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Total energies from variational functionals of the Green function and the renormalized four-point vertex

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We derive variational expressions for the grand potential or action in terms of the many-body Green function G which describes the propagation of particles and the renormalized four-point vertex Γ which describes the scattering of two particles in many-body systems. The main ingredient of the variational functionals is a term we denote as the Ξ-functional which plays a role analogously to the usual Φ-functional studied by Baym [G. Baym, Phys. Rev. **127**, 1391 (1962)] in connection with the conservation laws in many-body systems. We show that any Ξ-derivable theory is also Φ-derivable and therefore respects the conservation laws. We further set up a computational scheme to obtain accurate total energies from our variational functionals without having to solve computationally expensive sets of self-consistent equations. The input of the functional is an approximate Green function $\tilde{G}$ and an approximate four-point vertex $\tilde{\Gamma}$ obtained at a relatively low computational cost. The variational property of the functional guarantees that the error in the total energy is only of second order in deviations of the input Green function and vertex from the self-consistent ones that make the functional stationary. The functionals that we will consider for practical applications correspond to infinite order summations of ladder and exchange diagrams and are therefore particularly suited for applications to highly correlated systems. Their practical evaluation is discussed in detail.

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I. INTRODUCTION

Total energy calculations play an important role in condensed matter physics and quantum chemistry. For solid state physicists they are essential in predicting structural changes and bulk moduli in solids. In chemistry molecular bonding curves and potential energy surfaces are essential to understand phenomena such as molecular dissociation and chemical reactions. However, accurate total energy calculations are notoriously difficult and computationally demanding. In quantum chemistry there are advanced wave function methods such as configuration interaction and coupled cluster theory[1] to calculate energies but they can only be applied to relatively small molecules. In solid state physics most total energy calculations for crystals or surfaces are based on density functional theory[2] where the density functionals are mostly based on the local density approximation (LDA) and generalized gradient approximations (GGA).[3] These functionals have had great success but there are many cases where the functionals fail, in which case there is no clear systematic route to improvement. We have therefore recently advanced a different scheme which involves variational energy functionals of the many-body Green function and applied it successfully to calculate total energies of atoms, molecules,[4–8] and the electron gas.[9] A variety of such functionals can be systematically constructed using diagrammatic perturbation theory in which the different functionals correspond to different levels of perturbation theory. For these functionals we use input Green functions that are relatively easy to obtain at low computational cost, for instance from a local density or Hartree-Fock calculation. The variational property of the functional then assures that the errors in the energy are only of second order in the difference between our approximate Green function and the actual Green function that makes the functional stationary. This is the essential feature that allows one to obtain accurate total energies at a relatively low computational cost.[8] The remaining question is then how to select approximate variational functionals that yield good total energies.

In a diagrammatic expansion in many-body perturbation theory the building blocks are the Green function line G, which describes the propagation of particles and holes, and the interaction line v which in electronic systems is represented by the Coulomb repulsion between the electrons. From this diagrammatic structure one can proceed to construct variational functionals in several ways. First of all we can renormalize the Green function lines. This leads to a functional that has been studied by Luttinger and Ward[10] and leads to a functional we will call the Φ-functional $\Phi[G,v]$, depending on the dressed Green function and the bare two-particle interaction v. The Luttinger-Ward functional has been applied, with great success, to the calculation of total energies of the electron gas,[9,18] and atoms and molecules.[4–8,13] This type of functional has also received considerable attention for Hubbard lattice type systems.[11–16] Apart from renormalization of the Green function lines, we can also decide to renormalize the interaction lines by replacing the bare interaction by a dynamically screened one, usually denoted by W. This leads to the functional $\Psi[G,W]$ that was investigated in a paper by Hedin[17] and later more completely by Almbladh *et al.*[9,18] and which has been applied with success to calculations of the total energy of the electron gas[9,18] and atoms.[5] This type of functional has also received considerable attention in the dynamical mean field theory (DMFT) community.[19–22] The natural place to use this functional is in extended systems in which screening of the long range Coulomb interaction is essential. Finally there is also the possibility to renormalize the four-point vertices and replace them by a renormalized four-point vertex Γ. In this work we will concentrate on this type of functional.

