Approximation scheme for the three-particle propagator

A. Tarantelli and L. S. Cederbaum
Lehrstuhl für Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 253, D-6900 Heidelberg, Federal Republic of Germany
(Received 17 October 1991)

The three-particle (*ppp*) propagator, which is that component of the three-particle Green's function describing triple ionization, is investigated. In particular, a second-order approximation scheme for this propagator is presented, suitable for the calculation of triply charged electronic states. Two different methods are used to derive the explicit working equations. The first method is purely algebraic and is based on the connection of propagators and effective Hamiltonians. The second is the well-established algebraic-diagrammatic-construction method, which makes use of Feynman diagrams. These methods lead to equivalent working equations represented in different forms.

PACS number(s): 31.15.+q, 31.10.+z, 71.10.+x, 21.60.−n

I. INTRODUCTION

The theoretical study of positively charged ions is very unequally distributed among singly, doubly, and triply charged cations. Most of the research is directed to the investigation of singly charged systems and to the interpretation of single-ionization spectra. The study of doubly charged cations and of double-ionization processes increased drastically in recent years because of the development of new experimental techniques and the advent of larger computers which allow the theoretical description of such processes. Very little attention has been paid to the theoretical study of triply charged systems and of processes of triple ionization. One reason can be found in the enormous amount of states which have to be calculated for the description of triply charged systems.

On the other hand, triply charged states represent the final states of many electronic processes. One example is given by the so-called Auger satellite lines which can be experimentally detected in the Auger spectroscopy [1,2]. The assignment of these lines can be of fundamental importance for a correct interpretation of the normal Auger spectra. The Auger satellite lines arise when the initial core vacancy in the molecular system (the initial state of the Auger transition) is accompanied by simultaneous ionization of a second electron, usually from an orbital in which the electron is weakly bound. This "shakeoff" process results from a sudden change in the nuclear potential due to the rapid change in the electron shielding. The shakeoff process takes place with subsequent Auger emission and the final electronic state of the transition is triply positively charged.

Other processes which involve triply charged cations are dissociation processes of multiply charged molecules. Most of the information about these processes comes from photoionization experiments or collision spectroscopic methods involving the study of electron-capture or electron-loss processes in ion-neutral collisions [3–5]. Coulomb explosion [6] and mass spectroscopic experiments have also provided information about the dissociation and fragmentation properties of triply charged molecules. It should also be mentioned that the understanding of the internal structure of multiply charge cations can be of great interest itself, since it can offer a deeper insight into the nature of the chemical bond.

In recent years the development and refinement of the above-mentioned experimental techniques have led to an increase in the amount of experimental data on multiply charged systems and triple-ionization (direct or indirect) processes. This is not yet sufficiently counterbalanced by accurate theoretical studies, which can be of great help in the correct interpretation of the experimental results.

The calculation of triple-ionization energies by means of conventional methods such as self-consistent-field calculations lacks accuracy because these methods cannot account for possible strong correlation changes due to the loss of three electrons. More-sophisticated methods such as configuration-interaction (CI) methods present the problem of a very large numerical effort, owing to the necessity of calculating a great amount of states. Less-conventional or "direct" methods based on Green's functions [7,8] can therefore be viewed as very suitable theoretical instruments for the investigation of multiply charged electronic states. One advantage of these methods is that they allow for the direct calculation of the transition energies without resorting to separate calculations for the initial and final states.

Within the Green's functions the quantity suitable for the analysis of processes in which three electrons are ejected is the three-particle (*ppp*) propagator which can be obtained from the more general three-particle Green's function [9,10]. The purpose of this work is to present an approximation scheme for the *ppp* propagator consistent up to second order of perturbation theory. We should mention that an approximation scheme for this propagator based on the first-order approximation of the Bethe-Salpeter equation has been presented by Liegener [11]. The working equations of our second-order scheme are derived by means of two different and complementary methods. The first one is based on the perturbation expansion of a closed-form algebraic expression for the *ppp* propagator. This closed-form expression contains the ex-

act neutral ground state of the system as the only unknown quantity and its perturbation expansion is thus straightforward. This purely algebraic method has been recently presented and applied to the *pp* propagator for the theoretical investigation of double-ionization processes [12]. The second method used to derive the second-order working equations for the *ppp* propagator is the well-established ADC method (ADC denotes algebraic diagrammatic construction) [13–15]. The ADC approach is based on the diagrammatic representation of the perturbation expansion of the propagator. It should be mentioned that a closed-form formulation of the ADC approach has been recently presented [16]. Relevant in this context is also the work in Ref. [17].

II. DEFINITIONS

The most general form of the three-particle Green's function (six-point Green's function [9,10]) is given by a time-ordered expectation value of three creation and three annihilation operators in Heisenberg representation in the exact N-particle ground state $|\Psi_0^N\rangle$ of the system:

$$G_{\alpha\beta\nu,\gamma\delta\mu}=-i^3\langle\Psi_0^N|T\{a_\alpha a_\beta a_\nu a_\gamma^\dagger a_\delta^\dagger a_\mu^\dagger\}|\Psi_0^N\rangle \ . \tag{2.1}$$

The creation ($a_\alpha^\dagger$) and annihilation (a_α) operators are related to a suitable basis $\{|\varphi_\alpha\rangle\}$ of single-particle states. For example, in dealing with molecular systems it is common to choose the set $\{|\varphi_\alpha\rangle\}$ as the set of the molecular orbitals which derive from a self-consistent calculation for the ground state of the neutral molecule. In Eq. (2.1) the variables $\alpha,\beta,\ldots,\mu$ are supposed to include time; for example, $a_\alpha^\dagger=a_\alpha^\dagger(t_\alpha)$. The operator T is the Wick's time-ordering operator [8].

Depending on the possible time ordering of the creation and annihilation operators, the three-particle Green's function can be divided into a *ppp* and a *pph* part. The *ppp* part describes transition processes from the N-particle system to the $(N\pm3)$-particle system [10]. The *ppp* part reads as

$$\begin{aligned}G^{ppp}_{\alpha\beta\nu,\gamma\delta\mu}=&\,i\Theta(t_\alpha t_\beta t_\nu-t_\gamma t_\delta t_\mu)\sum_m\langle\Psi_0^N|T\{a_\alpha a_\beta a_\nu\}|\Psi_m^{N+3}\rangle\langle\Psi_m^{N+3}|T\{a_\gamma^\dagger a_\delta^\dagger a_\mu^\dagger\}|\Psi_0^N\rangle\\&-i\Theta(t_\gamma t_\delta t_\mu-t_\alpha t_\beta t_\nu)\sum_m\langle\Psi_0^N|T\{a_\gamma^\dagger a_\delta^\dagger a_\mu^\dagger\}|\Psi_m^{N-3}\rangle\langle\Psi_m^{N-3}|T\{a_\alpha a_\beta a_\nu\}|\Psi_0^N\rangle\\=&\,G^{ppp(+)}_{\alpha\beta\nu,\gamma\delta\mu}+G^{ppp(-)}_{\alpha\beta\nu,\gamma\delta\mu} \ .\end{aligned} \tag{2.2}$$

Here $|\Psi_m^{N\pm3}\rangle$ are the exact eigenstates of the Hamiltonian in the $(N\pm3)$-particle space. The function $\Theta(t_\alpha t_\beta t_\nu-t_\gamma t_\delta t_\mu)$ is a generalized step function defined as follows:

$$\Theta(t_\alpha t_\beta t_\nu-t_\gamma t_\delta t_\mu)=\begin{cases}1 & \text{for } t_\alpha,t_\beta,t_\nu\geq t_\gamma,t_\delta,t_\mu,\\ 0 & \text{for } t_\alpha,t_\beta,t_\nu<t_\gamma,t_\delta,t_\mu \ .\end{cases} \tag{2.3}$$

In this work we are interested in the theoretical description of the simultaneous attachment or ejection of three particles from the N-particle ground state. For this purpose we introduce the "*ppp* propagator." This quantity can be obtained from $\mathbf{G}^{ppp}$ [Eq. (2.2)] by a particular choice of the time arguments: the time arguments of the variables within each factor composing $\mathbf{G}^{ppp}$ are equal. The *ppp* propagator is defined as follows:

$$\begin{aligned}\Pi^{ppp}_{\alpha\beta\nu,\gamma\delta\mu}(t,t')=&-\lim_{\substack{t_\alpha,t_\beta,t_\nu\to t\\ t_\gamma,t_\delta,t_\mu\to t'}}G^{ppp}_{\alpha\beta\nu,\gamma\delta\mu}\\=&-i\Theta(t-t')\sum_m\langle\Psi_0^N|a_\alpha(t)a_\beta(t)a_\nu(t)|\Psi_m^{N+3}\rangle\langle\Psi_m^{N+3}|a_\gamma^\dagger(t')a_\delta^\dagger(t')a_\mu^\dagger(t')|\Psi_0^N\rangle\\&+i\Theta(t'-t)\sum_m\langle\Psi_0^N|a_\gamma^\dagger(t')a_\delta^\dagger(t')a_\mu^\dagger(t')|\Psi_m^{N-3}\rangle\langle\Psi_m^{N-3}|a_\alpha(t)a_\beta(t)a_\nu(t)|\Psi_0^N\rangle\\=&\,\Pi^{(+)}_{\alpha\beta\nu,\gamma\delta\mu}(t,t')+\Pi^{(-)}_{\alpha\beta\nu,\gamma\delta\mu}(t,t') \ .\end{aligned} \tag{2.4}$$

In this equation we indicated explicitly the time arguments of the creation and annihilation operators. By definition, the *ppp* propagator depends on two time arguments only. The first and the second terms in Eq. (2.4) describe the simultaneous attachment and removal of three particles from the ground state $|\Psi_0^N\rangle$, respectively. This becomes more apparent by considering the spectral representation of the *ppp* propagator in energy space, which can be obtained by Fourier transformation of Eq. (2.4). For a time-independent Hamiltonian the *ppp* propagator is a function of the time difference $(t-t')$ only and its spectral representation reads as

$$\begin{aligned}\Pi^{ppp}_{\alpha\beta\nu,\gamma\delta\mu}(\omega)=&\sum_m\frac{\langle\Psi_0^N|a_\alpha a_\beta a_\nu|\Psi_m^{N+3}\rangle\langle\Psi_m^{N+3}|a_\gamma^\dagger a_\delta^\dagger a_\mu^\dagger|\Psi_0^N\rangle}{\omega+E_0^N-E_m^{N+3}+i\eta}+\sum_m\frac{\langle\Psi_0^N|a_\gamma^\dagger a_\delta^\dagger a_\mu^\dagger|\Psi_m^{N-3}\rangle\langle\Psi_m^{N-3}|a_\alpha a_\beta a_\nu|\Psi_0^N\rangle}{\omega-E_0^N+E_m^{N-3}-i\eta}\\=&\,\Pi^{(+)}_{\alpha\beta\nu,\gamma\delta\mu}(\omega)+\Pi^{(-)}_{\alpha\beta\nu,\gamma\delta\mu}(\omega) \ .\end{aligned} \tag{2.5}$$

The infinitesimal quantity η appearing in this expression is only needed to guarantee the convergence of the Fourier transformation and will be omitted in the following. The poles of the *ppp* propagator

$$\Omega_m = \begin{cases} E_m^{N+3} - E_0^N & \text{for } m \in N+3 \ , \\ E_0^N - E_m^{N-3} & \text{for } m \in N-3 \ , \end{cases} \tag{2.6}$$

give the energy differences between the $(N\pm3)$-particle states $|\Psi_m^{N\pm3}\rangle$ and the N-particle ground state $|\Psi_0^N\rangle$. The residues

$$x_{\alpha\beta\nu}^m = \begin{cases} \langle \Psi_m^{N+3} | a_\alpha^\dagger a_\beta^\dagger a_\nu^\dagger | \Psi_0^N \rangle & \text{for } m \in N+3 \ , \\ \langle \Psi_m^{N-3} | a_\alpha a_\beta a_\nu | \Psi_0^N \rangle & \text{for } m \in N-3 \ , \end{cases} \tag{2.7}$$

represent the corresponding transition amplitudes.

