Configuration-interaction formulation of the Dyson equation

A. Tarantelli and L. S. Cederbaum
Lehrstuhl für Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 253, D-6900 Heidelberg, Germany
(Received 8 July 1991)

The Dyson equation represents a well-defined connection between the one-particle Green's function and the self-energy. By means of the Dyson equation, the evaluation of the one-particle Green's function can be reduced to the evaluation of the self-energy. As it is well known, the one-particle Green's function is composed of an advanced and a retarded part, which can be represented in the $(N+1)$- and $(N-1)$-particle configuration spaces, respectively. The Dyson equation combines these two spaces into a matrix in the union space. This is difficult to understand in configuration-interaction language, where the Hamiltonian matrices for systems containing different numbers of particles are naturally separated. Starting with the usual matrix representations of the Hamiltonian in the $(N+1)$- and $(N-1)$-particle spaces, it is shown that it is possible to define a class of unitary transformations that mixes the two parts and gives rise to an effective Hamiltonian matrix in the union space. This effective Hamiltonian leads to all possible representations of the Dyson equation. The transformations used arise from suitable combinations of the matrices of residues of the advanced and retarded Green's functions. Several specific members of the above class of unitary transformations are discussed in some detail also in connection with possible approximation schemes for the Green's function. Special attention is paid to those unitary transformations that depend on the ground state of the N-particle system as the only unknown quantity. This investigation has given rise to some general conclusions and to an alternative approach to the one-particle Green's function.

PACS number(s): 31.15.+q, 31.10.+z

I. INTRODUCTION

The one-particle Green's function $\mathbf{G}(\omega)$ contains relevant information on the physical properties of many-particle systems [1,2]. Using this function one can compute the ground-state energy, ground-state expectation values of one-particle operators, ionization potentials, electron affinities, ionization cross sections, and the optical potential for elastic electron-molecule scattering [1–7]. In energy representation the matrix element $G_{\alpha\beta}(\omega)$ of $\mathbf{G}(\omega)$ is explicitly given by

$$G_{\alpha\beta}(\omega)=\sum_m \frac{\langle \Psi_0^N|a_\alpha|\Psi_m^{N+1}\rangle\langle \Psi_m^{N+1}|a_\beta^\dagger|\Psi_0^N\rangle}{\omega+E_0^N-E_m^{N+1}+i\eta} + \sum_m \frac{\langle \Psi_0^N|a_\beta^\dagger|\Psi_m^{N-1}\rangle\langle \Psi_m^{N-1}|a_\alpha|\Psi_0^N\rangle}{\omega-E_0^N+E_m^{N-1}-i\eta} . \quad (1.1)$$

Here $|\Psi_m^{N\pm1}\rangle$ and $E_m^{N\pm1}$ are the exact $(N\pm1)$-particle states and energies, respectively. E_0^N represents the energy of the exact neutral (N-particle) ground state $|\Psi_0^N\rangle$ and the operators $a_\alpha^\dagger$ and a_α are creation and destruction operators related to a suitably chosen basis of one-particle states $\{|\varphi_\alpha\rangle\}$. The infinitesimal quantity η is necessary to guarantee the convergence of the Fourier transformation yielding Eq. (1.1) and does not have to be considered explicitly. The first term on the right-hand side of Eq. (1.1) is called the advanced Green's function $\mathbf{G}_+(\omega)$ and the second term the retarded Green's function $\mathbf{G}_-(\omega)$.

A basic equation in the theory of the one-particle Green's function is the Dyson equation [1,2]. This equation connects the Green's function to the self-energy $\mathbf{\Sigma}(\omega)$:

$$\mathbf{G}(\omega)=\mathbf{G}_0(\omega)+\mathbf{G}_0(\omega)\mathbf{\Sigma}(\omega)\mathbf{G}(\omega) . \quad (1.2)$$

$\mathbf{\Sigma}(\omega)$ is identical to the optical potential for elastic scattering [3]. $\mathbf{G}_0(\omega)$ represents the so-called free Green's function

$$\mathbf{G}_0(\omega)=(\omega\mathbf{1}-\boldsymbol{\varepsilon})^{-1} . \quad (1.3)$$

The poles of $\mathbf{G}_0$ are the energies of a chosen set of one-particle states $\{|\varphi_\alpha\rangle\}$ (orbitals), defining an unperturbed Hamiltonian $\hat{H}_0$:

$$\hat{H}_0=\sum_\alpha \varepsilon_\alpha a_\alpha^\dagger a_\alpha . \quad (1.4)$$

The self-energy $\mathbf{\Sigma}(\omega)$ in Eq. (1.2) can be written as a sum of a static (ω-independent) part $\mathbf{\Sigma}(\infty)$ and a dynamic (ω-dependent) part $\mathbf{M}(\omega)$ according to the following relation [5–7]:

$$\mathbf{\Sigma}(\omega)=\mathbf{\Sigma}(\infty)+\mathbf{M}(\omega) . \quad (1.5)$$

The static part can be determined from the dynamic part [7]. $\mathbf{\Sigma}(\omega)$ is, like $\mathbf{G}(\omega)$, a matrix the indices of which run over the one-particle states of the set $\{|\varphi_\alpha\rangle\}$. The dynamic part $\mathbf{M}(\omega)$ possesses a spectral representation which in matrix form reads

$$\mathbf{M}(\omega)=\mathbf{m}(\omega\mathbf{1}-\mathbf{\Omega})^{-1}\mathbf{m}^\dagger . \quad (1.6)$$

The matrix $\mathbf{\Omega}$ is the diagonal matrix of the spectral energies that are associated to the excitations of the $(N+1)$- and $(N-1)$-particle spaces. Taking into account Eq. (1.2) and Eqs. (1.5) and (1.6) one obtains that the poles of the Green's function $\mathbf{G}(\omega)$ are given by the eigenvalues of the following block matrix $\mathbf{A}$:

$$\mathbf{A}=\begin{bmatrix} \boldsymbol{\varepsilon}+\boldsymbol{\Sigma}(\infty) & \mathbf{m} \\ \mathbf{m}^{\dagger} & \mathbf{\Omega} \end{bmatrix} . \tag{1.7}$$

By introducing a unit matrix of the same dimension and block structure as $\mathbf{A}$

$$\mathbf{1}=\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \tag{1.8}$$

it is easy to see that $\mathbf{G}(\omega)$ is related to $\mathbf{A}$ according to the following equation:

$$\mathbf{G}(\omega)=(\omega\mathbf{1}-\mathbf{A})^{-1}_{\text{upper left block}} . \tag{1.9a}$$

This equation can also be formally rewritten as

$$\mathbf{G}(\omega)=(1 \quad 0)(\omega\mathbf{1}-\mathbf{A})^{-1}\begin{bmatrix} 1 \\ 0 \end{bmatrix} . \tag{1.9b}$$

From Eq. (1.1) it is seen that the one-particle Green's function contains information on the states and energies of different numbers of particles, namely, $N+1$ and $N-1$. In particular these quantities emerge as eigenvectors and eigenvalues of a single matrix $\mathbf{A}$.

In the present work we analyze the matrix $\mathbf{A}$, or equivalently the self-energy $\boldsymbol{\Sigma}(\omega)$, in the language of configuration interaction. In particular we are interested in the relation of the matrix $\mathbf{A}$ and the conventional Hamiltonian matrices of the $(N+1)$- and the $(N-1)$-particle systems. In performing our study we investigate the properties of the self-energy in its various representations. We pay special attention to those representations which depend solely on the ground state of the N-particle system as input data. One of these representations gives rise to an interesting equation for the Green's function.

The paper is organized as follows. In Sec. II we represent the advanced and the retarded parts of the Green's function in configuration space, i.e., in terms of Slater determinants. In the next step we cast the two parts of the Green's function into a single matrix which represents the starting point of our discussion. In Sec. III we establish the relation between this matrix and the self-energy $\boldsymbol{\Sigma}(\omega)$. We can show that they are related to each other by means of unitary transformations $\mathbf{T}$ which arise naturally from the structure of the one-particle Green's function. These unitary transformations lead to all possible representations of the dynamic self-energy and have in common that the static part of the self-energy is uniquely reproduced. Section IV is dedicated to a particular choice of $\mathbf{T}$, which seem to us to be the most obvious choice out of all possible transformations. With this $\mathbf{T}$ we obtain a closed-form formulation of the self-energy in terms of expectation values on the exact N-particle ground state $|\Psi_0^N\rangle$. Approximations for $|\Psi_0^N\rangle$ lead straightforwardly to approximations for the self-energy. The simplest way to analyze our closed-form expressions is to approximate $|\Psi_0^N\rangle$ by Rayleigh-Schrödinger perturbation theory. The perturbation expansion is carried out in detail up to third order and found to lead to the well-known algebraic diagrammatic construction (ADC) approximation scheme for the dynamic self-energy. The general situation encountered beyond third order is also addressed.

The dynamic self-energy can, in principle, be expressed as a sum of two parts assigned to different particle numbers. Since such a decoupling of the $(N+1)$- and $(N-1)$-particle contributions has theoretical and practical advantages, we investigate in Sec. V which transformations $\mathbf{T}$ give rise to this decoupling. In particular we pose the question whether it is possible to obtain a transformation using only $|\Psi_0^N\rangle$ as input data. By means of a simple counterexample which can be solved exactly we are able to give a negative answer to this question. This finding has led to a new approach to the self-energy and to the Green's function. The last section of the present work is devoted to this approach.

II. REPRESENTATION OF THE ONE-PARTICLE GREEN'S FUNCTION IN CONFIGURATION SPACE

As mentioned in the Introduction the one-particle Green's function is a sum of two independent parts, the so-called advanced $[\mathbf{G}_+(\omega)]$ and retarded $[\mathbf{G}_-(\omega)]$ Green's function:

$$\mathbf{G}(\omega)=\mathbf{G}_+(\omega)+\mathbf{G}_-(\omega) . \tag{2.1}$$

Each of these parts is easily expressed in configuration space:

$$\mathbf{G}_+(\omega)=(\mathbf{Y}_+)^{\dagger}(\omega\mathbf{1}-\mathbf{H}^{N+1})^{-1}\mathbf{Y}_+ , \tag{2.2a}$$

$$[\mathbf{G}_-(\omega)]^*=(\mathbf{Y}_-)^{\dagger}(\omega\mathbf{1}+\mathbf{H}^{N-1})^{-1}\mathbf{Y}_- . \tag{2.2b}$$

Here $\mathbf{H}^{N\pm1}$ represents the usual Hamiltonian matrix in the $(N\pm1)$-particle configuration space shifted along the diagonal by the energy E_0^N of the exact N-particle ground state $|\Psi_0^N\rangle$. Introducing the complete sets $\{|\Phi_q^{N+1}\rangle\}$ and $\{|\Phi_q^{N-1}\rangle\}$ of states in the $(N+1)$- and $(N-1)$-particle spaces, respectively, these matrices read

$$(\mathbf{H}^{N\pm1})_{qq'}=\langle\Phi_q^{N\pm1}|\hat{H}-E_0^N|\Phi_{q'}^{N\pm1}\rangle . \tag{2.3}$$

The choice of the $|\Phi_q^{N+1}\rangle$ is arbitrary; they can be, for instance, the exact eigenstates of the Hamiltonian $\hat{H}$ or the eigenstates of some unperturbed Hamiltonian $\hat{H}_0$. In Eqs. (2.2) $\mathbf{1}$ represents the unit matrix of the same dimension as $\mathbf{H}^{N\pm1}$. $\mathbf{Y}_+$ and $\mathbf{Y}_-$ are the matrices of the residues and read, respectively,

$$(\mathbf{Y}_+)_{q\alpha}=\langle\Phi_q^{N+1}|a_\alpha^{\dagger}|\Psi_0^N\rangle , \tag{2.4a}$$

$$(\mathbf{Y}_-)_{q\alpha}=\langle\Phi_q^{N-1}|a_\alpha|\Psi_0^N\rangle . \tag{2.4b}$$

The creation $a_\alpha^{\dagger}$ and destruction a_α operators are related to the one-particle basis set $\{|\varphi_\alpha\rangle\}$. By introducing a "composite" Hamiltonian matrix

$$\mathbf{H}=\begin{bmatrix} +\mathbf{H}^{N+1} & \mathbf{0} \\ \mathbf{0} & -(\mathbf{H}^{N-1})^* \end{bmatrix} \tag{2.5a}$$

and a "composite" matrix of the residues

$$\mathbf{Y}=\begin{bmatrix} \mathbf{Y}_+ \\ (\mathbf{Y}_-)^* \end{bmatrix} \tag{2.5b}$$

the Green's function [Eq. (2.1)] can be written as follows:

$$\mathbf{G}(\omega)=\mathbf{Y}^\dagger(\omega\mathbf{1}-\mathbf{H})^{-1}\mathbf{Y} \ . \tag{2.6}$$

Of course, the composite Hamiltonian matrix $\mathbf{H}$ [Eq. (2.5a)] and the matrix $\mathbf{A}$ of the Dyson equation [Eq. (1.7)] have the same dimension. However, the ordering of the blocks within the two matrices is different and of fundamental importance. The first important observation is that in $\mathbf{H}$ the two blocks along the diagonal are spanned by the configurations of the $(N+1)$- and $(N-1)$-particle spaces, respectively. These two blocks are obviously decoupled since the Hamiltonian is a particle number conserving operator. The matrix $\mathbf{A}$, on the other hand, is a matrix in which the $(N+1)$- and the $(N-1)$-particle spaces are strictly coupled together through the self-energy.

For the sake of convenience it is useful to divide the sets $\{|\Phi_q^{N\pm1}\rangle\}$ into subsets or "classes." Considering the N-particle ground state $|\Phi_0^N\rangle$ of an unperturbed Hamiltonian $\hat{H}_0$ as the reference state we can classify the states of the set $\{|\Phi_q^{N+1}\rangle\}$ as $1p$, $2p1h$, $3p2h$, etc. configuration states and the states of the set $\{|\Phi_q^{N-1}\rangle\}$ as $1h$, $2h1p$, $3h2p$, etc. configuration states. With this notation we indicate how many holes (h) and how many particles (p) have been created, respectively, in the occupied and unoccupied one-particle states of $|\Phi_0^N\rangle$. For example, an $(N-1)$-particle configuration state of the $2h1p$ class differ from $|\Phi_0^N\rangle$ by two holes in the occupied orbitals and one particle in the unoccupied orbitals. Formally one has

$$\begin{aligned}\{|\Phi_q^{N+1}\rangle\}&=\{|\Phi_{q(1p)}^{N+1}\rangle\}\cup\{|\Phi_{q(2p1h)}^{N+1}\rangle\}\cup\cdots \\ &=\{|\Phi_{q(1p)}^{N+1}\rangle\}\cup\{|\Phi_{q(\nu)}^{N+1}\rangle\} \ , \end{aligned} \tag{2.7a}$$

$$\begin{aligned}\{|\Phi_q^{N-1}\rangle\}&=\{|\Phi_{q(1h)}^{N-1}\rangle\}\cup\{|\Phi_{q(2h1p)}^{N-1}\rangle\}\cup\cdots \\ &=\{|\Phi_{q(1h)}^{N-1}\rangle\}\cup\{|\Phi_{q(\mu)}^{N-1}\rangle\} \ . \end{aligned} \tag{2.7b}$$

The indices ν and μ are here cumulative indices for the classes $2p1h$, $3p2h$, etc. and $2h1p$, $3h2p$, etc., respectively. We will refer to ν and μ also as to the classes of excitations of the $(N+1)$- and $(N-1)$-particle spaces, respectively.

As already mentioned, the upper left block of the matrix $\mathbf{A}$ is spanned by the one-particle states of the set $\{|\varphi_\alpha\rangle\}$ [see Eq. (1.7)]. Splitting the set $\{\varphi_\alpha\rangle\}$ into two subsets according to whether α labels as unoccupied (p) or an occupied (h) one-particle state in $|\Phi_0^N\rangle$

$$\{|\varphi_\alpha\rangle\}=\{|\varphi_{\alpha(p)}\rangle\}\cup\{|\varphi_{\alpha(h)}\rangle\} \ , \tag{2.8}$$

we can establish a one-to-one correspondence between the set $\{|\varphi_{\alpha(p)}\rangle\}$ ($\{|\varphi_{\alpha(h)}\rangle\}$) and $\{|\Phi_{q(1p)}^{N+1}\rangle\}$ ($\{|\Phi_{q(1h)}^{N-1}\rangle\}$). Bearing in mind this correspondence it follows that the lower right block $\mathbf{\Omega}$ of the matrix $\mathbf{A}$ is spanned by the classes of excitations of the $(N\pm1)$-particle spaces.