The natural place for variational functionals of the Green function G and the four-point vertex Γ is in systems where short range correlations play an important role such as in highly correlated systems. Such a type of theory was recently discussed in the work of Janiš[11,12] on the Hubbard model in which it was demonstrated how to derive the so-called parquet approximation from a functional of the Green function and the four-point vertex. Furthermore Katsnelson and Lichtenstein[23] have considered the electronic structure of correlated metals in which the building blocks of the theory are an approximate T matrix and a bare or noninteracting Green function (or a bare Green function in an effective correlated medium when using DMFT[24]). For describing the structural properties of such materials it would therefore be of great importance to be able to calculate the total energy from variational energy expressions in terms of the Green function and the four-point vertex where we use an approximate G and Γ as an input. The variational property then guarantees that the errors in the energy are only of second order in the deviations of the input Green function and vertex from the true quantities that make the functional stationary.

The construction of energy functionals in terms of G and Γ is most naturally done by the use of the Hugenholtz diagram technique[25–28] which has the bare four-point vertex as a diagrammatic building block. This procedure has been carried out in the early 1960s by De Dominicis[29,30] and later in more generality by De Dominicis and Martin[31,32] and leads to a functional we will call the Ξ-functional $\Xi[G,\Gamma]$. In the latter works the derivation has been carried out for a very general many-body system with not only one- and two-body interactions but also with $\frac{1}{2}$-body and $\frac{3}{2}$-body interactions that describe Bose-condensed and superconducting phases. Unfortunately this leads to rather involved equations and disguises the simpler case in which there are only one- and two-body interactions. For instance, in the general Bose-condensed and superconducting case no particle-particle and particle-hole contributions to the four-point vertex can be distinguished. The work of De Dominicis and Martin was aimed at demonstrating that one could express all thermodynamic quantities completely in terms of distribution functions rather than at a practical application of the formalism. In their work there is, therefore, no discussion of approximate functionals and of ways of evaluating them. However, nowadays the functionals can be subjected to numerical computation and it is therefore timely to discuss the formalism from this point of view and to present computational schemes to evaluate the functionals to calculate total energies. This is exactly the purpose of this work.

If we consider the first of the two papers of De Dominicis and Martin[31] we see that they use a purely algebraic approach to construct their functional which is not capable of displaying its full structure. Their second paper[32] uses a purely diagrammatic approach to derive in much more detail the structure of the functional but the derivation is quite difficult due to numerous intricate topological theorems that need to be discussed in order to avoid double counting of the diagrams. However, we found that a combination of both methods discussed in these two papers leads to a much quicker derivation of the final results. Therefore, in this work we derive, in an as simple as possible manner, a variational energy or action functional for normal systems using a purely algebraic method in combination with a diagrammatic analysis. We use, however, one generalization of the formalism of De Dominicis and Martin: since the Green functions are generated by differentiation of our functionals with respect to time-nonlocal potentials, the most natural framework to use is the Keldysh Green function technique.[33–36] We therefore consider generally time-dependent systems that are initially in thermodynamic equilibrium. This has two other advantages. First it allows for an elegant discussion of conservation laws which, as was shown by Baym,[37] are closely connected to Φ derivability. Such conservation laws were earlier discussed for variational energy and action functionals within the Φ and Ψ formalism in connection with time-dependent density-functional theory.[38] In particular we will show in this paper that also Ξ-derivable theories are conserving. Second, the use of finite temperature allows for an elegant treatment of the boundary conditions on the Green functions. These are, for instance, essential in going from the equations of motion for the Green function to the Dyson equation which will play an important role in our derivations.

