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Many-body theory of composite electronic-positronic systems

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The many-body theory of systems containing two types of charged light particles, like electrons and positrons, is investigated. The second quantized Hamiltonian, generalized Hartree-Fock equations and, in particular, the electron and positron Green's functions and self-energy parts (optical potentials) are addressed. Exact properties of the latter quantities are discussed in some detail. A systematic approximation scheme that has been successful in the case of electronic systems is applied to the Green's functions and self-energy parts of composite systems. Explicit working equations are derived.

I. INTRODUCTION

The method of Green's functions has been widely used to study quantum properties of many-body systems. The general theory (see, for instance, Refs. 1 and 2) has been applied, for example, to nuclei,[3,4] solids,[5,6] and atoms and molecules.[7,8] In each field different approximations to the exact Green's functions have to be introduced taking into account the specific interactions characteristic of the system under investigation.

The long-range interaction in solids and the short-range interaction in nuclear matter allow one to derive meaningful approximations by considering only partial summations of particular types of Feynman diagrams. These comprise the random-phase approximation (RPA) and the ladder diagrams, respectively.[1,9] For atoms, molecules, and possibly nuclei, the finite range of the system generally prevents a single series of diagrams from dominating the others.[10] To achieve reliable results it is, therefore, necessary to handle all Feynman diagrams up to a given order of perturbation theory on the same footing and to estimate the higher orders in a systematic way. This is explicitly attempted in the algebraic diagrammatic construction (ADC) scheme.[11,12] In the nth-order scheme all diagrams up to nth order are included as well as all series of diagrams arising from them. The ladder diagrams of second and third order, for example, thus generate the whole series of ladder diagrams. The ADC has been applied to atoms and, in particular, to numerous molecules.[13] We would like to mention that other approximations to Green's functions are available which have also been applied to atoms and molecules. An incomplete list of references includes Refs. 14–16 and 10.

In the present work we investigate the many-body theory of composite systems which contain two kinds of charged light particles. To be specific we consider electrons and positrons although the theory applies to other particles as well, e.g., muons. Particular attention is paid to the electron and positron Green's function and to the derivation of the ADC working equations. Green's functions provide a suitable tool to investigate the binding of particles to a system. The binding energy directly appears as a pole of the corresponding function. From the experience with electrons we expect the ADC to be useful in the calculations of the binding energy and other properties of the composite system. The literature on bound composite systems reports on exotic systems like positronium bound to an electron,[17,18] on muonic atoms,[19,20] and positronium hydride.[21] The literature on the binding of positrons to molecules is scarce. It is assumed, however, that bound positron-molecule systems should exist. In particular, it seems promising to search for positrons bound to negative ions and to molecules where they replace a proton. We are not aware of work on systems with more than one particle of each kind.

Most of the literature is concerned, however, with the scattering of positrons by atoms and molecules.[22] The majority of computations is on positron scattering by hydrogen and helium atoms and hydrogen molecules, but a number of systems like the oxygen and nitrogen molecules have also been investigated. Model potentials are commonly used in these calculations, and more recently *ab initio* calculations have been performed as well. For a review on the computational methods including a detailed account of the literature see Ref. 22. Since the self-energy part of the one-particle Green's function represents an optical potential,[23] scattering processes can also be calculated by Green's-function methods. For the ADC this has been successfully documented for electron-molecule scattering.[24,25] A few promising scattering calculations with different particles using Green's-function approaches are already available in the literature. These calculations comprise positron scattering by atomic helium,[26] by atomic hydrogen,[27] and by molecular hydrogen.[28]

The paper is organized as follows. In the next section the Hamiltonian and the generalized Hartree-Fock equations are introduced. The electron and positron Green's functions and their self-energies are discussed in Sec. III. Section IV is devoted to the discussion of the approximation scheme and to the derivation of the working equations.

II. HAMILTONIAN AND NOTATION

A. General

We consider a system composed of two types of light particles which move in the external field of heavy particles and concentrate on the dynamics of the former ones. To be specific we consider a molecule with N electrons and P positrons moving in the field of the fixed nuclei composing the molecular skeleton. It is clear that the electrons and/or positrons can be replaced by other particles, e.g., muons, and that the theory can easily be extended to systems having more than two types of light particles, although this case is not of practical relevance.

The Hamiltonian of the system reads

$$H=(T_{-}+V_{-}+V_{--})+(T_{+}+V_{+}+V_{++})+V_{+-} \tag{2.1}$$

where the first and second bracket on the right-hand side of the equation describe the electronic and positronic subsystems, respectively, and V_{+-} the interaction between them. T_{-} denotes the kinetic energy of the electrons, V_{-} their interaction with the nuclei, and V_{--} the electron-electron repulsion. The operators for the positrons carry a plus subscript and are defined analogously.

To write the Hamiltonian in its second quantized form, we introduce as usually[1] the field operator $\Psi(x,t)$ which annihilates a particle at space-spin coordinates x and at time t. Let $\Psi_{-}(x,t)$ and $\Psi_{+}(x,t)$ be the field operators for an electron and a positron, respectively. The appropriate commutation relations for $\Psi_{\pm}(x,t)$ will be

$$\{\Psi^{\dagger}(x,t),\Psi(y,t)\}=\delta(x-y)\ , \tag{2.2a}$$

$$\{\Psi(x,t),\Psi(y,t)\}=0\ , \tag{2.2b}$$

where $\delta(x-y)$ is the Dirac δ function and $\{\ ,\ \}$ is the anticommutator. Since we consider electrons and positrons to belong to different particle species, the field operators of electrons are chosen to commute with those of positrons

$$[\Psi_{+}^{\dagger}(x,t),\Psi_{-}(y,t)]=[\Psi_{+}(x,t),\Psi_{-}(y,t)]=0 \tag{2.2c}$$

where $[\ ,\ ]$ denotes the commutator. Choosing a commutator makes the evaluation of expectation values simpler. On the other hand, we may consider the electron and the positron as one-particle species, as is done in quantum electrodynamics, and choose instead of the commutator an anticommutator. This situation is similar to the one in nuclear physics, where neutron and proton are considered to belong to the same particle species, namely the nucleon. In the latter case also an anticommutator is chosen. As long as we are not concerned here with the annihilation of an electron-positron pair into photons or with conversion of neutrons into protons we may choose either commutators or anticommutators.

To proceed we expand the field operators according to

$$\Psi_{+}(x,t)=\sum_{s} b_s(t)\varphi_s(x)\ , \tag{2.3a}$$

$$\Psi_{-}(x,t)=\sum_{i} a_i(t)\chi_i(x)\ . \tag{2.3b}$$

The $\{\varphi_s\}$ and $\{\chi_i\}$ are complete orthonormal sets of suitable functions (orbitals) still to be determined. The annihilation operators a_i (or b_s) for the electron (or positron) in the one-particle state $|\varphi_s\rangle$ (or $|\chi_i\rangle$) obey the commutation relations

$$\{a_i^{\dagger},a_j\}=\delta_{ij}\ , \tag{2.4a}$$

$$\{b_r^{\dagger},b_s\}=\delta_{rs}\ , \tag{2.4b}$$

$$\{a_i,a_j\}=\{b_r,b_s\}=0\ , \tag{2.4c}$$

$$[b_r^{\dagger},a_i]=[b_r,a_i]=0 \tag{2.4d}$$

which follow immediately from (2.2).

Using Eqs. (2.2)–(2.4) the Hamiltonian (2.1) can easily be expressed in the notation of second quantization.[1] The only quantity which deserves some attention is the electron-positron interaction V_{+-} given in atomic units by

$$V_{+-}=-\sum_{i,s}\frac{1}{r_{is}} \tag{2.5}$$

where r_{is} is the distance between the electron i and positron s. Although V_{+-} is a two-particle interaction the particles involved are of different nature and can be quantized separately. This leads to

$$V_{+-}=-\sum_{r,s}\sum_{i,j} V_{risj}b_r^{\dagger}a_i^{\dagger}a_j b_s \tag{2.6a}$$

whereas the electron-electron and positron-positron interactions

$$V_{--}=\tfrac{1}{2}\sum_{i,j,k,l} V_{ijlk}a_i^{\dagger}a_j^{\dagger}a_k a_l\ , \tag{2.6b}$$

$$V_{++}=\tfrac{1}{2}\sum_{r,s,i,j} V_{rsut}b_r^{\dagger}b_s^{\dagger}b_t b_u \tag{2.6c}$$

contain an additional factor $\frac{1}{2}$.

In all cases the Coulomb matrix elements take on the same formal appearance

$$V_{abcd}=\int f_a^{*}(x_1)f_b^{*}(x_2)\frac{1}{|x_1-x_2|}f_d(x_2)\times f_c(x_1)d^3x_1d^3x_2\ . \tag{2.7a}$$

For later use we also define

$$V_{ab(cd)}=V_{abcd}-V_{abdc} \tag{2.7b}$$

for the case where all indices a,b,c,d belong to the same particle species. Here and in the following we use the indices i,j,k,l,m for electrons and r,s,t,u,v for positrons and define

$$f_a=\begin{cases}\chi_a & \text{for } a=i,j,k,l,m\\ \varphi_a & \text{for } a=r,s,t,u,v\ .\end{cases} \tag{2.8}$$

In second quantized form the Hamiltonian now reads

$$H=H_0+V\ , \tag{2.9a}$$

$$H_0=\sum_i \epsilon_i a_i^\dagger a_i+\sum_s e_s b_s^\dagger b_s\ , \tag{2.9b}$$

$$V=\sum_{i,j} W_{ij}a_i^\dagger a_j+\sum_{r,s} W_{rs}b_r^\dagger b_s+V_{--}+V_{++}+V_{+-}\ , \tag{2.9c}$$

where V_{--}, V_{++}, and V_{+-} have already been given above in (2.6). ϵ_i and e_s denote the one-particle energies of the electrons and of the positrons, respectively. For convenience W_{ij} and W_{rs}, which are the matrix elements of the one-particle potentials W_- and W_+, are only discerned by their subscripts. These potentials have been introduced to define the complete sets of orbitals

$$(T_+ +V_+ -W_+)\varphi_s=e_s\varphi_s\ , \tag{2.10a}$$

$$(T_- +V_- -W_-)\chi_i=\epsilon_i\chi_i\ . \tag{2.10b}$$

An interesting example for $W_\pm$ is discussed in the next subsection.

