} \frac{|V_{ij[kl]}|^2}{\epsilon_i+\epsilon_j-\epsilon_k-\epsilon_l}\,\bar{n}_i\bar{n}_j n_k n_l \;, \tag{60}$$

where

$$E_0^N(1)=\langle\Phi_0|\hat{H}|\Phi_0\rangle \tag{61}$$

is the first-order ground-state energy. The energy of the ionic state up to second order reads

$$E_q^{N-1}(2)= E_0^N(1)-\epsilon_q+W_q(\text{2h-1p}) + W_q(\text{3h-2p}) \;, \tag{62}$$

where the terms

$$W_q(\text{2h-1p})=-\sum_{j,k<l} \frac{|V_{qj[kl]}|^2}{\epsilon_q+\epsilon_j-\epsilon_k-\epsilon_l}\,\bar{n}_j n_k n_l \tag{63a}$$

and

$$W_q(\text{3h-2p})=-\sum_{\substack{i<j\\ k<l\neq q}} \frac{|V_{ij[kl]}|^2}{\epsilon_i+\epsilon_j-\epsilon_k-\epsilon_l}\,\bar{n}_i\bar{n}_j n_k n_l \tag{63b}$$

arise from the interaction of the ionic configuration $|\Phi_q\rangle$ with the 2h-1p and the 3h-2p excitations, respectively. The interaction $W_q(\text{1h})$ of $|\Phi_q\rangle$ with other hole configurations $|\Phi_p\rangle$, $p\neq q$, gives no second-order contribution according to Brillouin's theorem. Now the second-order ionization energy $I_q(2)$ follows by subtracting Eq. (60) from Eq. (62):

$$\begin{aligned} I_q(2) &= E_q^{N-1}(2) - E_0^N(2) \\ &= -\epsilon_q + W_q(\text{2h-1p}) + R_q \ . \end{aligned} \tag{64a}$$

Here,

$$R_q = - \sum_{j,k<l} \frac{|V_{qj[kl]}|^2}{\epsilon_q + \epsilon_j - \epsilon_k - \epsilon_l} n_j \bar{n}_k \bar{n}_l \tag{64b}$$

is the remainder of a partial cancellation of the 3h-2p contribution $W_q(\text{3h-2p})$ for the ionic state and the 2p-2h contribution for the ground state. A straightforward perturbation analysis of $I_q$ within the Green's-function approach yields the following second-order expression:

$$I_q(2) = -\epsilon_q - M_{qq}^{\text{I}(2)}(\epsilon_q) - M_{qq}^{\text{II}(2)}(\epsilon_q) \ , \tag{65}$$

where $\underline{M}_{qq}^{\text{I,II}(2)}(\omega)$ are given by Eqs. (31), (40), and (41).

Comparing the right-hand side of Eqs. (64) and (65) one immediately identifies the self-energy contributions I and II with $R_q$ and $W_q$ (2h-1p), respectively. This allows an interpretation of the role of the two second-order self-energy contributions. As expected, the $(N-1)$-particle part $\underline{M}^{\text{II}}(\omega)$ introduces the coupling of the one-hole configurations with the 2h-1p excitations. The $(N+1)$-particle part $\underline{M}^{\text{I}}(\omega)$, on the other hand, accounts simultaneously for the (second-order) ground-state correlation and for the interaction of the one-hole configurations with the 3h-2p excitations of the $(N-1)$-particle system. Thus, we see clearly the effect of the coupling of the $(N-1)$- and $(N+1)$-particle spaces in the Green's-function approach. Within a wave-function approach, e.g., the conventional configuration interaction (CI), one has to perform a double (2p-2h) excitation CI calculation for the ground state and a 1h, 2h-1p, plus 3h-2p CI calculation for the ionic states in order to obtain the (main) ionization energies consistent through second order. The second-order [ADC(2)] approximation for the Green's function $\underline{G}$, on the other hand, achieves this result by one diagonalization within the configuration space of 1h, 1p, 2h-1p, and 2p-1h excitations of $N \pm 1$ particles. The 1h—2p-1h and 1p—2p-1p coupling matrix elements cannot be derived within a wave-function approach.

### 2. *Transition amplitudes*

A similar analysis can be performed for the transition amplitudes

$$x_p^{(q)} = \langle \Psi_q^{N-1} | c_p | \Psi_0 \rangle \tag{66}$$

of the ionic main state $|\Psi_q^{N-1}\rangle$ considered above. Within the Green's-function approach $x_p^{(q)}$ is obtained as the $p$th component of the eigenvector corresponding to the solution $|\Psi_q^{N-1}\rangle$ for the eigenvalue problem (38) where, in the second-order scheme [ADC(2)], the matrix elements are given by Eqs. (40) and (41). Obviously, the second-order scheme reproduces the transition amplitude exactly to second order, that is,

$$x_p^{(q)}(2) = \begin{cases} 1 - \frac{1}{2} \sum\limits_{j,k<l} |V_{qj[kl]}|^2 (n_j \bar{n}_k \bar{n}_l + \bar{n}_j n_k n_l), & p = q \\ \sum\limits_{j,k<l} \dfrac{V_{pj[kl]} V_{qj[kl]}}{(\epsilon_q + \epsilon_j - \epsilon_k - \epsilon_l)(\epsilon_p - \epsilon_q)} (n_j \bar{n}_k \bar{n}_l + \bar{n}_j n_k n_l), & p \neq q . \end{cases} \tag{67}$$

We note that no first-order contributions occur.

Again, we compare these expressions with the result of the direct perturbation expansions for the wave functions $|\Psi_0\rangle$ and $|\Psi_q^{N-1}\rangle$ in Eq. (66):

$$x_p^{(q)}(2) = \langle c_q \Phi_0 | c_p | \Phi_0 \rangle + \langle c_q \Phi_0 | c_p | \Psi_0^{(2)} \rangle + \langle \Psi_q^{(2)} | c_p | \Phi_0 \rangle + \langle \Psi_q^{(1)} | c_p | \Psi_0^{(1)} \rangle \ . \tag{68}$$

Here, $|\Psi_q^{(\nu)}\rangle$ and $|\Psi_0^{(\nu)}\rangle$ denote the $\nu$th-order ionic- and ground-state wave functions, respectively. We may further specify the contributions on the right-hand side of Eq. (68) with respect to those $n$p-$m$h configurations $|\Psi^{(\nu)}(n\text{p-}m\text{h})\rangle$ which are involved. As a result, Eq. (68) can be written as

$$x_p^{(q)}(2) = \begin{cases} 1 + A_q^{(2)} + A_0^{(2)} + \langle \Psi_q^{(1)}(\text{3h-2p}) | c_p | \Psi_0^{(1)}(\text{2p-2h}) \rangle, & p = q & \text{(69a)} \\ \langle \psi_q^{(2)}(\text{1h}) | c_p | \Psi_0 \rangle + \langle \Psi_q^{(1)}(\text{3h-2p}) | c_p | \Psi_0^{(1)}(\text{2p-2h}) \rangle, & p \neq q, \ n_p = 1 & \text{(69b)} \\ \langle c_p \Phi_0 | c_p | \Psi_0^{(2)}(\text{1p-1h}) \rangle + \langle \Psi_q^{(2)}(\text{2h-1p}) | c_p | \Psi_0^{(1)}(\text{2p-2h}) \rangle, & p \neq q, \ n_p = 0. & \text{(69c)} \end{cases}$$

Here, $A_q^{(2)}$ and $A_0^{(2)}$ denote the second-order contributions for the normalization factors of the ionic- and ground-state wave functions, respectively. These terms and the remaining terms of Eq. (69) can easily be evaluated explicitly and one may check that indeed the expressions of Eq. (67) are reproduced. From Eq. (69) it can be seen that the correct wave-function description for the second-order transition amplitudes requires a single- plus double-excitation CI for the ground-state wave function and a 1h, 2h-1p, plus 3h-2p CI for the ionic state.