The purpose of the present work is to carry out a perturbation theoretical analysis of the *ppp* propagator [Eq. (2.5)] and to present the working equations for a second-order approximation scheme. The perturbation expansion is usually defined with respect to a Hamiltonian of the following general form:

$$\hat{H} = \hat{H}_0 + \hat{H}_I \ . \tag{2.8}$$

Here $\hat{H}_0$ represents the unperturbed Hamiltonian, diagonal in the chosen single-particle basis $\{|\varphi_\alpha\rangle\}$:

$$\hat{H}_0 = \sum_\alpha \epsilon_\alpha a_\alpha^\dagger a_\alpha \ . \tag{2.9}$$

The interaction term $\hat{H}_I$ is composed of a nondiagonal one-particle part $\hat{W}$ and of the Coulomb interelectronic interaction $\hat{V}$:

$$\hat{H}_I = \hat{W} + \hat{V} \ , \tag{2.10a}$$

$$\hat{W} = \sum_{\alpha,\beta} W_{\alpha\beta} a_\alpha^\dagger a_\beta \ , \tag{2.10b}$$

$$\hat{V} = \tfrac{1}{2} \sum_{\alpha,\beta,\gamma,\delta} V_{\alpha\beta\gamma\delta} a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma \ . \tag{2.10c}$$

Choosing $\hat{H}_0$ as the Hartree-Fock operator, ϵ_a in Eq. (2.9) is the energy of the αth molecular orbital and the one-particle term $\hat{W}$ assumes the following simple form:

$$\hat{W} = -\sum_{\alpha,\beta} \sum_k (V_{\alpha k \beta k} - V_{\alpha k k \beta}) a_\alpha^\dagger a_\beta \ , \tag{2.11}$$

where the sum over k runs over the occupied orbitals of the unperturbed N-particle ground state $|\Phi_0^N\rangle$ (Hartree-Fock determinant). The approximation scheme for the *ppp* propagator which we present in the following presupposes this form of $\hat{W}$. The transformation to any other choice of $\hat{H}_0$ and hence of $\hat{W}$ is easily done.

III. APPROXIMATION METHODS

The perturbation theoretical analysis of the *ppp* propagator has been performed by means of two conceptually different methods. The first one is a pure algebraic approach, which has recently been presented and applied to the *pp* propagator for the theoretical description of double-ionization processes [12]. The second one is the well-established ADC scheme (ADC denotes algebraic diagrammatic construction), based on Feynman diagrams [13–15]. Both methods represent general approaches and can be applied to any Green's function with slight natural modifications.

The major difference between the algebraic and the ADC methods lies in the following fact: in the former we make use of the connection between Green's functions and effective Hamiltonian [18,19]. The propagator of interest is reformulated as a closed-form expression which contains the exact N-particle ground state $|\Psi_0^N\rangle$ as the only unknown quantity [12]. This closed form is obtained by means of a unitary transformation which acts on the Hamiltonian matrix of the n-particle space. With n we indicate here the number of particles contained in the system after the transition has taken place. In the case of the *ppp* propagator n is $N\pm3$. Starting with this closed-form expression one obtains approximation schemes at each order of perturbation by expanding $|\Psi_0^N\rangle$ with the usual RSPT (Rayleigh-Schrödinger perturbation theory [8,20]). A characteristic of the approximation schemes obtained by the algebraic method is that the final equations can be expressed in "configuration form" [12], i.e., by matrix elements of the Hamiltonian taken with N- and $(N\pm3)$-particle electronic configurations (Slater determinants).

As already mentioned, the ADC approach [13,14] is based on the diagrammatic perturbation expansion of the Green's function under investigation. This can be carried out in terms of Feynman diagrams. By comparing order by order the power expansion of a general algebraic form with the corresponding diagrammatic expansion one obtains the matrices of the so-called effective interaction and effective transition amplitudes. These two matrices contain at each order of perturbation the same information as the matrix Ω of the exact energy differences [Eq. (2.6)] and the matrix $\mathbf{X}$ of the transition amplitudes [Eq. (2.7)], respectively. In ADC the working equations are obtained in "orbital form," i.e, in terms of products of two-particle integrals $V_{\alpha\beta\gamma\delta}$ and orbital energies ϵ_α.

The approximation which results from the algebraic closed-form expression for the propagator by expanding $|\Psi_0^N\rangle$ via RSPT is equivalent to that of the ADC and can be viewed as one of its algebraic formulations. In principle, other schemes can be obtained from the algebraic approach by employing different approximations for $|\Psi_0^N\rangle$. The explicit working equations obtained with both methods used here have a different appearance. Each set of working equations, in configuration form or in orbital form, may have its own advantages in numerical implementations. Another reason why we derived the approximation scheme of the *ppp* propagator by means of two methods is that the derivation of the approximation schemes for the *ppp* propagator is quite involved because of the appearance of six creation and annihilation operators in the definition [Eq. (2.4) and (2.5)]. Thus, the derivation of the working equation by means of two fundamentally different methods guarantees the correctness of the results. We should mention that by transforming the equations of the algebraic method into orbital form one obtains the ADC working equations.

In the next two sections we briefly discuss the algebraic

and the ADC approaches. For more details the reader is referred to Ref. [12] for the former and to Refs. [13–15] for the latter. We will carry out the discussion and explicitly present the approximation scheme up to second order for the second term $\mathbf{\Pi}^{(-)}$ of the *ppp* propagator which described triple ionization. It should be mentioned that the derivation of the working equations for the first term $\mathbf{\Pi}^{(+)}$ can be performed independently and in an analogous way. Furthermore, the equations for $\mathbf{\Pi}^{(+)}$ follow by a few manipulations from those of $\mathbf{\Pi}^{(-)}$.

IV. ALGEBRAIC METHOD AND WORKING EQUATIONS IN CONFIGURATION FORM

In this and in the next section we will consider the part $\mathbf{\Pi}^{(-)}$ of the *ppp* propagator. Whenever unambiguous, the superscript $(-)$ will be omitted. According to the definitions in Sec. II we rewrite this propagator $\mathbf{\Pi}$ in matrix form as follows:

$$\mathbf{\Pi}^*(\omega)=\mathbf{X}^\dagger(\omega-\mathbf{\Omega})^{-1}\mathbf{X} \ , \tag{4.1}$$

where $\mathbf{\Omega}$ is the diagonal matrix of elements Ω_m and $\mathbf{X}$ is the matrix of the transition amplitudes [see Eqs. (2.5)–(2.7)].

The matrix $\mathbf{\Omega}$ of the exact energy differences can be viewed as $(E_0^N-\hat{H})$ represented in the basis of its own eigenstates $|\Psi_m^{N-3}\rangle$ and is thus diagonal. The completeness of the set $\{|\Psi_m^{N-3}\rangle\}$ allows us to write the propagator in the following "representation-free" form:

$$\Pi_{\alpha\beta\nu,\gamma\delta\mu}=\langle\Psi_0^N|a_\gamma^\dagger a_\delta^\dagger a_\mu^\dagger(\omega-E_0^N+\hat{H})^{-1}a_\alpha a_\beta a_\nu|\Psi_0^N\rangle \ . \tag{4.2}$$

Here $\hat{H}$ is the Hamiltonian of the system defined in Eqs. (2.8)–(2.11). Alternatively, we can introduce in Eq. (4.2) a complete set of configuration states $\{|\Phi_q^{N-3}\rangle\}$ and obtain

$$\mathbf{\Pi}^*(\omega)=\mathbf{Y}^\dagger[(\omega-E_0^N)\mathbf{1}+\mathbf{H}]^{-1}\mathbf{Y} \ , \tag{4.3a}$$

where $\mathbf{H}$ denotes the usual Hamiltonian matrix in the $(N-3)$-particle configuration space

$$H_{qq'}=\langle\Phi_q^{N-3}|\hat{H}|\Phi_{q'}^{N-3}\rangle \ , \tag{4.3b}$$

and $\mathbf{Y}$ is a rectangular matrix of elements

$$Y_{q,\alpha\beta\nu}=\langle\Phi_q^{N-3}|a_\alpha a_\beta a_\nu|\Psi_0^N\rangle \ . \tag{4.3c}$$

Equations (4.1) and (4.3) are two different but equivalent representations of the general form in Eq. (4.2). In the former equation the Hamiltonian is represented in the eigenbasis and the Hamiltonian matrix is diagonal. In the latter equation the Hamiltonian matrix is built up on a suitable complete basis set of configurations and is nondiagonal.

The starting point of the algebraic method is the nondiagonal form in Eqs. (4.3) of the propagator. For later purposes it is reasonable to consider the configuration set $\{|\Phi_q^{N-3}\rangle\}$ appearing in Eqs. (4.3) as composed of the so-called $3h$, $4h\,1p$, $5h\,3p$, ... configuration states:

$$\{|\Phi_q^{N-3}\rangle\}=\{|\Phi_{q(3h)}^{N-3}\rangle\}\cup\{|\Phi_{q(4h1p)}^{N-3}\rangle\}\cup\cdots$$
$$=a\cup b \ . \tag{4.4}$$

In this equation we indicated with a the first subset $\{|\Phi_{q(3h)}^{N-3}\rangle\}$ and with b the sets complementary to the first one. The above classification is made with respect to the Hartree-Fock determinant $|\Phi_0^N\rangle$ (ground state of $\hat{H}_0$). With $mh(m-3)p$ we indicate how many holes (h) and how many particles (p) have been created, respectively, in the occupied and unoccupied orbitals of $|\Phi_0^N\rangle$.

Consistent with the notation used in Ref. [12] and Eq. (4.4), we introduce now the following block structure for the configuration-interaction matrix $\mathbf{H}$:

$$\mathbf{H}=\begin{bmatrix}\mathbf{H}_{aa} & \mathbf{H}_{ab}\\ \mathbf{H}_{ba} & \mathbf{H}_{bb}\end{bmatrix} . \tag{4.5}$$

Moreover, we introduce the following sets of auxiliary functions:

$$\mathcal{A}=\{a_i a_j a_k|\Psi_0^N\rangle,\ i<j<k\} \ , \tag{4.6a}$$

$$\mathcal{B}=\{a_u a_i a_j|\Psi_0^N\rangle,\ i<j\} \ , \tag{4.6b}$$

$$\mathcal{C}=\{a_u a_v a_i|\Psi_0^N\rangle,\ u<v\} \ , \tag{4.6c}$$

$$\mathcal{D}=\{a_u a_v a_w|\Psi_0^N\rangle,\ u<v<w\} \ . \tag{4.6d}$$

Here and in the following we specify with the indices $i,j,k,l,\ldots$ and $u,v,w,\ldots$ the orbitals which are occupied and unoccupied in the Hartree-Fock determinant, respectively. Taking into account the definition of the auxiliary functions [Eqs. (4.6)] and the splitting of the configuration states into the classes a and b [Eq. (4.4)], the matrix $\mathbf{Y}$ of the residues [Eq. (4.3c)] can be represented as a block matrix with the following structure:

$$\mathbf{Y}=\begin{bmatrix}\mathbf{Y}_{a\mathcal{A}} & \mathbf{Y}_{a\mathcal{B}} & \mathbf{Y}_{a\mathcal{C}} & \mathbf{Y}_{a\mathcal{D}}\\ \mathbf{Y}_{b\mathcal{A}} & \mathbf{Y}_{b\mathcal{B}} & \mathbf{Y}_{b\mathcal{C}} & \mathbf{Y}_{b\mathcal{D}}\end{bmatrix} . \tag{4.7}$$