B. Generalized Hartree-Fock equations

The Hamiltonian and the many-body formalism of the following sections do not depend on the choice of orbitals. On the other hand it is useful to choose orbitals, and thus an unperturbed Hamiltonian H_0, which are physically meaningful and advantageous in practical applications. In electronic systems the Hartree-Fock potential is of particular relevance and deserves attention also in the present case of composite systems. In analogy to the purely electronic case one seeks the orbitals minimizing the energy functional

$$E[\phi_0]=\langle\phi_0|H|\phi_0\rangle \tag{2.11a}$$

where the test function $|\phi_0\rangle$ is a product of an electronic and a positronic Slater determinant

$$|\phi_0\rangle=\prod_{s=1}^{P} b_s^\dagger \prod_{i=1}^{N} a_i^\dagger|0\rangle\ . \tag{2.11b}$$

$|0\rangle$ is the vacuum state with no particles in it. The minimization of $E[\phi_0]$ can be done in analogy to Ref. 4 and leads to the following coupled equations for the orbitals and orbital energies

$$(T_+ +V_+ +J_+ -K_+ -J_-)\varphi_s=e_s\varphi_s\ , \tag{2.12a}$$

$$(T_- +V_- +J_- -K_- -J_+)\chi_i=\epsilon_i\chi_i\ . \tag{2.12b}$$

As usual these equations must be solved in a self-consistent manner since the Coulomb and exchange operators J and K themselves depend on the orbitals occupied in the ground state $|\phi_0\rangle$. For completeness we give the explicit form of these operators:

$$J_+=\int\sum_{s=1}^{P}\frac{\varphi_s^*(x_2)\varphi_s(x_2)}{|x_2-x_1|}d^3x_2\ , \tag{2.13a}$$

$$J_-=\int\sum_{i=1}^{N}\frac{\chi_i^*(x_2)\chi_i(x_2)}{|x_2-x_1|}d^3x_2\ , \tag{2.13b}$$

$$K_+\varphi_r(x_1)=\int\sum_{s=1}^{P}\frac{\varphi_s^*(x_2)\varphi_r(x_2)}{|x_2-x_1|}d^3x_2\varphi_s(x_1)\ , \tag{2.13c}$$

$$K_-\chi_j(x_1)=\int\sum_{i=1}^{N}\frac{\chi_i^*(x_2)\chi_j(x_2)}{|x_2-x_1|}d^3x_2\chi_i(x_1)\ , \tag{2.13d}$$

with summation over doubly occurring indices of the ground-state orbitals. Clearly, an electron (positron) interacts via Coulomb and exchange with the other electrons (positrons), but in addition, it is also attracted by the charge distribution of the P positrons (N electrons) available.

The above coupled equations which we may call the generalized Hartree-Fock equations (GHF) define complete sets of orthonormal positronic and electronic functions φ and χ, respectively. In the case of bound systems the P orbitals φ_s and N orbitals χ_i which belong to the lowest orbital energies e_s and ϵ_i, respectively, define the so-called "occupied" orbitals. The complementary space comprises the "unoccupied" or "virtual" orbitals which describe states for an additional electron or positron, either bound or scattered. If the system is unbound, (2.12) define scattering states. Of particular interest is the case $P=0$, i.e., the target molecule does not contain positrons. In this case J_+ and K_+ vanish, (2.12b) describes the pure electronic system, and (2.12a) becomes

$$(T_+ +V_+ -J_-)\varphi_s=e_s\varphi_s \tag{2.14}$$

describing possible bound orbitals of an extra positron, but most of all, the scattering one-particle states of a positron from the electronic target system.

Finally, we give the explicit expressions for the matrix elements W_{ij} and W_{rs} needed to complete (2.9) for the full Hamiltonian of the system in the GHF picture

$$W_{ij}=-\sum_{k=1}^{N}(V_{ikjk}-V_{ikkj})+\sum_{r=1}^{P}V_{irjr}\ , \tag{2.15a}$$

$$W_{rs}=-\sum_{u=1}^{P}(V_{rusu}-V_{ruus})+\sum_{i=1}^{N}V_{risi}\ , \tag{2.15b}$$

as well as of the GHF total energy from (2.11a)

$$E_{\text{GHF}}=\sum_{i=1}^{N}\epsilon_i-\tfrac{1}{2}\sum_{i,j=1}^{N}(V_{ijij}-V_{ijji})+\sum_{s=1}^{P}e_s -\tfrac{1}{2}\sum_{r,s=1}^{P}(V_{rsrs}-V_{rssr})+\sum_{s=1}^{P}\sum_{i=1}^{N}V_{isis}\ . \tag{2.16}$$

The first two terms on the right-hand side of (2.16) describe the electronic energy, the following two terms the positronic energy, and the last term is due to the electron-positron interaction.

III. GREEN'S FUNCTIONS AND SELF-ENERGIES

A. One-particle Green's functions

The one-particle Green's function of a purely electronic system is well known and its diagrammatics can be found in any textbook on many-body problems (for instance, Refs. 1 and 29). For the composite system containing electrons as well as positrons we have to introduce two types of one-particle Green's functions, one for an electron and one for a positron. The electronic one-particle Green's function is defined as the time-ordered expectation value of the product of two field operators:

$$G_-(x_1,t_1;x_2,t_2)=-i\langle\psi_0|T(\Psi_-(x_1,t_1)\Psi_-^\dagger(x_2,t_2))|\psi_0\rangle \tag{3.1}$$

where $|\psi_0\rangle$ is the exact ground state of the system and T denotes the time ordering operator.[1] The positronic one-particle Green's function is defined analogously:

$$G_+(x_1,t_1;x_2,t_2) = -i\langle\psi_0|T(\Psi_+(x_1,t_1)\Psi_+^\dagger(x_2,t_2))|\psi_0\rangle \ . \tag{3.2}$$

We now use the expansion of the field operators to obtain

$$G_+(x_1,t_1;x_2,t_2)=\sum_{r,s}\varphi_r(x_1)\varphi_s^*(x_2)G_{+rs}(t_1,t_2) \tag{3.3}$$

where G_{+rs} is the time-ordered ground-state expectation value of the b operators in the Heisenberg picture:

$$G_{+rs}(t_1,t_2)=-i\langle\psi_0|T(b_r(t_1)b_s^\dagger(t_2))|\psi_0\rangle \ . \tag{3.4}$$

From now on we may drop the plus subscript in G_{+rs} because of our index convention (see Sec. II). For electrons a corresponding G_{ij} is defined. Remember that the indices refer to a specific basis system, for instance to the solutions of the generalized Hartree-Fock equations of Sec. II B. We call G_{rs} and G_{ij} the positron and electron Green's function, respectively.

As in the purely electronic case there is a spectral representation of G_+ and G_-. By standard manipulations it can be shown that the Fourier transform of a G consists of two parts given as

$$G_{rs}(\omega)=\langle\psi_0|b_r(\omega+E_0-H+i\eta)^{-1}b_s^\dagger|\psi_0\rangle + \langle\psi_0|b_s^\dagger(\omega-E_0+H-i\eta)^{-1}b_r|\psi_0\rangle \ . \tag{3.5}$$

Inserting in the first and second part of (3.5) a full set of exact $(P+1,N)$ and $(P-1,N)$ states (where P and N denote the number of positrons and electrons, respectively), i.e., solutions to the eigenvalue problems

$$H|P+1,N\rangle_m=E_m^+|P+1,N\rangle_m \tag{3.6a}$$

and

$$H|P-1,N\rangle_m=E_m^-|P-1,N\rangle_m \tag{3.6b}$$

will lead to the spectral representations

$$\begin{aligned}G_{rs}=&\sum_m\langle\psi_0|b_r|P+1,N\rangle_m\frac{1}{\omega+E_0-E_m^++i\eta}\\&\times{}_m\langle P+1,N|b_s^\dagger|\psi_0\rangle\\&+\sum_m\langle\psi_0|b_s^\dagger|P-1,N\rangle_m\frac{1}{\omega-E_0+E_m^--i\eta}\\&\times{}_m\langle P-1,N|b_r|\psi_0\rangle\end{aligned} \tag{3.7a}$$

where η is a positive infinitesimal. Note that m refers to $(P+1,N)$ states in the first term and to $(P-1,N)$ states in the second term. The superscripts plus and minus denote the $(P\pm1,N)$ state energies. It is clear that if $P=0$ the second term will be zero.

For the electron Green's function a similar analysis and similar formulas hold. In particular one finds the following spectral representation:

$$\begin{aligned}G_{ij}=&\sum_n\langle\psi_0|a_i|P,N+1\rangle_n\frac{1}{\omega+E_0-E_n^++i\eta}\\&\times{}_n\langle P,N+1|a_j^\dagger|\psi_0\rangle\\&+\sum_n\langle\psi_0|a_j^\dagger|P,N-1\rangle_n\frac{1}{\omega-E_0+E_n^--i\eta}\\&\times{}_n\langle P,N-1|a_i|\psi_0\rangle \ .\end{aligned} \tag{3.7b}$$

Here, of course, the quantities E_n^+ and E_n^- are the energies of the states $|P,N+1\rangle_n$ and $|P,N-1\rangle_n$, respectively.