The paper is divided as follows. We first discuss some definitions that form the basis of our subsequent analysis. We then derive self-consistent equations that relate the Green function and the renormalized four-point vertex. Then we provide a general construction of the variational functional using purely algebraic methods and we subsequently analyze the structure of the functional using diagrammatic methods. We then briefly discuss the conserving properties of the functional. Finally we discuss approximate functionals with details for their practical evaluation and present our conclusions and outlook.

II. DEFINING EQUATIONS

In the following we will consider a many-body system initially in thermodynamic equilibrium. At an initial time t_0 the system is subjected to a time-dependent external field. The Hamiltonian of the system in a time-dependent external potential $w(\mathbf{x}t)$ is (in atomic units) given by

$$\hat{H}(t) = \hat{h}(t) + \hat{V}, \tag{1}$$

where in the usual second quantization notation the one- and two-body parts of the Hamiltonian are given by

$$\hat{h}(t) = \int d\mathbf{x}\,\hat{\psi}^\dagger(\mathbf{x})h(\mathbf{x}t)\hat{\psi}(\mathbf{x}), \tag{2}$$

$$\hat{V} = \frac{1}{2}\int d\mathbf{x}d\mathbf{x}'\,v(\mathbf{r},\mathbf{r}')\hat{\psi}^\dagger(\mathbf{x})\hat{\psi}^\dagger(\mathbf{x}')\hat{\psi}(\mathbf{x}')\hat{\psi}(\mathbf{x}). \tag{3}$$

Here $\mathbf{x}=(\mathbf{r},\sigma)$ is a space-spin coordinate. The two-body interaction will usually be taken to be a Coulombic repulsion, i.e., $v(\mathbf{r},\mathbf{r}')=1/|\mathbf{r}-\mathbf{r}'|$. The one-body part of the Hamiltonian has the explicit form

$$h(\mathbf{x}t) = -\tfrac{1}{2}\nabla^2 + w(\mathbf{x}t) - \mu. \tag{4}$$

We further introduced the chemical potential μ in the one-body part of the Hamiltonian of Eq. (4) in anticipation of a finite temperature treatment of the system. We first consider the expectation value of an operator $\hat{O}$ for the case that the system is initially in an equilibrium state before a certain time t_0. For $t < t_0$ the expectation value of operator $\hat{O}$ in the Schrödinger picture is then given by $\langle\hat{O}\rangle = \mathrm{Tr}\{\hat{\rho}\hat{O}\}$, where $\hat{\rho} = e^{-\beta\hat{H}_0}/\mathrm{Tr}\, e^{-\beta\hat{H}_0}$ is the density matrix and $\hat{H}_0$ is the time-independent Hamiltonian that describes the system before the perturbation is switched on. We further defined $\beta = 1/k_B T$, with k_B the Boltzmann constant, to be the inverse temperature, and the trace involves a summation over a complete set of states in the Hilbert space. After we switch on the field the expectation value becomes a time-dependent quantity given by

$$\langle\hat{O}\rangle(t) = \mathrm{Tr}\{\hat{\rho}\hat{O}_H(t)\}, \tag{5}$$

where $\hat{O}_H(t) = \hat{U}(t_0,t)\hat{O}(t)\hat{U}(t,t_0)$ is the operator in the Heisenberg picture. The evolution operator $\hat{U}$ of the system is defined as the solution to the equations

$$i\partial_t \hat{U}(t,t') = \hat{H}(t)\hat{U}(t,t'), \tag{6}$$

$$i\partial_{t'} \hat{U}(t,t') = -\hat{U}(t,t')\hat{H}(t'), \tag{7}$$

with the boundary condition $\hat{U}(t,t) = 1$. The formal solution of Eq. (6) can be obtained by integration to yield the time-ordered expression $\hat{U}(t,t') = T\exp[-i\int_{t'}^{t} d\tau \hat{H}(\tau)]$ for $t > t'$ with a similar expression with antichronological time-ordering for $t' > t$. The operator $e^{-\beta\hat{H}_0}$ can now be regarded as an evolution operator in imaginary time, i.e., $\hat{U}(t_0 - i\beta, t_0) = e^{-\beta\hat{H}_0}$, if we define $\hat{H}(t)$ to be equal to $\hat{H}_0$ on the contour running straight from t_0 to $t_0 - i\beta$ in the complex time plane. We can therefore rewrite our expression for the expectation value as

$$\langle\hat{O}\rangle(t) = \frac{\mathrm{Tr}\{\hat{U}(t_0 - i\beta, t_0)\hat{U}(t_0,t)\hat{O}\hat{U}(t,t_0)\}}{\mathrm{Tr}\{\hat{U}(t_0 - i\beta, t_0)\}}. \tag{8}$$