### 3. *Higher excited ionic states*

Besides the ionic main states considered so far there occur secondary states (satellites) in the spectrum which are related to higher excited ionic configurations, e.g., the 2h-1p excited states $|\Psi_{jkl}\rangle$ which derive (in the sense of the adiabatic theorem) from the 2h-1p excitations

$$|\Phi_{jkl}\rangle = c_j^\dagger c_k c_l\,|\Phi_0\rangle,\quad \bar{n}_j n_k n_l = 1\ . \tag{70}$$

The 2h-1p excited states (and the 2p-1h excited states of $N+1$ particles) are explicitly considered in the second-order approach [ADC(2)] for $\underline{G}(\omega)$. Since their transition moments

$$x_p^{(jkl)} = \langle \Psi_{jkl}\,|\,c_p\,|\,\Psi_0\rangle \tag{71}$$

have no zeroth-order contribution,

$$x_p^{(jkl)}(0) = \langle \Phi_{jkl}\,|\,c_p\,|\,\Phi_0\rangle = 0\ , \tag{72}$$

the consistency of $\underline{G}(\omega)$ through second order implies that the transition amplitudes and ionization energies (electron affinities) of these states are consistent through first and zeroth order, respectively. A straightforward extension of the strict second-order scheme, namely, the consideration of the first-order interaction matrix $\underline{C}^{(1)}$ for the 2h-1p (2p-1h) excitations according to Eqs. (42) in the 2p-h—TDA scheme, yields also the ionization energies

$$I_{jkl} = \epsilon_j - \epsilon_k - \epsilon_l + C^{(1)}_{jkl,jkl} + O(2) \tag{73}$$

exact up to first order.

Within the wave-function description the consistency of the transition amplitudes $x_p^{(jkl)}$ through first order requires the first-order wave functions for the ground state and for the ionic state. The latter can be written as

$$\begin{aligned}|\Psi_{jkl}(1) = {} & |\Phi_{jkl}\rangle + |\Psi^{(1)}_{jkl}(1\text{h})\rangle \\ & + |\Psi^{(1)}_{jkl}(2\text{h-}1\text{p})\rangle + |\Psi^{(1)}_{jkl}(3\text{h-}2\text{p})\rangle \\ & + |\Psi^{(1)}_{jkl}(4\text{h-}3\text{p})\rangle\ ,\end{aligned} \tag{74}$$

where, similarly to Eq. (69), the first-order contributions are specified according to the respective $(n+1)$h-$n$p excitations. Only the 1h part $|\Psi^{(1)}_{jkl}(1\text{h})\rangle$ of the ionic wave function contributes to the first-order transition amplitudes

$$x_p^{(jkl)}(1) = \begin{cases} \langle \Psi^{(1)}_{jkl}(1\text{h-}0\text{p})\,|\,c_p\,|\,\Phi_0\rangle, & n_p = 1 \\ \langle \Phi_{jkl}\,|\,c_p\,|\,\Psi_0^{(1)}(2\text{p-}2\text{h})\rangle, & n_p = 0. \end{cases} \tag{75}$$

The explicit expression reads

$$x_p^{(jkl)}(1) = \frac{V_{pj[kl]}}{\epsilon_p + \epsilon_j - \epsilon_k - \epsilon_l}\ , \tag{76}$$

which is readily identified as the component of the first-order eigenvector for the solution $|\Psi_{jkl}\rangle$ of the eigenvalue problem (38) in the second-order approach.

## B. Third-order ADC scheme

As we have seen, the ADC(3) scheme (or extended 2p-h—TDA) defined by Eqs. (43) and (44) represents an infinite partial summation for the dynamic self-energy part $\underline{M}(\omega)$ which is complete through third order. Via the Dyson equation (13) using either the form (26) or (38), one obtains the ADC(3) approximation for $\underline{G}(\omega)$. Here, one has to employ a consistent static self-energy part $\underline{\Sigma}(\infty)$ that is at least complete through third order. As has been outlined in Sec. III B, the static part can be determined self-consistently from the approximation for $\underline{M}(\omega)$. Alternatively, one may use the third-order expression $\underline{\Sigma}^{(3)}(\infty)$ as obtained from the diagrammatic perturbation theory. In the latter case the ADC(3) working equations are identical with the third-order EOM equations.[18,22–24]

The explicit configuration space employed for the ADC(3) approach for $\underline{G}(\omega)$ is identical to that of the strict second-order scheme and of the 2p-h—TDA scheme, that is, it comprises the 1h and 2h-1p excitations of $N-1$ particles plus the 1p and 2p-1h excitations of $N+1$ particles. With respect to the 2p-h—TDA, the only modification consists in replacing the first-order coupling amplitudes $V_{pj[kl]}$ with the modified coupling amplitudes $U_{p,jkl}$, which are of second order in the perturbation.

For the ionic main states the resulting energies and transition amplitudes are now treated consistently through third order (see Table III). Again, it is instructive to compare in third order the Green's-function results with the expressions resulting from the perturbation expansion for the wave functions. However, since here the explicit expressions are already somewhat lengthy we restrict ourselves to a brief sketch of the procedure. The

Rayleigh-Schrödinger perturbation theory yields four contributions of third order:

$$I_q^{(3)} = W_q^{(3)}(\text{2h-1p}) + W_q^{(3)}(\text{3h-2p}) + W_q^{(3)}(\text{2h-1p—3h-2p}) - W_0^{(3)}(\text{2p-2h}) \tag{77}$$

for the ionization energy of the ionic state $|\Psi_q\rangle$ of Eq. (59). The first three terms on the right-hand side denote contributions to the ionic energy, the fourth term denotes the third-order contribution to the ground-state energy. All terms are specified according to the contributing configurations. The third-order contribution for the ionization energy within the ADC(3) scheme for $\underline{G}$ is readily obtained from a straightforward matrix perturbation theory for the diagonalization problem (38):

$$I_q^{(3)} = \Sigma_{qq}^{(3)}(\infty) + \{[\underline{U}_q^{(1)}(\epsilon_q \underline{\mathbb{1}} - \underline{K})^{-1}\underline{C}^{(1)}(\epsilon_q \underline{\mathbb{1}} - \underline{K})^{-1}\underline{U}_q^{(1)}]^{\text{I}} + (\cdots)^{\text{II}}\} + \{[\underline{U}_q^{(2)}(\epsilon_q \underline{\mathbb{1}} - K)^{-1}\underline{U}_q^{(1)} + \text{c.c.}]^{\text{I}} + (\cdots)^{\text{II}}\}\ . \tag{78}$$

The ADC(3) expressions for $\underline{U}_p$ and $\underline{C}$ are given in Eqs. (43) and (44). The third-order contribution $\Sigma_{qq}^{(3)}(\infty)$ for the static self-energy part can be taken from Ref. 6.