In (3.7a) and (3.7b) an important feature of the Green's function becomes apparent. The denominators give the energies of the $(P\pm1,N)$ and $(P,N\pm1)$ states, or more precisely, the changes in energy that the system experiences when we add or take away one positron, or when we add or take away one electron. This means, for instance, that, if we can calculate the positron Green's function for 0 positrons in the ground state we can get the binding energy of a positron to the system. In such a situation the GHF equations simplify considerably and boil down to the usual HF equations for the electrons and a single equation for the unoccupied orbitals of the positron in the field of the electrons. The positron Green's function also becomes simpler since the second term on the right-hand side of (3.7a) vanishes and the remaining term is easier to compute (see following sections).

B. The proper self-energy

We note that we have defined the Green's function of the fully interacting system, i.e., of the full Hamiltonian. We can now choose unperturbed Hamiltonians, for instance the GHF Hamiltonian, and define their so-called free Green's functions. In energy space the free Green's functions take on the following appearance:

$$G_{rs}^0=\frac{\delta_{rs}}{\omega-e_r\pm i\eta} \tag{3.7c}$$

for the positron and

$$G_{ij}^0=\frac{\delta_{ij}}{\omega-\epsilon_i\pm i\eta} \tag{3.7d}$$

for the electron. Here e_r and ϵ_i are the eigenvalues of the corresponding GHF equations. As usual we can connect the full Green's function and the free Green's function via the Dyson equation

$$G_{rs}=G^0_{rs}+G^0_{rt}\Sigma_{tu}G_{us} \tag{3.8a}$$

for the positron, and

$$G_{ij}=G^0_{ij}+G^0_{ik}\Sigma_{kl}G_{lj} \tag{3.8b}$$

for the electron. Σ_{rs} and Σ_{ij} are the positron and electron proper self-energies. In the last terms of (3.8a) and (3.8b) the summation convention is used for doubly occurring indices. Each of the equations (3.8a) and (3.8b) can be written in matrix notation

$$\underline{G}=\underline{G}^0+\underline{G}^0\underline{\Sigma}\,\underline{G} \tag{3.8c}$$

where all underlined quantities denote matrices. Particularly useful equations of the Dyson equations are obtained by inversion. One finds

$$\underline{G}_+(\omega)=(\omega\underline{1}-\underline{e}-\underline{\Sigma}_+)^{-1} \tag{3.8d}$$

and

$$\underline{G}_-(\omega)=(\omega\underline{1}-\underline{\epsilon}-\underline{\Sigma}_-)^{-1} \tag{3.8e}$$

where $\underline{e}$ and $\underline{\epsilon}$ denote the diagonal matrices of eigenvalues of the corresponding GHF equations, and $\underline{\Sigma}_+$ and $\underline{\Sigma}_-$ are the proper self-energy matrices. In (3.8d) and (3.8e) we omitted the infinitesimal imaginary terms $\pm i\eta$. "Diagonalizing" (3.8d) and (3.8e) enables us to calculate positron and electron ionization energies and positron and electron affinities as seen in (3.7a) and (3.7b). How to do the "diagonalization" will be shown in Sec. IV.

1. Static and dynamic parts

The proper self-energies for positrons and electrons consist of a static part $\Sigma(\infty)$ not depending on ω and a dynamic part M depending on ω:

$$\Sigma(\omega)_{\rho\sigma}=[\Sigma(\infty)+M(\omega)]_{\rho\sigma}\ . \tag{3.9}$$

The static parts can be obtained from the following equations analogous to the purely electronic case:[10]

$$\Sigma(\infty)_{uv}=W_{uv++}+\frac{1}{2\pi i}\sum_{r,s}V_{ur(vs)}\oint G_{rs}(\omega)d\omega +W_{uv+-}-\frac{1}{2\pi i}\sum_{i,j}V_{uivj}\oint G_{ij}(\omega)d\omega \tag{3.10a}$$

for the positron, and

$$\Sigma(\infty)_{kl}=W_{kl--}+\frac{1}{2\pi i}\sum_{i,j}V_{ki(lj)}\oint G_{ij}(\omega)d\omega +W_{kl-+}-\frac{1}{2\pi i}\sum_{r,s}V_{krls}\oint G_{rs}(\omega)d\omega \tag{3.10b}$$

for the electron [for the definitions of the symbols V_{abcd} and $V_{ab(cd)}$ see (2.7a) and (2.7b)]. The contour of integration is closed in the upper half of the complex energy plane. We have split up W_+ into the parts W_{++} (the purely positronic HF potential) and W_{+-} (the positron-electron HF potential) and W_- into the parts W_{--} and W_{-+}:

$$W_{uv++}=-\sum_{r=1}^{P}V_{ur(vr)}\ , \tag{3.11a}$$

$$W_{uv+-}=\sum_{i=1}^{N}V_{uivi}\ , \tag{3.11b}$$

$$W_{kl--}=-\sum_{i=1}^{N}V_{ki(li)}\ , \tag{3.11c}$$

$$W_{kl-+}=\sum_{r=1}^{P}V_{krlr}\ . \tag{3.11d}$$

The summation is always over GHF ground-state orbitals. The missing minus sign in (3.11b) and (3.11d) is due to the attraction of electrons and positrons. In the purely electronic case only the first line of (3.10b) shows up due to the fact that no positrons are present in the ground state. If positron-molecule scattering is to be described the first line on the right-hand side of (3.10a) vanishes.

We can now use the Dyson equations (3.8d) and (3.8e) for the positron and electron Green's functions to rewrite the right-hand sides of Eqs. (3.10a) and (3.10b) giving

$$\Sigma(\infty)_{uv}=W_{uv++}+\frac{1}{2\pi i}\sum_{r,s}V_{ur(vs)}\oint[G^0_{rs}(\omega)^{-1}-\Sigma(\infty)_{rs}-M_{rs}(\omega)]^{-1}d\omega +W_{uv+-}-\frac{1}{2\pi i}\sum_{i,j}V_{uivj}\oint[G^0_{ij}(\omega)^{-1}-\Sigma(\infty)_{ij}-M_{ij}(\omega)]^{-1}d\omega\ . \tag{3.12}$$

For the electronic proper self-energy a similar equation holds and is obtained by simply exchanging positronic and electronic indices. Equation (3.12) shows that the static self-energy part can be computed once the dynamic self-energy part is known. Consequently, we shall concentrate below on the evaluation of the latter. We mention that $\Sigma(\infty)$ has been found to be an important quantity in purely electronic systems[13] and should be of relevance also in composite systems. A converging iterative procedure for the numerical evaluation of $\Sigma(\infty)$ is described in Ref. 13.

For later purposes it is useful to note that the dynamic self-energy part possesses a spectral representation

$$M_{rs}=\sum_{\beta}\frac{m_r^{\beta}m_s^{\beta *}}{\omega-\omega_\beta+i\eta\sigma_\beta} \tag{3.13}$$

where $\sigma_\beta = \pm 1$. The terms with $\sigma_\beta = \pm 1$ are associated with excitations of $(P+1,N)$ or $(P-1,N)$ states, respectively. For electrons an analogous equation is valid with $\sigma_\beta = \pm 1$ associated with $(P,N\pm 1)$ states, respectively. In both cases the energies ω_β do not correspond to physical states, i.e., must not be confused with the energies $\pm(E_0 - E_m^\pm)$ appearing in the spectral representation of the Green's functions (3.7a) and (3.7b).

A few remarks on the physical meaning of the self-energy are in order. Equation (3.8) suggests that Σ can be viewed as an effective energy-dependent one-particle potential caused by correlation effects. The orbitals of a positron determined by

$$(T_+ + V_+ - W_+)\varphi_s = e_s \varphi_s \tag{3.14}$$

are modified by the self-energy part to give

$$(T_+ + V_+ - W_+ + \Sigma_+)\phi_\omega = \omega \phi_\omega \ . \tag{3.15}$$

In spatial representation Σ_+ is a nonlocal operator given by

$$\Sigma_+(x,x',\omega) = \sum_{r,s} \varphi_r(x) \Sigma_{rs}(\omega) \varphi_s^*(x') \ . \tag{3.16}$$

Considering a scattering situation, i.e., the scattering of a positron from the composite system as target, then ω is the energy of the incoming positron, and ϕ_ω is the optical wave function of the scattering positron. It is important to note that ϕ_ω fulfills the boundary condition that the *exact* scattering wave function of the full Hamiltonian splits up asymptotically into the product of the ground-state wave function and the optical wave function.[23,25] If Σ_+ is known Eq. (3.15) can be solved using as an incoming wave a free particle wave, and with the result one can easily obtain the exact elastic cross section. An analogous discussion holds for the case of electrons where Σ_- is the scattering potential (for applications see, e.g., Refs. 13 and 26).

To interpret the static self-energy $\Sigma_+(\infty)$ we introduce the common nonlocal density operators

$$\hat{\rho}_\pm(x,x') = \sum_{\text{spin}} \Psi_\pm^\dagger(x) \Psi_\pm(x') \tag{3.17}$$

where the summation is over the spin indices which are not written explicitly. The ground-state expectation value of these operators is simply given by

$$\rho_\pm(x,x') = \frac{1}{2\pi i} \oint d\omega \, \mathrm{Tr} G_\pm(x,x',\omega) \tag{3.18}$$

where the trace Tr is over the spin and the integration is in the upper half plane. With the aid of (3.18) and (3.10) we obtain the following expression for the static self-energy part:

$$\Sigma_+(x,x',\infty) = W_+(x,x') + \delta(x-x') \int dx_1 \frac{\rho_+(x_1) - \rho_-(x_1)}{|x-x_1|} - \frac{\rho_+(x,x')}{|x-x'|} \ . \tag{3.19}$$

Here $\rho(x) = \rho(x,x)$ is the local ground-state particle density. The static self-energy simply describes the Coulomb interaction (local and exchange) of the incoming positron with the ground-state charge distribution of the target. If the target itself does not contain positrons, the positron density $\rho_+(x,x')$ vanishes and (3.19) simplifies further. W_+ is the one-particle potential used to define the unperturbed Hamiltonian, see (2.10).