III. REPRESENTATION OF THE SELF-ENERGY IN CONFIGURATION SPACE

Several different analytical and numerical approaches have been presented in the past to determine the eigenvalues of the matrix $\mathbf{A}$ [7–10]. Most of the analytical methods are based on the analysis of the Feynman diagrams, which describe diagrammatically the perturbation expansion of the self-energy $\mathbf{\Sigma}(\omega)$. In this work we would like to investigate the self-energy and the Dyson equation from a completely different point of view, namely, in the language of configurations. We start with the composite Hamiltonian $\mathbf{H}$, which appears in the expression for the Green's function [Eqs. (2.5) and (2.6)] and arrive at a representation of the matrix $\mathbf{A}$ and hence of the self-energy $\mathbf{\Sigma}(\omega)$ by means of a unitary transformation. We would like to stress at this point that in our theory we will work with the composite Hamiltonian $\mathbf{H}$ equivalent to the full configuration-interaction matrices of the $(N\pm1)$-particle spaces. As it will become clear in the following we do not need to truncate the Hamiltonian matrices and to make any assumptions on their actual dimension and composition, since we will be able to use and to take account of the orthogonality and completeness of the sets $\{|\Phi_q^{N\pm1}\rangle\}$.

To establish the relation between the two different representations of the Green's function in Eqs. (1.9) and (2.6) we introduce a unitary transformation matrix. We start the discussion by analyzing in more detail the composite matrix $\mathbf{Y}$ of residues [Eq. (2.5b)]. Taking into account the usual anticommutation relations of the creation and destruction operators, it is easy to see that the columns of $\mathbf{Y}$ are normalized and orthogonal to each other. This can be shown by explicitly considering the scalar product of any two columns of $\mathbf{Y}$. This yields

$$\begin{aligned}(\mathbf{Y}^\dagger\mathbf{Y})_{\alpha\beta}&=\sum_q(\mathbf{Y}^\dagger)_{\alpha q}\mathbf{Y}_{q\beta} \\ &=\langle\Psi_0^N|a_\alpha a_\beta^\dagger|\Psi_0^N\rangle+\langle\Psi_0^N|a_\beta^\dagger a_\alpha|\Psi_0^N\rangle \\ &=\langle\Psi_0^N|\{a_\alpha,a_\beta^\dagger\}|\Psi_0^N\rangle=\delta_{\alpha\beta} \ . \end{aligned} \tag{3.1}$$

Here we indicated with $\{\ ,\ \}$ the anticommutator. Equation (3.1) shows a very peculiar property of the composite matrix of residues which derives from the fact that in the definition of $\mathbf{Y}$ the $(N+1)$- and the $(N-1)$-particle spaces are cast together in the union space. It is easy to see that the orthonormality property is lost if one considers separately the two matrices of the residues $\mathbf{Y}_+$ and $\mathbf{Y}_-$.

From the orthonormality of the columns of the matrix $\mathbf{Y}$ it follows that the composite matrix of residues $\mathbf{Y}$ can be viewed as one part of a unitary matrix. It is thus reasonable to build up the unitary transformation matrix $\mathbf{T}$ by suitably augmenting $\mathbf{Y}$. The resulting unitary matrix reads

$$\mathbf{T}=\begin{bmatrix} \mathbf{Y}_+ & \mathbf{T}_+ \\ (\mathbf{Y}_-)^* & (\mathbf{T}_-)^* \end{bmatrix} \ . \tag{3.2}$$

Remembering that the columns of $\mathbf{Y}$ are labeled with the index α which runs over the classes $1p$ [$(N+1)$-particle space] and $1h$ [$(N-1)$-particle space], it follows that in order to have a square matrix $\mathbf{T}$ the number of columns of $\mathbf{T}_+$ and $(\mathbf{T}_-)^*$ has to be equal to the number of configurations of the classes ν and μ together. We thus introduce

$$\begin{bmatrix} \mathbf{T}_+ \\ (\mathbf{T}_-)^* \end{bmatrix} = \begin{bmatrix} \mathbf{T}_{+(\nu)} & \mathbf{T}_{+(\mu)} \\ (\mathbf{T}_{-(\nu)})^* & (\mathbf{T}_{-(\mu)})^* \end{bmatrix} \tag{3.3}$$

for later purposes.

We now transform the composite Hamiltonian and residue matrices according to

$$\tilde{\mathbf{H}}=\mathbf{T}^\dagger\mathbf{H}\mathbf{T} , \tag{3.4a}$$

$$\tilde{\mathbf{Y}}=\mathbf{T}^\dagger\mathbf{Y} , \tag{3.4b}$$

and readily obtain the following expression for $\mathbf{G}(\omega)$ using Eq. (2.6):

$$\mathbf{G}(\omega)=\tilde{\mathbf{Y}}^\dagger(\omega\mathbf{1}-\tilde{\mathbf{H}})^{-1}\tilde{\mathbf{Y}} . \tag{3.5a}$$

Because of the unitarity of $\mathbf{T}$ we have $\tilde{\mathbf{Y}}^\dagger=(\mathbf{1} \quad \mathbf{0})$ and thus

$$\mathbf{G}(\omega)=(\omega\mathbf{1}-\tilde{\mathbf{H}})^{-1}_{\text{upper left block}} . \tag{3.5b}$$

$\tilde{\mathbf{Y}}$ can be viewed as a *projector* onto the classes $1p$ and $1h$. Comparison of Eqs. (3.5b) and (1.9) shows that he matrices $\tilde{\mathbf{H}}$ and $\mathbf{A}$ are equivalent. $\tilde{\mathbf{H}}$ is unequivocally determined by the transformation matrix $\mathbf{T}$ and can be used to determine the self-energy. It is important to note that the matrix $\tilde{\mathbf{H}}$ has the *same* block structure as the matrix $\mathbf{A}$ of the Dyson equation. For the following discussion it is thus useful to consider $\tilde{\mathbf{H}}$, like $\mathbf{A}$, as a block matrix:

$$\tilde{\mathbf{H}}=\begin{bmatrix} \tilde{\mathbf{H}}_{aa} & \tilde{\mathbf{H}}_{ab} \\ \tilde{\mathbf{H}}_{ba} & \tilde{\mathbf{H}}_{bb} \end{bmatrix}, \quad \tilde{\mathbf{H}}^\dagger=\tilde{\mathbf{H}} . \tag{3.6}$$

We note that the block $\tilde{\mathbf{H}}_{bb}$ possesses the following substructure:

$$\tilde{\mathbf{H}}_{bb}=\begin{bmatrix} \tilde{\mathbf{H}}^{\nu\nu}_{bb} & \tilde{\mathbf{H}}^{\nu\mu}_{bb} \\ \tilde{\mathbf{H}}^{\mu\nu}_{bb} & \tilde{\mathbf{H}}^{\mu\mu}_{bb} \end{bmatrix} . \tag{3.7}$$

A schematic representation of the action of $\mathbf{T}$ is shown in Fig. 1.

To better understand the relation between the matrix $\mathbf{A}$ of the Dyson equation and the matrix $\tilde{\mathbf{H}}$ derived in Eq. (3.6) we have to bear in mind that the first block of columns of the transformation matrix $\mathbf{T}$ is by construction identical to the composite matrix of residues $\mathbf{Y}$. As a consequence, the upper left block $\tilde{\mathbf{H}}_{aa}$ of the transformed Hamiltonian $\tilde{\mathbf{H}}$ is completely determined by $\mathbf{Y}$ and can be given explicitly. It does not depend on the choice of the second block of columns of $\mathbf{T}$. After simple algebra one obtains

$$(\tilde{\mathbf{H}}_{aa})_{\alpha\beta}=\langle\Psi_0^N|\{[a_\alpha,\hat{H}],a_\beta^\dagger\}|\Psi_0^N\rangle . \tag{3.8}$$

[,] denote the commutator. We note that this expression is identical to the upper left block of the matrix $\mathbf{A}$ in Eq. (1.7):

$$\tilde{\mathbf{H}}_{aa}=\boldsymbol{\varepsilon}+\boldsymbol{\Sigma}(\infty) . \tag{3.9}$$

For completeness, the equivalence between Eqs. (3.8) and (3.9) is shown in Appendix A.

Taking into account the above considerations, the following expression for the dynamic part $\mathbf{M}(\omega)$ of the self-energy holds:

$$\mathbf{M}(\omega)=\tilde{\mathbf{H}}_{ab}(\omega\mathbf{1}-\tilde{\mathbf{H}}_{bb})^{-1}\tilde{\mathbf{H}}_{ba} . \tag{3.10}$$

The static self-energy is reproduced uniquely while the dynamic part is given in one of its possible representations. The latter depends exclusively on the explicit form we can choose for the second block of columns of the transformation matrix $\mathbf{T}$. Choosing, for instance, $\mathbf{T}_+$ and $\mathbf{T}_-$ [see Eqs. (3.2) and (3.3)] such that $\tilde{\mathbf{H}}_{bb}$ is diagonal, one obtains $\tilde{\mathbf{H}}_{bb}=\boldsymbol{\Omega}$ and $\tilde{\mathbf{H}}_{ab}=\mathbf{m}$. The dynamic self-energy is then in its diagonal representation and Eq. (1.6) is recovered.

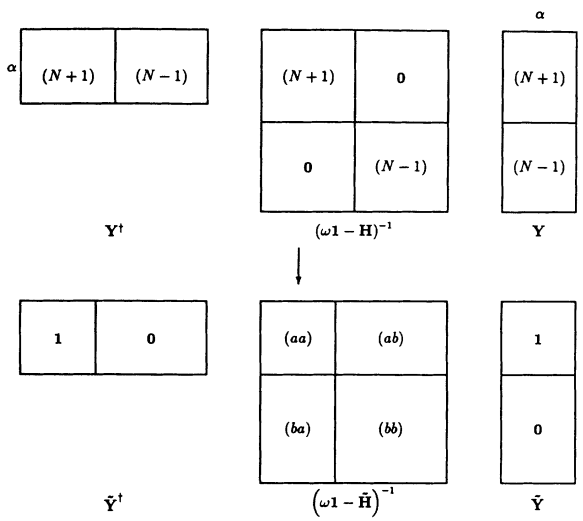

FIG. 1. Schematic drawing of the action of the unitary transformation $\mathbf{T}$ on the representation of the Green's function [see Eqs. (3.3)–(3.5)]. The $(N\pm1)$-particle spaces which are naturally decoupled in $\mathbf{H}$ now couple in the transformed composite Hamiltonian $\tilde{\mathbf{H}}$. In $\tilde{\mathbf{H}}$ the upper block (aa) is spanned by the classes $1p$ and $1h$ and the lower block (bb) by the classes of the $(N\pm1)$-particle excitations.

IV. NATURAL CHOICE OF T AND RELATION TO THE ADC SCHEME

A. General

In this section we investigate a particular choice of $\mathbf{T}$ which seems to us to be the most obvious choice out of all possible transformations.

The first column of blocks $\mathbf{Y}$ of the transformation matrix $\mathbf{T}$ introduced in the preceding section [Eqs. (3.2) and (3.3)] are essentially determined from the action of $a_\alpha^\dagger$ on the ground state $|\Psi_0^N\rangle$ [see Eqs. (2.4)]. Since $\mathbf{T}$ is a unitary matrix, the remaining columns of this transforma-

tion must rise from the action of that set of operators on $|\Psi_0^N\rangle$ which is the orthogonal complement of $\{a_\alpha^\dagger\}$. The simplest choice is based on the following consideration: we introduce explicitly the set of all creation and destruction operators which produce the configuration states $\{|\Phi_{q(\nu)}^{N+1}\rangle\}$ and $\{|\Phi_{q(\mu)}^{N-1}\rangle\}$ when acting on the reference state $|\Phi_0^N\rangle$. These operators $A_{0\gamma}$ are defined by the following relations:

$$|\Phi_{q(\nu)}^{N+1}\rangle = A_{0\nu}^\dagger|\Phi_0^N\rangle \ , \tag{4.1a}$$

$$|\Phi_{q(\mu)}^{N-1}\rangle = A_{0\mu}|\Phi_0^N\rangle \ . \tag{4.1b}$$

The $A_{0\nu}^\dagger$ operators contain the sets $\{a_{u2}^\dagger a_{u1}^\dagger a_{i1}\}$, $\{a_{u3}^\dagger a_{u2}^\dagger a_{u1}^\dagger a_{i1} a_{i2}\}$, etc. where u and i denote orbitals which are unoccupied and occupied in the reference configuration $|\Phi_0^N\rangle$, respectively. The $A_{0\mu}^\dagger$ operators are defined analogously but with occupied and unoccupied indices interchanged. The sets of operators $\{a_\alpha^\dagger\}\cup\{A_{0\gamma}^\dagger\}$ and $\{a_\alpha\}\cup\{A_{0\gamma}\}$ give rise to complete sets of functions for the $(N+1)$- and $(N-1)$-particle spaces, respectively, also when they act on any other N-particle state, and in particular on the exact ground state $|\Psi_0^N\rangle$ [11].

With this choice the elements of the second block of columns of the matrix $\mathbf{T}$ can be defined explicitly as

$$(\mathbf{T}_{+(\nu)})_{q\nu} = \langle \Phi_q^{N+1}|\,\tilde{A}_\nu^\dagger|\Psi_0^N\rangle \ , \tag{4.2a}$$

$$(\mathbf{T}_{-(\nu)})_{q\nu} = \langle \Phi_q^{N-1}|\,\tilde{A}_\nu|\Psi_0^N\rangle \ , \tag{4.2b}$$

$$(\mathbf{T}_{+(\mu)})_{q\mu} = \langle \Phi_q^{N+1}|\,\tilde{A}_\mu^\dagger|\Psi_0^N\rangle \ , \tag{4.2c}$$

$$(\mathbf{T}_{-(\mu)})_{q\mu} = \langle \Phi_q^{N-1}|\,\tilde{A}_\mu|\Psi_0^N\rangle \ , \tag{4.2d}$$

where the operators $\tilde{A}_\nu^\dagger$ and $\tilde{A}_\mu$ are defined as

$$\tilde{A}_\nu^\dagger = \sum_{\nu'}\left[A_{0\nu'}^\dagger - \sum_u a_u^\dagger\langle\Psi_0^N|\{a_u, A_{0\nu'}^\dagger\}|\Psi_0^N\rangle\right]\tilde{N}_{\nu'\nu} \ , \tag{4.3a}$$

$$\tilde{A}_\mu^\dagger = \sum_{\mu'}\left[A_{0\mu'}^\dagger - \sum_i a_i^\dagger\langle\Psi_0^N|\{a_i, A_{0\mu'}^\dagger\}|\Psi_0^N\rangle\right]\tilde{M}_{\mu'\mu} \ . \tag{4.3b}$$

Defining $\mathbf{T}_\pm$ as in Eqs. (4.2) but with the bare operators $A_{0\nu}^\dagger$ and $A_{0\mu}^\dagger$ instead of $\tilde{A}_\nu^\dagger$ and $\tilde{A}_\mu^\dagger$ does not lead to a unitary matrix $\mathbf{T}$. The latter operators are obtained by orthogonalizing the former ones on the $\{a_\alpha^\dagger\}$ and making use of the fact that the following pairs of operators anticommute: $\{A_{0\nu}, A_{0\mu}^\dagger\} = \{A_{0\nu}, a_i^\dagger\} = \{A_{0\mu}, a_u^\dagger\} = 0$. The matrices $\tilde{\mathbf{N}}$ and $\tilde{\mathbf{M}}$ represent normalization factors while the indices i and u specify occupied and unoccupied one-particle states, respectively. We note that $\mathbf{T}$ is a unitary matrix. As shown in Appendix C the operators $\tilde{A}_\gamma$ satisfy the following peculiar completeness relation:

$$\sum_\alpha a_\alpha^\dagger|\Psi_0^N\rangle\langle\Psi_0^N|a_\alpha + \sum_\gamma \tilde{A}_\gamma^\dagger|\Psi_0^N\rangle\langle\Psi_0^N|\,\tilde{A}_\gamma = 1 \ ; \quad \alpha = u,i \ , \ \gamma = \mu,\nu \tag{4.4a}$$

and

$$\sum_\alpha a_\alpha|\Psi_0^N\rangle\langle\Psi_0^N|a_\alpha^\dagger + \sum_\gamma \tilde{A}_\gamma|\Psi_0^N\rangle\langle\Psi_0^N|\,\tilde{A}_\gamma^\dagger = 1 \ ; \quad \alpha = u,i \ , \ \gamma = \mu,\nu \tag{4.4b}$$

in the spaces of $(N+1)$ and $(N-1)$ particles, respectively.