The central point of the algebraic method is to introduce in Eq. (4.3a) a unitary transformation $\mathbf{T}$ which transforms the Hamiltonian matrix $\mathbf{H}$ and the matrix $\mathbf{Y}$ according to the following equations:

$$\tilde{\mathbf{H}}=\mathbf{T}^\dagger\mathbf{H}\mathbf{T} \ , \tag{4.8a}$$

$$\tilde{\mathbf{Y}}=\mathbf{T}^\dagger\mathbf{Y} \ . \tag{4.8b}$$

The *ppp* propagator thus takes on the following appearance:

$$\mathbf{\Pi}^*(\omega)=\tilde{\mathbf{Y}}^\dagger[(\omega-E_0^N)\mathbf{1}+\tilde{\mathbf{H}}]^{-1}\tilde{\mathbf{Y}} \ . \tag{4.9}$$

The reason for the introduction of the unitary transformation $\mathbf{T}$ is the following: To obtain the triple-ionization energies one has to diagonalize the Hamiltonian matrix $\mathbf{H}$ [Eq. (4.3b)] or equivalently the transformed matrix $\tilde{\mathbf{H}}$ [Eq. (4.8a)]. For the matrix $\mathbf{H}$ [which represents the configuration-interaction (CI) matrix in the $(N-3)$-particle space] the dimension of the eigenvalue problem can be easily determined, depending on which "order of consistency" is required for the results. We could re-

quire, for instance, that the triple-ionization energies for transitions to $(N-3)$-particle states with large $3h$ component should be consistent at the second order of the perturbation theory. In this case a perturbation theoretical analysis shows that the configuration space of the matrix $\mathbf{H}$ must comprise the configuration classes $3h$, $4h\,1p$, and $5h\,2p$. The major characteristic of the transformation matrix $\mathbf{T}$ introduced in Eqs. (4.8) is that for a given order of consistency the eigenvalue problem of $\tilde{\mathbf{H}}$ requires a smaller working space than the matrix $\mathbf{H}$. In particular, to achieve consistency at second order for the triple-ionization energies for transitions to $3h$ states the necessary working space of $\tilde{\mathbf{H}}$ is composed only of the classes $3h$ and $4h\,1p$. In general, the matrix $\tilde{\mathbf{H}}$ allows us to calculate the triple-ionization energy by means of an eigenvalue problem which is the smallest possible for each required order of consistency. The fact that the working space is smaller than the working space of a comparable CI is a common characteristic of the approximation methods based on Green's functions and thus also of ADC [13–15].

The unitary transformation matrix $\mathbf{T}$ possesses the same block structure as the Hamiltonian matrix $\mathbf{H}$ [Eq. (4.5)] and reads as [12,21]

$$\mathbf{T}=\mathbf{U}(\mathbf{U}^{\dagger}\mathbf{U})^{-1/2}\,, \tag{4.10}$$

where

$$\mathbf{U}=\begin{pmatrix}\mathbf{1} & \mathbf{Z}\\ -\mathbf{Z}^{\dagger} & \mathbf{1}\end{pmatrix}\begin{pmatrix}\mathbf{1} & \mathbf{0}\\ \mathbf{0} & \mathbf{B}\end{pmatrix}=\begin{pmatrix}\mathbf{1} & \mathbf{ZB}\\ -\mathbf{Z}^{\dagger} & \mathbf{B}\end{pmatrix}. \tag{4.11}$$

The elements of the matrix $\mathbf{Z}$ appearing as the off-diagonal block in $\mathbf{U}$ satisfy the following relation:

$$(\mathbf{Z})^{\dagger}_{\mu,ijk}=-\frac{\langle\Phi^{N-3}_{q(\mu)}|a_i a_j a_k|\Psi^N_0\rangle}{\langle\Phi^N_0|\Psi^N_0\rangle}\,. \tag{4.12}$$

Here μ represents a cumulative index for the classes $4h\,1p$, $5h\,2p$, etc., i.e., for the configuration classes of the space b. The triple of indices $\{ijk\}$ can be considered a label for the configurations of the subset a, since for any $|\Phi^{N-3}_{q(3h)}\rangle$ we can write

$$|\Phi^{N-3}_{q(3h)}\rangle=|\Phi^{N-3}_{ijk}\rangle=a_i a_j a_k|\Phi^N_0\rangle,\ i<j<k\,.$$

Equation (4.12) shows that the matrix $\mathbf{Z}$ depends on the exact N-particle ground state of the system only. It is important to note also that the matrix $\mathbf{B}$ and thus $\mathbf{U}$ and the whole transformation matrix $\mathbf{T}$ contain the exact ground state as the sole unknown quantity. The explicit derivation of Eq. (4.12) and of the matrix $\mathbf{B}$ is discussed in detail in Refs. [12,21]. For the present purposes it is only sufficient to observe that the matrix $\mathbf{B}$ possesses a zeroth-order (which can be identified with the unit matrix $\mathbf{1}_b$ in the space b) and a vanishing first-order contribution. The second and higher orders of the matrix $\mathbf{B}$ contribute to the perturbation expansion of the propagator only in fourth order and beyond. Thus for a second-order approximation scheme of the propagator the matrix $\mathbf{B}$ can be set equal to $\mathbf{1}_b$.

For brevity of notation we introduce the following expression for the normalization matrix $(\mathbf{U}^{\dagger}\mathbf{U})^{-1/2}$ which appears in the definition of $\mathbf{T}$ [Eq. (4.10)]:

$$(\mathbf{U}^{\dagger}\mathbf{U})^{-1/2}=\begin{pmatrix}\mathbf{1}+\mathbf{ZZ}^{\dagger} & \mathbf{0}\\ \mathbf{0} & \mathbf{B}^{\dagger}(\mathbf{1}+\mathbf{Z}^{\dagger}\mathbf{Z})\mathbf{B}\end{pmatrix}^{-1/2}=\begin{pmatrix}\mathbf{P} & \mathbf{0}\\ \mathbf{0} & \mathbf{Q}\end{pmatrix}. \tag{4.13a}$$

We can now write the transformed matrix $\tilde{\mathbf{H}}$ [Eq. (4.8a)] and the residues $\tilde{\mathbf{Y}}$ [Eq. (4.8b)] in closed form. In particular, one finds that $\mathbf{P}$ has a simple appearance as a ground-state expectation value, since the following relation holds:

$$(\mathbf{1}+\mathbf{ZZ}^{\dagger})_{ijk,lmn}=\frac{\langle\Psi^N_0|a^{\dagger}_k a^{\dagger}_j a^{\dagger}_i a_l a_m a_n|\Psi^N_0\rangle}{|\langle\Phi^N_0|\Psi^N_0\rangle|^2}\,. \tag{4.13b}$$

Bearing in mind that $\tilde{\mathbf{H}}$ and $\tilde{\mathbf{Y}}$ have, respectively, the same block structure as $\mathbf{H}$ and $\mathbf{Y}$, one obtains for the transformed Hamiltonian

$$\tilde{\mathbf{H}}_{aa}=\mathbf{P}[(\mathbf{H}_{aa}-\mathbf{ZH}_{ba})-(\mathbf{H}_{ab}-\mathbf{ZH}_{bb})\mathbf{Z}^{\dagger}]\mathbf{P}\,, \tag{4.14a}$$

$$\tilde{\mathbf{H}}_{ab}=\mathbf{P}[(\mathbf{H}_{aa}-\mathbf{ZH}_{ba})\mathbf{Z}+(\mathbf{H}_{ab}-\mathbf{ZH}_{bb})]\mathbf{Q}\,, \tag{4.14b}$$

$$\tilde{\mathbf{H}}_{ba}=\mathbf{Q}[(\mathbf{Z}^{\dagger}\mathbf{H}_{aa}+\mathbf{H}_{ba})-(\mathbf{Z}^{\dagger}\mathbf{H}_{ab}+\mathbf{H}_{bb})\mathbf{Z}^{\dagger}]\mathbf{P}\,, \tag{4.14c}$$

$$\tilde{\mathbf{H}}_{bb}=\mathbf{Q}[(\mathbf{Z}^{\dagger}\mathbf{H}_{aa}+\mathbf{H}_{ba})\mathbf{Z}+(\mathbf{Z}^{\dagger}\mathbf{H}_{ab}+\mathbf{H}_{bb})]\mathbf{Q}\,, \tag{4.14d}$$

and analogously for the transformed matrix of the residues

$$\tilde{\mathbf{Y}}_{a\mathcal{A}}=\langle\Phi^N_0|\Psi^N_0\rangle(\mathbf{1}+\mathbf{ZZ}^{\dagger})^{1/2}\,, \tag{4.15a}$$

$$\tilde{\mathbf{Y}}_{a\mathcal{B}}=\mathbf{P}(\mathbf{Y}_{a\mathcal{B}}-\mathbf{ZY}_{b\mathcal{B}})\,, \tag{4.15b}$$

$$\tilde{\mathbf{Y}}_{a\mathcal{C}}=\mathbf{P}(\mathbf{Y}_{a\mathcal{C}}-\mathbf{ZY}_{b\mathcal{C}})\,, \tag{4.15c}$$

$$\tilde{\mathbf{Y}}_{a\mathcal{D}}=\mathbf{P}(\mathbf{Y}_{a\mathcal{D}}-\mathbf{ZY}_{b\mathcal{D}})\,, \tag{4.15d}$$

$$\tilde{\mathbf{Y}}_{b\mathcal{A}}=\mathbf{0}\,, \tag{4.15e}$$

$$\tilde{\mathbf{Y}}_{a\mathcal{B}}=\mathbf{Q}(\mathbf{Z}^{\dagger}\mathbf{Y}_{a\mathcal{B}}+\mathbf{Y}_{b\mathcal{B}})\,, \tag{4.15f}$$

$$\tilde{\mathbf{Y}}_{a\mathcal{C}}=\mathbf{Q}(\mathbf{Z}^{\dagger}\mathbf{Y}_{a\mathcal{C}}+\mathbf{Y}_{b\mathcal{C}})\,, \tag{4.15g}$$

$$\tilde{\mathbf{Y}}_{a\mathcal{D}}=\mathbf{Q}(\mathbf{Z}^{\dagger}\mathbf{Y}_{a\mathcal{D}}+\mathbf{Y}_{b\mathcal{D}})\,. \tag{4.15h}$$

It is interesting to observe that the block $\tilde{\mathbf{Y}}_{b\mathcal{A}}$ of $\tilde{\mathbf{Y}}$ vanishes identically. The above equations represent exact expressions for $\tilde{\mathbf{H}}$ and $\tilde{\mathbf{Y}}$ which depend only on $|\Psi^N_0\rangle$. Therefore the perturbation theoretical expansion of Eqs. (4.14) and (4.15) does not present problems of "intruder states" [22] or "dangerous denominators," i.e., denominators given by zeroth-order energy differences between degenerate or quasidegenerate states.

By means of Rayleigh-Schrödinger perturbation theory (RSPT), which is well defined for $|\Psi^N_0\rangle$, we will carry out in the following the calculation of the second-order approximation scheme for the *ppp* propagator. As already mentioned, for a second-order approximation scheme the working space of the transformed Hamiltonian $\tilde{\mathbf{H}}$ has to contain the configuration classes $3h$ and $4h\,1p$. Thus, we can identify the space b in Eqs. (4.14) and (4.15) with the class $4h\,1p$ of the $(N-3)$-particle configuration space.