If free particles are used then W_+ describes the positron-nuclei interaction (see 2.10a), i.e., $W_+ = V_+$. Using the GHF potential, on the other hand, leads to

$$\Sigma_+(x,x',\infty) = \delta(x-x') \int dx_1 \frac{\Delta\rho_+(x_1) - \Delta\rho_-(x_1)}{|x-x_1|} - \frac{\Delta\rho_+(x,x')}{|x-x'|} \tag{3.20a}$$

where

$$\Delta\rho_\pm = \rho_\pm - \rho_\pm^0 \tag{3.20b}$$

is the difference between the exact density and the one computed on the GHF level. It becomes evident that the static self-energy part (3.20a) represents a correction to the optical potential which depends only on the particles' correlation in the ground state. Indeed, the perturbation expansion of (3.20a) begins in third order owing to our choice of the GHF potential.

Finally we remark that

$$\Sigma_+(x,x',\infty) - W_+(x,x') \xrightarrow[|x|\to\infty]{} \delta(x-x') \frac{P-N}{|x|} \tag{3.21}$$

and, therefore, $\Sigma_+(x,x',\infty)$, vanishes at large distances if the GHF potential is used to define the particles, i.e., the free Green's function. The dynamic self-energy part $M_+(\omega)$, on the other hand, is proportional to $1/|x|^4$ asymptotically (see also Refs. 30 and 31).

2. *Feynman diagrams*

The Green's functions for positrons and electrons can be evaluated perturbationally by Feynman diagrams. Since our scheme to compute these functions (see next section) relies on Feynman diagrams, we discuss these diagrams in the following.

We introduce the following symbols (Fig. 1): A solid line with a direction from j to i denotes G_{ij}^0, a dashed line with a direction from s to r denotes G_{rs}^0. Analogously, double solid and dashed lines symbolize the electron and positron Green's functions G_{ij} and G_{rs}. A wavy line with two incoming and two outgoing lines stands for the Coulomb interaction matrix element V_{abcd}. A wavy line with a dot denotes W_{ac}. The indices in each pair of indices (a,c) and (b,d) denote either electronic or positronic orbitals. It should be noted that the elements V_{abcd} are matrix elements of $1/r_{12}$ not taking account of the sign of the particle charges [see (2.7)]. Therefore in the Feynman rules a minus sign for the electron-positron interaction has to be considered due to the different electrical charges of the particles. The diagrams are calculated going from the left to the right. The first two indices denote

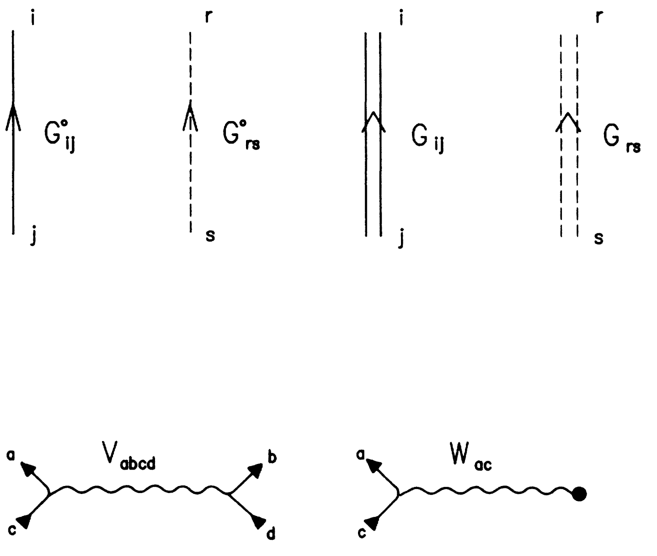

FIG. 1. Symbols used to draw the Feynman diagrams.

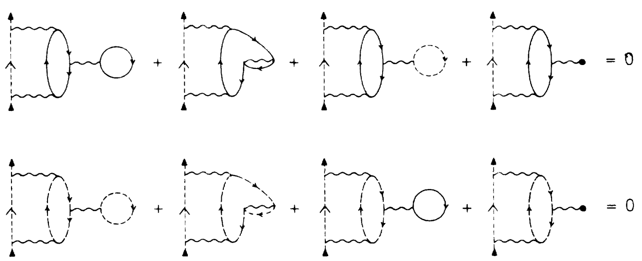

FIG. 3. The canceling of diagrams as a consequence of the equations shown in Fig. 2.

outgoing lines, the third and fourth incoming lines. The rules to draw and to evaluate the Feynman diagrams are collected in the Appendix.

If we choose the GHF Hamiltonian to be the unperturbed Hamiltonian, all first-order diagrams can be dropped owing to cancellations. These cancellations are depicted in Fig. 2 for the positron self-energy part. The purely positronic tadpoles together with their exchange are canceled by the matrix element of W_{++}. Of course, there is no exchange diagram corresponding to the diagram where an electronic loop is coupled to a positron line. The latter diagram cancels the matrix element of W_{+-}.

The above-mentioned cancellation of the first-order diagrams reduces considerably the number of diagrams to be considered in higher orders of perturbation theory. The diagrams of first order appear as parts of many higher-order diagrams and the sum of these diagrams vanishes. In Fig. 3 two series of diagrams are shown where in each series the diagrams cancel each other. As a consequence only those diagrams have to be considered where a free Green's-function line connects two different Coulomb interaction matrix elements V_{abcd}. The matrix elements of W do not appear at all.

Choosing, for instance, the GHF equation for the electrons but a different equation for the positrons we still encounter the compensation of many diagrams. The purely electronic tadpoles and their exchange still cancel the matrix elements of W_{--} and a similar result holds for W_{-+} and the positronic loop diagram. In passing we mention that if we consider a free particle equation instead of the GHF equation, the interaction W_{rs} stands for the interaction of the positron with the potential of the nuclei making up the molecular skeleton.

We briefly discuss the diagrams of the self-energy part related to the GHF Hamiltonian as the unperturbed one. The static self-energy part $\Sigma(\infty)_{ab}$ consists of all diagrams of the self-energy part for which the indices a and b are on the same Coulomb matrix element. The sum of these diagrams can be collected into a few diagrams if we may use the full Green's function G and not only the free one G^0. The diagrammatic equation for $\Sigma(\infty)$ is depicted in Fig. 4. If we investigate a target system with $P=0$ positrons, only the first two diagrams shown in the figure contribute to the positron static self-energy part. All other diagrams vanish. In general, $\Sigma(\infty)$ begins in third-order perturbation theory when the GHF potential is used. These diagrams of third order are collected in Fig. 5 for the positron Green's function. All diagrams except the top left one vanish in the important case $P=0$ describing positron-molecule scattering. The diagrams of the dynamic self-energy part are discussed in the follow-

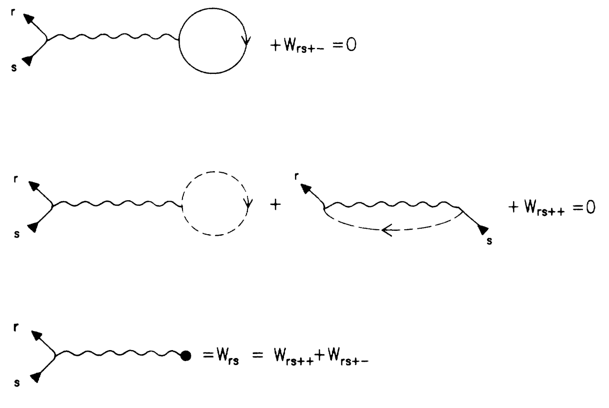

FIG. 2. The canceling of the first-order diagrams of the positron self-energy part when the GHF basis is used. Analogous relations hold for the electron self-energy part.

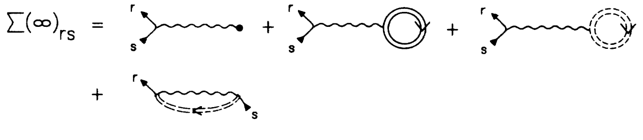

FIG. 4. The diagrammatic equation for the positron static self-energy part. The analogous equation for the electron static self-energy part is obtained by replacing r and s by i and j and interchanging the electron and positron Green's functions.

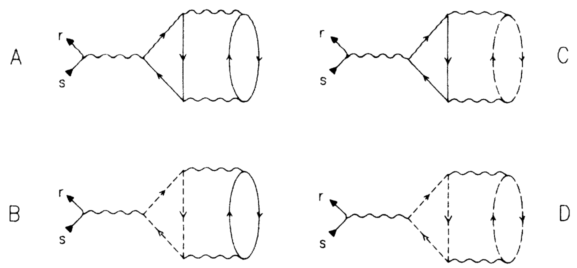

FIG. 5. The Feynman diagrams of third order of the positron static self-energy part. To the diagrams shown there may correspond exchange diagrams not shown here (one exchange diagram for A, one for B, none for C, and four for D).

ing chapter where they are explicitly needed for the construction of the working equations.

IV. APPROXIMATION SCHEME

A. A closer look at the dynamic self-energy part

For the discussion of approximations to the dynamic self-energy part it is useful to investigate in more detail relevant exact properties of this quantity. As briefly mentioned in Sec. III B 1, the dynamic self-energy part $\underline{M}(\omega)$ has a spectral representation. $\underline{M}$ can be written as the sum of two parts $\underline{M}^{(\mathrm{I})}$ and $\underline{M}^{(\mathrm{II})}$ analytical in the upper and lower half of the complex ω plane, respectively,

$$M_{rs}(\omega)=M_{rs}^{(\mathrm{I})}(\omega)+M_{rs}^{(\mathrm{II})}(\omega) \ . \tag{4.1}$$

Here and in the following we confine ourselves to the discussion of the positron self-energy. In the general case of N electrons and P positrons in the target's ground state the electron self-energy is easily obtained from the positron one by a simple interchange of the appearing indices and of P and N. Using matrix notation we may write

$$\underline{M}^{(\mathrm{I})}=\underline{m}^{(\mathrm{I})\dagger}(\omega\underline{1}-\underline{\Omega}^{(\mathrm{I})}+i\eta)^{-1}\underline{m}^{(\mathrm{I})} \tag{4.2}$$

where $\underline{1}$ is the unit matrix, $\underline{\Omega}^{(\mathrm{I})}$ denotes the diagonal matrix having the poles ω_β of $\underline{M}^{(\mathrm{I})}$ as elements and the matrix $\underline{m}^{(\mathrm{I})}$ has elements $m_r^{\beta *}$ [see Eq. (3.13)]:

$$\underline{m}^{\dagger}=(m_r^{\beta}) \ . \tag{4.3}$$

Analogous expressions hold for $\underline{M}^{(\mathrm{II})}$.