With the aid of the transformation defined in Eqs. (3.2), (3.3), (4.2), and (4.3) the transformed composite Hamiltonian $\tilde{\mathbf{H}} = \mathbf{T}^\dagger\mathbf{H}\mathbf{T}$ which determines the Green's function and the self-energy can be given explicitly as a ground-state expectation value:

$$(\tilde{\mathbf{H}}_{aa})_{\alpha\beta} = \langle\Psi_0^N|\{[a_\alpha, \hat{H}], a_\beta^\dagger\}|\Psi_0^N\rangle \ , \quad \alpha,\beta = u,i \tag{4.5a}$$

$$(\tilde{\mathbf{H}}_{ab})_{\alpha\gamma} = \langle\Psi_0^N|\{[a_\alpha, \hat{H}], A_\gamma^\dagger\}|\Psi_0^N\rangle \ , \quad \gamma = \mu,\nu \tag{4.5b}$$

$$(\tilde{\mathbf{H}}_{ba})_{\gamma\beta} = \langle\Psi_0^N|\{[\tilde{A}_\gamma, \hat{H}], a_\beta^\dagger\}|\Psi_0^N\rangle \ , \quad \gamma = \mu,\nu \tag{4.5c}$$

$$(\tilde{\mathbf{H}}_{bb})_{\gamma\gamma'} = \langle\Psi_0^N|\{[\tilde{A}_\gamma, \hat{H}], \tilde{A}_{\gamma'}^\dagger\}|\Psi_0^N\rangle \ , \quad \gamma,\gamma' = \mu,\nu \ . \tag{4.5d}$$

These expressions give the Hamiltonian $\tilde{\mathbf{H}}$ in closed form. Two important observations have to be made about the above formulas. First of all we note that they contain the ground state $|\Psi_0^N\rangle$ as the sole unknown quantity. Therefore the evaluation of Eqs. (4.5) depends exclusively on $|\Psi_0^N\rangle$. Different approximations for $|\Psi_0^N\rangle$ lead to different approximations for $\tilde{\mathbf{H}}$ and thus for the self-energy. The second point concerns the block $\tilde{\mathbf{H}}_{bb}$ of the transformed matrix $\tilde{\mathbf{H}}$. It can be easily seen from Eq. (4.5d) that the coupling block $\tilde{\mathbf{H}}_{bb}^{\mu\nu}$ between the $(N\pm1)$-particle excitations does not vanish identically. We mention that there exist representations of $\mathbf{M}(\omega)$ in which the coupling block vanishes (see Sec. V).

B. Perturbation expansion of the transformed Hamiltonian $\tilde{\mathbf{H}}$

In the following we analyze the results which we have obtained by simply expanding $|\Psi_0^N\rangle$ by Rayleigh-Schrödinger perturbation theory (RSPT). For this purpose we substitute $|\Psi_0^N\rangle$ in Eqs. (4.5) with its perturbation expansion

$$|\Psi_0^N\rangle = \sum_q c_q|\Phi_q^N\rangle \tag{4.6}$$

where $|\Phi_q^N\rangle$ are configuration states spanning the N-particle space. It is reasonable to construct these states on the same set of orbitals as done for the configurations of the $(N\pm1)$-particle space and thus to define

$$\{|\Phi_q^N\rangle\} = |\Phi_0^N\rangle\cup\{|\Phi_{q(1h1p)}^N\rangle\}\cup\{|\Phi_{q(2h2p)}^N\rangle\}\cup\cdots \ . \tag{4.7}$$

With this choice the action of the creation and destruction operators on the $|\Phi_q^N\rangle$ is well defined. In the following we present the expansion of the dynamic self-energy up to and including third order of perturbation. For this we need to consider the contributions up to second order for the off-diagonal blocks $\tilde{\mathbf{H}}_{ab}$ and $\tilde{\mathbf{H}}_{ba}$ and the contributions up to first order to the block $\tilde{\mathbf{H}}_{bb}$ [see Eq. (3.10)]. The only classes of excitations which must be considered

are $\nu=2p1h$ and $\mu=2h1p$. One readily obtains for the zeroth and first order $\tilde{\mathbf{H}}_{bb}^{(0)}$ and $\tilde{\mathbf{H}}_{bb}^{(1)}$ the following relations:

$$(\tilde{\mathbf{H}}_{bb}^{\nu\nu})_{\nu\nu'}^{(0)}=\langle\Phi_0^N|A_{0\nu}(\hat{H}_0-E_0^{N(0)})A_{0\nu'}^\dagger|\Phi_0^N\rangle\ , \tag{4.8a}$$

$$(\tilde{\mathbf{H}}_{bb}^{\nu\nu})_{\nu\nu'}^{(1)}=\langle\Phi_0^N|A_{0\nu}(\hat{H}_I-E_0^{N(1)})A_{0\nu'}^\dagger|\Phi_0^N\rangle\ , \tag{4.8b}$$

$$(\tilde{\mathbf{H}}_{bb}^{\mu\mu})_{\mu\mu'}^{(0)}=-\langle\Phi_0^N|A_{0\mu'}^\dagger(\hat{H}_0-E_0^{N(0)})A_{0\mu}|\Phi_0^N\rangle\ , \tag{4.9a}$$

$$(\tilde{\mathbf{H}}_{bb}^{\mu\mu})_{\mu\mu'}^{(1)}=-\langle\Phi_0^N|A_{0\mu'}^\dagger(\hat{H}_I-E_0^{N(1)})A_{0\mu}|\Phi_0^N\rangle\ . \tag{4.9b}$$

The coupling block $\tilde{\mathbf{H}}_{bb}^{\mu\nu}$ vanishes in zeroth and first order:

$$(\tilde{\mathbf{H}}_{bb}^{\mu\nu})^{(0)}=(\tilde{\mathbf{H}}_{bb}^{\mu\nu})^{(1)}=\mathbf{0}\ . \tag{4.10}$$

The superscript (n) indicates the order of the quantity in question and $\hat{H}_I=\hat{H}-\hat{H}_0$. The expressions for the elements of $\tilde{\mathbf{H}}_{ba}$ are somewhat more lengthy and are needed up to second order. We have to distinguish between occupied (i) and unoccupied (u) orbitals. The expressions read

$$(\tilde{\mathbf{H}}_{ba}^{\nu u})^{(0)}=0\ , \tag{4.11a}$$

$$(\tilde{\mathbf{H}}_{ba}^{\nu u})_{\nu u}^{(1)}=\langle\Phi_0^N|A_{0\nu}(\hat{H}_I-E_0^{N(1)})a_u^\dagger|\Phi_0^N\rangle\ , \tag{4.11b}$$

$$(\tilde{\mathbf{H}}_{ba}^{\nu u})_{\nu u}^{(2)}=\sum_q\Big[\langle\Phi_0^N|A_{0\nu}(\hat{H}_I-E_0^{N(1)})a_u^\dagger|\Phi_{q(2h2p)}^N\rangle c_{q(2h2p)}^{(1)}+\langle\Phi_0^N|A_{0\nu}(\hat{H}_0-E_0^{N(0)})a_u^\dagger|\Phi_{q(1h1p)}^N\rangle c_{q(1h1p)}^{(2)}$$
$$-\sum_v\langle\Phi_0^N|A_{0\nu}a_v^\dagger|\Phi_{q(1h1p)}^N\rangle c_{q(1h1p)}^{(2)}\langle\Phi_0^N|a_v(\hat{H}_0-E_0^{N(0)})a_u^\dagger|\Phi_0^N\rangle\Big]\ , \tag{4.11c}$$

$$(\tilde{\mathbf{H}}_{ba}^{vi})^{(0)}=0\ , \tag{4.12a}$$

$$(\tilde{\mathbf{H}}_{ba}^{vi})_{vi}^{(1)}=\sum_q[\langle\Phi_0^N|A_{0\nu}(\hat{H}_0-E_0^{N(0)})a_i^\dagger|\Phi_{q(2h2p)}^N\rangle c_{q(2h2p)}^{(1)}-\langle\Phi_0^N|a_i^\dagger(\hat{H}_0-E_0^{N(0)})A_{0\nu}|\Phi_{q(2h2p)}^N\rangle c_{q(2h2p)}^{(1)}]\ , \tag{4.12b}$$

$$(\tilde{\mathbf{H}}_{ba}^{vi})_{vu}^{(2)}=\sum_q[\langle\Phi_0^N|A_{0\nu}(\hat{H}_0-E_0^{N(0)})a_i^\dagger|\Phi_{q(2h2p)}^N\rangle c_{q(2h2p)}^{(2)}+\langle\Phi_0^N|A_{0\nu}(\hat{H}_I-E_0^{N(1)})a_i^\dagger|\Phi_{q(2h2p)}^N\rangle c_{q(2h2p)}^{(1)}$$
$$-\langle\Phi_0^N|a_i^\dagger(\hat{H}_0-E_0^{N(0)})A_{0\nu}|\Phi_{q(2h2p)}^N\rangle c_{(2h2p)}^{(2)}-\langle\Phi_0^N|a_i^\dagger(\hat{H}_I-E_0^{N(1)})A_{0\nu}|\Phi_{q(2h2p)}^N\rangle c_{q(2h2p)}^{(1)}]\ , \tag{4.12c}$$

$$(\tilde{\mathbf{H}}_{ba}^{\mu u})^{(0)}=0\ , \tag{4.13a}$$

$$(\tilde{\mathbf{H}}_{ba}^{\mu u})_{\mu u}^{(1)}=\sum_q[c_{q(2h2p)}^{*(1)}\langle\Phi_{q(2h2p)}^N|A_{0\mu}(\hat{H}_0-E_0^{N(0)})a_u^\dagger|\Phi_0^N\rangle-c_{q(2h2p)}^{*(1)}\langle\Phi_{q(2h2p)}^N|a_u^\dagger(\hat{H}_0-E_0^{N(0)})A_{0\mu}|\Phi_0^N\rangle]\ , \tag{4.13b}$$

$$(\tilde{\mathbf{H}}_{ba}^{\mu u})_{\mu u}^{(2)}=\sum_q[c_{q(2h2p)}^{*(2)}\langle\Phi_{q(2h2p)}^N|A_{0\mu}(\hat{H}_0-E_0^{N(0)})a_u^\dagger|\Phi_0^N\rangle+c_{q(2h2p)}^{*(1)}\langle\Phi_{q(2h2p)}^N|A_{0\mu}(\hat{H}_I-E_0^{N(1)})a_u^\dagger|\Phi_0^N\rangle$$
$$-c_{q(2h2p)}^{*(2)}\langle\Phi_{q(2h2p)}^N|a_u^\dagger(\hat{H}_0-E_0^{N(0)})A_{0\mu}|\Phi_0^N\rangle-c_{q(2h2p)}^{*(1)}\langle\Phi_{q(2h2p)}^N|a_u^\dagger(\hat{H}_1-E_0^{N(1)})A_{0\mu}|\Phi_0^N\rangle]\ , \tag{4.13c}$$

$$(\tilde{\mathbf{H}}_{ba}^{\mu i})^{(0)}=0\ , \tag{4.14a}$$

$$(\tilde{\mathbf{H}}_{ba}^{ui})_{\mu i}^{(1)}=-\langle\Phi_0^N|a_i^\dagger(\hat{H}_I-E_0^{N(1)})A_{0\mu}|\Phi_0^N\rangle\ , \tag{4.14b}$$

$$(\tilde{\mathbf{H}}_{ba}^{\mu i})_{\mu i}^{(2)}=\sum_q\Big[-c_{q(2h2p)}^{*(1)}\langle\Phi_{q(2h2p)}^N|a_i^\dagger(\hat{H}_I-E_0^{N(1)})A_{0\mu}|\Phi_0^N\rangle-c_{q(1h1p)}^{*(2)}\langle\Phi_{q(1h1p)}^N|a_i^\dagger(\hat{H}_0-E_0^{N(0)})A_{0\mu}|\Phi_0^N\rangle$$
$$+\sum_j c_{q(2h2p)}^{*(2)}\langle\Phi_{q(2h2p)}^N|a_j^\dagger A_{0\mu}|\Phi_0^N\rangle\langle\Phi_0^N|a_i^\dagger(\hat{H}_0-E_0^{N(0)})a_j|\Phi_0^N\rangle\Big]\ . \tag{4.14c}$$

In the above formulas we expressed the operators $\tilde{A}_\gamma^\dagger$ in terms of the bare operators $A_{0\gamma}^\dagger$ according to the definitions in Eqs. (4.1) and (4.3). In the expansion of the dynamic self-energy up to third order the operators $\tilde{A}_\gamma^\dagger$ can be identified with the bare ones except for the last terms in Eqs. (4.11c) and (4.14c). These terms are due to the components of the $\tilde{A}_\gamma^\dagger$ which derive from the orthogonalization to the $a_\alpha^\dagger$. For convenience, these formulas are obtained under the explicit assumption that the one-particle basis set $\{|\varphi_\alpha\rangle\}$ is the set deriving form a self-consistent restricted Hartree-Fock calculation on the ground state $|\Psi_0^N\rangle$. Thus there are no first-order contributions to $|\Psi_0^N\rangle$ from the first class of excitations $\gamma=1h1p$.

The formulas in Eqs. (4.8)–(4.14) are naturally given as products of matrix elements of the Hamiltonian between configuration classes and the coefficient $c_q^{(n)}$ which is the nth-order contribution of the state $|\Phi_q^N\rangle$ to the perturbation expansion of $|\Psi_0^N\rangle$. If one takes explicitly account of the form of the Hamiltonian (see Appendix A) the above expressions can be transformed into products of two-particle integrals $V_{\alpha\beta\gamma\delta}$ and one-particle energies ε_α. The

formulation in these integrals can be obtained in a lengthy but quite straightforward way and some illustrative examples are presented in Appendix B. When expressed in terms of two-particle integrals, it becomes possible to carry out a direct comparison of our result with the well-established ADC approach [12] to the self-energy. ADC is a general approach to the Green's function. It is essentially based on the analysis of Feynman diagrams which describe the perturbation expansion of $\mathbf{M}(\omega)$. By comparing order by order the power expansion of a general algebraic expression (ADC form) with the corresponding diagrammatic expansion, one obtains an effective nondiagonal interaction matrix $(\mathbf{K}+\mathbf{C})$ and an effective coupling matrix $\mathbf{U}$. The matrices $(\mathbf{K}+\mathbf{C})$ and $\mathbf{U}$ can be viewed as particular representations of the submatrices $\mathbf{\Omega}$ and $\mathbf{m}$ of the matrix $\mathbf{A}$ [see Eq. (1.7)]. The relation between our approach and ADC can be established by comparing the blocks $\tilde{\mathbf{H}}_{bb}$ and $\tilde{\mathbf{H}}_{ba}$ of our transformed composite Hamiltonian $\tilde{\mathbf{H}}$ with the ADC effective matrices $(\mathbf{K}+\mathbf{C})$ and $\mathbf{U}$, respectively. We have rewritten all the expressions in Eqs. (4.8)–(4.14) in terms of two-particle integrals $V_{\alpha\beta\gamma\delta}$ and orbital energies ε_α. The final result has been found to be identical with the ADC equations, i.e., the self-energy $\mathbf{M}(\omega)$ given in Eq. (3.10) with $\tilde{\mathbf{H}}_{ab}$ and $\tilde{\mathbf{H}}_{bb}$ of Eqs. (4.8–4.14) is *identical* to that obtained in the third-order ADC scheme.

In principle, starting with the closed-form expressions of Eqs. (4.5) one could proceed in the same way as done above up to third order and calculate the approximation schemes in any order of perturbation theory for $\mathbf{M}(\omega)$. However, this straightforward application of RSPT presents some problems, which we discuss briefly in the following.