The only necessary quantity for the perturbation expansion of the propagator is the RSPT for $|\Psi_0^N\rangle$. This can be formally written as

$$|\Psi_0^N\rangle = |\Psi_0^{(0)N}\rangle + |\Psi_0^{(1)N}\rangle + |\Psi_0^{(2)N}\rangle + \cdots \ . \tag{4.16}$$

The explicit form of the contributions $|\Psi_0^{(i)N}$ up to third order can be found for instance in Ref. [12(a)]. As usual, each of the $|\Psi_0^{(i)N}\rangle$ can be expressed as a linear combination of configurations $|\Phi_q^N\rangle$. Analogously to the classification introduced for the $(N-3)$-particle configuration states, we subdivide the set $\{|\Phi_q^N\rangle\}$ into classes according to

$$\{|\Phi_q^N\rangle\} = \{|\Phi_0^N\rangle\} \cup \{|\Phi_{q(\gamma)}^N\rangle\} \ , \tag{4.17}$$

where the set $\{|\Phi_{q(\gamma)}^N\rangle\}$ contains the configuration classes $1h\,1p$, $2h\,2p$,.... Using the expansion (4.16) of $|\Psi_0^N\rangle$, we can write the perturbation expansion of the transformed matrices $\tilde{\mathbf{H}}$ [Eq. (4.8a)] and $\tilde{\mathbf{Y}}$ [Eq. (4.8b)] as follows:

$$\tilde{\mathbf{H}} = \tilde{\mathbf{H}}^{(0)} + \tilde{\mathbf{H}}^{(1)} + \tilde{\mathbf{H}}^{(2)} + \cdots = \tilde{\mathbf{H}}^{(0)} + \tilde{\mathbf{H}}_I \ , \tag{4.18a}$$

$$\tilde{\mathbf{Y}} = \tilde{\mathbf{Y}}^{(0)} + \tilde{\mathbf{Y}}^{(1)} + \tilde{\mathbf{Y}}^{(2)} + \cdots = \tilde{\mathbf{Y}}^{(0)} + \tilde{\mathbf{Y}}_I \ . \tag{4.18b}$$

It is easy to see that the zeroth-order contribution $\tilde{\mathbf{H}}^{(0)}$ to $\tilde{\mathbf{H}}$ is identical to the zeroth-order contribution to the configuration-interaction matrix $\mathbf{H}$:

$$\tilde{\mathbf{H}}^{(0)} = \begin{bmatrix} \tilde{\mathbf{H}}_{aa}^{(0)} & \mathbf{0} \\ \mathbf{0} & \tilde{\mathbf{H}}_{bb}^{(0)} \end{bmatrix} . \tag{4.19a}$$

$\tilde{\mathbf{H}}^{(0)}$ is diagonal and its matrix elements read as

$$\tilde{H}_{qq'}^{(0)} = \langle \Phi_q^{N-3} | \hat{H}_0 | \Phi_{q'}^{N-3} \rangle \delta_{qq'} \ . \tag{4.19b}$$

In this equation $\delta_{qq'}$ represents the Kronecker symbol. It should be mentioned that the equality $\tilde{\mathbf{H}}$ and $\mathbf{H}$ in zeroth order holds in all $(N-3)$-particle configuration subspaces. The zeroth order of the transformed matrix of the residues $\tilde{\mathbf{Y}}$ is given by the following matrix:

$$\tilde{\mathbf{Y}}^{(0)} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} . \tag{4.20}$$

At first order the matrix $\tilde{\mathbf{H}}^{(1)}$ reads as

$$\tilde{\mathbf{H}}^{(1)} = \begin{bmatrix} \tilde{\mathbf{H}}_{aa}^{(1)} & \tilde{\mathbf{H}}_{ab}^{(1)} \\ \tilde{\mathbf{H}}_{ba}^{(1)} & \tilde{\mathbf{H}}_{bb}^{(1)} \end{bmatrix} . \tag{4.21a}$$

We remember that the space b can be identified with the class $4h\,1p$ only. The matrix elements of $\tilde{\mathbf{H}}^{(1)}$ can be easily obtained by Eqs. (4.14) in terms of the Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}_I$ and the matrix $\mathbf{Z}$:

$$\tilde{\mathbf{H}}_{aa}^{(1)} = \mathbf{H}_{Iaa} \ , \tag{4.21b}$$

$$\tilde{\mathbf{H}}_{ba}^{(1)} = \mathbf{Z}^{\dagger(1)} \mathbf{H}_{0aa} + \mathbf{H}_{Iba} - \mathbf{H}_{0bb} \mathbf{Z}^{(1)} \ , \tag{4.21c}$$

$$\tilde{\mathbf{H}}_{bb}^{(1)} = \mathbf{H}_{Ibb} \ , \tag{4.21d}$$

$$\tilde{\mathbf{H}}_{ab}^{(1)} = (\tilde{\mathbf{H}}_{ba}^{(1)})^{\dagger} \ . \tag{4.21e}$$

Taking into account that the matrix $\mathbf{Z}^{(1)}$ vanishes identically for $\mu = 4h\,1p$, if the unperturbed state $|\Psi_0^N\rangle$ is the Hartree-Fock determinant [see Eq. (4.12)], it follows that the transformed Hamiltonian matrix is identical to the configuration-interaction matrix, i.e.,

$$\tilde{H}_{qq'}^{(1)} = \langle \Phi_q^{N-3} | \hat{H}_I | \Phi_{q'}^{N-3} \rangle \quad \text{for } q,q' \in 3h, 4h\,1p \ . \tag{4.21f}$$

The first-order coupling block $\tilde{\mathbf{H}}_{ba}^{(1)}$ vanishes for the higher classes of configurations ($5h\,2p, 6h\,3p, \ldots$) of the space b.

The transformed matrix of the residues in first order takes on the following form:

$$\tilde{\mathbf{Y}}^{(1)} = \begin{bmatrix} 0 & 0 & \tilde{\mathbf{Y}}_{a\mathcal{C}}^{(1)} & 0 \\ 0 & \tilde{\mathbf{Y}}_{b\mathcal{B}}^{(1)} & 0 & 0 \end{bmatrix} . \tag{4.22}$$

In order to write the nonvanishing blocks of $\tilde{\mathbf{Y}}^{(1)}$ in explicit form one has to consider the first-order contribution $|\Psi_0^{(1)N}\rangle$ to the N-particle ground state:

$$|\Psi_0^{(1)N}\rangle = \sum_q c_q^{(1)} |\Phi_q^N\rangle \ . \tag{4.23}$$

If $|\Phi_0^N\rangle$ is the Hartree-Fock determinant, only the $2h\,2p$ configurations contribute to $|\Psi_0^{(1)N}\rangle$ (Brillouin theorem). The nonvanishing elements of the matrix $\tilde{\mathbf{Y}}^{(1)}$ can thus be written as

$$(\tilde{\mathbf{Y}}_{a\mathcal{C}}^{(1)})_{ijk,uvm} = \langle \Phi_{ijk}^{N-3} | a_u a_v a_m | \Psi_0^{(1)N} \rangle \ , \tag{4.24a}$$

$$(\tilde{\mathbf{Y}}_{b\mathcal{B}}^{(1)})_{uijkl,vmn} = \langle \Phi_{uijkl}^{N-3} | a_v a_m a_n | \Psi_0^{(1)N} \rangle \ . \tag{4.24b}$$

In the latter equation we used the label $\{uijkl\}$ to indicate explicitly the $4h\,1p$ configuration state

$$|\Phi_{q(4h1p)}^{N-3}\rangle = |\Phi_{uijkl}^{N-3}\rangle = a_u^{\dagger} a_i a_j a_k a_l |\Phi_0^N\rangle \ .$$

To complete the second-order approximation scheme for the *ppp* propagator we further need the second-order contribution $\tilde{\mathbf{H}}_{aa}^{(2)}$ of the transformed Hamiltonian in the subspace a and the second-order contributions to the first row of blocks of the matrix $\tilde{\mathbf{Y}}$, i.e., the blocks $\tilde{\mathbf{Y}}_{a\mathcal{A}}^{(2)}$, $\tilde{\mathbf{Y}}_{a\mathcal{B}}^{(2)}$, $\tilde{\mathbf{Y}}_{a\mathcal{C}}^{(2)}$, and $\tilde{\mathbf{Y}}_{a\mathcal{D}}^{(2)}$. The blocks $\tilde{\mathbf{H}}_{bb}$ and $\tilde{\mathbf{H}}_{ba}$ of $\tilde{\mathbf{H}}$ and the second row of blocks of $\tilde{\mathbf{Y}}$ are needed only up to first order (see below).

One obtains for the transformed Hamiltonian

$$\tilde{\mathbf{H}}_{aa}^{(2)} = \mathbf{P}^{(2)} \mathbf{H}_{0aa} + \mathbf{H}_{0aa} \mathbf{P}^{(2)} - \mathbf{Z}^{(1)} \mathbf{H}_{Iba} - \mathbf{H}_{Iab} \mathbf{Z}^{\dagger(1)} + \mathbf{Z}^{(1)} \mathbf{H}_{0bb} \mathbf{Z}^{\dagger(1)} \tag{4.25a}$$

or, explicitly,

$$(\tilde{\mathbf{H}}^{(2)}_{aa})_{ijk,lmn} = -\tfrac{1}{2}\langle\Psi_0^{(1)N}|a_k^\dagger a_j^\dagger a_i^\dagger a_l a_m a_n|\Psi_0^{(1)N}\rangle(\langle\Phi_{lmn}^{N-3}|\hat{H}_0|\Phi_{lmn}^{N-3}\rangle + \langle\Phi_{ijk}^{N-3}|\hat{H}_0|\Phi_{ijk}^{N-3}\rangle)$$
$$+ \sum_\mu \langle\Psi_0^{(1)N}|a_k^\dagger a_j^\dagger a_i^\dagger|\Phi_{q(\mu)}^{N-3}\rangle\langle\Phi_{q(\mu)}^{N-3}|\hat{H}_I|\Phi_{lmn}^{N-3}\rangle + \sum_\mu \langle\Phi_{ijk}^{N-3}|\hat{H}_I|\Phi_{q(\mu)}^{N-3}\rangle\langle\Phi_{q(\mu)}^{N-3}|a_l a_m a_n|\Psi_0^{(1)N}\rangle$$
$$+ \sum_\mu \langle\Psi_0^{(1)N}|a_k^\dagger a_j^\dagger a_i^\dagger|\Phi_{q(\mu)}^{N-3}\rangle\langle\Phi_{q(\mu)}^{N-3}|\hat{H}_0|\Phi_{q(\mu)}^{N-3}\rangle\langle\Phi_{q(\mu)}^{N-3}|a_l a_m a_n|\Psi_0^{(1)N}\rangle \ . \tag{4.25b}$$

It is interesting to observe that this expression contains a sum over the configurations μ of the subspace b. It is easy to see that this sum can be restricted to the class $\mu = 5h2p$ only. Furthermore, only the first-order term of $|\Psi_0^N\rangle$ contributes.

The second-order contributions to the matrix $\tilde{\mathbf{Y}}$ necessary for the second-order approximation scheme are given by the following expressions:

$$(\tilde{\mathbf{Y}}^{(2)}_{a\mathcal{A}})_{ijk,lmn} = \langle\Phi_0^N|\Psi_0^{(2)N}\rangle\delta_{il}\delta_{jm}\delta_{kn} + \tfrac{1}{2}\langle\Psi_0^{(1)N}|a_k^\dagger a_j^\dagger a_i^\dagger a_l a_m a_n|\Psi_0^{(1)N}\rangle \ , \tag{4.26a}$$

$$(\tilde{\mathbf{Y}}^{(2)}_{a\mathcal{B}})_{ijk,umn} = \langle\Phi_{ijk}^{N-3}|a_u a_m a_n|\Psi_0^{(2)N}\rangle \ , \tag{4.26b}$$

$$(\tilde{\mathbf{Y}}^{(2)}_{a\mathcal{C}})_{ijk,uvm} = \langle\Phi_{ijk}^{N-3}|a_u a_v a_m|\Psi_0^{(2)N}\rangle \ , \tag{4.26c}$$

$$(\tilde{\mathbf{Y}}^{(2)}_{a\mathcal{D}})_{ijk,uvw} = \langle\Phi_{ijk}^{N-3}|a_u a_v a_w|\Psi_0^{(2)N}\rangle \ . \tag{4.26d}$$

To calculate these matrix elements it is now necessary to evaluate the second-order contribution $|\Psi_0^{(2)N}\rangle$ to $|\Psi_0^N\rangle$.