With the aid of (4.2) one can cast the Dyson equation (3.8) into algebraic form. For this purpose we introduce a matrix which takes on the following appearance:

$$\underline{A}=\begin{bmatrix} \underline{e}+\underline{\Sigma}(\infty) & (\underline{m}^{(\mathrm{I})})^{\dagger} & (\underline{m}^{(\mathrm{II})})^{\dagger} \\ \underline{m}^{(\mathrm{I})} & \underline{\Omega}^{(\mathrm{I})} & \underline{0} \\ \underline{m}^{(\mathrm{II})} & \underline{0} & \underline{\Omega}^{(\mathrm{II})} \end{bmatrix} . \tag{4.4}$$

Here, $\underline{e}$ denotes the diagonal matrix of all positron orbital energies and $\underline{\Sigma}(\infty)$ stands for the static self-energy matrix. We remind the reader that the latter can be computed exactly once the dynamic self-energy part is known (see Sec. III B 1). The one-particle Green's function is determined as the upper left block of the inverse of the matrix $\underline{T}(\omega)=\omega\underline{1}-\underline{A}$. More precisely

$$G_{rs}(\omega)=(\underline{T}^{-1})_{rs}=[\omega\underline{1}-\underline{A}]_{rs}^{-1} \ . \tag{4.5}$$

The Dyson equation immediately follows from the usual relation between the elements of a matrix and its inverse. Let

$$\underline{T}=\begin{bmatrix} \underline{a} & \underline{b}^{\dagger} \\ \underline{b} & \underline{d} \end{bmatrix}, \quad \underline{T}^{-1}=\begin{bmatrix} \underline{g} & \underline{c}^{\dagger} \\ \underline{c} & \underline{h} \end{bmatrix} \tag{4.6a}$$

where $\underline{a}=\omega\underline{1}-\underline{e}-\underline{\Sigma}(\infty)$. The usual relation

$$\underline{g}=(\underline{a}-\underline{b}^{\dagger}\underline{d}^{-1}\underline{b})^{-1} \tag{4.6b}$$

is nothing but the Dyson equation in its version in (3.8d).

Equation (4.5) makes clear that the poles and residues of the Green's function can be obtained by solving the eigenvalue equation of the Hermitian matrix $\underline{A}$ given above. The secular equation for $\underline{A}$ in matrix notation reads

$$\underline{A}\,\underline{X}=\underline{X}\,\underline{E}, \quad \underline{X}^{\dagger}\underline{X}=\underline{1} \tag{4.7}$$

where $\underline{E}$ is the diagonal matrix of eigenvalues and $\underline{X}$ the unitary eigenvector matrix. Comparing with (3.7a) shows that the elements X_{rm} and X_{rn} of $\underline{X}$ are equal to ${}_m\langle P+1,N|b_r^{\dagger}|\psi_0\rangle$ and $\langle\psi_0|b_r^{\dagger}|P-1,N\rangle_n$, respectively.

As known in the purely electronic case, the dynamic self-energy is intimately related to the so-called two-particle–one-hole response function.[11] A similar relation can be established for the positron and electron self-energies of a composite electronic-positronic system. However, we now have two types of particles which must be taken into consideration explicitly. We define a Green's function with several indices which can be electronic and positronic and give as an example a six-point function

$$G_{rik,sjl}=(-i)^3\langle\psi_0|T(b_r(t_r)a_i(t_i)a_k(t_k)a_l^{\dagger}(t_l)a_j^{\dagger}(t_j)b_s^{\dagger}(t_s))|\psi_0\rangle \ . \tag{4.8}$$

As seen, the last three indices refer to the Hermite conjugate operators and the sequence of the indices in front of the comma runs in the given order of the operators, whereas the indices behind the comma run in the opposite direction of the Hermite conjugate operators. We introduce a short-hand notation for the response functions

$$R_{123,1'2'3'}=G_{123,1'2'3'}-G_{23,3'4}G^{-1}_{45}G_{51,1'2'} \tag{4.9a}$$

where summation and time integration over doubly occurring indices is implied. The primed times, t'_1 for instance, refer to the primed indices in this definition, i.e., t'_1 refers to $1'$. The number of electronic indices must be even, the same being true for positronic indices. An example where indices are written explicitly reads

$$R_{rik,sjl}=G_{rik,sjl}-G_{ik,lm}G^{-1}_{mn}G_{nr,sj} \ . \tag{4.9b}$$

The response function needed in connection with the dynamic self-energy part is obtained by

$$\Pi_{123,1'2'3'}(t,t')=\lim_{\substack{t_1,t_2,t_3\mapsto t\\ t'_1,t'_2,t'_3\mapsto t'}} R_{1'23,2'3'1} \tag{4.10a}$$

and depends only on the time difference $t-t'$. As an example we give $\Pi_{jsk,lvm}$:

$$\begin{aligned}\Pi_{jsk,lvm}(t,t')&=\lim_{\substack{t_j,t_s,t_k\mapsto t\\ t_1,t_v,t_m\mapsto t'}} R_{lsk,vmj}\\ &=\lim_{\substack{t_j,t_s,t_k\mapsto t\\ t_1,t_v,t_m\mapsto t'}} (G_{lsk,vmj}-G_{sk,jx}G^{-1}_{xy}G_{yl,vm}) \ .\end{aligned} \tag{4.10b}$$

Carrying out a similar calculation as done for the purely electronic case, we obtain for the dynamic self-energy the following result:

$$\begin{aligned}M_{\rho\sigma}=\sum[\,&\tfrac{1}{4}V_{\rho r(st)}\Pi_{rst,uvw}V^*_{\sigma u(vw)}\\ &+(-V_{\rho jsk})\Pi_{jsk,lvm}(-V^*_{\sigma lvm})\\ &+\tfrac{1}{2}(-V_{\rho ksj})\Pi_{ksj,uvw}V^*_{\sigma u(vw)}\\ &+\tfrac{1}{2}V_{\rho r(st)}\Pi_{rst,lvm}(-V^*_{\sigma lvm})]\end{aligned} \tag{4.11}$$

where summation is supposed over all indices except ρ and σ. The negative sign of the electron-positron attraction is explicitly indicated. The notation is as in the preceding sections: i,j,k,l,m denote electronic indices, r,s,t,u,v denote positronic indices. ρ and σ denote positronic indices of the self-energy. Of course, if we consider the electronic self-energy we have only to change all positronic indices into electronic ones and vice versa. Note that a factor $\frac{1}{2}$ is attached to each positronic interaction matrix element V_{uvsr}. In the purely positronic case only the first term on the right-hand side of (4.11) has to be considered.

We now introduce an index restriction whenever a purely positronic V appears and define two column vectors

$$\begin{aligned}(\underline{V}_{++\rho})_{stu}&=V^*_{\rho s(tu)}, \quad \text{with } t<u\\ (\underline{V}_{+-\rho})_{isj}&=-V^*_{\rho isj} \ .\end{aligned} \tag{4.12a}$$

These vectors can be put together into a single vector which reads

$$\underline{V}_\rho=\begin{bmatrix}\underline{V}_{++\rho}\\ \underline{V}_{+-\rho}\end{bmatrix} \ . \tag{4.12b}$$

Analogously we define a 2×2 block matrix for the four types of Π which appear in (4.11):

$$\underline{\Pi}=\begin{bmatrix}\Pi_{rst,uvw} & \Pi_{rst,lvm}\\ \Pi_{ksj,uvw} & \Pi_{jsk,lvm}\end{bmatrix} \ . \tag{4.12c}$$

The final result for the dynamic self-energy part

$$M(\omega)_{\rho\sigma}=\underline{V}^\dagger_\rho\underline{\Pi}(\omega)\underline{V}_\sigma \tag{4.13}$$

now takes on the same formal appearance as in the purely electronic case. Equations (4.12) and (4.13) make clear that the situation is more complex than in the latter case. In particular, more elements appear and the configuration space of $\underline{M}(\omega)$ contains additional types of excitations which have to be taken care of when working equations are derived (see next section).

B. Algebraic diagrammatic construction scheme

The algebraic diagrammatic construction (ADC) is a scheme to carry out in a systematic manner infinite partial summations of Feynman diagrams. The nth-order scheme ADC(n) is complete to nth order, i.e., it contains *all* the Feynman diagrams up to nth order and infinitely many diagrams of higher orders. The choice of the latter diagrams is automatically dictated by the former ones and the analytic structure of the exact dynamic self-energy part. The scheme can be applied to a single component of the Green's function[12,32,33] or directly to the dynamic self-energy part.[11] In the present work we follow the latter possibility. Since the method is described in detail in the literature[11] for electronic systems, we discuss it here only briefly and concentrate on the differences arising due to the presence of positrons.