As already mentioned, the coupling block $\tilde{\mathbf{H}}^{\mu\nu}_{bb}$, obtained by setting $\gamma=\mu$ and $\gamma'=\nu$ in Eq. (4.5d), does not vanish identically. As shown above it is indeed zero in zeroth and first order, but there appear nonvanishing contributions in second and higher orders (see also Appendix B). A similar problem is encountered also in using the equation of motion (EOM) method for the approximation of the Dyson equation [13,14]. There, one starts from a completely different point of attack but one also obtains second-order coupling terms between the spaces of the $(N+1)$- and $(N-1)$-particle excitations. The presence of second-order coupling elements prevents the possibility of reproducing analytically the fourth-order ADC scheme. In fact the ADC approach takes explicitly into account that the dynamic self-energy can be split into two independent contributions deriving from the classes of the $(N+1)$- and $(N-1)$-particle excitations. The Feynman diagrams associated to $\mathbf{M}(\omega)$ can also be separated into two independent sets, which respect this splitting of the dynamic self-energy (see next section).

In order to get rid of the coupling terms between the blocks ν and μ of $\tilde{\mathbf{H}}_{bb}$ one could obviously proceed by introducing an ulterior unitary transformation matrix which block diagonalizes $\tilde{\mathbf{H}}_{bb}$. After the block-diagonalization transformation, the resulting matrix possesses blocks along the diagonal which, by construction, are decoupled from each other. In general there are infinitely many unitary transformations which block-diagonalize a Hermitian matrix. A recent investigation showed, however, that under very simple and convincing conditions the unitary transformation which block diagonalizes a given Hermitian matrix can be unequivocally constructed [15]. In this way it is thus possible to obtain for the dynamic self-energy a uniquely defined formulation in which the $(N+1)$- and the $(N-1)$-particle excitations are decoupled from each other. To analyze this procedure we have investigated the simple case of a one-particle Hamiltonian. We can show that in this case the block diagonalization of $\tilde{\mathbf{H}}_{bb}$ leads to expressions in closed form for the dynamic self-energy. This example is quite interesting for itself and is illustrated and discussed in detail in Appendix C.

In the general case of a two-particle Hamiltonian the block diagonalization of $\tilde{\mathbf{H}}_{bb}$ does not lead to closed-form expressions. The reason is that the block-diagonalization matrix depends explicitly on the eigenvector matrix of $\tilde{\mathbf{H}}_{bb}$, which is in general not known. The block-diagonalization procedure can therefore be carried out only order by order in perturbation theory. The result gives rise to approximation schemes for the dynamic self-energy, in which the $(N\pm1)$-particle excitations are, by construction, decoupled from each other at each given order of perturbation.

V. ON THE DECOUPLING OF THE SELF-ENERGY INTO $(N+1)$- AND $(N-1)$-PARTICLE CONTRIBUTIONS

The dynamic self-energy $\mathbf{M}(\omega)$ can be written as a sum of two parts:

$$\mathbf{M}(\omega)=\mathbf{M}^{(\nu)}(\omega)+\mathbf{M}^{(\mu)}(\omega) \tag{5.1}$$

where $\mathbf{M}^{(\nu)}(\omega)$ and $M^{(\mu)}(\omega)$ can be uniquely assigned to the configuration spaces of $(N+1)$ and $(N-1)$ particles [5–7]. Indeed, the perturbation expansion of the self-energy, which is commonly done in terms of Feynman diagrams, automatically gives rise to two distinct sets of diagrams, which unequivocally can be assigned to $\mathbf{M}^{(\nu)}(\omega)$ and $M^{(\mu)}(\omega)$ [1,2]. The ADC scheme for the self-energy explicitly makes use of this fact [12].

Clearly, the self-energy represented in configuration space [Eq. (3.10)] does not decouple into $(N+1)$- and $(N-1)$-particle contributions for arbitrary transformations $\mathbf{T}$. Even the appealing choice of $\mathbf{T}$ introduced in the preceding section does not lead to a representation of $\mathbf{M}(\omega)$ which decouples according to Eq. (5.1). The diagonal representation of $\tilde{\mathbf{H}}_{bb}$ in Eq. (1.6) obviously leads to this decoupling. Another representation which fulfills Eq. (5.1) is obtained (per construction) by block diagonalizing $\tilde{\mathbf{H}}_{bb}$ as discussed in the preceding section.

In the following we investigate the general question of whether a representation of $\mathbf{M}(\omega)$ exists which fulfills Eq. (5.1) and makes use only of the exact ground state, i.e., the transformation matrix is determined by $|\Psi_0^N\rangle$. This requirement is motivated by the fact that the Green's function itself and the matrix of the residues $\mathbf{Y}$ [see Eqs. (2.2) and (2.4)], which is an indispensable part of the transformation $\mathbf{T}$, are defined via $|\Psi_0^N\rangle$. Furthermore,

this opens the possibility to straightforwardly expand $\mathbf{T}$ in terms of perturbation series which are well established for the ground state.

The most obvious way to fulfill Eq. (5.1) is achieved by setting to zero those blocks of the transformation $\mathbf{T}$ which give rise to the coupling of the $(N+1)$- and $(N-1)$-particle spaces in $\tilde{\mathbf{H}}_{bb}$. By writing

$$\mathbf{T}=\begin{pmatrix} \mathbf{Y}_+ & \mathbf{T}_{+(\nu)} & \mathbf{0} \\ (\mathbf{Y}_-)^* & \mathbf{0} & (\mathbf{T}_{-(\mu)})^* \end{pmatrix} \tag{5.2}$$

the submatrix $\tilde{\mathbf{H}}_{bb}$ of the composite Hamiltonian $\tilde{\mathbf{H}}$ becomes block diagonal, i.e., $\tilde{\mathbf{H}}_{bb}^{\mu\nu}=\mathbf{0}$, and the self-energy $\mathbf{M}(\omega)$ in Eq. (3.10) trivially decouples into two distinct parts $\mathbf{M}^{(\nu)}(\omega)$ and $M^{(\mu)}(\omega)$.

The matrix $\mathbf{T}$ defined above thus possesses the two required characteristics: it automatically renders the block $\tilde{\mathbf{H}}_{bb}$ block diagonal and can be given as a function of $|\Psi_0^N\rangle$ only. However, the matrix $\mathbf{T}$ is unfortunately singular, since some of its columns (precisely as many as the dimension of the one-particle basis set $\{|\varphi_\alpha\rangle\}$) vanish identically. This statement can be proven by a simple argument of combinatorial analysis. Suppose that the one-particle basis set $\{|\varphi_\alpha\rangle\}$ is composed of $n+v$ states, where n and v indicate the number of occupied and unoccupied one-particle states in $|\Phi_0^N\rangle$, respectively. $n+v$ is thus the number of column vectors included in the component $\mathbf{Y}$ of $\mathbf{T}$. Let us first consider the upper part of $\mathbf{T}$ indicated by the subscript $+$ [see Eq. (5.2)]. If d is the dimension of the $(N+1)$-particle space, i.e., the total number of $(N+1)$-particle states, then the number of column vectors in $\mathbf{T}_{+(\nu)}$ is obviously $d-v$. This is the dimension of the class ν. $\mathbf{Y}_+^\dagger\mathbf{Y}_+$ (and $\mathbf{Y}_-^\dagger\mathbf{Y}_-$) are directly related to the one-particle density matrices [see Eqs. (2.4)], which for an interacting many-body system has no vanishing eigenvalues, i.e, the matrix $\mathbf{Y}_+$ does not contain linearly dependent column vectors. Hence we have produced in $(\mathbf{Y}_+ \quad \mathbf{T}_+)$ as many as $n+v+d-v=n+d$ linearly independent and even orthogonal column vectors of length d. This is clearly a contradiction. Because of the assumed unitary of $\mathbf{T}$, the vectors of $\mathbf{T}_{+(\nu)}$ are orthogonal to those of $\mathbf{Y}_+$ (and to each other) and therefore we can conclude for a given vector that it can be chosen to be either really orthogonal to $\mathbf{Y}_+$ or it vanishes identically. In particular, the number of vanishing columns in the matrix $\mathbf{T}_{+(\nu)}$ is n and the number of nonvanishing orthogonal columns is $d-n$. Similar arguments apply to the matrix $\mathbf{T}_{-(\mu)}$. Denoting the dimension of the $(N-1)$-particle space by $\bar{d}$, the number of nonvanishing columns in $\mathbf{T}_{-(\mu)}$ is $\bar{d}-v$ and the number of vanishing columns is v [16].

We conclude that for a generic interacting many-body system it is, in principle, *impossible* to construct a matrix which is unitary and at the same time possesses the block structure indicated in Eq. (5.2). The rank of the $(d+\bar{d})$-dimensional matrix $\mathbf{T}$ as given in Eq. (5.2) is at most $(d+\bar{d})-(n+v)$. In the special case where the Hamiltonian of the system is a one-particle operator, n columns of $\mathbf{Y}_+$ and v columns of $\mathbf{Y}_-$ become linear dependent and a unitary matrix $\mathbf{T}$ as in Eq. (5.2) can be constructed. The explicit determination of the elements of $\mathbf{T}$ in this case is interesting and discussed in Appendix C.

If valid, the ansatz in Eq. (5.2) would have allowed us to construct $\mathbf{T}$ in terms of $|\Psi_0^N\rangle$ only. Since $\mathbf{Y}_\pm$ are determined in terms of $|\Psi_0^N\rangle$, it would have been sufficient to obtain $\mathbf{T}_{+(\nu)}$ and $\mathbf{T}_{-(\mu)}$ by orthogonalizing on $\mathbf{Y}_+$ and $\mathbf{Y}_-$, respectively. As shown above, the ansatz in Eq. (5.2) is inapplicable and we have to resort to a full matrix $\mathbf{T}$ and impose the decoupling of $\mathbf{M}(\omega)$ as a condition on $\mathbf{T}$. However, we have been able to find an example that helps to clarify the situation. The example consists of a two-electron system in a restricted space of two spatial orbitals and can be solved exactly. By means of this example we reached the following important conclusion: it is not possible to obtain a block-diagonal submatrix $\tilde{\mathbf{H}}_{bb}$ of $\tilde{\mathbf{H}}$ or, equivalently, to decouple $\mathbf{M}(\omega)$ according to Eq. (5.1), by a unitary matrix $\mathbf{T}$ which contains $|\Psi_0^N\rangle$ as the sole unknown quantity.

VI. AN ALTERNATIVE APPROACH TO THE ONE-PARTICLE GREEN'S FUNCTION

We have demonstrated in the preceding sections that it is in general not possible to decouple the dynamic self-energy into parts of different particle numbers by a transformation $\mathbf{T}$ that depends on $|\Psi_0^N\rangle$ as the only unknown quantity. The question now arises of how the transformation matrix $\mathbf{T}$ looks, which depends only on $|\Psi_0^N\rangle$ and produces a "maximally decoupled" dynamic self-energy. By maximally decoupled we mean that the $(N+1)$- and the $(N-1)$-particle contributions to the dynamic self-energy arise decoupled from each other as much as possible.

We begin with the structure of $\mathbf{T}$ in Eq. (5.2) which would have led to a block diagonal $\tilde{\mathbf{H}}_{bb}$ if this $\mathbf{T}$ were not singular. A convenient choice of the blocks $\mathbf{T}_{+(\nu)}$ and $(\mathbf{T}_{-(\mu)})^*$ reads

$$(\mathbf{T}_{+(\nu)})_{q\nu}=\langle\Phi_q^{N+1}|A_\nu^\dagger|\Psi_0^N\rangle\ , \tag{6.1a}$$

$$(\mathbf{T}_{-(\mu)})_{q\mu}^*=\langle\Psi_0^N|A_\mu^\dagger|\Phi_q^{N-1}\rangle\ . \tag{6.1b}$$

The operators $A_\nu^\dagger$ and $A_\mu^\dagger$ are here defined according to

$$A_\nu^\dagger=\sum_{\nu'}\left[A_{0\nu'}^\dagger-\sum_{\alpha,\beta}a_\alpha^\dagger(\boldsymbol{\sigma}^{-1})_{\alpha\beta}\langle\Psi_0^N|a_\beta A_{0\nu'}^\dagger|\Psi_0^N\rangle\right]N_{\nu'\nu}\ , \tag{6.2a}$$

$$A_\mu^\dagger=\sum_{\mu'}\left[A_{0\mu'}^\dagger-\sum_{\alpha,\beta}a_\alpha^\dagger(\boldsymbol{\rho}^{-1})_{\alpha\beta}\langle\Psi_0^N|A_{0\mu}^\dagger a_\beta|\Psi_0^N\rangle\right]M_{\mu'\mu}\ . \tag{6.2b}$$

Again the operators $A_{0\nu}^\dagger$ and $A_{0\mu}^\dagger$ represent the bare creation and destruction operator strings according to Eq. (4.1). The matrices $\mathbf{N}$ and $\mathbf{M}$ in Eqs. (6.2) are normalization factors [17] while the matrices $\boldsymbol{\rho}$ and $\boldsymbol{\sigma}$ are the two complementary density matrices defined according to

$$\rho_{\alpha\beta}=\langle\Psi_0^N|a_\beta^\dagger a_\alpha|\Psi_0^N\rangle\ , \tag{6.3a}$$

$$\sigma_{\alpha\beta}=\langle\Psi_0^N|a_\alpha a_\beta^\dagger|\Psi_0^N\rangle\ . \tag{6.3b}$$

This choice arises straightforwardly from that given in Sec. IV by putting $\mathbf{T}_{+(\nu)}=\mathbf{T}_{-(\mu)}=\mathbf{0}$ to maintain the desired block structure as in Eq. (5.2) with orthogonal

vectors. As we have seen in Sec. V, n columns of $\mathbf{T}_{+(\nu)}$ and ν columns of $\mathbf{T}_{-(\mu)}$ vanish identically. To obtain a unitary transformation $\mathbf{T}$ it is necessary to replace these vectors by $n+\nu$ "long" vectors, i.e., by vectors which have nonvanishing components in both $\mathbf{T}_+$ and $\mathbf{T}_-$ parts [see Eqs. (3.2) and (3.3)]. It is easy to convince oneself that this construction yields the maximal decoupling in the spaces of the $(N\pm1)$-particle excitations (see also Fig. 2). To proceed we introduce the matrices

$$\mathbf{C}=\begin{bmatrix}\mathbf{C}_+\\ \mathbf{0}\end{bmatrix}=\begin{bmatrix}\langle\Phi_q^{N+1}|A_\nu^\dagger|\Psi_0^N\rangle\\ \mathbf{0}\end{bmatrix},\quad \mathbf{C}\neq\mathbf{0} \tag{6.4a}$$

$$\mathbf{D}=\begin{bmatrix}\mathbf{0}\\ (\mathbf{D}_-)^*\end{bmatrix}=\begin{bmatrix}\mathbf{0}\\ \langle\Psi_0^N|A_\mu^\dagger|\Phi_q^{N-1}\rangle\end{bmatrix},\quad \mathbf{D}\neq\mathbf{0} \tag{6.4b}$$

which contain only the nonvanishing columns of $\mathbf{T}$ in Eq. (6.1). The vanishing columns of $\mathbf{T}$ will now be replaced by some suitable vectors. Since we know that they are as many as $n+\nu$, which corresponds to the number of one-particle states of the set $\{|\varphi_\alpha\rangle\}$, we can label them with the one-particle index α, as is the situation for $\mathbf{Y}$. Casting these new vectors into a matrix $\mathbf{X}$, it is easy to see that this matrix possesses exactly the same block structure and dimension of $\mathbf{Y}$. We define

$$\mathbf{X}=\begin{bmatrix}\mathbf{X}_+\\ (\mathbf{X}_-)^*\end{bmatrix}=\begin{bmatrix}\langle\Phi_q^{N+1}|x_{+\alpha}^\dagger|\Psi_0^N\rangle\\ \langle\Psi_0^N|x_{-\alpha}^\dagger|\Phi_q^{N-1}\rangle\end{bmatrix}. \tag{6.5}$$

The operators $x_{\pm\alpha}^\dagger$ have to be determined under the condition that the whole $\mathbf{T}$ matrix

$$\mathbf{T}=(\mathbf{Y}\quad\mathbf{X}\quad\mathbf{C}\quad\mathbf{D}) \tag{6.6}$$

is unitary.