The comparison of the expressions in Eqs. (77) and (78) is somewhat more intricate than in the second-order case. Only the second term on the right-hand side of Eq. (78) can directly be identified with the contribution $W_q^{(2)}(\text{2h-1p})$ of the wave-function approach in Eq. (77). The remaining four terms of Eq. (78) reproduce in a complicated way the remaining three terms of Eq. (77) which we shall not discuss further at this point. We mention that the CI spaces required for a consistent second-order treatment also allow consistency through third order for the main ionization energies. This does not apply to the transition amplitudes $x_p^{(q)}$. Here, the analysis of the third-order contributions shows that already 3p-3h excitations have to be considered for the ground-state wave function.

We finally note that the energies of the higher excited 2h-1p (2p-1h) states are, as in the 2p-h—TDA, treated consistently through first order, whereas the transition amplitudes are already exact to second order.

### C. Beyond third order

Certainly, the most remarkable achievement of the general ADC approach is the explicit construction of the fourth-order scheme [ADC(4)] defined by the Eqs. (B1)—(B16) of Appendix B, and we would emphasize that the ADC(4) constitutes infinite partial summations for the self-energy $\underline{M}(\omega)$ and (via the Dyson equation) for the Green's function $\underline{G}(\omega)$ which are complete up to fourth order. Concomitantly, the ionization (attachment) energies and the transition amplitudes for the ionic main states are treated consistently through fourth order. In the wave-function picture this means that one has to employ all excitations up to 4p-4h excitations (quadruple excitations) for the ground state and all excitations up to 5h-4p (5p-4h) excitations for the ionic states. The explicit ADC(4) space for $\underline{G}(\omega)$, on the other hand, is spanned by the 1h, 2h-1p, and 3h-2p excitations of $N-1$ particles and the 1p, 2p-1h, and 3p-2h excitations of $N+1$ particles. Again, this shows that in the ADC approach both the ground-state correlation and the effect of higher excitations (here 4h-3p, 5h-4p, or 4p-3h, 5p-4h) on the ionic states are implicitly taken into account by means of the coupling of the $(N+1)$- and the $(N-1)$-particle spaces in the Dyson equation and by the use of higher-order matrix elements for $\underline{C}$ and $\underline{U}_p$.

Of particular importance is the improvement achieved for the secondary 2h-1p (2p-1h) excited states: In the ADC(4) scheme their ionization (attachment) energies and the transition amplitudes are

TABLE III. Orders of consistent treatment for ionization/attachment energies $I_n$ and transition amplitudes $x_p^{(n)}$ in the first ADC approximations.

| | Main state | | | Secondary states | | | |
|---|---|---|---|---|---|---|---|
| | 1h, 1p | | 2h-1p, 2p-1h | | 3h-2p, 3p-2h | | · · · |
| | $I_q$ | $x^{(q)}$ | $I_{jkl}$ | $x^{(jkl)}$ | $I_{jklm}$ | $x^{(ijklm)}$ | · · · |
| ADC(2) | 2 | 2 | 0 | 1 | | | · · · |
| 2p-h—TDA | 2 | 2 | 1 | 1 | | | · · · |
| ADC(3) | 3 | 3 | 1 | 2 | | | · · · |
| ADC(4) | 4 | 4 | 2 | 3 | 0 | 2 | · · · |

calculated consistently through second and third order, respectively. With respect to the energies this means that the ground-state correlation is correctly described through second order. Furthermore, the contributions of the ionic 4h-3p (4p-3h) excitations which are not present in the ADC(4) space, are implicitly taken into account.

In the fourth-order scheme the 3h-2p and 3p-2h excitations, which implicitly have been considered already in second order, are introduced explicitly, thus making the next higher class of secondary states, namely, the 3h-2p (3p-2h) excited states, accessible to calculation in the Green's-function approach. Since the transition amplitudes of these states are at least of second order, the ADC(4) scheme treats the transition amplitudes and the energies consistently through second and zeroth order, respectively. Similar to the extension of the strict second-order scheme (2p-h—TDA), the ADC(4) may be extended by introducing the first-order contribution $\underline{C}^{(1)}$ for the 3h-2p (3p-2h) block [see Eqs. (B10) and (B16) of Appendix B]. In this case the ionization (attachment) energies obtained are exact up to first order.

The result that the transition amplitudes for the 3h-2p (3p-2h) excited states vanish in first order is not trivial. To see this, let us consider the 3h-2p excited state $|\Psi_{ijklm}\rangle$ associated with the unperturbed configuration

$$|\Phi_{ijklm}\rangle = c_i^\dagger c_j^\dagger c_k c_l c_m |\Phi_0\rangle, \quad \bar{n}_i \bar{n}_j n_k n_l n_m = 1 \ . \tag{79}$$

For the transition amplitudes

$$x_p^{(ijklm)} = \langle \Psi_{ijklm} | c_p | \Psi_0 \rangle \tag{80}$$

there occur two nonvanishing first-order contributions,

$$x_p^{(ijklm)} = \langle \Psi_{ijklm}^{(1)}(1\mathrm{h}) | c_p | \Phi_0 \rangle + \langle \Phi_{ijklm} | c_p | \Psi_0^{(1)}(2\mathrm{p}\text{-}2\mathrm{h}) \rangle \ , \tag{81}$$

arising from the hole excitations $|\Psi_{ijklm}^{(1)}(1\mathrm{h})\rangle$ of the ionic state and the 2p-2h excitations $|\Psi_0^{(1)}(2\mathrm{p}\text{-}2\mathrm{h})\rangle$ of the ground state. It is readily verified that both contributions cancel each other.

As we have seen explicitly, the transition moments of the 2h-1p (2p-1h) and 3h-2p (3p-2h) excited states are at least of first and second order, respectively. This finding can easily be generalized: The transition amplitudes for $(n+1)$h-$n$p and $(n+1)$p-$n$h excited states, $n=0,1,\ldots$, are at least of order $n$ in the perturbation:

$$\langle \Psi^{N-1}_{(n+1)\mathrm{h}\text{-}n\mathrm{p}} | c_p | \Psi_0^N \rangle \equiv O(n) \ , \tag{82a}$$

$$\langle \Psi^{N+1}_{(n+1)\mathrm{p}\text{-}n\mathrm{h}} | c_p | \Psi_0^N \rangle \equiv O(n) \ . \tag{82b}$$

A proof of this assertion is found in Appendix C. Here we mention an immediate consequence of this property: Inspection of the spectral representation (4) of $\underline{G}$ shows that the $(n+1)$h-$n$p and $(n+1)$p-$n$h excited states occur explicitly in $\underline{G}$ in (and beyond) the order $2n$, $n=0,1,\ldots$. To state this differently we may say that in each even order of $\underline{G}$ the next higher class of excitations comes explicitly into consideration. This proves the rule (4) of Sec. III A.