To generally make clear which term of $\tilde{\mathbf{H}}$ and $\tilde{\mathbf{Y}}$ contributes to which order of the propagator we expand the matrix $[(\omega - E_0^N)\mathbf{1} + \tilde{\mathbf{H}}]^{-1}$ of Eq. (4.9) in power of $(\omega\mathbf{1} - E_0^{(0)N}\mathbf{1} + \tilde{\mathbf{H}}^{(0)})^{-1}(\tilde{\mathbf{H}}_I - E_{0,I}^N)$. We note that $\tilde{\mathbf{H}} = \tilde{\mathbf{H}}^{(0)} + \tilde{\mathbf{H}}_I$ and bear in mind the RSPT expansion of the neutral ground-state energy E_0^N:

$$E_0^N = E_0^{(0)N} + E_0^{(1)N} + E_0^{(2)N} + \cdots = E_0^{(0)N} + E_{0,I}^N \ . \tag{4.27}$$

One obtains the following expression:

$$\mathbf{\Pi}^*(\omega) = \tilde{\mathbf{Y}}^\dagger\{[(\omega - E_0^{(0)N})\mathbf{1} + \tilde{\mathbf{H}}^{(0)}]^{-1}$$
$$- [(\omega - E_0^{(0)N})\mathbf{1} + \tilde{\mathbf{H}}^{(0)}]^{-1}(\tilde{\mathbf{H}}_I - E_{0,I}^N)[(\omega - E_0^{(0)N})\mathbf{1} + \tilde{\mathbf{H}}^{(0)}]^{-1}$$
$$+ [(\omega - E_0^{(0)N})\mathbf{1} + \tilde{\mathbf{H}}^{(0)}]^{-1}(\tilde{\mathbf{H}}_I - E_{0,I}^N)[(\omega - E_0^{(0)N})\mathbf{1} + \tilde{\mathbf{H}}^{(0)}]^{-1}$$
$$\times(\tilde{\mathbf{H}}_I - E_{0,I}^N)[(\omega - E_0^{(0)N})\mathbf{1} + \tilde{\mathbf{H}}^{(0)}]^{-1} + \cdots\}\tilde{\mathbf{Y}} \ . \tag{4.28}$$

By means of this expression we can determine which blocks of $\tilde{\mathbf{H}}$ and $\tilde{\mathbf{Y}}$ are necessary to obtain a consistent representation of the propagator at a given order of perturbation theory. In particular, a glance at Eqs. (4.19) and (4.20) is sufficient to demonstrate that for a second-order approximation scheme the only second-order contributions needed are those of the block $\tilde{\mathbf{H}}_{aa}$ and of the upper row of blocks of the matrix $\tilde{\mathbf{Y}}$.

In summary, in our first-order approximation the *ppp* propagator is given by Eq. (4.9), where the space of the matrices spans the $3h$ configurations (subspace a). The effective Hamiltonian $\tilde{\mathbf{H}}$ is just given by $\tilde{\mathbf{H}}^{(0)}_{aa} + \tilde{\mathbf{H}}^{(1)}_{aa}$ [see Eqs. (4.19b) and (4.21b)]. The matrix of the effective residues $\tilde{\mathbf{Y}}$ is nonvanishing only in the blocks of columns labeled $\mathcal{A}$ and $\mathcal{C}$. Up to first order the block $\tilde{\mathbf{Y}}_{a\mathcal{A}}$ can be identified with the unit matrix [see Eq. (4.20)], while the block $\tilde{\mathbf{Y}}_{a\mathcal{C}}$ has the simple form as given in Eq. (4.24a).

In the second-order scheme the space of the matrices in Eq. (4.9) spans the $3h$ and the $4h1p$ configurations. The latter constitute the first configuration class of the subspace b. The second-order term of the effective Hamiltonian $\tilde{\mathbf{H}}_{aa}$ is given by Eq. (4.25). The coupling block $\tilde{\mathbf{H}}_{ba}$ and the block $\tilde{\mathbf{H}}_{bb}$ are needed only at first order and are equal to the Hamiltonian matrix $\mathbf{H}$ [see Eqs. (4.21)]. The needed matrix $\tilde{\mathbf{Y}}$ has second-order contributions only in the first row of blocks according to Eqs. (4.26). In the lower row of blocks the first-order contributions are sufficient for a consistent second-order approximation scheme of the propagator. Here there are nonvanishing terms only in the block of columns labeled $\mathcal{B}$ [see Eqs. (4.22) and (4.24b)].

Finally, we note that in our algebraic method the explicit formulation of the perturbation scheme is given in "configuration form," i.e., the formulas presented in this section for the contributions $\tilde{\mathbf{H}}^{(i)}$ and $\tilde{\mathbf{Y}}^{(i)}$ are expressed in terms of matrix elements of the Hamiltonian between configuration classes of the $(N-3)$-particle space and of coefficients c_q [see Eq. (4.23)]. The latter are essentially matrix elements of the Hamiltonian matrix in the N-particle space. Writing explicitly the states which compose the different configuration classes in terms of creation and annihilation operators acting on $|\Phi_0^N\rangle$ and using the second quantization form of the Hamiltonian [Eqs. (2.8–(2.11)], the formulas in configuration form can be transformed into products of two-particle integrals $V_{\alpha\beta\gamma\delta}$ and orbital energies ϵ_α. The procedure is, in principle, quite simple but lengthy. An example showing the technical characteristics is illustrated in Ref. [12(a)]. We

have carried out this transformation into orbital form. The results are the ADC equations which are presented in the following section.

V. ADC APPROACH AND WORKING EQUATIONS IN ORBITAL FORM

It is well known that the perturbation theoretical analysis of any Green's function can be carried out in terms of Feynman diagrams [7,8,20]. ADC is a well-established method of constructing approximation schemes for Green's functions and propagators based on Feynman diagrams. The diagrammatic expansion at nth order of the complete *ppp* propagator [Eq. (2.4)] can be obtained by drawing all topologically distinct diagrams which contain n interaction vertices and $2n+3$ arrowed solid lines (free Green's-function lines). All Feynman diagrams start and end with three solid lines pointing upwards. The Feynman diagrams of the *ppp* propagator up to second order are drawn in Fig. 1. The upper (lower) extreme of each diagram is characterized by the time t (t'). In Fig. 1 and in the following pictures we use the Abrikosov notation according to which each interaction point represents an antisymmetrized element $(V_{\alpha\beta\gamma\delta}-V_{\alpha\beta\delta\gamma})$ of the interaction term $\hat{H}_I$ of the Hamiltonian. In each interaction point four (two outgoing and two incoming) arrowed lines meet. The use of the Abrikosov notation is very advantageous compared with the Feynman notation because of the reduced number of diagrams to be analyzed. We reiterate that in the Feynman notation the interaction vertices are represented by wavy lines corresponding to nonantisymmetrized matrix elements $V_{\alpha\beta\gamma\delta}$.

As can be seen from Fig. 1 there are three types of diagrams. The zeroth-order diagram and the first diagram of second order are composed of three disjoint lines. The second type contains those diagrams with two lines connected together by interaction points and one disjoint line. Up to second order this is the most common type of diagram. The third type of diagrams shows all three lines connected together by interaction points. There is only one diagram of this type in the diagrammatic expansion up to second order.

Feynman diagrams can be interpreted in time space or in energy space. In the latter case there are two different procedures to evaluate them: One can perform the Fourier transformation of the analytical expressions obtained from the diagrams in time space or, equivalently, one can consider the so-called time-ordered Goldstone diagrams, which can be directly interpreted in energy space. The Goldstone diagrams can be obtained from the Feynman diagrams by permuting in all possible ways the extremes and the interaction points. The number of Goldstone diagrams for a given nth-order Feynman diagram is thus $(n+2)!$. The set of Goldstone diagrams can be exactly divided into two subsets which describe separately the perturbation expansion of $\Pi^{(+)}$ and $\Pi^{(-)}$. The two subsets of diagrams are characterized by the ordering of the external times t and t'. The diagrams of $\Pi^{(-)}$ are characterized by $t'>t$. The first- and second-order Goldstone diagrams of $\Pi^{(-)}$ are drawn in Figs. 2 and 3, respectively. We use the convention that the time axis points upwards. It is interesting to note that the Feynman diagram of second order labeled C gives rise to only 6 topologically different Goldstone diagrams while the other second-order diagrams give rise to 12.

In the following we list the rules for reading the Goldstone diagrams of the *ppp* propagator.

(1) *Particle and hole lines.* To each particle (hole) line is associated a particle (hole) index and a negative (positive) one-particle energy $-(+)\epsilon_\alpha$. A particle (hole) line is a line pointing upwards (downwards).

(2) *ω line.* The sign of the energy variable ω is defined by the so-called ω line, an auxiliary arrowed line which has to be taken into account in each Goldstone diagram. The ω line starts at the time t and ends at the time t', flowing in direction $t\rightarrow t'$. If the ω line points upwards (downwards), the ω variable carries a $-(+)$ sign. In the case of $\Pi^{(-)}$ the ω line points upwards and the ω variable has a minus sign.

(3) *Interaction points.* Each interaction point is connected with four arrowed lines, two outgoing and two incoming. It represents an antisymmetrized matrix element of the two-particle interaction $\hat{H}_I$: $V_{\alpha\beta[\gamma\delta]}=V_{\alpha\beta\gamma\delta}-V_{\alpha\beta\delta\gamma}$. The four indices $\alpha,\beta,\gamma,\delta$ are the labels of the four lines converging to the interaction point.

(4) *Denominators.* The horizontal line which can be drawn between any two neighboring connection points (including the extrema) gives rise to a denominator of the form

$$\sigma\omega+\epsilon_i+\epsilon_j+\cdots-\epsilon_u-\epsilon_v+\cdots\ .$$

Each particle $(u,v,\ldots)$ or hole $(i,j,\ldots)$ line which is cut by the horizontal line gives a negative or positive contribution (see rule 1), respectively. If the ω line is also cut, the denominator is said to be ω dependent. In this case the variable ω has a positive ($\sigma=1$) or negative ($\sigma=-1$) sign according to rule 2. If the ω line is not cut the denominator is said ω independent and $\sigma=0$.

(5) *Pairs.* Each pair of equivalent lines of a Goldstone diagram gives a factor of $\frac{1}{2}$.

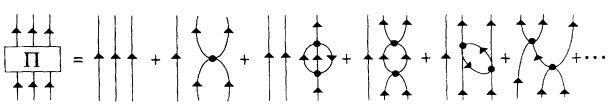

FIG. 1. Perturbation expansion of the *ppp* propagator up to second order in terms of Feynman diagrams.

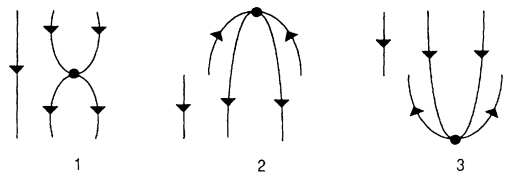

FIG. 2. First-order time-ordered Goldstone diagrams of the *ppp* propagator $\Pi^{(-)}$.

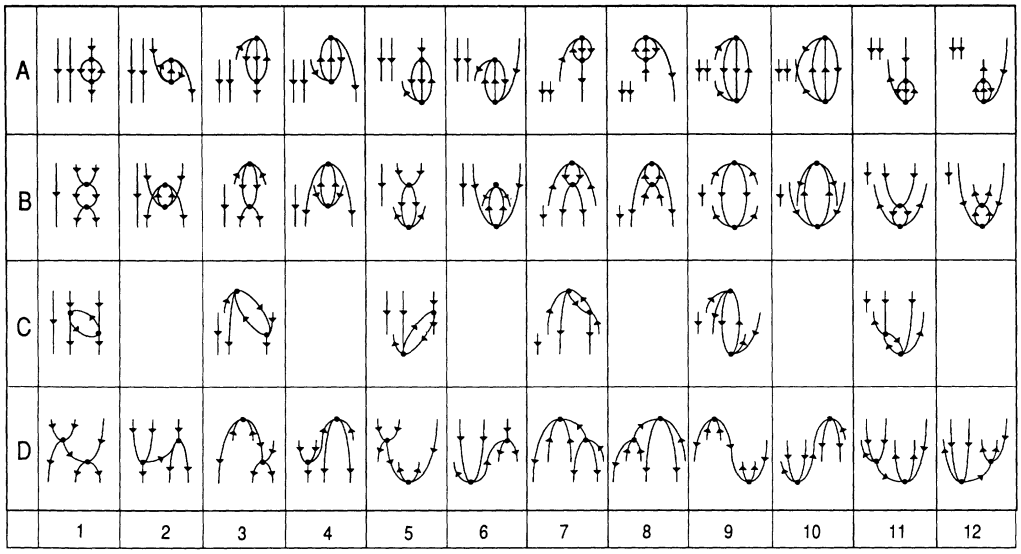

FIG. 3. Second-order time-ordered Goldstone diagrams of the *ppp* propagator $\mathbf{\Pi}^{(-)}$.