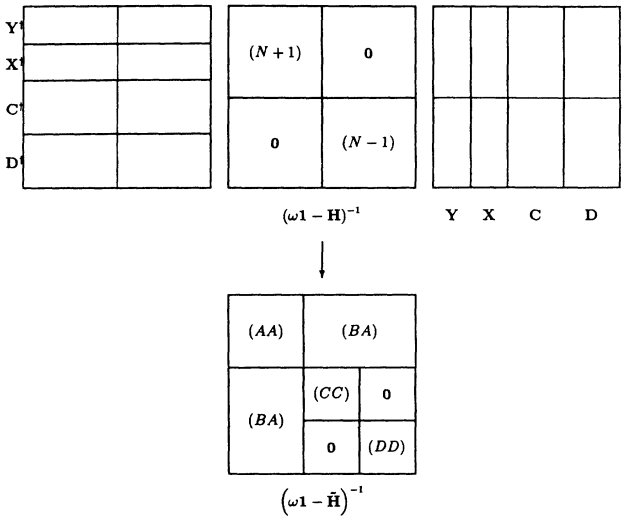

FIG. 2. Schematic representation of the transformed composite Hamiltonian which leads to the maximally decoupled dynamic self-energy. The upper left block (AA) of $\tilde{\mathbf{H}}$ is twice as large as the $\tilde{\mathbf{H}}_{aa}$ part of the composite Hamiltonian of Fig. 1. The large blocks (CC) and (DD) of the $(N\pm1)$-particle excitation are exactly decoupled from each other.

A. The extended Green's function

Before specifying the new matrix $\mathbf{X}$ we make some general remarks on the transformation matrix $\mathbf{T}$ as defined in Eq. (6.6). The transformed composite Hamiltonian obtained by means of $\mathbf{T}$ now possesses the following block structure:

$$\tilde{\mathbf{H}}=\begin{bmatrix}\tilde{\mathbf{H}}_{AA} & \tilde{\mathbf{H}}_{AB}\\ \tilde{\mathbf{H}}_{BA} & \tilde{\mathbf{H}}_{BB}\end{bmatrix}. \tag{6.7}$$

Note that the block $\tilde{\mathbf{H}}_{BB}$ has a block-diagonal structure, where the $(N+1)$- and $(N-1)$-particle contributions decouple exactly from each other:

$$\tilde{\mathbf{H}}_{BB}=\begin{bmatrix}\tilde{\mathbf{H}}_{CC} & 0\\ 0 & \tilde{\mathbf{H}}_{DD}\end{bmatrix}. \tag{6.8a}$$

$\tilde{\mathbf{H}}_{CC}$ and $\tilde{\mathbf{H}}_{DD}$ correspond to the $(N+1)$- and $(N-1)$-particle spaces, respectively. Because of the appearance of the transformation (6.6), the dimension of $\tilde{\mathbf{H}}_{AA}$ is twice as large as that of $\tilde{\mathbf{H}}_{aa}$ in the preceding sections. $\tilde{\mathbf{H}}_{AA}$ is a block matrix with the following block structure:

$$\tilde{\mathbf{H}}_{AA}=\begin{bmatrix}\mathbf{Y}^\dagger\\ \mathbf{X}^\dagger\end{bmatrix}\mathbf{H}(\mathbf{Y}\quad\mathbf{X})=\begin{bmatrix}\tilde{\mathbf{H}}_{aa} & \tilde{\mathbf{H}}_{ax}\\ \tilde{\mathbf{H}}_{xa} & \tilde{\mathbf{H}}_{xx}\end{bmatrix}. \tag{6.8b}$$

It should also be noted that the block $\tilde{\mathbf{H}}_{aa}$ is still contained in the $\tilde{\mathbf{H}}_{AA}$.

The elements of the transformed Hamiltonian in the above new representation explicitly read

$$(\tilde{\mathbf{H}}_{aa})_{\alpha\beta}=\langle\Psi_0^N|\{[a_\alpha,\hat{H}],a_\beta^\dagger\}|\Psi_0^N\rangle, \tag{6.9a}$$

$$(\tilde{\mathbf{H}}_{xa})_{\alpha\beta}=\langle\Psi_0^N|x_{+\alpha}[\hat{H},a_\beta^\dagger]|\Psi_0^N\rangle+\langle\Psi_0^N|[\hat{H},a_\beta^\dagger]x_{-\alpha}|\Psi_0^N\rangle, \tag{6.9b}$$

$$(\tilde{\mathbf{H}}_{xx})_{\alpha\beta}=\langle\Psi_0^N|x_{+\alpha}[\hat{H},x_{+\beta}^\dagger]|\Psi_0^N\rangle+\langle\Psi_0^N|[\hat{H},x_{-\beta}^\dagger]x_{-\alpha}|\Psi_0^N\rangle, \tag{6.9c}$$

$$(\tilde{\mathbf{H}}_{Ca})_{\nu\beta}=\langle\Psi_0^N|A_\nu[\hat{H},a_\beta^\dagger]|\Psi_0^N\rangle, \tag{6.9d}$$

$$(\tilde{\mathbf{H}}_{Cx})_{\nu\beta}=\langle\Psi_0^N|A_\nu[\hat{H},x_{+\beta}^\dagger]|\Psi_0^N\rangle, \tag{6.9e}$$

$$(\tilde{\mathbf{H}}_{CC})_{\nu\nu'}=\langle\Psi_0^N|A_\nu[\hat{H},A_{\nu'}^\dagger]|\Psi_0^N\rangle, \tag{6.9f}$$

$$(\tilde{\mathbf{H}}_{Da})_{\mu\beta}=-\langle\Psi_0^N|A_\mu^\dagger[\hat{H},a_\beta]|\Psi_0^N\rangle, \tag{6.9g}$$

$$(\tilde{\mathbf{H}}_{Dx})_{\mu\beta}=-\langle\Psi_0^N|A_\mu^\dagger[\hat{H},x_{-\beta}]|\Psi_0^N\rangle, \tag{6.9h}$$

$$(\tilde{\mathbf{H}}_{DD})_{\mu\mu'}=-\langle\Psi_0^N|A_{\mu'}^\dagger[\hat{H},A_\mu]|\Psi_0^N\rangle. \tag{6.9i}$$

The evaluation of these expressions can lead to useful approximation schemes, since only $|\Psi_0^N\rangle$ appears and the $\tilde{\mathbf{H}}_{CC}$ and $\tilde{\mathbf{H}}_{DD}$ are *a priori* decoupled. A possible choice of the operators $x_{\pm\alpha}^\dagger$ will be given below. A schematic representation of $\mathbf{T}$ and of its action on the composite Hamiltonian $\mathbf{H}$ [Eq. (2.5a)] is given in Fig. 2.

The block structure of $\tilde{\mathbf{H}}$ suggests the introduction of a Green's function which is not exactly the usual textbook Green's function. $\tilde{\mathbf{H}}_{AA}$ can now be considered as related to a new static self-energy $\tilde{\boldsymbol{\Sigma}}(\infty)$. Correspondingly we can introduce the dynamical component as

$$\tilde{\mathbf{M}}(\omega)=\tilde{\mathbf{H}}_{AB}(\omega\mathbf{1}-\tilde{\mathbf{H}}_{BB})^{-1}\tilde{\mathbf{H}}_{BA} \ . \tag{6.10}$$

The transformed Hamiltonian and the self-energy function $\tilde{\mathbf{\Sigma}}(\omega)$

$$\tilde{\mathbf{\Sigma}}(\omega)=\tilde{\mathbf{\Sigma}}(\infty)+\tilde{\mathbf{M}}(\omega) \tag{6.11}$$

give rise to a new Green's function $\tilde{\mathbf{G}}(\omega)$ which satisfies the following Dyson-like equation:

$$\tilde{\mathbf{G}}(\omega)=\tilde{\mathbf{G}}_0(\omega)+\tilde{\mathbf{G}}_0(\omega)\tilde{\mathbf{\Sigma}}(\omega)\tilde{\mathbf{G}}(\omega) \ . \tag{6.12}$$

Most importantly, the dynamic part $\tilde{\mathbf{M}}(\omega)$ splits into two independent terms

$$\tilde{\mathbf{M}}(\omega)=\tilde{\mathbf{M}}^{(C)}(\omega)+\tilde{\mathbf{M}}^{(D)}(\omega) \tag{6.13}$$

representing the $(N+1)$- and $(N-1)$-particle excitation spaces, respectively. The decoupling of the blocks *CC* and *DD* is very important for practical purposes, since their dimensions are very large compared to that of $\tilde{\mathbf{H}}_{AA}$. The price we have to pay for this decoupling is that $\tilde{\mathbf{H}}_{AA}$ is twice as large as $\tilde{\mathbf{H}}_{aa}$, which is the corresponding term in the usual Green's function theory. This doubling of the upper left block cannot be considered a disadvantage if one bears in mind that we reached the maximal decoupling of the $(N\pm1)$-particle excitations by means of a transformation that contains $|\Psi_0^N\rangle$ as the sole unknown quantity. It would be of interest to investigate the quality of the results (ionization potentials, for instance) obtained by diagonalizing $\tilde{\mathbf{H}}_{AA}$ alone.

Starting with the transformed Hamiltonian $\tilde{\mathbf{H}}$ [Eqs. (6.7)–(6.9)] and the Dyson-like equation [Eq. (6.12)], it is not difficult to derive the spectral representation of $\tilde{\mathbf{G}}(\omega)$. It reads

$$\tilde{\mathbf{G}}(\omega)=\begin{bmatrix}\mathbf{Y}_+ & (\mathbf{Y}_-)^* \\ \mathbf{X}_+ & (\mathbf{X}_-)^*\end{bmatrix}(\omega\mathbf{1}-\mathbf{H})^{-1}\begin{bmatrix}\mathbf{Y}_+ & \mathbf{X}_+ \\ (\mathbf{Y}_-)^* & (\mathbf{X}_-)^*\end{bmatrix} \tag{6.14}$$

where $\mathbf{H}$ is the Hamiltonian defined in Eq. (2.5a).

The Green's function $\tilde{\mathbf{G}}(\omega)$ can be viewed as a block matrix composed of four blocks:

$$\tilde{\mathbf{G}}(\omega)=\begin{bmatrix}\tilde{\mathbf{G}}_{11}(\omega) & \tilde{\mathbf{G}}_{12}(\omega) \\ \tilde{\mathbf{G}}_{21}(\omega) & \tilde{\mathbf{G}}_{22}(\omega)\end{bmatrix} \tag{6.15}$$

where the upper left block $\tilde{\mathbf{G}}_{11}(\omega)$ can be easily identified with the textbook Green's function:

$$\begin{aligned}\tilde{\mathbf{G}}_{11}(\omega)&=(\mathbf{Y}_+)^\dagger(\omega\mathbf{1}-\mathbf{H}^{N+1})^{-1}\mathbf{Y}_+ \\ &\quad+[(\mathbf{Y}_-)^\dagger(\omega\mathbf{1}+\mathbf{H}^{N-1})^{-1}\mathbf{Y}_-]^* \\ &\equiv\mathbf{G}_+(\omega)+\mathbf{G}_-(\omega)=\mathbf{G}(\omega) \ .\end{aligned} \tag{6.16a}$$

The other blocks read explicitly

$$\begin{aligned}\tilde{\mathbf{G}}_{21}(\omega)&=(\mathbf{X}_+)^\dagger(\omega\mathbf{1}-\mathbf{H}^{N+1})^{-1}\mathbf{Y}_+ \\ &\quad+[(\mathbf{X}_-)^\dagger(\omega\mathbf{1}+\mathbf{H}^{N-1})^{-1}\mathbf{Y}_-]^* \ ,\end{aligned} \tag{6.16b}$$

$$\begin{aligned}\tilde{\mathbf{G}}_{12}(\omega)&=(\mathbf{Y}_+)^\dagger(\omega\mathbf{1}-\mathbf{H}^{N+1})^{-1}\mathbf{X}_+ \\ &\quad+[(\mathbf{Y}_-)^\dagger(\omega\mathbf{1}+\mathbf{H}^{N-1})^{-1}\mathbf{X}_-]^* \ ,\end{aligned} \tag{6.16c}$$

$$\begin{aligned}\tilde{\mathbf{G}}_{22}(\omega)&=(\mathbf{X}_+)^\dagger(\omega\mathbf{1}-\mathbf{H}^{N+1})^{-1}\mathbf{X}_+ \\ &\quad+[(\mathbf{X}_-)^\dagger(\omega\mathbf{1}+\mathbf{H}^{N-1})^{-1}\mathbf{X}_-]^* \ .\end{aligned} \tag{6.16d}$$

Concerning the construction of the rectangular matrix $\mathbf{X}$ introduced in Eq. (6.5), it is clear that the condition of unitarity of $\mathbf{T}$ is not sufficient to determine it unequivocally. We postulate here the following form for the operators $x^\dagger_{+\alpha}$ and $x^\dagger_{-\alpha}$:

$$x^\dagger_{+\alpha}=\sum_\beta a^\dagger_\beta(\boldsymbol{\sigma}^{-1/2}\boldsymbol{\rho}^{1/2})_{\beta\alpha} \ , \tag{6.17a}$$

$$x^\dagger_{-\alpha}=-\sum_\beta a^\dagger_\beta(\boldsymbol{\rho}^{-1/2}\boldsymbol{\sigma}^{1/2})_{\beta\alpha} \ . \tag{6.17b}$$

Here $\boldsymbol{\rho}$ and $\boldsymbol{\sigma}=\mathbf{1}-\boldsymbol{\rho}$ are the two complementary density matrices defined in Eqs. (6.3). The first two blocks of columns of the transformation matrix $\mathbf{T}$ now read

$$\begin{aligned}(\mathbf{Y}\quad\mathbf{X})&=\begin{bmatrix}\mathbf{Y}_+ & \mathbf{Y}_+\boldsymbol{\sigma}^{-1/2}\boldsymbol{\rho}^{1/2} \\ (\mathbf{Y}_-)^* & -(\mathbf{Y}_-)^*\boldsymbol{\rho}^{-1/2}\boldsymbol{\sigma}^{1/2}\end{bmatrix} \\ &=\begin{bmatrix}\langle\Phi_q^{N+1}|a^\dagger_\alpha|\Psi_0^N\rangle & \sum_\beta\langle\Phi_q^{N+1}|a^\dagger_\beta|\Psi_0^N\rangle(\boldsymbol{\sigma}^{-1/2}\boldsymbol{\rho}^{1/2})_{\beta\alpha} \\ \langle\Psi_0^N|a^\dagger_\alpha|\Phi_q^{N-1}\rangle & -\sum_\beta\langle\Psi_0^N|a^\dagger_\beta|\Phi_q^{N-1}\rangle(\boldsymbol{\rho}^{-1/2}\boldsymbol{\sigma}^{1/2})_{\beta\alpha}\end{bmatrix} \ .\end{aligned} \tag{6.18}$$

It is interesting to observe that the operators $x^\dagger_{\pm\alpha}$ can be viewed as linear combinations of the bare creation operators $a^\dagger_\alpha$ with coefficients determined by the density matrices $\boldsymbol{\rho}$ and $\boldsymbol{\sigma}$. The vectors composing the matrices $\mathbf{Y}$, $\mathbf{X}$, $\mathbf{C}$, and $\mathbf{D}$ form an orthonormalized set, i.e, $\mathbf{T}$ is a unitary transformation. Inserting the definitions in Eq. (6.18) into the general expression of $\tilde{\mathbf{G}}(\omega)$ [Eqs. (6.16)] we have

$$\tilde{\mathbf{G}}(\omega)=\begin{bmatrix}\mathbf{1} & \mathbf{1} \\ \boldsymbol{\rho}^{1/2}\boldsymbol{\sigma}^{-1/2} & -\boldsymbol{\sigma}^{1/2}\boldsymbol{\rho}^{-1/2}\end{bmatrix}\begin{bmatrix}\mathbf{G}_+(\omega) & \mathbf{0} \\ \mathbf{0} & \mathbf{G}_-(\omega)\end{bmatrix}\begin{bmatrix}\mathbf{1} & \boldsymbol{\sigma}^{-1/2}\boldsymbol{\rho}^{1/2} \\ \mathbf{1} & -\boldsymbol{\rho}^{-1/2}\boldsymbol{\sigma}^{1/2}\end{bmatrix} \ . \tag{6.19}$$

From this expression it is possible to recognize that the components of $\tilde{\mathbf{G}}(\omega)$ are specific linear combinations of the textbook advanced and retarded Green's functions. As already mentioned the block $\tilde{\mathbf{G}}_{11}(\omega)$ is the simple sum of $\mathbf{G}_+(\omega)$ and $\mathbf{G}_-(\omega)$.