Within the framework of the EOM and the equivalent superoperator formalism one arrives, in general, at secular equations that are structurally related to the ADC equations. The EOM equations also exhibit the coupling between the $(N+1)$- and $(N-1)$-particle spaces and the respective configuration spaces are constructed in terms of the physical ionic excitations 1p, 1h, 2p-1h, 2h-1p, etc. In particular, second- and third-order schemes have been derived that are essentially equivalent to the ADC(2) and the ADC(3) scheme, respectively.[18,22–25] On the other hand, there are obvious differences between the two procedures. The basic EOM equation is formulated in terms of ground-state expectation values of exact excitation operators. Approximation schemes result by expanding the exact excitation operators in terms of basis operators and by employing a finite Rayleigh-Schrödinger expansion for the ground state. This procedure introduces several problems which render the derivation of extended approximation schemes increasingly complicated. First, we note that in the EOM approach the restriction to the physical 1p, 1h, 2p-1h,... excitation operators is by no means obvious.[24] One cannot rule out the necessity to employ "unphysical" excitation operators, e.g., 3p(3h) operators, in the basis in order to be complete. Second, the resulting secular matrices are not *a priori* Hermitian and it is not clear in which way the non-Hermiticity should preferably be dealt with. Third, the basic excitations are not orthogonal and, moreover, the nonorthogonality depends on the approximation employed for the ground state. Finally, we remark that the derivation of a consistent higher-order approximation scheme requires in general a rather high-order expansion of the ground-state wave function. For example, the second-order ground-state wave function is needed for the derivation of the third-order equations. Besides the formal differences between the EOM and the diagrammatic approach the resulting equations also seem to be essentially different beyond third order. According to Herman *et al.*[27] the EOM method introduces direct second-order coupling matrix elements between the 2p-1h and 2h-1p excitations of $N+1$ and $N-1$ particles, respectively, which do not appear in the ADC scheme.

## V. CONCLUSIONS

The algebraic diagrammatic construction (ADC) presented in this article reformulates the diagrammatic perturbation expansion for the dynamic self-energy part $\underline{M}(\omega)$ in terms of an exact algebraic form. The poles of $\underline{M}(\omega)$ are derived as the eigenvalues $\omega_k$ of the Hermitian modified interaction matrix $\underline{K}+\underline{C}$ and the Dyson amplitudes $m_p^{(k)}$ are obtained as the products of the eigenvectors $\underline{X}^{(k)}$ and the vectors of modified transition amplitudes $\underline{U}_p$. The configuration space for the ADC equation is spanned by the physical $(n+1)$p-$n$h excitations of $N+1$ particles and by the physical $(n+1)$h-$n$p excitations of $N-1$ particles, $n=1,2,\ldots$. There is no coupling between the $(N+1)$-particle space I and the $(N-1)$-particle space II and both self-energy parts $\underline{M}^{\mathrm{I}}(\omega)$ and $\underline{M}^{\mathrm{II}}(\omega)$ can be calculated independently. The matrix elements of $\underline{C}$ and $\underline{U}_p$ are defined by perturbation expansions which can be constructed successively by comparison with the lowest orders of the diagrammatic expansion for $\underline{M}(\omega)$. The modified transition amplitudes $\underline{U}_p$ are hereby obtained as linear forms in the "outer" two-particle interaction (Coulomb) matrix elements $V_{pr[st]}$. This allows the determination of the (more general) 2p-h—polarization propagator $\underline{\Pi}(\omega)$ and any transition function of the form $T(\omega)=\underline{Z}^{\dagger}\underline{\Pi}(\omega)\underline{Z}'$, where $\underline{Z}$ and $\underline{Z}'$ denote vectors of arbitrary transition matrix elements $Z_{jkl}$.

The general ADC scheme defines in a natural and systematic way a set of $n$th-order approximations $\underline{M}(\omega;n)\rightarrow\underline{M}(\omega)$, $n=2,3,\ldots$, representing infinite partial summations complete through $n$th order. Here, one employs low-order expansions $\underline{U}_p(n)$ and $\underline{C}(n)$ for the modified transition amplitudes and the modified interaction matrix, respectively. We emphasize that the $n$th-order equations are Hermitian and that the required configuration space is restricted to low excited configurations. Via the Dyson equation the $n$th-order ADC approximation for $\underline{M}(\omega)$ induces a consistent approximation for the one-particle Green's function. We note that the Dyson equation introduces an explicit coupling between the spaces of $N+1$ and $N-1$ particles. With respect to this feature the Green's-function approach differs markedly from the conventional wave-function approach. Another difference is the instance that the ADC equations employ effective matrix elements which are no longer first-order expressions in the two-particle interaction, but which include higher-order terms. As the analysis of the ADC results in the lowest orders of perturbation theory has demonstrated, these means allow, on the one hand, a consistent consideration of the ground-state correlation and, on the other hand, the implicit consideration of higher excited ionic configurations that are not taken into account in the explicit configuration space.

The second-, third-, and fourth-order ADC schemes have been explicitly constructed and discussed. The ADC(2) scheme is trivial and recovers the well-known second-order approximation for the self-energy. The corresponding approximation for $\underline{G}(\omega)$ treats the ionization energies and transition amplitudes of the ionic main states consistently through second order. This means that in a wave-function picture one has to employ 2p-2h excitations for the ground state and up to 3h-2p (3p-2h) excitations for the ionic states, which are not contained in the configuration space of the second-order scheme. However, as is well known,[37] the second-order approximation does not provide accurate results for the main ionization energies and one has to proceed to an approach which is at least complete through third order.

The third-order [ADC(3)] equations have been identified with previously derived approximations, namely, the third-order EOM (Refs. 18 and 22—24) and the extended 2p-h—TDA equations.[14] In this approximation the ionic main states are treated consistently through third order and, as a consequence, quite accurate results are obtained.[14,15] The higher excited (2h-1p, 2p-1h) ionic states are treated consistently through first order which allows for a qualitatively adequate description of the energy regions where these higher excited ionic states play a major role.[13] These properties designate the ADC(3) scheme as a useful standard method for generating theoretical ionization (and attachment) spectra.

The fourth-order scheme [ADC(4)] constitutes from both a theoretical and a practical point of view a decisive step beyond previous approaches. It allows the incorporation in a systematic and transparent way of the large bulk of fourth-order diagrams and it enables us to interpret the various contributions in terms of the simpler expansion of the ADC representation. The ADC(4) approximation for the one-particle Green's function yields the ionization (attachment) energies and the transition amplitudes of the main ionic states exact up to fourth order. In order to achieve consistency through this order within the wave-function treatment one has to consider up to 4p-4h excitations for $|\Psi_0\rangle$ and up to 5h-4p (5p-4h) excitations for the ionic states of the $(N\mp1)$-particle system. A decisive improvement of the results with respect to the ADC(3) scheme can be expected for the higher 2h-1p (2p-1h) excited states, which now are treated consistently through second order. As has been mentioned, the adequate treatment of these secondary states is particularly important for the inner valence and the core region, which may now become accessible to an even quantitatively good description. However, it is apparent that the numerical requirements of the ADC(4) scheme surmount those of the ADC(3) considerably and that further approximations have to be introduced in order to cope with the large matrices which are to be diagonalized.