If we read the time arguments of the evolution operators in the numerator of this expression from left to right we may say that the system evolves from t_0 along the real time axis to t after which the operator $\hat{O}$ acts. Then the system evolves back along the real axis from time t to t_0 and finally parallel to the imaginary axis from t_0 to $t_0 - i\beta$ (see Fig. 1). This observation motivates us to define the following action functional (compare with the action functionals used in Refs. 37 and 39)

$$Y = i \ln \mathrm{Tr}\{\hat{U}(t_0 - i\beta, t_0)\}, \tag{9}$$

where we define the evolution operator on the contour as

$$\hat{U}(t_0 - i\beta, t_0) = T_C \exp\left(-i\int dt \hat{H}(t)\right). \tag{10}$$

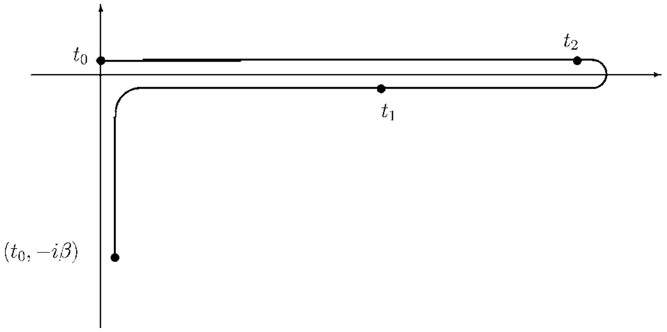

FIG. 1. The Keldysh contour drawn in the complex time plane.

Here the time integral is taken on the contour displayed in Fig. 1 and T_C denotes time-ordering along the contour.[34,36] When we evaluate this quantity for the equilibrium system we see that

$$iY = -\ln \mathrm{Tr}\{e^{-\beta\hat{H}_0}\} = \beta\Omega, \tag{11}$$

where Ω is the grand potential. Therefore the total energy E of the system is obtained from the zero-temperature limit

$$\lim_{T\to 0} \frac{iY}{\beta} = \lim_{T\to 0} \Omega = E - \mu N, \tag{12}$$

where N denotes the number of particles in the system. Let us now see how this functional can be used as a generating functional by making variations with respect to parameters in the Hamiltonian. To do this one needs to consider changes in the evolution operator $\hat{U}$ which are readily evaluated using Eqs. (6) and (7). For instance, when we make a perturbation $\delta\hat{V}(t)$ in the Hamiltonian we have using Eq. (6),

$$i\partial_t \delta\hat{U}(t,t') = \delta\hat{V}(t)\hat{U}(t,t') + \hat{H}(t)\delta U(t,t'), \tag{13}$$

with a similar differential equation with respect to t' and boundary condition $\delta\hat{U}(t,t) = 0$. The solution to this equation is given by

$$\delta\hat{U}(t,t') = -i\int_{t'}^{t} d\tau \hat{U}(t,\tau)\delta\hat{V}(\tau)U(\tau,t'), \tag{14}$$

from which variations in the action can be calculated. For instance, if we choose the perturbation to be a time-dependent and spatially nonlocal potential of the form

$$\delta\hat{V}(t) = \int d\mathbf{x}_1 d\mathbf{x}_2 \delta u(\mathbf{x}_1,\mathbf{x}_2,t)\hat{\psi}^\dagger(\mathbf{x}_1)\hat{\psi}(\mathbf{x}_2), \tag{15}$$

we obtain the time-dependent one-particle density matrix as a functional derivative with respect to Y,

$$\langle \hat{\psi}^{\dagger}(\mathbf{x}_1)\hat{\psi}(\mathbf{x}_2)\rangle(t) = \frac{\delta Y}{\delta u(\mathbf{x}_1,\mathbf{x}_2,t)}. \tag{16}$$