B. The unperturbed Green's function $\tilde{\mathbf{G}}_0(\omega)$

Interestingly, the Green's function $\tilde{\mathbf{G}}(\omega)$ cannot be straightforwardly reduced to the free one $\tilde{\mathbf{G}}_0(\omega)$, where the Hamiltonian is identified with its unperturbed part $\hat{H}_0$ [Eq. (1.4)]. This becomes apparent from the definitions [Eqs. (6.14) and (6.17)] and the obvious observation that the density matrices $\boldsymbol{\rho}$ and $\boldsymbol{\sigma}$ become singular matrices for $\hat{H}=\hat{H}_0$. However, we can show that the limit of the Green's function $\tilde{\mathbf{G}}(\omega)$ for $\hat{H}\rightarrow\hat{H}_0$ exists and that it is possible to derive a corresponding $\tilde{\mathbf{G}}_0(\omega)$. We anticipate here that the block $\tilde{\mathbf{G}}_{0,11}(\omega)$ of the unperturbed Green's function $\tilde{\mathbf{G}}_0(\omega)$ is identical with the usual free Green's function [see Eq. (1.3)].

As we can easily see from the definition of the new Green's function, the elements which could possibly give rise to divergences derive from the matrix $\mathbf{X}$. In the following we first demonstrate that $\mathbf{X}$ ntself cannot contain divergent matrix elements and then give the final form of the free Green's function $\tilde{\mathbf{G}}_0(\omega)$.

In order to prove that $\mathbf{X}$ does not contain divergent terms it is sufficient to bear in mind that the single columns composing $\mathbf{X}$ are normalized and orthogonal to each other. Explicitly this can be written as follows:

$$
\begin{aligned}
(\mathbf{X}^\dagger\mathbf{X})_{\alpha\beta} &= \sum_{\gamma,\varepsilon}(\boldsymbol{\rho}^{1/2}\boldsymbol{\sigma}^{-1/2})_{\alpha\gamma}\langle\Psi_0^N|a_\gamma a_\varepsilon^\dagger|\Psi_0^N\rangle(\boldsymbol{\sigma}^{-1/2}\boldsymbol{\rho}^{1/2})_{\varepsilon\beta}+\sum_{\gamma,\varepsilon}(\boldsymbol{\sigma}^{1/2}\boldsymbol{\rho}^{-1/2})_{\alpha\gamma}\langle\Psi_0^N|a_\varepsilon^\dagger a_\gamma|\Psi_0^N\rangle(\boldsymbol{\rho}^{-1/2}\boldsymbol{\sigma}^{1/2})_{\varepsilon\beta} \\
&= \sum_{\gamma,\varepsilon}(\boldsymbol{\rho}^{1/2}\boldsymbol{\sigma}^{-1/2})_{\alpha\gamma}\sigma_{\gamma\varepsilon}(\boldsymbol{\sigma}^{-1/2}\boldsymbol{\rho}^{1/2})_{\varepsilon\beta}+\sum_{\gamma,\varepsilon}(\boldsymbol{\sigma}^{1/2}\boldsymbol{\rho}^{-1/2})_{\alpha\gamma}\rho_{\gamma\varepsilon}(\boldsymbol{\rho}^{-1/2}\boldsymbol{\sigma}^{1/2})_{\varepsilon\beta} \\
&= \rho_{\alpha\beta}+\sigma_{\alpha\beta}=\delta_{\alpha\beta}\ . \qquad (6.20)
\end{aligned}
$$

The vectors themselves composing $\mathbf{X}$ have to be finite for the above relation to be valid. Otherwise at least one element of the product matrix $\mathbf{X}^\dagger\mathbf{X}$ would be infinite. Moreover Eq. (6.19) is a formal equation and holds for any choice for the Hamiltonian, and in particular for the unperturbed choice $\hat{H}=\hat{H}_0$. This leads to the conclusion that the divergencies contained in the matrices $\boldsymbol{\rho}^{-1/2}$ and $\boldsymbol{\sigma}^{-1/2}$ cancel necessarily together with the other factors in $\mathbf{X}$.

To perform the calculation of the limit of $\tilde{\mathbf{G}}(\omega)$ for $\hat{H}\rightarrow\hat{H}_0$ we proceed now in the following way: we consider a Hamiltonian composed of two terms $\hat{H}=\hat{H}_0+\lambda(\hat{H}-\hat{H}_0)$ and take λ to be a small parameter. The limit $\hat{H}\rightarrow\hat{H}_0$ is defined by suitably switching off the interaction, i.e., by $\lambda\rightarrow 0$ The form of $\tilde{\mathbf{G}}_0(\omega)$ reads

$$
\tilde{\mathbf{G}}_0(\omega)=\begin{bmatrix}\tilde{\mathbf{G}}_{0,11}(\omega) & 0\\ 0 & \tilde{\mathbf{G}}_{0,22}(\omega)\end{bmatrix} \qquad (6.21)
$$

where

$$
\tilde{\mathbf{G}}_{0,11}(\omega)=\mathbf{G}_0(\omega)\ . \qquad (6.22)
$$

As expected, the block $\tilde{\mathbf{G}}_{0,11}(\omega)$ can be identified with the usual free Green's function and is therefore the simple inverse-diagonal matrix of the one-particle energies [see Eq. (1.3)]. The remaining part $\tilde{\mathbf{G}}_{0,22}(\omega)$ is block-diagonal matrix in the sense that the spaces spanned by unoccupied and occupied one-particle states are decoupled from each other. Labeling u and i unoccupied and occupied one-particle indices, respectively, $\tilde{\mathbf{G}}_{0,22}(\omega)$ thus reads

$$
\tilde{\mathbf{G}}_{0,22}(\omega)=\begin{bmatrix}\tilde{\mathbf{G}}^u_{0,22}(\omega) & 0\\ 0 & \tilde{\mathbf{G}}^i_{0,22}(\omega)\end{bmatrix} \qquad (6.23)
$$

where

$$
[\tilde{\mathbf{G}}^u_{0,22}(\omega)]_{uu'}=\sum_{w,x}(\mathbf{B}^{-1/2})_{uw}\left[\frac{1}{2}\sum_{\substack{i,j\\ z}}\frac{\Gamma_{ijwz}\Gamma^*_{ijxz}}{(\omega+\varepsilon_z-\varepsilon_i-\varepsilon_j)}\right]\times(B^{-1/2})_{xu'}\ , \qquad (6.24a)
$$

$$
[\tilde{\mathbf{G}}^i_{0,22}(\omega)]_{ii'}=\sum_{m,n}(\mathbf{B}^{-1/2})_{im}\left[\frac{1}{2}\sum_{\substack{u,v\\ k}}\frac{\Gamma_{mkuv}\Gamma^*_{nkuv}}{\omega-\varepsilon_u-\varepsilon_v+\varepsilon_k}\right]\times(B^{-1/2})_{ni'}\ , \qquad (6.24b)
$$

and

$$
B_{uv}=\tfrac{1}{2}\sum_{\substack{k,l\\ z}}\Gamma_{klzv}\Gamma^*_{klzu}\ , \qquad (6.25a)
$$

$$
B_{ij}=\tfrac{1}{2}\sum_{\substack{x,y\\ l}}\Gamma_{ilxy}\Gamma^*_{jlxy}\ . \qquad (6.25b)
$$

In the above formulas we specified with i,j,k,l,m,n occupied one-particle indices and with u,v,w,x,y,z unoccupied one-particle indices. The symbol $\Gamma_{\alpha\beta\gamma\delta}$ is defined as

$$
\Gamma_{\alpha\beta\gamma\delta}=\frac{V_{\alpha\beta[\gamma\delta]}}{\varepsilon_\alpha+\varepsilon_\beta-\varepsilon_\gamma-\varepsilon_\delta} \qquad (6.25c)
$$

where $V_{\alpha\beta[\gamma\delta]}=V_{\alpha\beta\gamma\delta}-V_{\alpha\beta\delta\gamma}$ is the antisymmetrized matrix element of the two-particle interaction.

The matrix elements of $\tilde{\mathbf{G}}_{0,22}(\omega)$ are peculiar linear combinations of the zeroth-order energies of the $2p\,1h$ and $2h\,1p$ configuration states. In the sense of perturbation theory they are effectively of zeroth order in the two-particle interaction, but are given as fractions of second-order terms. The physical meaning of the $\tilde{\mathbf{G}}_{0,22}(\omega)$ component of the free Green's function $\tilde{\mathbf{G}}_0(\omega)$ as well as of the complete Green's function $\tilde{\mathbf{G}}(\omega)$ is not completely clear yet and deserves further investigation.

VII. SUMMARY

The one-particle Green's function contains information on the states and energies of different number of particles, namely, $(N+1)$ and $(N-1)$. By means of the Dyson equation the one-particle Green's function is connected to the self-energy function and the energies of the $(N\pm1)$-particle states emerge as eigenvalues of a single matrix in the union space of the $(N\pm1)$-particle configurations.

The major task of this work was to start with the usual configuration-interaction matrices of the $(N\pm1)$-particle spaces and to mix them by means of a unitary transformation in such a way that the Dyson equation and the self-energy are recovered. The transformed composite Hamiltonian obtained is generally represented by a full matrix in the union space. We have derived the class of unitary transformations which give rise to the different representations of the self-energy. The properties of the self-energy in several specific representations have been investigated also in connection with possible approximation schemes for the Green's function.

The static part of the self-energy is invariant to these transformations. Concerning the dynamic part of the self-energy, various choices for the elements of the unitary transformation are possible. We first attempted to construct a transformation matrix which contains the exact ground state $|\Psi_0^N\rangle$ of the system as the only unknown quantity. This request is motivated by the fact that the Green's function itself is defined via $|\Psi_0^N\rangle$ and that the perturbation expansion of this state is straightforward. The first natural choice takes account of the completeness of the set of creation and destruction operator strings that can be associated to the configuration states of the $(N\pm1)$-particle spaces. This choice leads to a composite Hamiltonian in the union space and to a specific representation of the dynamic self-energy in terms of the exact ground state. We carried out a perturbation theoretical analysis of this composite Hamiltonian and we could show that the approximation scheme obtained up to and including third order of the self-energy is equivalent to the well established ADC (3) scheme based on Feynman diagrams. Proceeding in the same way it is possible to obtain approximation schemes at any order of perturbation. However, in higher orders than the third one, the contributions from the $(N+1)$- and $(N-1)$-particle excitations to the dynamic self-energy appear coupled to each other. Their decoupling is possible but somewhat tedious.

It is known that the dynamic self-energy can be split into two independent parts, deriving from the contributions of the $(N+1)$ and $(N-1)$-particle spaces, respectively. Therefore it is interesting to investigate the question whether it is possible to find a suitable unitary transformation which depends only on $|\Psi_0^N\rangle$ and decouples the $(N\pm1)$-particle spaces of the dynamic self-energy. By means of a counterexample we are able to show that for a generic Hamiltonian it is not possible to fulfill the two required conditions on the transformation matrix simultaneously. This is only possible if we neglect the correlation and the interelectronic interaction, i.e., if the Hamiltonian of the system under investigation is a one-particle operator.

In the general case of an interacting many-particle system the decoupling of the $(N\pm1)$-particle contributions to the dynamic self-energy is of fundamental importance for practical calculations. Being interested in a transformation in closed form which depends only on $|\Psi_0^N\rangle$, we introduced a unitary transformation which gives rise to a representation of the self-energy where the contributions of the $(N+1)$- and $(N-1)$-particle spaces are maximally decoupled. Defining the resulting decoupled function as a new self-energy function leads to a new approach to the Green's function. The striking characteristic of this new self-energy is that its static component is represented by a matrix of double the dimension of the usual static self-energy. The new self-energy suggests the introduction of a corresponding Green's function, which contains the usual textbook Green's function as one of its components. Some properties of the extended Green's function are discussed.

ACKNOWLEDGMENTS

We thank H.-D. Meyer and J. Schirmer for discussions. Financial support by the Deutsche Forschungsgemeinschaft is acknowledged.

APPENDIX A

In this appendix we prove the equivalence of Eqs. (3.8) and (3.9). We consider in the following a Hamiltonian of the following general form:

$$\hat{H}=\hat{H}_0+\hat{H}_I \tag{A1}$$

where $\hat{H}_0$ is the unperturbed diagonal part

$$\hat{H}_0=\sum_\alpha \varepsilon_\alpha a_\alpha^\dagger a_\alpha \tag{A2}$$

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

$$\hat{H}_I=\hat{W}+\hat{V}\ , \tag{A3a}$$

$$\hat{W}=\sum_{\alpha,\beta} W_{\alpha\beta}a_\alpha^\dagger a_\beta\ , \tag{A3b}$$

$$\hat{V}=\tfrac{1}{2}\sum_{\alpha,\beta,\gamma,\delta} V_{\alpha\beta\gamma\delta}a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma\ . \tag{A3c}$$

The equations of motion of the Green's functions lead to the following expression for the constant part $\Sigma(\infty)$ of the self-energy in terms of the one-particle Green's function [5–7]:

$$\Sigma(\infty)_{\alpha\beta}=W_{\alpha\beta}+\sum_{\gamma,\delta}(V_{\alpha\gamma\beta\delta}-V_{\alpha\gamma\delta\beta})\frac{1}{2\pi i}\oint G_{\delta\gamma}(\omega)d\omega\ . \tag{A4}$$

Closing the interaction path in the upper complex plain, this equation yields, after integration

$$\Sigma(\infty)_{\alpha\beta}=W_{\alpha\beta}+\sum_{\gamma,\delta}(V_{\alpha\gamma\beta\delta}-V_{\alpha\gamma\delta\beta})\langle\Psi_0^N|a_\gamma^\dagger a_\delta|\Psi_0^N\rangle\ . \tag{A5}$$

Taking into account this explicit formulation of $\Sigma(\infty)$ we show in the following that the block $\tilde{\mathbf{H}}_{aa}$ [Eq. (3.8)] exactly reproduces the upper left block of the matrix $\mathbf{A}$ [Eq. (1.7)]. Making use of the explicit form of the Hamiltonian and of the anticommutation relations between creation and destruction operators, Eq. (3.8) yields

$$\begin{aligned}(\tilde{\mathbf{H}}_{aa})_{\alpha\beta}&=\langle\Psi_0^N|\{[a_\alpha,\hat{H}],a_\beta^\dagger\}|\Psi_0^N\rangle\\&=\left[\varepsilon_\alpha\delta_{\alpha\beta}+W_{\alpha\beta}+\sum_{\alpha,\beta,\gamma,\delta}(V_{\alpha\gamma\beta\delta}-V_{\alpha\gamma\delta\beta})\times\langle\Psi_0^N|a_\gamma^\dagger a_\delta|\Psi_0^N\rangle\right]\end{aligned} \tag{A6}$$

so that

$$(\tilde{\mathbf{H}}_{aa})_{\alpha\beta}=[\boldsymbol{\varepsilon}+\boldsymbol{\Sigma}(\infty)]_{\alpha\beta}\ . \tag{A7}$$

APPENDIX B

1. Transformation into orbital form

In the following we describe the procedure of transforming from configuration form into orbital form. We consider the general form of the Hamiltonian given by Eqs. (A2) and (A3) and choose the unperturbed Hamiltonian $\hat{H}_0$ to be the Hartree-Fock operator, i.e., the term $\hat{W}$ of the Hamiltonian takes on the following appearance:

$$\hat{W}=-\sum_{\alpha,\beta}\sum_k V_{\alpha k[\beta k]}a_\alpha^\dagger a_\beta n_k \tag{B1a}$$

where n_k is the occupation number of the kth orbital in the unperturbed ground state $|\Phi_0^N\rangle$ (Hartree-Fock determinant) and

$$V_{\alpha k[\beta k]}=V_{\alpha k\beta k}-V_{\alpha kk\beta}\ . \tag{B1b}$$

As an illustrative example we transform into orbital form the second-order contribution of the coupling block ($\tilde{\mathbf{H}}_{ba}^{\nu u}$) (see Sec. IV). We begin with the first term [see Eq. (4.11c)]. In configuration form it reads

$$(\tilde{\mathbf{H}}_{ba}^{\nu u})^{(2)}_{\nu u,\text{first term}}=\sum_q\langle\Phi_0^N|A_{0\nu}(\hat{H}_I-E_0^{N(1)})a_u^\dagger|\Phi^N_{q(2h2p)}\rangle c^{(1)}_{q(2h2p)}\ . \tag{B2}$$