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## APPENDIX A: FOURTH-ORDER DIAGRAMS WITH A SEVEN-LINE CUT

In fourth order there occur 16 diagrams, namely, the time orderings (2), (5), (6), and (12), for U1, U2, V1, and V2, which introduce 4p-3h (4h-3p) denominators. In the following we shall demonstrate explicitly that these denominators cancel out. We shall restrict ourselves to the diagrams U2. The treatment of the other cases is analogous. The sum $D$ of the four U2 diagrams

$$\mathrm{U2}(2)+\mathrm{U2}(5)+\mathrm{U2}(6)+\mathrm{U2}(12) \tag{A1}$$

can be written as

$$D=\frac{1}{2}\sum_{\substack{j,k<l,\\ j',k'<l',\\ u,v}} V_{pj[kl]}\delta_{jj'}V_{kl[uv]}V_{uv[k'l']}V^{*}_{qj'[k'l']}hn_u n_v \times n_j\bar{n}_k\bar{n}_l n_{j'}\bar{n}_{k'}\bar{n}_{l'}\ , \tag{A2a}$$

where

$$\begin{aligned}
h&=\omega_{12}^{-1}(\omega_1^{-1}\omega_2^{-1}+\omega_1^{-1}\epsilon_1^{-1}+\omega_2^{-1}\epsilon_2^{-1}+\epsilon_1^{-1}\epsilon_2^{-1})\ ,\\
\omega_{12}&=(\omega+\epsilon_j+\epsilon_u+\epsilon_v-\epsilon_k-\epsilon_l-\epsilon_{k'}-\epsilon_{l'})\ ,\\
\omega_1&=\omega+\epsilon_j-\epsilon_k-\epsilon_l\ ,\\
\omega_2&=\omega+\epsilon_{j'}-\epsilon_{k'}-\epsilon_{l'}\ ,\\
\epsilon_1&=\epsilon_u+\epsilon_v-\epsilon_k-\epsilon_l\ ,\\
\epsilon_2&=\epsilon_u+\epsilon_v-\epsilon_{k'}-\epsilon_{l'}\ .
\end{aligned} \tag{A2b}$$

Obviously, $h$ can be simplified to

$$\begin{aligned}
h&=\omega_1^{-1}\omega_2^{-1}\epsilon_1^{-1}\epsilon_2^{-1}\tfrac{1}{2}(\epsilon_1+\epsilon_2+\omega_1+\omega_2)\\
&=\omega_1^{-1}\omega_2^{-1}\frac{(\epsilon_1+\epsilon_2)/2}{\epsilon_1\epsilon_2}+\tfrac{1}{2}(\omega_1^{-1}+\omega_2^{-1})\frac{1}{\epsilon_1\epsilon_2}\ ,
\end{aligned} \tag{A3}$$

where the 4p-3h denominator $\omega_{12}$ is canceled. Inserting the last expression for $h$ in the right-hand side of Eq. (A2a) one obtains

$$D=\sum_{\substack{j,k<l\\ j',k'<l'}} V_{pj[kl]}\frac{\widetilde{C}_{jkl,j'k'l'}n_j\bar{n}_k\bar{n}_l n_{j'}\bar{n}_{k'}\bar{n}_{l'}}{(\omega+\epsilon_j-\epsilon_k-\epsilon_l)(\omega+\epsilon_{j'}-\epsilon_{k'}-\epsilon_{l'})}V^{*}_{qj'[k'l']} + \sum_{j,k<l}\frac{n_j\bar{n}_k\bar{n}_l}{\omega+\epsilon_j-\epsilon_k-\epsilon_l}(V_{pj[kl]}\widetilde{U}_{q,jkl}+\widetilde{U}^{*}_{p,jkl}V^{*}_{qj[kl]})\ , \tag{A4a}$$

where

$$\widetilde{C}_{jkl,j'k'l'}=\frac{1}{2}\sum_{u,v}\delta_{jj'}V_{kl[uv]}V_{uv[k'l']}\frac{\epsilon_u+\epsilon_v-(\epsilon_k+\epsilon_l+\epsilon_{k'}+\epsilon_{l'})/2}{(\epsilon_u+\epsilon_v-\epsilon_k-\epsilon_l)(\epsilon_u+\epsilon_v-\epsilon_{k'}-\epsilon_{l'})}n_u n_v\ , \tag{A4b}$$

$$\widetilde{U}^{*}_{p,jkl}=\frac{1}{8}\sum_{\substack{u,v\\ k',l'}}\frac{V_{kl[uv]}V_{uv[k'l']}n_u n_v}{(\epsilon_u+\epsilon_v-\epsilon_k-\epsilon_l)(\epsilon_u+\epsilon_v-\epsilon_{k'}-\epsilon_{l'})}V_{pj[k'l']}\ . \tag{A4c}$$

The first sum on the right-hand side of Eq. (A4a) has the form of the term (5a) in Table I and $\widetilde{C}_{jkl,j'k'l'}$ is identified as a contribution to $C^{(2)}_{jkl,j'k'l'}$. Similarly, the second sum contributes to the term (1a) of Table I and $\widetilde{U}_{p,jkl}$ represents a contribution to the third-order modified transition matrix elements $U^{(3)}_{p,jkl}$.

## APPENDIX B: EXPLICIT EXPRESSIONS FOR THE FOURTH-ORDER ADC SCHEME

Here we present the explicit expressions for the modified coupling amplitudes $\underline{U}_p$ and the modified interaction matrix $\underline{C}$ of the fourth-order ADC scheme. We start with the case of $\underline{M}^{1}(\omega)$. Here, the configuration space is spanned by the 2p-1h and 3p-2h excitations:

$$(j,k,l),\ \text{with}\ n_j\bar{n}_k\bar{n}_l=1,\quad k<l\ ;$$
$$(i,j,k,l,m),\ \text{with}\ n_i n_j\bar{n}_k\bar{n}_l\bar{n}_m=1,\quad i<j\ ,\quad k<l<m\ . \tag{B1}$$