Similarly, when we consider a time-dependent two-body potential of the form

$$\delta\hat{V}(t) = \int d(\mathbf{x}_1\mathbf{x}_2\mathbf{x}_3\mathbf{x}_4)\,\delta V(\mathbf{x}_1\mathbf{x}_2\mathbf{x}_3\mathbf{x}_4,t) \times \hat{\psi}^{\dagger}(\mathbf{x}_1)\hat{\psi}^{\dagger}(\mathbf{x}_2)\hat{\psi}(\mathbf{x}_3)\hat{\psi}(\mathbf{x}_4), \tag{17}$$

we obtain the time-dependent two-particle density matrix as a derivative

$$\langle \hat{\psi}^{\dagger}(\mathbf{x}_1)\hat{\psi}^{\dagger}(\mathbf{x}_2)\hat{\psi}(\mathbf{x}_3)\hat{\psi}(\mathbf{x}_4)\rangle(t) = \frac{\delta Y}{\delta V(\mathbf{x}_1\mathbf{x}_2\mathbf{x}_3\mathbf{x}_4,t)}. \tag{18}$$

Note that in order to derive Eqs. (16) and (18) we had to make variations δu and δV for time variables on the contour. After the variation is made all observables are, of course, evaluated for physical quantities that are the same on the upper and lower branch of the contour. In the remainder of the paper we will heavily use the action functional as a generating functional for the many-body Green functions. To do this we have to generalize the time-local potentials u and V to time-nonlocal ones, such that the derivatives of Y with respect to these potentials become time-ordered expectation values that we can identify with the one- and two-particle Green functions G and G_2. By a subsequent Legendre transform we then can construct a variational functional in terms of G and G_2. Let us start out by defining the n-body Green function as

$$G_n(1\dots n,1'\dots n') = (-i)^n\langle T_C[\hat{\psi}_H(1)\dots\hat{\psi}_H(n)\hat{\psi}_H^{\dagger}(1')\dots\hat{\psi}_H^{\dagger}(n')]\rangle, \tag{19}$$

where we introduced the short notation $1=(\mathbf{x}_1t_1)$ and where we defined the expectation value of a Heisenberg operator as

$$\langle\hat{O}\rangle = \frac{\mathrm{Tr}\{\hat{U}(t_0-i\beta,t_0)\hat{O}_H(t)\}}{\mathrm{Tr}\{\hat{U}(t_0-i\beta,t_0)\}}. \tag{20}$$

The many-body Green functions satisfy the following hierarchy equations[40,41] which connect the n-body Green function to the $n+1$ and $n-1$ body Green function:

$$[i\partial_{t_1}-h(1)]G_n(1\dots n,1'\dots n') = \sum_{j=1}^{n}\delta(1j')(-1)^{n-j}G_{n-1}(2\dots n,1'\dots j'-1,j'+1\dots n') - i\int d\mathbf{x}\,v(\mathbf{x}_1,\mathbf{x})G_{n+1}(1\dots n,\mathbf{x}t_1,\mathbf{x}t_1^{+},1'\dots n'). \tag{21}$$

These equations follow directly from the definition of the Green functions, the anticommutation relations of the field operators, and the equations of motion of the evolution operators in Eqs. (6) and (7). The Green functions are defined for time arguments on the time contour. Such contour Green functions were first introduced by Keldysh[33] and are often denoted as Keldysh Green functions[34–36] and play an important role in nonequilibrium systems. The one-particle Green function $G_1=G$ obeys the boundary condition $G(\mathbf{x}_1t_0,2)=-G(\mathbf{x}_1t_0-i\beta,t_2)$ as is readily derived using the cyclic property of the trace. The property $G(1,\mathbf{x}_2t_0)=-G(1,\mathbf{x}_2t_0-i\beta)$ for the other argument is likewise easily verified as well as similar relations for the n-body Green functions. These boundary conditions are sometimes referred to as the Kubo-Martin-Schwinger conditions[40,42] and are essential in solving the equations of motion for the Green function.[36] After these preliminaries we are now ready to derive the equations that connect the one- and two-body Green functions which we will use to construct the variational functional Y.