The self-energy is given in the preceding section in the diagonal representation where its poles are explicitly displayed. A general nondiagonal representation is obtained by inserting unity $\underline{Y}\,\underline{Y}^\dagger=\underline{1}$, where $\underline{Y}$ is a unitary matrix, twice into Eq. (4.2). The result takes on the following appearance:

$$\underline{M}^{(\mathrm{I})}=\underline{U}^{(\mathrm{I})\dagger}(\omega\underline{1}-\underline{K}^{(\mathrm{I})}-\underline{C}^{(\mathrm{I})})^{-1}\underline{U}^{(\mathrm{I})} \tag{4.14a}$$

where

$$\underline{U}^{(\mathrm{I})}=\underline{Y}^\dagger\underline{m}^{(\mathrm{I})} \ , \tag{4.14b}$$

$$\underline{K}^{(\mathrm{I})}+\underline{C}^{(\mathrm{I})}=\underline{Y}^\dagger\underline{\Omega}^{(\mathrm{I})}\underline{Y} \ . \tag{4.14c}$$

Analogous relations hold for $\underline{M}^{(\mathrm{II})}$ with a different choice of the transformation $\underline{Y}$, of course. With the above, the matrix $\underline{A}$ in (4.4) is transformed to

$$\underline{A}'=\begin{bmatrix}\underline{e}+\underline{\Sigma}(\infty) & \underline{U}^{(\mathrm{I})\dagger} & \underline{U}^{(\mathrm{II})\dagger}\\ \underline{U}^{(\mathrm{I})} & (\underline{K}+\underline{C})^{(\mathrm{I})} & \underline{0}\\ \underline{U}^{(\mathrm{II})} & \underline{0} & (\underline{K}+\underline{C})^{(\mathrm{II})}\end{bmatrix} \tag{4.15a}$$

and the equation (4.5) for the Green's function remains unaltered:

$$G_{rs}(\omega)=[\omega\underline{1}-\underline{A}']^{-1}_{rs}\ . \tag{4.15b}$$

From now on we shall drop the superscripts (I) and (II) whenever necessary. The ADC makes use of the perturbation expansion of the effective coupling matrix $\underline{U}$ and the effective interaction matrix $\underline{C}$ in terms of the electron-electron and positron-positron repulsion, and positron-electron attraction:

$$\underline{U}=\underline{U}^{(1)}+\underline{U}^{(2)}+\underline{U}^{(3)}+\cdots\ , \tag{4.16a}$$

$$\underline{C}=\underline{C}^{(1)}+\underline{C}^{(2)}+\underline{C}^{(3)}+\cdots\ . \tag{4.16b}$$

It is noted that the expansion of the effective coupling and effective interaction matrices begins in first order of perturbation theory. $\underline{K}$ is defined as the zeroth order of the right-hand side of (4.14c). The perturbation expansion of the self-energy itself immediately follows from (4.16) and

$$\begin{aligned}(\omega\underline{1}-\underline{K}-\underline{C})^{-1}=(\omega\underline{1}-\underline{K})^{-1}\\ \times[\,\underline{1}+\underline{C}(\omega\underline{1}-\underline{K})^{-1}\\ +\underline{C}(\omega\underline{1}-\underline{K})^{-1}\underline{C}(\omega\underline{1}-\underline{K})^{-1}+\cdots\,]\end{aligned} \tag{4.17}$$

The result reads

$$\begin{aligned}\underline{M}(\omega)=\ &\underline{U}^{(1)\dagger}(\omega\underline{1}-\underline{K})^{-1}\underline{U}^{(1)}+\underline{U}^{(2)\dagger}(\omega\underline{1}-\underline{K})^{-1}\underline{U}^{(1)}\\ &+\underline{U}^{(1)\dagger}(\omega\underline{1}-\underline{K})^{-1}\underline{U}^{(2)}\\ &+\underline{U}^{(1)\dagger}(\omega\underline{1}-\underline{K})^{-1}\underline{C}^{(1)}(\omega\underline{1}-\underline{K})^{-1}\underline{U}^{(1)}+\cdots\end{aligned} \tag{4.18}$$

where all terms up to third order are displayed explicitly. In the ADC the expansions of $\underline{U}$ and $\underline{C}$ are determined by comparing (4.18) with the expansion of the self-energy via Feynman diagrams. As can be seen from (4.18) the expansion of the dynamic self-energy begins in second order. Equating the Feynman diagrams of second order and the first term on the right-hand side of (4.18) allows the determination of $\underline{U}^{(1)}$. The Feynman diagrams of third order can be divided into two sets according to their dependence on $(\omega\underline{1}-\underline{K})^{-1}$. Since $\underline{U}^{(1)}$ is already known, one set of diagrams determines $\underline{U}^{(2)}$ and the other allows the evaluation of $\underline{C}^{(1)}$ [see last term on the right-hand side of (4.18)]. Higher orders are computed analogously. The Feynman diagrams up to nth order are used to evaluate $\underline{U}$ and $\underline{C}$. The resulting quantities are then inserted into (4.14a) to obtain the dynamic self-energy part in ADC(n). The Dyson equation is solved via the eigenvalue equation for the matrix $\underline{A}'$ in (4.15). It should be noted that the resulting self-energy and Green's function are in ADC(n) correct up to nth order and contain infinitely many terms of higher orders. On the other hand, the perturbation expansion (4.18) used to determine $\underline{U}$ and $\underline{C}$ only includes terms up to nth order, and, more importantly, exhibits an incorrect dependence on ω not shared by the exact and ADC self-energy parts which are both subject to a spectral representation.

From the spectral representation of the one-particle Green's function (3.7a) we see that the space of the matrix $\underline{A}'$ comprises all possible states in the $(N,P+1)$ and $(N,P-1)$ systems. Since the target system is (N,P), i.e., contains N electrons and P positrons, we may classify this space by $p, 2p1h, 3p2h, \ldots$ and $h, 2h1p, 3h2p, \ldots$ excitations, where h and p denote holes and particles, respectively. In contrast to the purely electronic case, the excitation can now be electronic and/or positronic. We indicate by the superscripts plus and minus positronic and electronic excitations, respectively. As can be seen from (4.15), the particle and hole space of $\underline{\epsilon}+\underline{\Sigma}(\infty)$ is positronic, i.e., p^+ and h^+, if the positronic Green's function is studied. Equation (4.15a) implies that the space of $\underline{M}^{(\mathrm{I})}$ comprises the excitations $2p1h, 3p2h, \ldots,$ which explicitly include

$$2p^+1h^+,1p^+1p^-1h^-\ ,$$

$$3p^+2h^+,2p^+1p^-1h^+1h^-,1p^+2p^-2h^-\ ,$$

etc. The space $1p^+1p^-1h^-$, for instance, is spanned by all possible excitations where a positron is added to a vacant orbital and an electron is removed from an occupied orbital and inserted into an orbital vacant in the unperturbed ground state of the (N,P) target system. The resulting system is characterized by N electrons and $P+1$ positrons. Analogously, $\underline{M}^{(\mathrm{II})}$ comprises the excitations $2h1p, 3h2p, \ldots,$ which explicitly include

$$2h^+1p^+,1h^+1h^-1p^-\ ,$$

$$3h^+2p^+,2h^+1h^-1p^+1p^-,1h^+2h^-2p^-\ ,$$

etc. which characterize a system with N electrons and $P-1$ positrons. If the electronic Green's function of (N,P) is studied, we just have to interchange P and N as well as plus and minus.

Finally, we mention that the size of the configuration space needed in ADC(n) is restricted. In ADC(2) the space comprises $2p1h$ and $2h1p$ excitations and grows by $1p1h$ excitation at every higher order at which n is even. The configuration space required by ADC(n) is substantially smaller than that which is required by Rayleigh-Schrödinger perturbation theory for obtaining the same energies accurate to nth order. For a detailed discussion of this relevant aspect of ADC, see Ref. 11.

C. Positron-molecule bound and scattering states

The case where the target system is purely electronic, for example, a molecule, is of particular interest and is treated first. The positronic Green's function then describes the attachment of a positron to the system. If the positron is bound we may compute its binding energy (or positron affinity), else only its scattering states, and relate them to available experiments. Since $P=0$, we cannot remove a positron from the target and the positronic Green's function consists only of the first term shown on the right-hand side of (3.7a). Analogously, the expression for the dynamic self-energy part simplifies considerably and reads

$$M_{p\sigma}=\sum V_{pjsk}\Pi_{jsk,lvm}V^{*}_{\sigma lvm} \tag{4.19}$$

with summation over doubly occurring indices on the right-hand side of (4.19). In particular, $\underline{M}^{(\mathrm{II})}=0$ and we can omit the last column and row of $\underline{A}$ and $\underline{A}'$.

The ADC simplifies as well since we are left with $\underline{U}^{(\mathrm{I})}$ and $\underline{C}^{(\mathrm{I})}$ and the number of Feynman diagrams is small. All time-ordered diagrams which contain a positron line pointing downwards vanish. In ADC(2) and ADC(3) the configuration space is restricted to $1p^{+}1p^{-}1h^{-}$ excitations and the nonvanishing elements of $\underline{K}^{(\mathrm{I})}$ read

$$K^{(\mathrm{I})}_{jsk,jsk}=e_s+\epsilon_k-\epsilon_j;\quad \bar{n}_s\bar{n}_k n_j=1 \tag{4.20}$$

where n_p is the occupation number of orbital p which can be either 1 or 0 and $\bar{n}_p=1-n_p$. Since $\underline{U}^{(\mathrm{I})}$ begins at first order, the dynamic self-energy at second order is readily obtained from (4.19) if Π is calculated to zeroth order. The same result follows, of course, by evaluating the diagram of second order depicted in Fig. 6. Since $P=0$, only a single time-ordered diagram of second order is available giving

$$M(\omega)_{p\sigma}=\sum_{s,k,j}(-V_{pjsk})\frac{\bar{n}_s\bar{n}_k n_j}{\omega-e_s-\epsilon_k+\epsilon_j}(-V_{sk\sigma j})\,. \tag{4.21}$$

A brief comparison with the first term on the right-hand side (4.18) determines $\underline{U}^{(1)}$

$$U^{(1)}_{\sigma jsk}=-V^{*}_{\sigma jsk}=-V_{sk\sigma j} \tag{4.22}$$

and completes the calculation of $\underline{M}(\omega)$ on the ADC(2) level.