(6) *Evaluation.* To evaluate a Goldstone diagram multiply the contribution of all the n interaction points (rule 3) and all the $n+1$ cuts (rule 4) and sum over all the internal particle and hole indices. Multiply the result by a factor

$$(-i)(-i)^n(i)^{n+1}(-1)^h(\tfrac{1}{2})^p=(-1)^h(\tfrac{1}{2})^p ,$$

where h is the number of hole lines and p is the number of pairs of equivalent lines. The factor $-i$ arises from the definition in Eqs. (2.1) and (2.4).

Remark. The overall sign of a Goldstone diagram in Abrikosov notation is not uniquely determined. In order to settle it, it is necessary to analyze one of the corresponding diagrams in Feynman notation. The rules for these diagrams are the same as above except for rule 3 and that each loop (closed line) appearing in the considered diagram in Feynman notation contributes a factor of -1. Instead of interaction points, one has wavy lines representing $V_{\alpha\beta\gamma\delta}$, where α and β are the indices of the outgoing lines and γ and δ are the indices of the incoming lines of the corresponding vertices.

The ADC approach has been discussed in detail elsewhere [13–15]. Here we confine ourselves to the necessary equations, considering explicitly only the part $\mathbf{\Pi}^{(-)}$.

The central point of ADC is to express the *ppp* propagator in the following nondiagonal representation of the general expression in Eq. (4.2), which is equivalent to the specific formulation of the algebraic approach [Eq. (4.3a)]:

$$\mathbf{\Pi}(\omega)=\mathbf{f}^{\dagger}(\omega-\mathbf{K}-\mathbf{C})^{-1}\mathbf{f} . \tag{5.1}$$

The configuration space of the matrices **K**, **C** and **f** is the $(N-3)$-particle space. The matrix **K** is the diagonal matrix of the zeroth-order energy differences. **C** is called the matrix of the effective interaction and **f** is the matrix of the effective transition amplitudes. **C** and **f** can be considered as equivalent to the matrices $(\tilde{\mathbf{H}}_I-E^N_{0,I})$ and to the transformed matrix of the residues $\tilde{\mathbf{Y}}$ of the algebraic method, respectively. The ADC form in Eq. (5.1) can be expressed in power series of the matrix $(\omega-\mathbf{K})^{-1}\mathbf{C}$. In zeroth, first, and second order one obtains, respectively,

$$\mathbf{\Pi}(\omega)^{(0)}=\mathbf{f}^{(0)\dagger}(\omega\mathbf{1}-\mathbf{K})^{-1}\mathbf{f}^{(0)} , \tag{5.2a}$$

$$\mathbf{\Pi}(\omega)^{(1)}=[\mathbf{f}^{(0)\dagger}(\omega\mathbf{1}-\mathbf{K})^{-1}\mathbf{f}^{(1)}]+\text{H.c.} + \mathbf{f}^{(0)\dagger}(\omega\mathbf{1}-\mathbf{K})^{-1}\mathbf{C}^{(1)}(\omega\mathbf{1}-\mathbf{K})^{-1}\mathbf{f}^{(0)} , \tag{5.2b}$$

$$\begin{aligned}\mathbf{\Pi}(\omega)^{(2)}=&[\mathbf{f}^{(0)\dagger}(\omega\mathbf{1}-\mathbf{K})^{-1}\mathbf{f}^{(2)}]+\text{H.c.}\\ &+[\mathbf{f}^{(0)\dagger}(\omega\mathbf{1}-\mathbf{K})^{-1}\mathbf{C}^{(1)}(\omega\mathbf{1}-\mathbf{K})^{-1}\mathbf{f}^{(1)}]+\text{H.c.}\\ &+\mathbf{f}^{(0)\dagger}(\omega\mathbf{1}-\mathbf{K})^{-1}\mathbf{C}^{(1)}(\omega\mathbf{1}-\mathbf{K})^{-1}\\ &\times\mathbf{C}^{(1)}(\omega\mathbf{1}-\mathbf{K})^{-1}\mathbf{f}^{(0)}\\ &+\mathbf{f}^{(0)\dagger}(\omega\mathbf{1}-\mathbf{K})^{-1}\mathbf{C}^{(2)}(\omega\mathbf{1}-\mathbf{K})^{-1}\mathbf{f}^{(0)} ,\end{aligned} \tag{5.2c}$$

where the following perturbation expansions of the matrices **f** and **C** have been used:

$$\mathbf{f}=\mathbf{f}^{(0)}+\mathbf{f}^{(1)}+\mathbf{f}^{(2)}+\cdots , \tag{5.3a}$$

$$\mathbf{C}=\mathbf{C}^{(1)}+\mathbf{C}^{(2)}+\cdots . \tag{5.3b}$$

By comparing order by order the expressions in Eqs. (5.2) with the corresponding diagrammatic expansion in terms of Goldstone diagrams (Figs. 2 and 3) it is possible to derive the matrix elements of the matrices **K**, **C**, and **f**. This derivation is carried out below.

In most applications of ADC it turned out to be advantageous to consider the so-called transition function instead of the propagator itself. The transition function is defined as

$$\mathbf{P}(\omega)=\mathbf{F}^{\dagger}(\omega-\mathbf{K}-\mathbf{C})^{-1}\mathbf{F} , \tag{5.4a}$$

where

$$\mathbf{F}=\mathbf{f}\mathbf{D} . \tag{5.4b}$$

D is a vector of general parameters which can assume precise physical meaning depending on the specific transition process under investigation. The indices of the elements composing **D** are all triple combinations $\{\alpha\beta\gamma\}$ of one-particle indices. The elements $D_{\alpha\beta\gamma}$ are assumed to be symmetric under cyclic permutations:

$$D_{\alpha\beta\gamma}=D_{\beta\gamma\alpha}=D_{\gamma\alpha\beta}=-D_{\alpha\gamma\beta}=-D_{\beta\alpha\gamma}=-D_{\gamma\beta\alpha} .$$

With the introduction of the vector **D** the transition function is a scalar quantity. The power expansion of the transition function yields expressions which are formally identical to Eqs. (5.2) with the substitution $\mathbf{f}\rightarrow\mathbf{F}$. From the diagrammatic point of view **D** can be viewed as a dashed line connecting the external lines of each Goldstone diagram. After having obtained from the diagrams the matrix element of the vector **F** it is not difficult to derive the matrix **f**. This can be done by taking into account the symmetry properties of the auxiliary vector **D**.

The analysis of the diagrams in zeroth and first order is quite simple. In zeroth order there is only one diagram. This diagram has to be compared with the corresponding zeroth-order form [Eq. (5.2a)]. From the comparison one obtains the matrix elements of the diagonal matrix **K** in the $3h$ space,

$$K_{ijk,ijk}=\epsilon_i+\epsilon_j+\epsilon_k , \tag{5.5a}$$

and the zeroth-order contribution to the vector **F** in the same space. The latter is identical to the vector **D**. From this consideration it follows that the block $3h,3h$ of the matrix **f** is identical to the unit matrix:

$$f_{ijk,ijk}=\delta_{ii'}\delta_{jj'}\delta_{kk'} . \tag{5.5b}$$

In first order the analytical form in Eq. (5.2b) has to be compared with the three first-order Goldstone diagrams of Fig. 2. The assignment is also in this case straightforward. The first diagram has to be compared with the last term of Eq. (5.2b). The second diagram of Fig. 2 is associated to the first term of Eq. (5.2b). The third diagram can be considered as the Hermitian conjugate diagram of the first one and does not give rise to new relevant information. From the comparison one easily obtains

$$F^{(1)}_{ijk}=\left[\frac{1}{2}\sum_{u,v}\Gamma_{jkuv}D_{iuv}\right]+(ijk\rightarrow jki)+(ijk\rightarrow kil) , \tag{5.6a}$$

$$\begin{aligned}C^{(1)}_{ijk,lmn}=&[(-V_{jk[mn]}\delta_{il})+(i,j,k\rightarrow j,k,i)\\&+(i,j,k\rightarrow k,i,j)]\\&+[l,m,n\rightarrow m,n,l]+[l,m,n\rightarrow n,l,m] .\end{aligned} \tag{5.6b}$$

In these expressions and in the following we use the notation

$$\Gamma_{\alpha\beta\gamma\delta}=\frac{V_{\alpha\beta[\gamma\delta]}}{\epsilon_\alpha+\epsilon_\beta-\epsilon_\gamma-\epsilon_\delta} \tag{5.7a}$$

with

$$V_{\alpha\beta[\gamma\beta]}=V_{\alpha\beta\gamma\delta}-V_{\alpha\beta\delta\gamma} . \tag{5.7b}$$

In second order the diagrammatic analysis is more involved. There are 4 Feynman diagrams and each of them generates 12 time-ordered Goldstone diagrams (excluding the diagram C which generates only 6). Equation (5.2c) shows that in the second-order ADC scheme the elements $F^{(2)}_{ijk}$, $F^{(1)}_{uijkl}$, $C^{(2)}_{ijk,lmn}$, and $C^{(1)}_{uijkl,mnp}$ contribute to the *ppp* propagator.

The element $F^{(2)}_{ijk}$ is found to be composed of nine different terms. Seven of these nine terms can be obtained by direct comparison of the expression $[\mathbf{F}^{(0)\dagger}(\omega\mathbf{1}-\mathbf{K})^{-1}\mathbf{F}^{(2)}]$ and the diagrams labeled $A7$, $A8$, $B7$, $B8$, $C7$, $D7$, and $D8$ of Fig. 3. The Hermitian conjugate diagrams are, respectively, $A11$, $A12$, $B11$, $B12$, $C11$, $D11$, and $D12$. They correspond to the term $[\mathbf{F}^{(2)\dagger}(\omega\mathbf{1}-\mathbf{K})^{-1}\mathbf{F}^{(0)}]$ and give rise to the same information as the preceding ones. We will discuss below the derivation of the last two terms.

The coupling element $C^{(1)}_{uijkl,mnp}$ appears in the expansion term

$$[\mathbf{F}^{(1)\dagger}(\omega\mathbf{1}-\mathbf{K})^{-1}\mathbf{C}^{(1)}(\omega\mathbf{1}-\mathbf{K})^{-1}\mathbf{F}^{(0)}]$$

and

$$[\mathbf{F}^{(0)\dagger}(\omega\mathbf{1}-\mathbf{K})^{-1}\mathbf{C}^{(1)}(\omega\mathbf{1}-\mathbf{K})^{-1}\mathbf{C}^{(1)}(\omega\mathbf{1}-\mathbf{K})^{-1}\mathbf{F}^{(0)}] .$$

The sets of diagrams corresponding to these terms are $\{A5,C5,D6\}$ and $\{A1,C1,D2\}$. Indeed, for the calculation of $C^{(1)}_{uijkl,mnp}$ it is sufficient to consider the last set of diagrams $\{A1,C1,D2\}$. The first set is only needed to determine the relative sign of the elements $C^{(1)}_{uijkl,mnp}$ and $F^{(1)}_{uijkl}$. Once $C^{(1)}_{uijkl,mnp}$ is determined, it is easy to derive $F^{(1)}_{ulmnp}$ from any of the two sets of diagrams.