The modified coupling amplitudes for the 2p-1h space read

$$U_{p,jkl}=U^{(1)}_{p,jkl}+U^{(2)}_{p,jkl}+U^{(3)}_{p,jkl}\ , \tag{B2}$$

where $U^{(1)}_{p,jkl}$ and $U^{(2)}_{p,jkl}$ are given by Eqs. (40a) and (43b), respectively. The third-order term

$$U^{(3)}_{p,jkl}=\sum_{I=1}^{23} W^{(3,I)*}_{pjkl} \tag{B3a}$$

is the sum of the following 23 contributions:

$$W^{(3,1)}_{pjkl}=\left[-\tfrac{1}{2}\sum_{j',k',r,v}\gamma_{ujkr}\gamma_{sruv}V_{pv[sl]}\bar{n}_r\bar{n}_s n_u n_v\right]-(k\leftrightarrow l)\ , \tag{B3b}$$

$$W^{(3,2)}_{pjkl}=-\tfrac{1}{8}\sum_{k',l',u,v}\gamma_{uvkl}\gamma_{rsuv}V_{pj[rs]}\bar{n}_r\bar{n}_s n_u n_v\ , \tag{B3c}$$

$$W^{(3,3)}_{pjkl}=\tfrac{1}{4}\sum_{r,s,u,v}\gamma_{jvrs}\gamma_{rsuv}V_{pu[kl]}\bar{n}_r\bar{n}_s n_u n_v\ , \tag{B3d}$$

$$W^{(3,4)}_{pjkl}=\left[\tfrac{1}{4}\sum_{u,v,r,s}\gamma_{uvlr}\gamma_{sruv}V_{pj[ks]}\bar{n}_r\bar{n}_s n_u n_v\right]-(k\leftrightarrow l)\ , \tag{B3e}$$

$$W^{(3,5)}_{pjkl}=\left[-\sum_{r,u,v,w}\gamma_{uvrl}\frac{V_{wr[ku]}V_{pj[wv]}}{\epsilon_v+\epsilon_w-\epsilon_k-\epsilon_l}\bar{n}_r n_u n_v n_w\right]-(k\leftrightarrow l)\ , \tag{B3f}$$

$$W^{(3,6)}_{pjkl}=\left[\sum_{u,v,r,s}\gamma_{ujrs}\frac{V_{vr[ku]}V_{ps[vl]}}{\epsilon_j+\epsilon_v-\epsilon_k-\epsilon_s}\bar{n}_r\bar{n}_s n_u n_v\right]-(k\leftrightarrow l)\ , \tag{B3g}$$

$$W^{(3,7)}_{pjkl}=\left[\sum_{u,v,r,s}\gamma_{uvrl}\frac{V_{jr[su]}V_{ps[vk]}}{\epsilon_j+\epsilon_v-\epsilon_l-\epsilon_s}\bar{n}_r\bar{n}_s n_u n_v\right]-(k\leftrightarrow l)\ , \tag{B3h}$$

$$W^{(3,8)}_{pjkl}=\left[\tfrac{1}{2}\sum_{r,u,v,w}\gamma_{uvrl}\frac{V_{jw[uv]}V_{pr[wk]}}{\epsilon_j+\epsilon_w-\epsilon_r-\epsilon_l}\bar{n}_r n_u n_v n_w\right]-(k\leftrightarrow l)\ , \tag{B3i}$$

$$W^{(3,9)}_{pjkl}=\left[\tfrac{1}{2}\sum_{r,s,t,v}\gamma_{jvrs}\frac{V_{rs[kt]}V_{pt[vl]}}{\epsilon_j+\epsilon_v-\epsilon_k-\epsilon_t}\bar{n}_r\bar{n}_s\bar{n}_t n_v\right]-(k\leftrightarrow l)\ , \tag{B3j}$$

$$W^{(3,10)}_{pjkl}=\left[\sum_{u,v,r,s}\gamma_{uvrs}\frac{V_{rj[kv]}V_{ps[ul]}}{\epsilon_j+\epsilon_u-\epsilon_k-\epsilon_s}\bar{n}_r\bar{n}_s n_u n_v\right]-(k\leftrightarrow l)\ , \tag{B3k}$$

$$W^{(3,11)}_{pjkl}=\left[\sum_{u,v,r,s}\gamma_{ujkr}\frac{V_{vr[us]}V_{ps[vl]}}{\epsilon_v+\epsilon_j-\epsilon_k-\epsilon_s}\bar{n}_r\bar{n}_s n_u n_v\right]-(k\leftrightarrow l)\ , \tag{B3l}$$

$$W^{(3,12)}_{pjkl}=\tfrac{1}{4}\sum_{u,v,r,s}\gamma_{uvrs}\frac{V_{rs[kl]}V_{pj[uv]}}{\epsilon_u+\epsilon_v-\epsilon_k-\epsilon_l}\bar{n}_r\bar{n}_s n_u n_v\ , \tag{B3m}$$

$$W^{(3,13)}_{pjkl}=\tfrac{1}{4}\sum_{u,v,u',v'}\gamma_{uvkl}\frac{V_{u'v'[uv]}V_{pj[u'v']}}{\epsilon_{u'}+\epsilon_{v'}-\epsilon_k-\epsilon_l}n_u n_v n_{u'} n_{v'}\ , \tag{B3n}$$

$$W^{(3,14)}_{pjkl}=\sum_{r,s,u,v}\gamma_{ujrs}\frac{V_{rv[kl]}V_{ps[uv]}}{\epsilon_u+\epsilon_v+\epsilon_j-\epsilon_k-\epsilon_l-\epsilon_s}\times\bar{n}_r\bar{n}_s n_u n_v\ , \tag{B3o}$$

$$W^{(3,15)}_{pjkl}=-\sum_{r,u,v,w}\gamma_{uvkl}\frac{V_{wj[ur]}V_{pr[wv]}}{\epsilon_v+\epsilon_w+\epsilon_j-\epsilon_k-\epsilon_l-\epsilon_r}\times\bar{n}_r n_u n_v n_w\ , \tag{B3p}$$

$$W^{(3,16)}_{pjkl}=\left[\tfrac{1}{2}\sum_{r,s,u,v}\gamma_{uvrl}\frac{V_{rj[ks]}V_{ps[uv]}}{\epsilon_u+\epsilon_v+\epsilon_j-\epsilon_k-\epsilon_l-\epsilon_s}\bar{n}_r\bar{n}_s n_u n_v\right]-(k\leftrightarrow l)\ , \tag{B3q}$$

$$W^{(3,17)}_{pjkl}=\left[-\tfrac{1}{2}\sum_{r,u,v,w}\gamma_{wjkr}\frac{V_{uv[wl]}V_{pr[uv]}}{\epsilon_u+\epsilon_v+\epsilon_j-\epsilon_k-\epsilon_l-\epsilon_r}\bar{n}_r n_u n_v n_w\right]-(k\leftrightarrow l)\ , \tag{B3r}$$

$$W^{(3,18)}_{pjkl}=\left[\sum_{r,u,v,w}\gamma_{uvrl}\frac{V_{wj[kv]}V_{pr[wu]}}{\epsilon_u+\epsilon_w+\epsilon_j-\epsilon_k-\epsilon_l-\epsilon_r}\bar{n}_r n_u n_v n_w\right]-(k\leftrightarrow l)\ , \tag{B3s}$$

$$W_{pjkl}^{(3,19)}=\left[-\sum_{r,s,u,v}\gamma_{ujrl}\frac{V_{rv[ks]}V_{ps[uv]}}{\epsilon_u+\epsilon_v+\epsilon_j-\epsilon_k-\epsilon_l-\epsilon_s}\bar{n}_r\bar{n}_s n_u n_v\right]-(k\leftrightarrow l)\ , \tag{B3t}$$

$$W_{pjkl}^{(3,20)}=-\frac{1}{2}\sum_{u,v,r,s}\gamma_{uvrs}\frac{V_{js[uv]}V_{pr[kl]}}{\epsilon_j-\epsilon_r}\bar{n}_r\bar{n}_s n_u n_v\ , \tag{B3u}$$

$$W_{pjkl}^{(3,21)}=\frac{1}{2}\sum_{v,r,s,t}\gamma_{jvrs}\frac{V_{rs[tv]}V_{pt[kl]}}{\epsilon_j-\epsilon_t}\bar{n}_r\bar{n}_s\bar{n}_t n_v\ , \tag{B3v}$$

$$W_{pjkl}^{(3,22)}=\left[-\frac{1}{2}\sum_{u,v,r,s}\gamma_{uvrs}\frac{V_{rs[lv]}V_{pj[ku]}}{\epsilon_u-\epsilon_l}\bar{n}_r\bar{n}_s n_u n_v\right]-(k\leftrightarrow l)\ , \tag{B3w}$$

$$W_{pjkl}^{(3,23)}=\left[\frac{1}{2}\sum_{r,u,v,w}\gamma_{uvlr}\frac{V_{wr[uv]}V_{pj[kw]}}{\epsilon_w-\epsilon_l}\bar{n}_r n_u n_v n_w\right]-(k\leftrightarrow l)\ . \tag{B3x}$$