To proceed we need the Feynman diagrams of third order. Each Feynman diagram of nth order stands for $n!$ time-ordered diagrams. For $P=0$ most Feynman diagrams vanish and this is also true for the time-ordered diagrams of a contributing Feynman diagram. From the six time-ordered diagrams of second order only a single one does not vanish. In third order we encounter 108 time-ordered diagrams which contribute to the dynamic self-energy if $P\neq0$. Their number is reduced to 8 by setting $P=0$. These diagrams are shown in Fig. 6. Following the rules to evaluate Feynman diagrams, the diagrams $A1$, $B1$, C, and D have denominators quadratic in ω owing to the two cuts available. Accordingly, these diagrams are seen to contribute to the term

$$\underline{U}^{(1)\dagger}(\omega\underline{1}-\underline{K})^{-1}\underline{C}^{(1)}(\omega\underline{1}-\underline{K})^{-1}\underline{U}^{(1)}$$

in the expansion of the self-energy. Adding up the contributions of the above diagrams leads to

$$C^{(1)}_{jsk,j's'k'}=\delta_{ss'}V_{kj'(jk')}-\delta_{jj'}V_{sks'k'}+\delta_{kk'}V_{sj's'j} \tag{4.23}$$

for the first order of the effective interaction. For the external indices jsk and $j's'k'$ we have used here $n_j\bar{n}_s\bar{n}_k=1$ and $n_{j'}\bar{n}_{s'}\bar{n}_{k'}=1$, respectively. The first term on the right-hand side of (4.23) arises from diagrams $A1$ and $B1$, the second and third terms from the diagrams C and D, respectively.

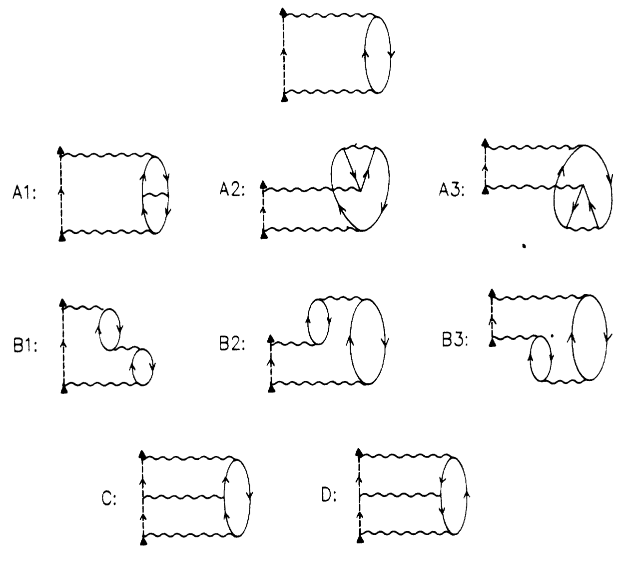

FIG. 6. The time-ordered diagrams contributing to the dynamic positron self-energy part in the absence of positrons in the target system. All diagrams of second and third order are shown.

The remaining time-ordered diagrams of Fig. 6 contribute to the second and third terms in the expansion of $\underline{M}(\omega)$ given in (4.18). The diagrams $A2$ and $B2$ clearly correspond to the second term in this expansion. They are sufficient for obtaining the effective coupling to second order. The result takes on the following appearance:

$$U^{(2)}_{\sigma jsk}=-\sum_{j'k'}V_{kk'(jj')}\frac{n_{j'}\bar{n}_{k'}}{\epsilon_j+\epsilon_{j'}-\epsilon_k-\epsilon_{k'}}V_{sj'\sigma k'}\,. \tag{4.24}$$

The computation of $\underline{U}^{(\mathrm{I})}$ to second order completes the calculation of $\underline{M}(\omega)$ on the ADC(3) level. The ADC(3) dynamic self-energy is obtained by inserting

$$\begin{aligned}&\underline{U}=\underline{U}^{(1)}+\underline{U}^{(2)}\,,\\&\underline{C}=\underline{C}^{(1)}\end{aligned} \tag{4.25}$$

into Eq. (4.14a). The static self-energy can be determined as explained in Sec. III B 1 and the Dyson equation can subsequently be solved either directly or by solving the secular equation for the matrix $\underline{A}'$. The binding energy of the positron and/or the scattering cross sections obtained are correct to third order and enjoy the advantage of being determined in a size-consistent manner.

D. ADC(3) working equations for a composite system

In the general case where the target system contains electrons and positrons both parts $\underline{M}^{(\mathrm{I})}$ and $\underline{M}^{(\mathrm{II})}$ contribute to the one-particle Green's function. Furthermore, the excitation space grows due to the presence of positrons in the target. In ADC(2) and ADC(3) this space comprises $1p^{+}1p^{-}1h^{-}$ and $2p^{+}1h^{+}$ excitations for $\underline{M}^{(\mathrm{I})}$

and $1h^+1h^-1p^-$ and $2h^+1p^+$ for $\underline{M}^{(\mathrm{II})}$. The nonvanishing elements of $\underline{K}^{(\mathrm{I})}$ now read

$$K^{(\mathrm{I})}_{jsk,jsk}=e_s+\epsilon_k-\epsilon_j;\quad \bar{n}_s\bar{n}_k n_j=1\ , \tag{4.26a}$$

$$K^{(\mathrm{I})}_{rst,rst}=e_s+e_t-e_r;\quad \bar{n}_s\bar{n}_t n_r=1\ , \tag{4.26b}$$

and those of $\underline{K}^{(\mathrm{II})}$ have the same appearance except that particles and holes must be exchanged, i.e., $n_s n_k \bar{n}_j=1$ and $n_s n_t \bar{n}_r=1$ hold instead of $\bar{n}_s\bar{n}_k n_j=1$ and $\bar{n}_s\bar{n}_t n_r=1$, respectively.

In second order one encounters six time-ordered diagrams and their number grows to as much as 108 in third order. Fortunately, the 60 time-ordered diagrams of third order in which all the hole and particle lines are positronic are, up to a trivial renaming of indices, identical to those already investigated in Ref. 11 for the purely electronic case. This also applies to quantities of the ADC resulting from these diagrams. The additional Feynman diagrams arising due to the fact that we have a composite system are the diagrams of second order and the diagrams *A*1, *B*1, *C*, and *D* of third order depicted in Fig. 6 (now as Feynman diagrams, i.e., all possible time orderings must be considered) as well as the diagrams collected in Fig. 7.

We first discuss $\underline{M}^{(\mathrm{I})}$ and drop the superscript (I) unless explicitly needed. The effective coupling matrix $\underline{U}$ must be calculated for both excitation spaces indicated in (4.26). In first order we find

$$U^{(1)}_{\sigma,jsk}=-V^{*}_{\sigma jsk}\ , \tag{4.27a}$$

$$U^{(1)}_{\sigma,rst}=V^{*}_{\sigma r(st)}\ . \tag{4.27b}$$

The term $U^{(1)}_{\sigma,jsk}$ is obviously the same as in the $P=0$ case and $U^{(1)}_{\sigma,rst}$ can be obtained from the second-order diagrams where all lines are positronic. Equations (4.26) and (4.27) complete the evaluation of the ADC(2). The evaluation of the ADC(3) is much more complicated since even $U^{(2)}_{\sigma,jsk}$ contains a number of terms not appearing in the $P=0$ situation. Some of these terms arise from the remaining time-ordered diagrams corresponding to *C* and *D* in Fig. 6. The diagrams shown in Fig. 7 contribute, on the other hand, to both $U^{(2)}_{\sigma,jsk}$ and $U^{(2)}_{\sigma,rst}$. For the $1p^+1p^-1h^-$ configuration space our final result reads

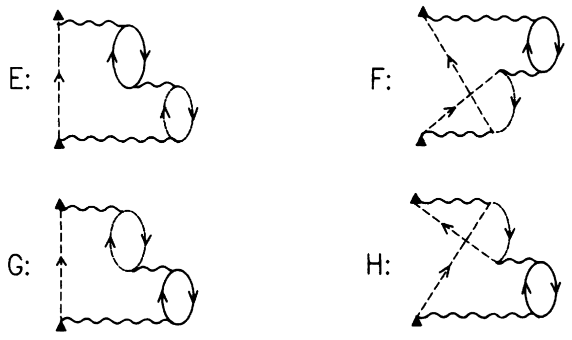

FIG. 7. Feynman diagrams contributing to the dynamic positron self-energy part in the presence of positrons in the target system. To have all the Feynman diagrams in second and third order one has to add the Feynman diagrams of the purely positronic case (these diagrams have only positron lines and are identical to those given in the literature for the purely electronic case), the second-order and third-order diagrams *A*1, *B*1, *C* and *D* shown in Fig. 6, but considered as Feynman diagrams.

$$\begin{aligned}U^{(2)}_{\sigma,jsk}=\ &U^{(2)}_{\sigma,jsk}(P=0)\\ &-\sum_{k',v}V_{sk'vj}\frac{n_v\bar{n}_{k'}}{\epsilon_j+e_v-\epsilon_{k'}-e_s}V^{*}_{\sigma k'vk}\\ &+\sum_{j',v}V_{skvj'}\frac{n_v n_{j'}}{\epsilon_{j'}+e_v-\epsilon_k-e_s}V^{*}_{\sigma jvj'}\\ &-\sum_{u,v}V_{kujv}\frac{n_v\bar{n}_u}{\epsilon_j+e_v-\epsilon_k-e_u}V^{*}_{\sigma u(sv)}\end{aligned} \tag{4.28a}$$

where the first term on the right-hand side stands for the result obtained for the purely electronic target and given in (4.24). For the $2p^+1h^+$ configuration space the result can be written more compactly:

$$U^{(2)}_{\sigma,rst}=U^{(2)}_{\sigma,rst}(N=0)+\sum_{k,j}V_{ktjr}\frac{\bar{n}_k n_j}{\epsilon_j+e_r-\epsilon_k-e_t}V^{*}_{\sigma ksj} \tag{4.28b}$$

since most of the contributing terms are included in the first expression on the right-hand side of the equation. This expression stands for the result of a purely positronic target and is easily determined from the analogous expression in Ref. 11 for electrons.