The expansion term $[\mathbf{F}^{(0)\dagger}(\omega\mathbf{1}-\mathbf{K})^{-1}\mathbf{C}^{(2)}(\omega\mathbf{1}-\mathbf{K})^{-1}\mathbf{F}^{(0)}]$ is the only expansion term of the second-order ADC which contains $C^{(2)}_{ijk,lmn}$. To find out the analytical expression of $C^{(2)}_{ijk,lmn}$ one has to consider the set of diagrams $\{A2,A4,A6,A10,B2,B4,B6,B10\}$. However, this set of diagrams contains ω-dependent cuts which belong to the higher configuration class $5h2p$. This class does not appear in the second-order ADC scheme. These apparently inconsistent denominators disappear when the contributions of the above diagrams are added together. After this summation one obtains analytical expressions which possess the same algebraic structure of the expansion terms appearing in the second-order ADC form in Eq. (5.2). From these expressions it is thus possible to derive $C^{(2)}_{ijk,lmn}$ and the last two missing contributions to $F^{(2)}_{ijk}$.

The explicit final expressions for the elements of the matrices **C** and **f** in the second-order ADC scheme are collected in Tables I and II, respectively. We remind that the elements of **f** can be easily obtained from the elements of the vector **F**. In Table I we report also the matrix elements $C^{(1)}_{uijkl,vmnpq}$ which in fact are superfluous in the strict second-order ADC scheme. However, these elements can be considered as an integral part of the

TABLE I. Elements of the matrices **K** and **C** necessary for the ADC-approximation scheme up to and including second order of perturbation. The labels $i,j,k,l,\ldots$ refer to occupied orbitals and the labels $u,v,w,\ldots$ refer to unoccupied orbitals in the Hartree-Fock ground state. The notation $V_{\alpha\beta[\gamma\delta]}=V_{\alpha\beta\gamma\delta}-V_{\alpha\beta\delta\gamma}$ is used throughout. ϵ_α denotes the energy of the αth orbital. The set $\{ijk, i<j<k\}$ of one-particle indices spans the subspace a ($3h$). The set $\{uijkl, i<j<k<l\}$ of one-particle indices spans the subspace b ($4h\,1p$).

$$K_{ijk,lmn}=(E_0^N\mathbf{1}-\tilde{\mathbf{H}}^*_{aa})^{(0)}_{ijk,lmn}=(\epsilon_i+\epsilon_j+\epsilon_k)\delta_{il}\delta_{jm}\delta_{kn}$$

$$K_{uijkl,vmnpq}=(E_0^N\mathbf{1}-\tilde{\mathbf{H}}^*_{bb})^{(0)}_{uijkl,vmnpq}=(-\epsilon_u+\epsilon_i+\epsilon_j+\epsilon_k+\epsilon_l)\delta_{uv}\delta_{im}\delta_{jn}\delta_{kp}\delta_{lq}$$

$$C^{(1)}_{ijk,lmn}=(E_0^N\mathbf{1}-\tilde{\mathbf{H}}^*_{aa})^{(1)}_{ijk,lmn}=[(-V_{jk[mn]}\delta_{il})+(i,j,k\rightarrow j,k,i)+(i,j,k\rightarrow k,i,j)]+[l,m,n\rightarrow m,n,l]+[l,m,n\rightarrow n,l,m]$$

$$\begin{aligned}C^{(2)}_{ijk,lmn}=(E_0^N\mathbf{1}-\tilde{\mathbf{H}}^*_{aa})^{(2)}_{ijk,lmn}=&\left\{\left[-\frac{1}{4}\sum_{\substack{p,\\u,v}}V_{kp[uv]}V_{uv[np]}\left\{\frac{1}{\epsilon_u+\epsilon_v-\epsilon_k-\epsilon_p}+\frac{1}{\epsilon_u+\epsilon_v-\epsilon_n-\epsilon_p}\right\}\delta_{il}\delta_{jm}\right]\right.\\&\left.-[m\leftrightarrow n]+[l,m,n\rightarrow m,n,l]\right\}-\{j\leftrightarrow k\}+\{i,j,k\rightarrow j,k,i\}\\&+\left\{\left[\frac{1}{4}\sum_{u,v}V_{jk[uv]}V_{uv[mn]}\left\{\frac{1}{\epsilon_u+\epsilon_v-\epsilon_j-\epsilon_k}+\frac{1}{\epsilon_u+\epsilon_v-\epsilon_m-\epsilon_n}\right\}\delta_{il}\right]\right.\\&\left.+[i,j,k\rightarrow j,k,i]+[i,j,k\rightarrow k,i,j]\right\}+\{l,m,n\rightarrow m,n,l\}+\{l,m,n\rightarrow n,l,m\}\end{aligned}$$

$$\begin{aligned}C^{(1)}_{uijkl,mnp}=(-\tilde{\mathbf{H}}^*_{ba})^{(1)}_{uijkl,mnp}=&[-(V_{kl[pu]}\delta_{im}\delta_{jn}+V_{il[pu]}\delta_{jm}\delta_{kn}-V_{jl[pu]}\delta_{im}\delta_{kn}+V_{ki[pu]}\delta_{jm}\delta_{ln}\\&-V_{kj[pu]}\delta_{im}\delta_{ln}+V_{ij[pu]}\delta_{km}\delta_{ln})]-[n\leftrightarrow p]+[m,n,p\rightarrow n,p,m]\end{aligned}$$

$$\begin{aligned}C^{(1)}_{uijkl,vmnpq}=(E_0^N\mathbf{1}-\tilde{\mathbf{H}}^*_{bb})^{(1)}_{uijkl,vmnpq}=&(V_{vi[um]}\delta_{jn}\delta_{kp}\delta_{lq}-V_{vj[um]}\delta_{in}\delta_{kp}\delta_{lq}+V_{vk[um}[\delta_{in}\delta_{jp}\delta_{lq}-V_{vl[um]}\delta_{in}\delta_{jp}\delta_{kq})\\&-(m\leftrightarrow n)+(m,n,p,q\rightarrow p,m,n,q)-(m,n,p,q\rightarrow q,m,n,p)\\&+[\delta_{uv}(-V_{ij[mn]}\delta_{kp}\delta_{lq}+V_{ik[mn]}\delta_{jp}\delta_{lq}-V_{il[mn]}\delta_{jp}\delta_{kq}-V_{jk[mn]}\delta_{ip}\delta_{lq}\\&-V_{kl[mn]}\delta_{ip}\delta_{jq}+V_{jl[mn]}\delta_{ip}\delta_{kq})]\\&-[n\leftrightarrow p]+[n,p,q\rightarrow q,n,p]-[m\leftrightarrow p]+[m,p,q\rightarrow q,m,p]+[m\leftrightarrow p,n\leftrightarrow q]\end{aligned}$$

second-order approximation scheme as done previously for other propagators [13,14]. The inclusion of this term may be of great importance in improving the results for the $4h\,1p$ satellite states, which in this way result to be treated consistently at first order of perturbation. This term can be determined from a few diagrams of third order or from the algebraic method discussed in the preceding section.

The expressions in Tables I and II are given in terms of two-electron integrals. This is the natural form of the expressions deriving from Feynman diagrams. As discussed in the preceding section one obtains from the algebraic method expressions in the more compact configuration form. The configuration form can be transformed into orbital form. After carrying out this transformation we could show that the algebraic method yields exactly the same working equations as ADC.

Finally, we should mention that the ADC approximation scheme for the propagator $\mathbf{\Pi}^{(+)}(\omega)$, describing the simultaneous attachment of three particles to the system, can be obtained by simple manipulations from the approximation scheme presented here for $\mathbf{\Pi}^{(-)}(\omega)$. The Goldstone diagrams of $\mathbf{\Pi}^{(+)}$ can be obtained from those of $\mathbf{\Pi}^{(-)}$ by simply turning them upside down. It follows that to obtain the matrix elements of **f**, **K**, and **C** one has to exchange the particle $(u,v,w,\ldots)$ and the hole $(i,j,k,\ldots)$ labels in the expressions of Tables I and II. Taking into account the rules given above for the analysis of Goldstone diagrams and in particular bearing in mind that the auxiliary ω line now points downwards one obtains the following relations for the elements **f**, **K**, and **C** which enter in the second-order ADC scheme of $\mathbf{\Pi}^{(+)}$:

$$\begin{aligned}&f_{\alpha\beta\gamma,\delta\epsilon\zeta}=\bar{f}^{(0)}_{\alpha\beta\gamma,\delta\epsilon\zeta}-\bar{f}^{(1)}_{\alpha\beta\gamma,\delta\epsilon\zeta}+\bar{f}^{(2)}_{\alpha\beta\gamma,\delta\epsilon\zeta}\,,\\&K_{\alpha\beta\gamma,\alpha\beta\gamma}=\bar{K}_{\alpha\beta\gamma,\alpha\beta\gamma}\,,\\&K_{\alpha\beta\gamma\delta,\alpha\beta\gamma\delta}=\bar{K}_{\alpha\beta\gamma\delta,\alpha\beta\gamma\delta}\,,\\&C_{\alpha\beta\gamma,\delta\epsilon\zeta}=-\bar{C}^{(1)}_{\alpha\beta\gamma,\delta\epsilon\zeta}+\bar{C}^{(2)}_{\alpha\beta\gamma,\delta\epsilon\zeta}\,,\\&C_{\alpha\beta\gamma\delta\epsilon,\zeta\eta\theta}=\bar{C}^{(1)}_{\alpha\beta\gamma\delta\epsilon,\zeta\eta\theta}\,,\\&C_{\alpha\beta\gamma\delta\epsilon,\zeta\eta\theta\iota\kappa}=-\bar{C}^{(1)}_{\alpha\beta\gamma\delta\epsilon,\zeta\eta\theta\iota\kappa}\,.\end{aligned}\tag{5.8}$$

Here the $\bar{\mathbf{f}}$, $\bar{\mathbf{K}}$, and $\bar{\mathbf{C}}$ are obtained from the elements **f**, **K**, and **C** of Tables I and II by interchanging the particle and hole indices.

TABLE II. Elements of the matrix f necessary for the ADC-approximation scheme up to and including second order of perturbation. The notation used is the same as in Table I. The subspaces $\mathcal{A}$, $\mathcal{B}$, $\mathcal{C}$, $\mathcal{D}$, i.e., the columns of blocks of the matrix f (or, equivalently $\tilde{\mathbf{Y}}$) are spanned by the sets of one-particle indices $\{lmn, l<m<n\}$, $\{umn, m<n\}$, $\{uvm, u<v\}$, $\{uvw, u<v<w\}$, respectively.