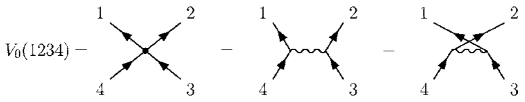

FIG. 2. Four-point vertex corresponding to the Hugenholtz diagram technique.

III. RELATION BETWEEN THE FOUR-POINT VERTEX AND THE GREEN FUNCTION

In order to derive a variational energy functional in terms of the Green function G and the renormalized four-point vertex Γ we start out by deriving coupled equations between these quantities, similar to the familiar Hedin equations.[17] However, instead of the usual coupled equations in terms of the Green function G and the screened interaction W we have equations in terms of the Green function G and the four-point vertex Γ. Since our aim is to derive equations in terms of the renormalized four-point vertex it is advantageous to write our equations in terms of the bare four-point vertex first. This is most conveniently done within the Hugenholtz diagram technique.[25–28] We will therefore first rewrite the two-particle interaction as a four-point function as

$$\hat{V} = \frac{1}{2}\int d\mathbf{x}d\mathbf{x}'\,v(\mathbf{r},\mathbf{r}')\hat{\psi}^{\dagger}(\mathbf{x})\hat{\psi}^{\dagger}(\mathbf{x}')\hat{\psi}(\mathbf{x}')\hat{\psi}(\mathbf{x}) = \frac{1}{4}\int d(\mathbf{x}_1\mathbf{x}_2\mathbf{x}_3\mathbf{x}_4)V_0(\mathbf{x}_1\mathbf{x}_2\mathbf{x}_3\mathbf{x}_4) \times \hat{\psi}^{\dagger}(\mathbf{x}_1)\hat{\psi}^{\dagger}(\mathbf{x}_2)\hat{\psi}(\mathbf{x}_3)\hat{\psi}(\mathbf{x}_4), \tag{22}$$

where we defined

$$V_0(\mathbf{x}_1\mathbf{x}_2\mathbf{x}_3\mathbf{x}_4) = v(\mathbf{r}_1,\mathbf{r}_2)[\delta(\mathbf{x}_2-\mathbf{x}_3)\delta(\mathbf{x}_1-\mathbf{x}_4) - \delta(\mathbf{x}_1-\mathbf{x}_3)\delta(\mathbf{x}_2-\mathbf{x}_4)]. \tag{23}$$

This term is used as a basic entity in the Hugenholtz diagram technique and is displayed pictorially in Fig. 2. We now make use of the fact that the Green function can be obtained as a derivative of the functional

$$iY[u] = -\ln \mathrm{Tr}\{U[u](t_0-i\beta,t_0)\} \tag{24}$$

with respect to a nonlocal (in space and time) potential $u(12)$, where

$$\hat{U}[u](t_0 - i\beta, t_0) = T_C \exp\left(-i\int dt\hat{H}(t) - i\int d1\int d2\hat{\psi}^{\dagger}(\mathbf{x}_1)u(12)\hat{\psi}(\mathbf{x}_2)\right). \tag{25}$$