The states appearing in this formula can be easily expressed in terms of creation and annihilation operator strings acting on $|\Phi_0^N\rangle$ as follows:

$$A_{0\nu}^\dagger|\Phi_0^N\rangle=a_y^\dagger a_x^\dagger a_i|\Phi_0^N\rangle\ , \tag{B3a}$$

$$|\Phi^N_{q(2h2p)}\rangle=a_z^\dagger a_w^\dagger a_m a_n|\Phi_0^N\rangle \tag{B3b}$$

with $n_i n_m n_n \bar{n}_x \bar{n}_y \bar{n}_z \bar{n}_w=1$. Here $\bar{n}=1-n$. The RSPT expansion coefficient $c^{(1)}_{q(2h2p)}$ of the N-particle configuration $|\Phi^N_{q(2h2p)}\rangle$ reads

$$c^{(1)}_{q(2h2p)}=\langle\Phi^N_{q(2h2p)}|\hat{H}_I|\Phi_0^N\rangle=\frac{V_{wz[mn]}}{\varepsilon_m+\varepsilon_n-\varepsilon_w-\varepsilon_z}\ . \tag{B4}$$

Taking into account that

$$a_u^\dagger|\Phi^N_{q(2h2p)}\rangle=a_u^\dagger a_z^\dagger a_w^\dagger a_m a_n|\Phi_0^N\rangle \tag{B5}$$

represents an $(N+1)$-particle configuration of the class $3p2h$, the first factor in Eq. (B2) is simply the matrix element of the interaction term $\hat{H}_I$ between the configurations in Eqs. (B3a) and (B5). One obtains

$$\begin{aligned}\langle\Phi_0^N|A_{0\nu}(\hat{H}_I-E_0^{N(1)})a_u^\dagger|\Phi^N_{q(2h2p)}\rangle=&[(V_{ym[zu]}\delta_{xw}\delta_{in})+(u,z,w\to z,w,u)+(u,z,w\to w,u,z)]\\&-[x\leftrightarrow y]-[m\leftrightarrow n]+[x\leftrightarrow y,m\leftrightarrow n]\\&+[(V_{mn[iu]}\delta_{yz}\delta_{xw})+(u,z,w\to z,w,u)+(u,z,w\to w,u,z)]-[x\leftrightarrow y]\ .\end{aligned} \tag{B6}$$

The sum over q in Eq. (B2) is now equivalent to a sum over the one-particle states z,w,m,n. The formulation in orbital form finally reads

$$\begin{aligned}(\tilde{\mathbf{H}}_{ba}^{\nu u})^{(2)}_{\nu u,\text{first term}}=&\tfrac{1}{2}\sum_{m,n}\frac{V_{mn[iu]}V_{xy[mn]}}{\varepsilon_m+\varepsilon_n-\varepsilon_x-\varepsilon_y}\\&+\left[\sum_{\substack{z\\m}}\frac{V_{ym[zu]}V_{xz[mi]}}{\varepsilon_m+\varepsilon_i-\varepsilon_x-\varepsilon_z}+\tfrac{1}{2}\delta_{xu}\left[\sum_{\substack{w,z\\m}}\frac{V_{ym[wz]}V_{wz[mi]}}{\varepsilon_m+\varepsilon_i-\varepsilon_w-\varepsilon_z}+\sum_{\substack{m,n\\z}}\frac{V_{mn[iz]}V_{yz[mn]}}{\varepsilon_m+\varepsilon_n-\varepsilon_y-\varepsilon_z}\right]\right]-[x\leftrightarrow y]\ .\end{aligned} \tag{B7}$$

Analogously, the remaining two terms contributing to the coupling block are evaluated. The terms in Eq. (B7) which

contain the factor δ_{xu} cancel exactly with the other contributions appearing in Eq. (4.11c). The final expression in orbital form for $\tilde{\mathbf{H}}^{vu}_{ba}$ reads thus

$$(\tilde{\mathbf{H}}^{vu}_{ba})^{(2)}_{xyi,u}=\tfrac{1}{2}\sum_{m,n}\frac{V_{mn[iu]}V_{xy[mn]}}{\varepsilon_m+\varepsilon_n-\varepsilon_x-\varepsilon_y}+\left[\sum_{\substack{z\\ m}}\frac{V_{ym[zu]}V_{xz[mi]}}{\varepsilon_m+\varepsilon_i-\varepsilon_x-\varepsilon_z}\right]-(x\leftrightarrow y)\ . \tag{B8}$$

In the formulas (B6)–(B8) the symbol $(\alpha\leftrightarrow\beta)$ stands for a term that has the same appearance as the preceding one, but with the indices α and β interchanged. For practical calculations it can be advantageous to consider the restriction $x<y$ over the external indices x and y which run over the same (unoccupied) space.

2. On the coupling between $(N\pm1)$-particle excitations

This appendix is directly related to Sec. IV B. We show here that the coupling block $\tilde{\mathbf{H}}^{\mu\nu}_{bb}$ between the $(N\pm1)$-particle excitations has a nonvanishing second-order contribution. As discussed in the text, the presence of this contribution prevents the possibility of reproducing the fourth-order ADC scheme for the dynamic self-energy by starting with the closed-form expressions of Eqs. (4.5). Starting with Eq. (4.5d) one obtains at second order for $\gamma=\mu$ and $\gamma'=\nu$ the following expression:

$$\begin{aligned}(\tilde{\mathbf{H}}^{\mu\nu}_{bb})^{(2)}_{\mu\nu}=&\sum_q c^{(1)*}_{q(2h2p)}\langle\Phi^N_{q(2h2p)}|A_\mu(\hat{H}_I-E_0^{N(1)})A^\dagger_\nu|\Phi^N_0\rangle+\sum_q c^{(2)*}_{q(3h3p)}\langle\Phi^N_{q(3h3p)}|A_\mu(\hat{H}_0-E_0^{N(0)})A^\dagger_\nu|\Phi^N_0\rangle\\&-\sum_q c^{(1)*}_{q(2h2p)}\langle\Phi^N_{q(2h2p)}|A^\dagger_\nu(\hat{H}_I-E_0^{N(1)})A_\mu|\Phi^N_0\rangle-\sum_q c^{(2)*}_{q(3h3p)}\langle\Phi^N_{q(3h3p)}|A^\dagger_\nu(\hat{H}_0-E_0^{N(0)})A_\mu|\Phi^N_0\rangle\ .\end{aligned} \tag{B9}$$

Here $c^{(2)}_{q(3h3p)}$ is the second-order RSPT expansion coefficient of an N-particle configuration of the class $3h3p$. By using the same procedure as discussed in Appendix B 1 we transformed this expression into orbital form. The result is lengthy and is hence not given here. It is seen that $(\tilde{\mathbf{H}}^{\mu\nu}_{bb})^{(2)}$ is not zero and thus the $(N\pm1)$-particle excitations couple at second order of perturbation theory. As discussed in the main text we can get rid of the coupling contributions by block-diagonalizing the block $\tilde{\mathbf{H}}_{bb}$. In general, this procedure can be carried out only order by order and does not lead to closed-form expressions for the dynamic self-energy. We should mention that there exists a simple case where the block diagonalization of $\tilde{\mathbf{H}}_{bb}$ leads to closed-form expressions. This is the case of a one-particle Hamiltonian and is discussed in detail in Appendix C.

APPENDIX C

In the following we analyze in detail the case of a system, the Hamiltonian of which is a one-particle operator. As discussed in the text, we show that in this case it is possible to block diagonalize the part $\tilde{\mathbf{H}}_{bb}$ of the transformed composite Hamiltonian $\tilde{\mathbf{H}}$ [Eqs. (4.5)] by means of a unitary transformation that depends on the N-particle ground state only.

The eigenvalues of the transformed Hamiltonian $\tilde{\mathbf{H}}$ obtained in Sec. IV [Eqs. (4.5)] are the same as those of $\mathbf{H}$ [Eq. (2.5a)] and represent the exact attachment and ionization energies. We define the eigenvector matrix of $\mathbf{H}$ as

$$\mathbf{S}=\begin{bmatrix}\mathbf{S}^{N+1}&\mathbf{0}\\ \mathbf{0}&(\mathbf{S}^{N-1})^*\end{bmatrix} \tag{C1a}$$

where

$$(\mathbf{S}^{N+1})_{qm}=\langle\Phi^{N+1}_q|\Psi^{N+1}_m\rangle\ , \tag{C1b}$$

$$(\mathbf{S}^{N-1})_{qm}=\langle\Phi^{N-1}_q|\Psi^{N-1}_m\rangle\ . \tag{C1c}$$

Here the set $\{|\Psi^{N\pm1}_m\rangle\}$ is the set of the exact eigenstates of $\mathbf{H}^{N\pm1}$. Taking into account that the transformation matrix $\mathbf{T}$, as given in Eqs. (3.2), (4.2), and (4.3) is a unitary matrix it is easy to see that the eigenvector matrix of $\tilde{\mathbf{H}}$ can be written as follows:

$$\tilde{\mathbf{S}}=\mathbf{T}^\dagger\mathbf{S}=\begin{bmatrix}\langle\Psi^N_0|a_\alpha|\Psi^{N+1}_m\rangle&\langle\Psi^{N-1}_m|a_\alpha|\Psi^N_0\rangle\\ \langle\Psi^N_0|\tilde{A}_\nu|\Psi^{N+1}_m\rangle&\langle\Psi^{N-1}_m|\tilde{A}_\nu|\Psi^N_0\rangle\\ \langle\Psi^N_0|\tilde{A}_\mu|\Psi^{N+1}_m\rangle&\langle\Psi^{N-1}_m|\tilde{A}_\mu|\Psi^N_0\rangle\end{bmatrix}\ . \tag{C2}$$

It will be useful to split the sets $\{|\Psi^{N\pm1}_m\rangle\}$ according to

$$\{|\Psi^{N+1}_m\rangle\}=\{|\Psi^{N+1}_p\rangle\}\cup\{|\Psi^{N+1}_s\rangle\}\ , \tag{C3a}$$

$$\{|\Psi^{N-1}_m\rangle\}=\{|\Psi^{N-1}_h\rangle\}\cup\{|\Psi^{N-1}_r\rangle\}\ , \tag{C3b}$$

where we distinguished from which class of configuration states the eigenstates in a perturbation theoretical analysis derive. The following associations between exact eigenstates and configuration states hold:

$$|\Psi^{N+1}_p\rangle\leftrightarrow|\Phi^{N+1}_{q(1p)}\rangle\ , \tag{C4a}$$

$$|\Phi^{N+1}_s\rangle\leftrightarrow|\Phi^{N+1}_{q(\nu)}\rangle\ , \tag{C4b}$$

$$|\Psi^{N-1}_h\rangle\leftrightarrow|\Phi^{N-1}_{q(1h)}\rangle\ , \tag{C4c}$$

$$|\Psi^{N-1}_r\rangle\leftrightarrow|\Phi^{N-1}_{q(\mu)}\rangle\ . \tag{C4d}$$

After interchanging the columns of blocks in $\tilde{\mathbf{S}}$ and specifying with u and i the unoccupied and occupied one-particle state of the set $\{|\varphi_\alpha\rangle\}$, respectively, we obtain for the eigenvector matrix of $\tilde{\mathbf{H}}$

$$\tilde{\mathbf{S}}=\begin{bmatrix} \langle\Psi_0^N|a_u|\Psi_p^{N+1}\rangle & \langle\Psi_h^{N-1}|a_u|\Psi_0^N\rangle & \langle\Psi_0^N|a_u|\Psi_s^{N+1}\rangle & \langle\Psi_r^{N-1}|a_u|\Psi_0^N\rangle \\ \langle\Psi_0^N|a_i|\Psi_p^{N+1}\rangle & \langle\Psi_h^{N-1}|a_i|\Psi_0^N\rangle & \langle\Psi_0^N|a_i|\Psi_s^{N+1}\rangle & \langle\Psi_r^{N-1}|a_i|\Psi_0^N\rangle \\ \langle\Psi_0^N|\tilde{A}_\nu|\Psi_p^{N+1}\rangle & \langle\Psi_h^{N-1}|\tilde{A}_\nu|\Psi_0^N\rangle & \langle\Psi_0^N|\tilde{A}_\nu|\Psi_s^{N+1}\rangle & \langle\Psi_r^{N-1}|\tilde{A}_\nu|\Psi_0^N\rangle \\ \langle\Psi_0^N|\tilde{A}_\mu|\Psi_p^{N+1}\rangle & \langle\Psi_h^{N-1}|\tilde{A}_\mu|\Psi_0^N\rangle & \langle\Psi_0^N|\tilde{A}_\mu|\Psi_s^{N+1}\rangle & \langle\Psi_r^{N-1}|\tilde{A}_\mu|\Psi_0^N\rangle \end{bmatrix} . \tag{C5}$$

From the unitarity of the eigenvector matrix $\tilde{\mathbf{S}}$ the following peculiar completeness relations can be derived:

$$\sum_\alpha a_\alpha^\dagger|\Psi_0^N\rangle\langle\Psi_0^N|a_\alpha+\sum_\gamma \tilde{A}_\gamma^\dagger|\Psi_0^N\rangle\langle\Psi_0^N|\tilde{A}_\gamma=1 ; \quad \alpha=u,i , \quad \gamma=\mu,\nu , \tag{C6a}$$

$$\sum_\alpha a_\alpha|\Psi_0^N\rangle\langle\Psi_0^N|a_\alpha^\dagger+\sum_\gamma \tilde{A}|\Psi_0^N\rangle\langle\Psi_0^N|\tilde{A}_\gamma^\dagger=1 ; \quad \alpha=u,i , \quad \gamma=\mu,\nu \tag{C6b}$$

which hold in the $(N+1)$- and $(N-1)$-particle spaces, respectively.

The above-presented formulas are still quite general and hold for any choice of the Hamiltonian. In the following we will consider explicitly the case of a one-particle Hamiltonian. In this case it is not difficult to see that the matrix $\tilde{\mathbf{H}}$ acquires a block-diagonal structure:

$$\tilde{\mathbf{H}}=\begin{bmatrix} \tilde{\mathbf{H}}_{aa} & 0 & 0 \\ 0 & \tilde{\mathbf{H}}_{bb}^{\nu\nu} & \tilde{\mathbf{H}}_{bb}^{\nu\mu} \\ 0 & \tilde{\mathbf{H}}_{bb}^{\mu\nu} & \tilde{\mathbf{H}}_{bb}^{\mu\mu} \end{bmatrix} . \tag{C7}$$

Indeed, considering for the Hamiltonian the simple expression

$$\hat{H}=\sum_{\alpha,\beta} H_{\alpha\beta}a_\alpha^\dagger a_\beta \tag{C8}$$

and taking explicitly into account that the columns of the transformation matrix $\mathbf{T}$ are orthonormal

$$\langle\Psi_0^N|\{a_\alpha,\tilde{A}_\gamma^\dagger\}|\Psi_0^N\rangle\equiv 0 \tag{C9}$$

we can see that the matrix elements of the off-diagonal block of $\tilde{\mathbf{H}}$ vanish identically:

$$\begin{aligned}(\tilde{\mathbf{H}}_{ab})_{\alpha\gamma}&=\langle\Psi_0^N|\{[a_\alpha,\hat{H}],\tilde{A}_\gamma^\dagger\}|\Psi_0^N\rangle \\ &=\sum_{\beta\delta}H_{\beta\delta}\langle\Psi_0^N|\{(a_\alpha a_\beta^\dagger a_\delta-a_\beta^\dagger a_\delta a_\alpha),\tilde{A}_\gamma^\dagger\}|\Psi_0^N\rangle \\ &=\sum_{\beta\delta}H_{\beta\delta}\delta_{\alpha\beta}\langle\Psi_0^N|\{a_\delta,\tilde{A}_\gamma^\dagger\}|\Psi_0^n\rangle\equiv 0 .\end{aligned} \tag{C10}$$

In other words, any matrix element of the off-diagonal block $\tilde{\mathbf{H}}_{ab}$ is exactly zero since it can be expressed as the product of a matrix element of the Hamiltonian $\hat{H}$ and the anticommutator of the operator strings.