$$f^{(0)}_{ijk,lmn}=(\tilde{\mathbf{Y}}^{*}_{a\mathcal{A}})^{(0)}_{ijk,lmn}=\delta_{il}\delta_{jm}\delta_{kn}$$

$$f^{(1)}_{ijk,lmn}=(\tilde{\mathbf{Y}}^{(1)}_{a\mathcal{A}})^{(1)}_{ijk,lmn}=0$$

$$f^{(2)}_{ijk,lmn}=(\tilde{\mathbf{Y}}^{*}_{a\mathcal{A}})^{(2)}_{ijk,lmn}=\left\{-\frac{1}{4}\sum_{\substack{q,\\u,v}}(\Gamma_{jquv}\Gamma_{uvlq}\delta_{im}\delta_{kn}-\Gamma_{jquv}\Gamma_{uvmq}\delta_{il}\delta_{kn}+\Gamma_{jquv}\Gamma_{uvnq}\delta_{il}\delta_{km})\right\}-(j\leftrightarrow k)+(i,j,k\rightarrow k,i,j)$$

$$+\left\{\left\{-\frac{1}{4}\sum_{u,v}\Gamma_{jkuv}\Gamma_{uvmn}\delta_{il}\right\}+(l,m,n\rightarrow m,n,l)+(l,m,n\rightarrow n,l,m)\right\}+[i,j,k\rightarrow j,k,i]+[i,j,k\rightarrow k,i,j]$$

$$f^{(0)}_{ijk,umn}=(\tilde{\mathbf{Y}}^{*}_{a\mathcal{B}})^{(0)}_{ijk,umn}=0$$

$$f^{(1)}_{ijk,umn}=(\tilde{\mathbf{Y}}^{*}_{a\mathcal{B}})^{(1)}_{ijk,umn}=0$$

$$f^{(2)}_{ijk,umn}=(\tilde{\mathbf{Y}}^{*}_{a\mathcal{B}})^{(2)}_{ijk,umn}=\left\{\frac{1}{2}\left\{\sum_{\substack{p,\\y,z}}\frac{\Gamma_{pkyz}V_{yz[up]}}{\epsilon_u-\epsilon_k}-\sum_{\substack{p,q\\y}}\frac{V_{yk[pq]}\Gamma_{pquy}}{\epsilon_u-\epsilon_k}\right\}\delta_{im}\delta_{jn}\right\}-[j\leftrightarrow k]+[i,j,k\rightarrow j,k,i]$$

$$f^{(0)}_{ijk,uvm}=(\tilde{\mathbf{Y}}^{*}_{a\mathcal{C}})^{(0)}_{ijk,uvm}=0$$

$$f^{(1)}_{ijk,uvm}=(\tilde{\mathbf{Y}}^{*}_{a\mathcal{C}})^{(1)}_{ijk,uvm}=\{\Gamma_{jkuv}\delta_{im}\}+\{i,j,k\rightarrow j,k,i\}+\{i,j,k\rightarrow k,i,j\}$$

$$f^{(2)}_{ijk,uvm}=(\tilde{\mathbf{Y}}^{*}_{a\mathcal{C}})^{(2)}_{ijk,uvm}=\left\{\left\{-\frac{1}{2}\left\{\sum_{z,y}\frac{\Gamma_{jkzy}V_{zy[uv]}}{\epsilon_u+\epsilon_v-\epsilon_j-\epsilon_k}+\sum_{p,q}\frac{V_{jk[pq]}\Gamma_{pquv}}{\epsilon_u+\epsilon_v-\epsilon_j-\epsilon_k}\right\}+\left\{\sum_{\substack{p\\y}}\frac{V_{yj[up]}\Gamma_{pkuy}}{\epsilon_u+\epsilon_v-\epsilon_j-\epsilon_k}\right\}\right.\right.$$

$$\left.\left.-(j\leftrightarrow k)-(u\leftrightarrow v)+(j\leftrightarrow k,u\leftrightarrow v)\right\}\delta_{im}\right\}+\{i,j,k\rightarrow j,k,i\}+\{i,j,k\rightarrow k,i,j\}$$

$$f^{(0)}_{ijk,uvw}=(\tilde{\mathbf{Y}}^{*}_{a\mathcal{D}})^{(0)}_{ijk,uvw}=0$$

$$f^{(1)}_{ijk,uvw}=(\tilde{\mathbf{Y}}^{*}_{a\mathcal{D}})^{(1)}_{ijk,uvw}=0$$

$$f^{(2)}_{ijk,uvw}=(\tilde{\mathbf{Y}}^{*}_{a\mathcal{D}})^{(2)}_{ijk,uvw}=\left\{\left\{-\frac{1}{\epsilon_u+\epsilon_v+\epsilon_w-\epsilon_i-\epsilon_j-\epsilon_k}\left\{\sum_{m}V_{jk[wm]}\Gamma_{miuv}+\sum_{y}\Gamma_{jkyu}V_{yi[vw]}\right\}\right\}\right.$$

$$\left.+[u,v,w\rightarrow v,w,u]+[u,v,w\rightarrow w,u,v]\right\}+\{i,j,k\rightarrow j,k,i\}+\{i,j,k\rightarrow k,i,j\}$$

$$f_{uijkl,mnp}=(\tilde{\mathbf{Y}}^{*}_{b\mathcal{A}})_{ijk,mnp}=0 \quad \text{all orders}$$

$$f^{(0)}_{uijkl,vmn}=(\tilde{\mathbf{Y}}^{*}_{b\mathcal{B}})^{(0)}_{uijkl,vmn}=0$$

$$f^{(1)}_{uijkl,vmn}=(\tilde{\mathbf{Y}}^{*}_{b\mathcal{B}})^{(1)}_{uijk,vmn}=+\Gamma_{kluv}\delta_{im}\delta_{jn}+\Gamma_{iluv}\delta_{jm}\delta_{kn}-\Gamma_{jluv}\delta_{im}\delta_{kn}+\Gamma_{kiuv}\delta_{jm}\delta_{ln}-\Gamma_{kjuv}\delta_{im}\delta_{ln}+\Gamma_{ijuv}\delta_{km}\delta_{ln}$$

$$f^{(0)}_{uijkl,vwm}=(\tilde{\mathbf{Y}}^{*}_{b\mathcal{C}})^{(0)}_{uijkl,vwm}=0$$

$$f^{(1)}_{uijkl,vwm}=(\tilde{\mathbf{Y}}^{*}_{b\mathcal{C}})^{(1)}_{uijkl,vwm}=0$$

$$f^{(0)}_{uijkl,vwz}=(\tilde{\mathbf{Y}}^{*}_{b\mathcal{D}})^{(0)}_{uijkl,vwz}=0$$

$$f^{(1)}_{uijkl,vwz}=(\tilde{\mathbf{Y}}^{*}_{b\mathcal{D}})^{(1)}_{uijkl,vwz}=0$$

VI. BRIEF SUMMARY

In this work we have presented the working equations of the second-order approximation scheme for the *ppp* propagator. This propagator can be obtained from the more general three-particle Green's function by a particular choice of the time arguments and is suitable for the description of triple-ionization processes and triply charged systems. Examples of triple-ionization processes can be found in the so-called satellite Auger processes which can occur simultaneously to the normal Auger process and in the dissociation or fragmentation processes of highly ionized systems.

To calculate triple-ionization energies we used a Green's-function approach and derived the working equations for an approximation scheme consistent at second order of perturbation. For this purpose we used conceptually different methods, a purely algebraic one and the diagrammatic ADC approach. We have demonstrated that both methods give rise to equivalent sets of working equations.

The working equations obtained by the algebraic method are expressed in configuration form, i.e., as products of matrix elements of the Hamiltonian taken with N- and $(N-3)$-particle electronic configurations. With the ADC approach one obtains the final equations in orbital form, i.e., in terms of products of two-particle integrals and orbital energies. This is the natural form of the expressions deriving from Feynman diagrams. Transforming the formulas in configuration form of the algebraic method into orbital form, we could show that the two methods lead to identical equations. It should be mentioned that each set of working equations, in configuration form or in orbital form, may have its own advantages in numerical implementations.

Furthermore, since the two procedures are fundamentally different, the equivalence of the results is an important test for their correctness. This is a relevant point in the case of the *ppp* propagator because it contains six creation and destruction operators in the definition and thus the derivation of the explicit working equations is quite involved. Both methods lead to working equations which allow for a size-consistent calculation of triple-ionization energies without resorting to separate calculations for the initial and final states involved in the transition.

The approximation scheme ensures, moreover, that the change in electronic correlations and relaxation energy in the molecular system due to the loss of three electrons is taken consistently into account. It is to expect that the implementation of our working equations leads to satisfactory numerical results with much less numerical effort than conventional methods of comparable accuracy. This is due to the fact that the configuration space of our scheme contains the $(N-3)$-particle configuration states of the classes $3h$ and $4h\,1p$, while for a comparable configuration-interaction calculation the higher excited $5h\,2p$ class has to be explicitly taken into account in the configuration space.

Finally, we should mention that from the presented approximation scheme for the propagator describing the simultaneous triple ionization one easily obtains the approximation scheme for the propagator describing the attachment of three particles to the system.

ACKNOWLEDGMENT

The authors acknowledge financial support by the Deutsche Forschungsgemeinschaft.

[1] M. O. Krause, T. A. Carlson, and W. E. Moddeman, J. Phys. (Paris) Colloq. **32**, C4-139 (1971).

[2] W. E. Moddeman, T. A. Carlson, M. O. Krause, B. P. Pullen, W. E. Bull, and G. K. Schweitzer, J. Chem. Phys. **55**, 2317 (1971).

[3] D. Mathur, in *Multiply Charged Ions in Electronic and Atomic Collisions,* edited by H. B. Gilbody, W. R. Newell, F. H. Read, and A. C. H. Smith (Elsevier, New York, 1988), and references therein; D. Mathur, C. Badrinathan, P. A. Rajgara, and U. T. Raheja, Chem. Phys. **103**, 447 (1986).

[4] W. Koch, N. Heinrich, H. Schwarz, F. Maquin, and D. Stahl, Int. J. Mass Spectrom. Ion Proc. **67**, 305 (1985).

[5] D. Mathur, R. G. Kingston, F. M. Harris, and J. H. Beynon, J. Phys. B **19**, 1575 (1986).

[6] D. S. Gemmell, E. P. Kanter, and W. J. Pietsch, Chem. Phys. Lett. **55**, 331 (1978).

[7] A. A. Abrikosov, L. P. Gorkov, and J. E. Dzyaloskinski, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, New York, 1963).

[8] A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, New York, 1971).

[9] A. B. Migdal, *Theory of Finite Fermi Systems* (Interscience/Wiley, New York, 1967).

[10] S. E. Ethofer and P. Schuck, Z. Phys. **228**, 264 (1969).

[11] C.-H. Liegener, Chem. Phys. **76**, 397 (1983).

[12] (a) A. Tarantelli and L. S. Cederbaum, Phys. Rev. A **39**, 1639 (1989); (b) A. Tarantelli and L. S. Cederbaum, in *Many-Body Methods in Quantum Chemistry,* edited by U. Kaldor, Lecture Notes in Chemistry Vol. 52 (Springer, Berlin, 1989).

[13] J. Schirmer, Phys. Rev. A **26**, 2395 (1982).

[14] J. Schirmer, L. S. Cederbaum, and O. Walter, Phys. Rev. A **28**, 1237 (1983).

[15] A. Tarantelli and L. S. Cederbaum, Phys. Rev. A **39**, 1656 (1989).

[16] J. Schirmer, Phys. Rev. A **43**, 4647 (1991).

[17] D. Mukherjee and W. Kutzelnigg, in *Many-Body Methods in Quantum Chemistry* [Ref. 12(b)].

[18] B. H. Brandow, in *Effective Interction and Operators in Nuclei,* edited by J. Ehlers, K. Hepp, R. Kippenhahn, H. A. Weidenmüller, and J. Zittartz, Lecture Notes in Physics Vol. 40 (Springer, Berlin, 1975); W. Kvasnicka, in *Advances in Chemical Physics,* edited by I. Prigogine and S. A. Rice (Wiley, New York, 1977), Vol. 36; I. Lindgren and J. Morrison, *Atomic Many-Body Theory* (Springer, Berlin,

1982).

[19] L. S. Cederbaum, J. Schirmer, and H.-D. Meyer, J. Phys. A **22**, 2427 (1989).

[20] N. H. March, W. H. Young, and S. Sampanthar, *The Many-Body Problem in Quantum Mechanics* (Cambridge University, Cambridge, 1967).

[21] A. Tarantelli and L. S. Cederbaum, J. Math. Phys. **31**, 828 (1990).

[22] Ph. Durant and J. P. Malrieu, in *Advances in Chemical Physics,* edited by I. Prigogine and S. A. Rice (Wiley, New York, 1987), Vol. 67, and references therein; H. A. Weidenmüller, in *Effective Interactions and Operators in Nuclei,* Lecture Notes in Physics Vol. 40, edited by J. Ehlers, K. Hepp, R. Kippenhahn, H. A. Weidenmüller, and J. Zittartz (Springer, Berlin, 1975), and references therein.