Due to the enlarged excitation space the effective interaction $\underline{C}$ contains four kinds of matrix elements. In first order $C^{(1)}_{jsk,j's'k'}$ is identical with the result (4.23) obtained for a positron-free target. The elements $C^{(1)}_{rst,r's't'}$ are identical with the result of Ref. 11 for the electronic Green's function if we rename the positronic indices to electronic ones. We are left to determine the effective interaction matrix elements which couple the spaces $1p^+1p^-1h^-$ and $2p^+1h^+$. These elements easily follow from diagrams *E* and *G* in Fig. 7. Only the time ordering as depicted in the figure contributes to $\underline{C}^{(1)}$. From *E* and *G* we readily find

$$C^{(1)}_{jsk,rs't}=-\delta_{ss'}V_{krjt}\ , \tag{4.29a}$$

$$C^{(1)}_{rst,js'k}=-\delta_{ss'}V_{tjrk}\ , \tag{4.29b}$$

respectively.

The above completes the evaluation of $\underline{M}^{(\mathrm{I})}$ on the ADC(3) level. Generally, the knowledge of explicit expressions of $\underline{C}^{(\mathrm{I})}$ and $\underline{U}^{(\mathrm{I})}$ is sufficient to determine the analogous expressions of $\underline{C}^{(\mathrm{II})}$ and $\underline{U}^{(\mathrm{II})}$ and hence of $\underline{M}^{(\mathrm{II})}$. The *q*th order of these quantities specified by (II) follows directly from those of (I):

$$\underline{M}^{(\mathrm{II})(q)}(n,\bar{n})=(-1)^q\underline{M}^{(\mathrm{I})(q)}(\bar{n},n)\ , \tag{4.30a}$$

$$\underline{C}^{(\mathrm{II})(q)}(n,\bar{n})=(-1)^q\underline{C}^{(\mathrm{I})(q)}(\bar{n},n)\ , \tag{4.30b}$$

$$\underline{U}^{(\mathrm{II})(q)}(n,\bar{n})=(-1)^{q+1}\underline{U}^{(\mathrm{I})(q)}(\bar{n},n)\ . \tag{4.30c}$$

Note the extra $+1$ in the exponent of the latter expression. n denotes holes and $\bar{n}$ particles. To obtain the quantities specified by (II) from those specified by (I) one has to replace the hole indices by particle indices and vice versa.

V. CONCLUDING REMARKS

The generalized Hartree-Fock particles of the composite system represent the best independent particles in analogy to the Hartree-Fock particles in an electronic or nuclear system. Although the diagrammatic analysis can be carried out with any choice of an unperturbed Hamiltonian, the use of the generalized Hartree-Fock Hamiltonian simplifies the analysis by considerably reducing the number of contributing Feynman diagrams. The electron and positron Green's functions are evaluated via the Dyson equation which, as usually, relates them to their self-energies. These play the role of optical potentials in scattering calculations. The self-energies consist of a static and a dynamic part. The static part is of particular relevance in cases of strongly correlated target systems. It is shown that this part can be calculated from the dynamic part. Particular attention has, therefore, been paid to the exact properties and approximate evaluation of the latter.

After the identification of the contributing elementary excitations, the ideas behind the ADC can also be used for composite systems. The working equations of the ADC(3) have been derived explicitly. For a general composite system, the equations, of course, contain several terms more than for a purely, e.g., electronic, system. However, the numerical evaluation of the ADC(3) should be manageable also for a composite system. On the other hand, if we are interested in the bonding (or scattering) of a single particle to (by) a system of different particles, the ADC(3) working equations as well as the Dyson equation become particularly simple. It is then even possible to derive and apply ADC(4) equations.

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APPENDIX: RULES FOR FEYNMAN DIAGRAMS OF ELECTRONIC-POSITRONIC COMPOSITE SYSTEMS

Drawing rules. To obtain the nth-order Feynman diagrams of the one-particle Green's function draw all *connected* topologically distinct diagrams with all possible combinations of n_1 interactions V_{abcd} and n_2 interactions W_{ac} connected by $2n_1+n_2+1$ G^0 lines. Of course, $n_1+n_2=n$. The symbols for the interactions and G^0 lines are given in Fig. 1. The n interactions are drawn one above the other, the vertical axis being the time axis. Two G^0 lines enter and two exit each interaction V_{abcd}. Analogously, one G^0 line enters and one exits each W_{ac}. Each Feynman diagram begins with a G^0 line connected to an interaction only at its upper end and ends with a G^0 line connected to an interaction only at its lower end. If these external G^0 lines are positron (electron) lines, the diagram belongs to the positron (electron) Green's function. Note that each pair of indices (a,c) and (b,d) can be electronic or positronic. Consequently, if a positron G^0 line enters the interaction W_{ac}, a positron line must exit it, etc.

We remind the reader that the use of the generalized Hartree-Fock potential reduces the number of diagrams. Then $n_2=0$, i.e., only the interactions V_{abcd} must be taken into account, and, in addition, diagrams have to be omitted in which the same G^0 line enters and exits the interaction V_{abcd}.

The Feynman diagrams for the self-energy part are easily obtained from those of the Green's function. Only those diagrams contribute which do not disconnect upon cutting a single G^0 line into two lines. After identifying the contributing diagrams just remove its external G^0 lines.

Evaluation rules. To each interaction in a diagram of a Green's function a time variable t_ν is attributed. The external times of the diagram are t' and t. Multiply all interactions and all G^0 functions appearing in the diagram, integrate over all internal times t_ν and sum over all internal indices. Multiply the result by an overall factor $i^n(-1)^{L+n_3}$. L is the number of loops in the diagram and n_3 is the number of interactions V_{abcd} between electrons and positrons, i.e., two of the indices are positronic and two electronic.

With slight modifications these rules also apply to diagrams of the self-energy part. Since the external G^0 lines have been removed from the diagrams, the corresponding interactions carry the external times t' and t. Therefore there are two time variables t_ν less to integrate over. Otherwise all rules stay the same as above except that the overall factor now reads $i^n(-1)^{L+n_3+1}$.

We now turn to the rules to evaluate diagrams directly in ω space. These rules can be derived from the rules in time space. Draw all time-ordered diagrams. From each nth-order Feynman diagram of the Green's function $(n+2)!$ time-ordered diagrams result ($n!$ for the self-energy part) by permuting the times t', t, and the t_ν. Each of these time-ordered diagrams must be evaluated separately. We note that the diagrams of the self-energy part with $t>t'$ contribute to $\underline{M}^{(\mathrm{I})}$, those with $t<t'$ to $\underline{M}^{(\mathrm{II})}$, and those with $t=t'$ to the static self-energy (the external G^0 lines which have been removed to obtain the latter diagrams were both attached to the same interaction element).

Draw auxiliary horizontal lines between all two successive times, i.e., $n+1$ and $n-1$ auxiliary lines for a Green's function and self-energy diagram, respectively. Each auxiliary line contributes a multiplicative term $1/x$ to the diagram. x is easy to calculate: each G^0_{aa} line cut by the auxiliary line contributes additively ϵ_a (or e_a if a is a positron index) to x. The orbital energy enters with a plus (minus) sign if the G^0 line points downwards (upwards). If the auxiliary line is between t and t' add $+\omega$ or $-\omega$ to x according to whether $t>t'$ or $t<t'$. Remember that a hole line (particle line) [G^0 line pointing downwards (upwards)] is associated with an occupied (empty) orbital.

Multiply all the interactions and the contributions of the auxiliary lines and sum over all the internal indices. The final expression of the diagram is obtained by multiplying the result by the overall factor $-(-1)^{n_3+L+H}$ for a Green's-function diagram and by $(-1)^{n_3+L+H}$ for a self-energy diagram, where H is the number of hole lines.

As an example we briefly discuss the evaluation of a particular time-ordered diagram $E1$ obtained from the Feynman diagram E in Fig. 8 by choosing the time ordering $t_1 > t > t'$. In this figure both diagrams are shown together with time variables and all necessary indices. (Since G^0_{ab} vanishes if $a \neq b$, it is sufficient to attribute a single index to each G^0 line). Obviously the diagram belongs to $M^{(\mathrm{I})}_{rs}$. In ω space the expression for the time-ordered diagram takes on the appearance

$$E1=(-1)^6 \sum_{k,j,u,u',v} V_{jvku} \frac{n_j n_v \bar{n}_k \bar{n}_u}{\epsilon_j + e_v - \epsilon_k - e_u} \times V_{rku'j} \frac{\bar{n}_{u'}}{\omega + e_v - e_u - e_{u'}} V_{u'usv} \, .$$

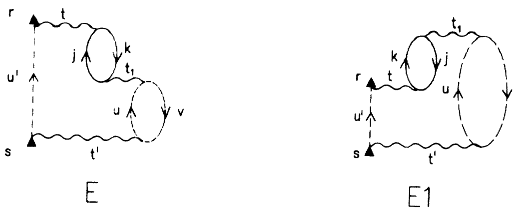

FIG. 8. A self-energy Feynman diagram E and a time-ordered diagram $E1$. Since E is a Feynman diagram, t, t', and t_1 are not related and each runs independently from $-\infty$ to $+\infty$. Since $E1$ has been defined to be a time-ordered diagram, we have to take the depicted time ordering literally: The internal time t_1 is larger than the external times t and t' ($t > t'$). r and s are (positronic) external indices.

The diagram contains two loops ($L=2$), two hole lines ($H=2$), and two Coulomb interactions between positrons and electrons ($n_3=2$). Only one auxiliary line is between t and t' leading to a single ω-dependent contribution.

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