Since $\tilde{\mathbf{H}}$ is block diagonal, its eigenvector matrix $\tilde{\mathbf{S}}$ is block diagonal as well and Eq. (B5) reduces to

$$\tilde{\mathbf{S}}=\begin{bmatrix} \langle\Psi_0^N|a_u|\Psi_p^{N+1}\rangle & \langle\Psi_h^{N-1}|a_u|\Psi_0^N\rangle & 0 & 0 \\ \langle\Psi_0^N|a_i|\Psi_p^{N+1}\rangle & \langle\Psi_h^{N-1}|a_i|\Psi_0^N\rangle & 0 & 0 \\ 0 & 0 & \langle\Psi_0^N|\tilde{A}_\nu|\Psi_s^{N+1}\rangle & \langle\Psi_r^{N-1}|\tilde{A}_\nu|\Psi_0^N\rangle \\ 0 & 0 & \langle\Psi_0^N|\tilde{A}_\mu|\Psi_s^{N+1}\rangle & \langle\Psi_r^{N-1}|\tilde{A}_\mu|\Psi_0^N\rangle \end{bmatrix} . \tag{C11}$$

From Eq. (B11) follows a very interesting characteristic of the eigenstates of the classes r and s: they build separately a complete set of states in *their* space. This can be written as

$$\sum_r|\Psi_r^{N-1}\rangle\langle\Psi_r^{N-1}|=1_r , \tag{C12a}$$

$$\sum_s|\Psi_s^{N+1}\rangle\langle\Psi_s^{N+1}|=1_s . \tag{C12b}$$

Moreover, since the space spanned by the index α is independent from the space of the $(N\pm1)$ excitations ν and μ, Eqs. (B6) reduce to the following equations:

$$\sum_\alpha a_\alpha^\dagger|\Psi_0^N\rangle\langle\Psi_0^N|a_\alpha=1 , \quad \alpha=u,i , \tag{C13a}$$

$$\sum_\alpha a_\alpha|\Psi_0^N\rangle\langle\Psi_0^N|a_\alpha^\dagger=1 , \quad \alpha=u,i , \tag{C13b}$$

$$\sum_\gamma \tilde{A}_\gamma^\dagger|\Psi_0^N\rangle\langle\Psi_0^N|\tilde{A}_\gamma=1 , \quad \gamma=\mu,\nu , \tag{C13c}$$

$$\sum_\gamma \tilde{A}_\gamma|\Psi_0^N\rangle\langle\Psi_0^N|\tilde{A}_\gamma^\dagger=1 , \quad \gamma=\mu,\nu . \tag{C13d}$$

The first two completeness relations are valid in the space spanned by the index α while the second two are valid in the space spanned by the indices ν and μ.

Our purpose is now to block diagonalize the lower block $\tilde{\mathbf{H}}_{bb}$ of $\tilde{\mathbf{H}}$. We remember that a Hermitian matrix can be unequivocally block diagonalized [15]. Accordingly, we build up the following unitary matrix, which has the same block structuer of $\tilde{\mathbf{S}}$:

$$\mathbf{U}=\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \langle \Psi_0^N|\tilde{A}_\nu|\Psi_s^{N+1}\rangle & \langle \Psi_r^{N-1}|\tilde{A}_\nu|\Psi_0^N\rangle \\ 0 & 0 & \langle \Psi_0^N|\tilde{A}_\mu|\Psi_s^{N+1}\rangle & \langle \Psi_r^{N-1}|\tilde{A}_\mu|\Psi_0^N\rangle \end{bmatrix} \tag{C14}$$

and its block-diagonal part:

$$\mathbf{U}_{\mathrm{BD}}=\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \langle \Psi_0^N|\tilde{A}_\nu|\Psi_s^{N+1}\rangle & 0 \\ 0 & 0 & 0 & \langle \Psi_r^{N-1}|\tilde{A}_\mu|\Psi_0^N\rangle \end{bmatrix}. \tag{C15}$$

It follows:

$$\mathbf{U}\mathbf{U}_{\mathrm{BD}}^\dagger=\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \sum_s \langle \Psi_0^N|\tilde{A}_\nu|\Psi_s^{N+1}\rangle\langle \Psi_s^{N+1}|\tilde{A}_{\nu'}^\dagger|\Psi_0^N\rangle & \sum_r \langle \Psi_0^N|\tilde{A}_{\mu'}^\dagger|\Psi_r^{N-1}\rangle\langle \Psi_r^{N-1}|\tilde{A}_\nu|\Psi_0^N\rangle \\ 0 & 0 & \sum_s \langle \Psi_0^N|\tilde{A}_\mu|\Psi_s^{N+1}\rangle\langle \Psi_s^{N+1}|\tilde{A}_{\nu'}^\dagger|\Psi_0^N\rangle & \sum_r \langle \Psi_0^N|\tilde{A}_{\mu'}^\dagger|\Psi_r^{N-1}\rangle\langle \Psi_r^{N-1}|\tilde{A}_\mu|\Psi_0^N\rangle \end{bmatrix} \tag{C16}$$

and

$$\mathbf{U}_{\mathrm{BD}}\mathbf{U}_{\mathrm{BD}}^\dagger=\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \sum_s \langle \Psi_0^N|\tilde{A}_\nu|\Psi_s^{N+1}\rangle\langle \Psi_s^{N+1}|\tilde{A}_{\nu'}^\dagger|\Psi_0^N\rangle & 0 \\ 0 & 0 & 0 & \sum_r \langle \Psi_0^N|\tilde{A}_{\mu'}^\dagger|\Psi_r^{N-1}\rangle\langle \Psi_r^{N-1}|\tilde{A}_\mu|\Psi_0^N\rangle \end{bmatrix}. \tag{C17}$$

To simplify the notation we introduce now the following two matrices $\mathbf{P}$ and $\mathbf{Q}$, the indices of which belong to the union space of the classes ν and μ:

$$P_{\gamma\gamma'}=\sum_s \langle \Psi_0^N|\tilde{A}_\gamma|\Psi_s^{N+1}\rangle\langle \Psi_s^{N+1}|\tilde{A}_{\gamma'}^\dagger|\Psi_0^N\rangle = \langle \Psi_0^N|\tilde{A}_\gamma \tilde{A}_{\gamma'}^\dagger|\Psi_0^N\rangle\ ,\quad \gamma,\gamma'=\mu,\nu\ , \tag{C18a}$$

$$Q_{\gamma\gamma'}=\sum_r \langle \Psi_0^N|\tilde{A}_{\gamma'}^\dagger|\Psi_r^{N-1}\rangle\langle \Psi_r^{N-1}|\tilde{A}_\gamma|\Psi_0^N\rangle = \langle \Psi_0^N|\tilde{A}_{\gamma'}^\dagger \tilde{A}_\gamma|\Psi_0^N\rangle\ ,\quad \gamma,\gamma'=\mu,\nu\ . \tag{C18b}$$

Equations (B18) can be written because of the completeness relation given in Eq. (B12). It is not difficult to see that the following important relations hold

$$\mathbf{P}=\mathbf{P}^\dagger \tag{C19a}$$

$$\mathbf{Q}=\mathbf{Q}^\dagger\ , \tag{C19b}$$

$$\mathbf{P}+\mathbf{Q}=\mathbf{1}\ . \tag{C19c}$$

Moerover, taking account of Eq. (B13)

$$\mathbf{P}=\mathbf{P}^2\ , \tag{C19d}$$

$$\mathbf{Q}=\mathbf{Q}^2\ , \tag{C19e}$$

Eqs. (B16) and (B17) can now be reformulated in terms of $\mathbf{P}$ and $\mathbf{Q}$:

$$\mathbf{U}\mathbf{U}_{\mathrm{BD}}^\dagger=\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \mathbf{P}_{\nu\nu} & \mathbf{Q}_{\nu\mu} \\ 0 & 0 & \mathbf{P}_{\mu\nu} & \mathbf{Q}_{\mu\mu} \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \mathbf{P}_{\nu\nu} & -\mathbf{P}_{\nu\mu} \\ 0 & 0 & \mathbf{P}_{\mu\nu} & (\mathbf{1}-\mathbf{P})_{\mu\mu} \end{bmatrix}, \tag{C20}$$

$$\mathbf{U}_{\mathrm{BD}}\mathbf{U}_{\mathrm{BD}}^\dagger=\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \mathbf{P}_{\nu\nu} & 0 \\ 0 & 0 & 0 & \mathbf{Q}_{\mu\mu} \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \mathbf{P}_{\nu\nu} & 0 \\ 0 & 0 & 0 & (\mathbf{1}-\mathbf{P})_{\mu\mu} \end{bmatrix}. \tag{C21}$$

The matrix $\mathbf{U}\mathbf{U}_{\mathrm{BD}}^\dagger(\mathbf{U}_{\mathrm{BD}}\mathbf{U}_{\mathrm{BD}}^\dagger)^{-1/2}$ is the unitary matrix which unequivocally block diagonalizes the lower block $\tilde{\mathbf{H}}_{bb}$ of $\tilde{\mathbf{H}}$. We proceed now to analyze the complete unitary transformation $\tilde{\mathbf{T}}$ matrix, with which we want to transform the composite Hamiltonian $\mathbf{H}$:

$$\tilde{\mathbf{T}}=\mathbf{T}\mathbf{U}\mathbf{U}_{\mathrm{BD}}^\dagger(\mathbf{U}_{\mathrm{BD}}\mathbf{U}_{\mathrm{BD}}^\dagger)^{-1/2}\ . \tag{C22}$$

$\mathbf{T}$ here is the unitary matrix defined by Eqs. (3.2), (4.2), and (4.3).

Clearly the first two blocks of columns of $\tilde{\mathbf{T}}$ (labeled with u and i) are identical to those of $\mathbf{T}$ and hence to the composite matrix of the residues $\mathbf{Y}$. We analyze now the third (ν) block of columns. It reads

$$\begin{bmatrix} \mathbf{T}_{+(\nu)} \\ (\mathbf{T}_{-(\nu)})^* \end{bmatrix}=\sum_{\nu'} \begin{bmatrix} \sum_\gamma \langle \Phi_q^{N+1}|\tilde{A}_\gamma^\dagger|\Psi_0^N\rangle\langle \Psi_0^N|\tilde{A}_\gamma \tilde{A}_{\nu'}^\dagger|\Psi_0^N\rangle \\ \sum_\gamma \langle \Psi_0^N|\tilde{A}_\gamma^\dagger|\Phi_q^{N-1}\rangle\langle \Psi_0^N|\tilde{A}_\gamma \tilde{A}_{\nu'}^\dagger|\Psi_0^N\rangle \end{bmatrix} \times(\mathbf{U}_{\mathrm{BD}}\mathbf{U}_{\mathrm{BD}}^\dagger)_{\nu'\nu}^{-1/2}\ . \tag{C23}$$

Taking into account the completeness relation in Eq. (B13b) and the anticommutation property of the opera-

tors $a_\alpha^\dagger$ and $\tilde{A}_\gamma^\dagger$, the last equation reduces to

$$\begin{bmatrix} \mathbf{T}_{+(\nu)} \\ (\mathbf{T}_{-(\nu)})^* \end{bmatrix} = \sum_{\nu'} \begin{bmatrix} \langle \Phi_q^{N+1} | \tilde{A}_{\nu'}^\dagger | \Psi_0^N \rangle \\ 0 \end{bmatrix} (\mathbf{U}_{\mathrm{BD}} \mathbf{U}_{\mathrm{BD}}^\dagger)_{\nu'\nu}^{-1/2} . \tag{C24}$$

Analogously one obtains for the fourth block of columns

$$\begin{bmatrix} \mathbf{T}_{+(\mu)} \\ (\mathbf{T}_{-(\mu)})^* \end{bmatrix} = \sum_{\nu'} \begin{bmatrix} 0 \\ \langle \Psi_0^N | \tilde{A}_{\mu'}^\dagger | \Phi_q^{N-1} \rangle \end{bmatrix} (\mathbf{U}_{\mathrm{BD}} \mathbf{U}_{\mathrm{BD}}^\dagger)_{\mu'\mu}^{-1/2} . \tag{C25}$$

The final transformation $\tilde{\mathbf{T}}$ which brings $\tilde{\mathbf{H}}$ in Eq. (B7) into block-diagonal form $\tilde{\mathbf{T}}^\dagger \tilde{\mathbf{H}} \tilde{\mathbf{T}}$ reads

$$\tilde{\mathbf{T}} = \begin{bmatrix} \langle \Phi_q^{N+1} | a_u^\dagger | \Psi_0^N \rangle & \langle \Phi_q^{N+1} | a_i^\dagger | \Psi_0^N \rangle & \langle \Phi_q^{N+1} | \bar{A}_\nu | \Psi_0^N \rangle & 0 \\ \langle \Psi_0^N | a_u^\dagger | \Phi_q^{N+1} \rangle & \langle \Psi_0^N | a_i^\dagger | \Phi_q^{N+1} \rangle & 0 & \langle \Psi_0^N | \bar{A}_\nu^\dagger | \Phi_q^{N-1} \rangle \end{bmatrix} \tag{C26}$$

where the operators $\bar{A}_\gamma$ are given by

$$\bar{A}_\nu = \sum_{\nu'} \tilde{A}_{\nu'}^\dagger (\mathbf{U}_{\mathrm{BD}} \mathbf{U}_{\mathrm{BD}}^\dagger)_{\nu'\nu}^{-1/2} , \tag{C27a}$$

$$\bar{A}_\mu = \sum_{\mu'} \tilde{A}_{\mu'}^\dagger (\mathbf{U}_{\mathrm{BD}} \mathbf{U}_{\mathrm{BD}}^\dagger)_{\mu'\mu}^{-1/2} . \tag{C27b}$$

Interestingly the new operators $\bar{A}_\gamma^\dagger$ are, apart from the normalization factor, identical to the original operators $\tilde{A}_\gamma^\dagger$.

The matrix $\tilde{\mathbf{T}}$ possesses a very peculiar block structure and is unitary. As we discussed in the main text, in the general case of a correlated system it is not possible to obtain a unitary matrix with the block structure as given in Eq. (B26). In the present case, however, where we supposed the Hamiltonian to be a one-particle operator, it becomes possible since the matrices

$$(\mathbf{Y}_+)_{q\alpha} = \langle \Phi_q^{N+1} | a_\alpha^\dagger | \Psi_0^N \rangle$$

and

$$(\mathbf{Y}_-)_{q\alpha}^* = \langle \Psi_0^N | a_\alpha^\dagger | \Phi_q^{N-1} \rangle$$

contains linear dependent column vectors.

[1] A. A. Abrikosov, L. P. Gorkov, and J. E. Dzyaloskinski, *Methods of Quantum Field Theory in Statistical Physcis* (Prentice-Hall, Englewood Cliffs, NJ, 1963).

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

[3] S. J. Bell and E. Squires, Phys. Rev. Lett. **3**, 96 (1959).

[4] H.-D. Meyer, Phys. Rev. A **40**, 5605 (1989), and references therein.

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

[6] J. Winter, Nucl. Phys. A **194**, 535 (1972).

[7] L. S. Cederbaum and W. Domcke, in *Advances in Chemical Physics,* edited by I. Prigogine and S. A. Rice (Wiley, New York, 1977), Vol. 36, p. 205.

[8] W. von Niessen, J. Schirmer, and L. S. Cederbaum, Comput. Phys. Rep. **1**, 59 (1984).

[9] L. S. Cederbaum, W. Domcke, J. Schirmer, and W. von Niessen, in *Advances in Chemical Physics,* edited by I. Prigogine and S. A. Rice (Wiley, New York, 1986), Vol. 65, p. 115.

[10] G. Angonoa, O. Walter, and J. Schirmer, J. Chem. Phys. **87**, 6789 (1987).

[11] R. Manne, Chem. Phys. Lett. **45**, 470 (1977).

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

[13] Y. Öhrn and G. Born, Adv. Quantum Chem. **13**, 1 (1981).

[14] M. F. Herman, K. F. Freed, and D. L. Yeager, Adv. Chem. Phys. **48**, 1 (1981).

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

[16] We should mention that in order to prove that the transformation matrix as in Eq. (5.2) is singular, we have made explicit use of the fact that the one-particle basis set $\{|\varphi_\alpha\rangle\}$ contains an arbitrary but finite number of orbitals. It follows that the number of configurations which span the $(N\pm1)$-particle spaces is finite as well. It is of interest to investigate the case of an infinite one-partice basis set $\{|\varphi_\alpha\rangle\}$, e.g., by incuding explicitly continuum states. In particular, the question arises whether the matrix is then nonsingular. Since for practical tasks one is constrained to a finite number of basis functions, this investigation would go beyond the purposes of the present work.

[17] According to the results of the preceding section, the matrices **M** and **N** can be chosen to eliminate the linear dependency among the columns of $\mathbf{T}_{+(\nu)}$ and $\mathbf{T}_{-(\mu)}$ and to make the remaining vectors normalized and orthogonal to each other.