Here and in the following we use the first-order coefficient

$$\gamma_{ijkl}=\frac{V_{ij[kl]}}{\epsilon_i+\epsilon_j-\epsilon_k-\epsilon_l}\ . \tag{B4}$$

The first four contributions (B3b)—(B3e) originate from the time orderings (2), (5), (6), and (12) of the diagrams U1, U2, V1, and V2. The remaining 19 contributions (B3f)—(B3x) correspond to the diagrams W1(8), W*X*(8), W*X*(10), *X*=2,3; U*X*(8), U*X*(10), *X*=1, . . . , 5; and V*X*(8), V*X*(10), *X*=1,2—in this order.

The modified coupling matrix elements for the 3p-2h space read

$$U_{p,ijklm}=U_{p,ijklm}^{(2)}\ , \tag{B5a}$$

$$U_{p,ijklm}^{(2)}=\left[-\sum_r\gamma_{ijrm}^{*}V_{pr[kl]}^{*}\bar{n}_r+\left(\sum_v\gamma_{vjkm}^{*}V_{pi[vl]}^{*}n_v\right)-(i\leftrightarrow j)\right]+[(k,l,m)\leftrightarrow(m,k,l)]+[(k,l,m)\leftrightarrow(l,m,k)]\ . \tag{B5b}$$

The modified 2p-1h interaction matrix elements

$$C_{jkl,j'k'l'}=C_{jkl,j'k'l'}^{(1)}+C_{jkl,j'k'l'}^{(2)} \tag{B6}$$

consist of a first-order term given by Eq. (42c) and the second-order term

$$C_{jkl,j'k'l'}^{(2)}=\delta_{jj'}A_{kl,k'l'}-\delta_{kk'}\delta_{ll'}B_{jj'}+(\delta_{ll'}D_{jk,j'k'}-\delta_{jj'}\delta_{kk'}E_{l,l'})-(k\leftrightarrow l)-(k'\leftrightarrow l')+(k\leftrightarrow l,\ \ k'\leftrightarrow l')\ , \tag{B7a}$$

$$A_{kl,k'l'}=-\frac{1}{2}\sum_{u,v}\gamma_{kluv}\gamma_{uvk'l'}[\epsilon_u+\epsilon_v-\tfrac{1}{2}(\epsilon_k+\epsilon_{k'}+\epsilon_l+\epsilon_{l'})]n_u n_v\ , \tag{B7b}$$

$$B_{j,j'}=-\frac{1}{2}\sum_{r,s,v}\gamma_{rsjv}\gamma_{j'vrs}[\epsilon_v-\epsilon_r-\epsilon_s+\tfrac{1}{2}(\epsilon_j+\epsilon_{j'})]\bar{n}_r\bar{n}_s n_v\ , \tag{B7c}$$

$$D_{jk,j'k'}=-\sum_{r,v}\gamma_{krvj}\gamma_{vj'k'r}[\epsilon_v-\epsilon_r+\tfrac{1}{2}(\epsilon_j+\epsilon_{j'}-\epsilon_k-\epsilon_{k'})]\bar{n}_r n_v\ , \tag{B7d}$$

$$E_{l,l'}=-\frac{1}{2}\sum_{u,v,r}\gamma_{lruv}\gamma_{uvl'r}[\epsilon_u+\epsilon_v-\epsilon_r-\tfrac{1}{2}(\epsilon_l+\epsilon_{l'})]\bar{n}_r n_u n_v\ . \tag{B7e}$$

The modified 2p-h—3p-2h interaction matrix elements

$$C_{jkl,i'j'k'l'm'}=C_{jkl,i'j'k'l'm'}^{(1)} \tag{B8}$$

are identical with the wave-function expression

$$\begin{aligned}C_{jkl,i'j'k'l'm'}^{(1)}&=\langle\Phi_0\,|\,c_l c_k c_j^{\dagger}\hat{H}c_{i'}c_{j'}c_{k'}^{\dagger}c_{l'}^{\dagger}c_{m'}^{\dagger}\,|\,\Phi_0\rangle\\&=\{[(\delta_{kk'}\delta_{ll'}\tfrac{1}{2}V_{i'j'[jm']}+\delta_{kk'}\delta_{jj'}V_{li'[l'm']})+((k',l',m')\leftrightarrow(l',m',k'))\\&\qquad+((k',l',m')\leftrightarrow(m',k',l'))]-[i'\leftrightarrow j']\}-\{k\leftrightarrow l\}\ .\end{aligned} \tag{B9}$$

In the strict fourth-order ADC scheme the modified 3p-2h interaction matrix vanishes. It is a straightforward extension to take into account the first-order 3p-2h interaction matrix elements

$$\begin{aligned}C^{(1)}_{ijklm,i'j'k'l'm'} &= \langle \Phi_0 | c_m c_l c_k c_j^\dagger c_i^\dagger \hat{H} c_{i'} c_{j'} c_{k'}^\dagger c_{l'}^\dagger c_{m'}^\dagger | \Phi_0 \rangle - \delta_{ii'}\delta_{jj'}\delta_{kk'}\delta_{ll'}\delta_{mm'}[E_0(1) - \epsilon_i - \epsilon_j + \epsilon_k + \epsilon_l + \epsilon_m] \\ &= \delta_{kk'}\delta_{ll'}\delta_{mm'} V_{i'j'[ij]} + [(\delta_{ii'}\delta_{jj'}\delta_{kk'} V_{lm[l'm']}) + ((k,l,m) \leftrightarrow (l,m,k)) + ((k,l,m) \leftrightarrow (m,k,l))] \\ &\quad + [(k',l',m') \leftrightarrow (l',m',k')] + [(k',l',m') \leftrightarrow (m',k',l')] \\ &\quad + \{[(-\delta_{ii'}\delta_{kk'}\delta_{ll'} V_{j'm[jm']}) - ((k,l,m) \leftrightarrow (k,m,l)) + ((k,l,m) \leftrightarrow (l,m,k))] \\ &\qquad + [(k',l',m') \leftrightarrow (l',m',k')] - [(k',l',m') \leftrightarrow (k',m',l')]\} \\ &\quad - \{i \leftrightarrow j\} - \{i' \leftrightarrow j'\} + \{i \leftrightarrow j,\ i' \leftrightarrow j'\} \; . \end{aligned} \tag{B10}$$

Here $E_0(1)$ denotes the first-order ground-state energy, $E_0(1) = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle$.

For the case of $\underline{M}^{\mathrm{II}}(\omega)$ the configuration space is spanned by the 2h-1p and 3h-2p excitations

$$\begin{aligned}&(j,k,l), \text{ with } \bar{n}_j n_k n_l, \quad k < l \\ &(i,j,k,l,m), \text{ with } \bar{n}_i \bar{n}_j n_k n_l n_m, \quad i < j, \quad k < l < m \; .\end{aligned} \tag{B11}$$

The resulting expressions are formally similar to the previous case:

$$U_{p,jkl} = U^{(1)}_{p,jkl} - \bar{U}^{(2)}_{p,jkl} + \bar{U}^{(3)}_{p,jkl} \; , \tag{B12}$$

$$U_{p,ijklm} = \bar{U}^{(2)}_{p,ijklm} \; , \tag{B13}$$

$$C_{jkl,j'k'l'} = -C^{(1)}_{jkl,j'k'l'} + \bar{C}^{(2)}_{jkl,j'k'l'} \; , \tag{B14}$$

$$C_{jkl,i'j'k'l'm'} = C^{(1)}_{jkl,i'j'k'l'm'} \; , \tag{B15}$$

$$C_{ijklm,i'j'k'l'm'} = -C^{(1)}_{ijklm,i'j'k'l'm'} \; . \tag{B16}$$

Here, $\bar{U}^{(\nu)}_{p,jkl}$ and $\bar{C}^{(\nu)}_{jkl,j'k'l'}$ are obtained from the previous expressions by simply exchanging the occurring occupation numbers according to $n_i \leftrightarrow \bar{n}_i$ [see Eq. (44c)].

We emphasize that the fourth-order ADC equations reflect the symmetry properties of the underlying Hamiltonian $\hat{H}$. For a spin-independent Hamiltonian one arrives straightforwardly at a spin-free formulation of the ADC equations.

## APPENDIX C: ON THE PERTURBATION EXPANSION OF THE TRANSITION AMPLITUDES

In the following we shall sketch a proof of the assertion (82) which states that the transition amplitudes for $(n+1)$h-$n$p and $(n+1)$p-$n$h excited states are at least of order $n$, $n = 0,1,\ldots$. Let us consider the amplitudes

$$x_p^{(\mu)} = \langle \Psi_\mu^{N-1} | c_p | \Psi_0^N \rangle \tag{C1}$$

for an exact $(N-1)$-particle state $|\Psi_\mu^{N-1}\rangle$ deriving from a $(n+1)$h-$n$p configuration. In order to establish a perturbation expansion for $x_p^{(\mu)}$ we may express the ground state and the ionic state according to the adiabatic theorem (see, e.g., Fetter and Walecka[4]):

$$|\Psi_0^N\rangle = \lim_{\epsilon \to 0} \frac{\hat{U}_\epsilon(0, \pm\infty) | \Phi_0^N \rangle}{\langle \Phi_0 | U_\epsilon(0, \pm\infty) | \Phi_0 \rangle} \; , \tag{C2}$$

$$|\Psi_\mu^{N-1}\rangle = \lim_{\epsilon \to 0} \frac{\hat{U}_\epsilon(0, \pm\infty) | \Phi_0^{N-1} \rangle}{\langle \Phi_0^{N-1} | U_\epsilon(0, \pm\infty) | \Phi_0^{N-1} \rangle} \; . \tag{C3}$$

Here $\hat{U}_\epsilon(t,t')$ denotes the time-evolution operator in the interaction picture for the adiabatic Hamiltonian $\hat{H} = \hat{H}_0 + e^{-\epsilon|t|}\hat{H}_I$, $|\Phi_0^N\rangle$ is the unperturbed (HF) ground state, and

$$|\Phi_\mu^{N-1}\rangle = c_{j_1}^\dagger \cdots c_{j_n}^\dagger c_{i_1} \cdots c_{i_{n+1}} | \Phi_0^N \rangle \tag{C4}$$

stands for an unperturbed $(n+1)$h-$n$p excited ionic state. Since the wave functions in Eqs. (C2) and (C3) are not normalized, one has to replace the expression (C1) by

$$x_p^{(\mu)} = \frac{\langle \Psi_\mu^{N-1} | c_p | \Psi_0^N \rangle}{(\langle \Psi_\mu^{N-1} | \Psi_\mu^{N-1} \rangle \langle \Psi_0^N | \Psi_0^N \rangle)^{1/2}} \; . \tag{C5}$$

For our purpose it is sufficient to consider the numerator

$$A_\epsilon(-\infty) = \langle \Phi_\mu^{N-1} | \hat{U}_\epsilon^\dagger(0, -\infty) c_p \hat{U}_\epsilon(0, -\infty) | \Phi_0 \rangle \; . \tag{C6}$$

It should be noted that this quantity may not exist separately as $\epsilon \to 0$. Since the following argument is not affected by the complications arising from the limits we may instead of (C6) consider the expression

$$\begin{aligned}A(t) &= \lim_{\epsilon \to 0} A_\epsilon(t) \\ &= \langle \Phi_\mu^{N-1} | \hat{U}^\dagger(0,t) c_p \hat{U}(0,t) | \Phi_0 \rangle \; ,\end{aligned} \tag{C7}$$

which for finite $t$ is well defined. Here

$$\hat{U}(t,t')=e^{i\hat{H}_0 t}e^{-i\hat{H}(t-t')}e^{-i\hat{H}_0 t'} \tag{C8}$$

is the usual time-evolution operator in the interaction picture. Using Eq. (C8) one obtains

$$A(t)=\exp\{i[E_\mu^{N-1}(0)-E_0^N(0)]t\} \times \langle \Phi_\mu^{N-1} | e^{-i\hat{H}t}c_p e^{i\hat{H}t} | \Phi_0 \rangle , \tag{C9}$$

where $E_\mu^{N-1}(0)$ and $E_0^N(0)$ denote the zeroth-order ionic-state and ground-state energies. With the help of the well-known relation

$$e^{-i\hat{H}t}c_p e^{-i\hat{H}t}=c_p+it[c_p,\hat{H}] +\tfrac{1}{2}(it)^2[[c_p,\hat{H}],\hat{H}]+\cdots , \tag{C10}$$

the expectation value on the right-hand side of Eq. (C9) can be written as a sum of terms

$$A_l=\langle \Phi_\mu^{N-1} | [[\ldots[c_p,\hat{H}],\ldots],\hat{H}] | \Phi_0^N \rangle , \tag{C11}$$

where $l$ indicates the number of commutators. Recalling that $\hat{H}=\hat{H}_0+\hat{H}_I$, where $\hat{H}_0$ is one-particle operator and $\hat{H}_I$ is a two-particle operator, one easily sees that the expectation values (C11) vanish unless $\hat{H}_I$ occurs at least $n$ times, that is, unless $A_l$ and thus $A(t)$ is at least of $n$th order. Obviously, this argument also holds as $t \to -\infty$, which completes our proof.

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