Since this expression contains a double time integral one has to define precisely how the time ordering in this equation is defined. This leads to often overlooked subtleties the details of which are presented in Appendix A where we further show that

$$G(12) = i\frac{\delta Y[u]}{\delta u(21)}. \tag{26}$$

By a subsequent differentiation (see Appendix A) we can obtain the two-particle Green function as

$$G_2(1234) = -\frac{\delta G(14)}{\delta u(32)} + G(14)G(23). \tag{27}$$

If the derivatives are taken at $u=0$ we obtain the Green functions as defined in Eq. (19). If the derivative is taken at nonzero u then there is no direct relation between the Green function and expectation values of time-ordered field operators. However, as shown in Appendix A the Green functions in the presence of a nonlocal potential u still satisfy a set of hierarchy equations. The first ones are

$$[i\partial_{t_1} - h(1)]G(11') = \delta(11') + \int d2[u(12) + \Sigma(12)]G(21'), \tag{28}$$

$$[-i\partial_{t_1'} - h(1')]G(11') = \delta(11') + \int d2G(12)\times[u(21') + \tilde{\Sigma}(21')], \tag{29}$$

where we defined the self-energy operator Σ and its adjoint $\tilde{\Sigma}$ by the equations

$$\int d2\Sigma(12)G(21') = -\frac{i}{2}\int d(234)V(1234)G_2(4321'), \tag{30}$$

$$\int d2G(12)\tilde{\Sigma}(21') = -\frac{i}{2}\int d(234)G_2(1234)V(4321'). \tag{31}$$

Here we defined

$$V(1234) = v(\mathbf{r}_1,\mathbf{r}_2)\delta(t_1,t_2)[\delta(23)\delta(14) - \delta(13)\delta(24)]\theta_{1234} \tag{32}$$

where $\delta(ij)=\delta(t_i,t_j)\delta(\mathbf{x}_i-\mathbf{x}_j)$ and $\theta_{1234}=1$ if $t_1>t_2>t_3>t_4$ (on the contour) and zero otherwise. The function θ_{1234} therefore ensures that the operators have the proper time-ordering before the equal time limits, described by the δ functions, are taken. In the next section we will also allow for more general forms of $V(1234)$ in order to obtain the two-particle Green function as a functional derivative with respect to V. In order to derive a self-consistent set of equations we have to give a relation between the two-particle Green function and the self-energy. We first note that $\Sigma=\tilde{\Sigma}$. This can be derived by applying to Eq. (31) the operator $[i\partial_{t_1}-h(1)]$ and to Eq. (30) the operator $[-i\partial_{t_1'}-h(1')]$. With the use of the equations of motion of the one- and two-particle Green functions from Eq. (21) the result then follows. As a remark we note that for more general initial conditions Σ is no longer equal to $\tilde{\Sigma}$.[43] From the equality of Σ and $\tilde{\Sigma}$ it follows that the Green function has a unique inverse given by the Dyson equation

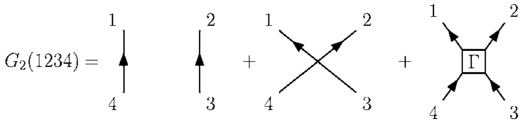

FIG. 3. Definition of the renormalized four-point vertex Γ.

$$\begin{aligned}G^{-1}(12) &= [i\partial_{t_1} - h(1)]\delta(12) - u(12) - \Sigma(12)\\ &= G_0^{-1}(12) - u(12) - \Sigma(12)\end{aligned} \tag{33}$$

which satisfies

$$\int d2G^{-1}(12)G(21) = \int d2G(12)G^{-1}(21') = \delta(11'). \tag{34}$$

For later reference we also defined the inverse G_0^{-1} of the noninteracting Green function in Eq. (33). We now define the renormalized four-point vertex by the equation

$$G_2(1234) = G(14)G(23) - G(13)G(24) + \int d(5678)G(15)G(27)\Gamma(5786)G(83)G(64). \tag{35}$$

This expression is displayed pictorially in Fig. 3. The four-point vertex Γ has the interpretation of a renormalized interaction that describes the scattering of two particles and will play an important role in our energy functional later. By differentiating Eq. (34) with respect to the nonlocal potential u and using Eqs. (27), (30), and (33) we can readily derive (along the lines of Ref. 17) the equations

$$\begin{aligned}\Sigma(18) = &-i\int d(23)V(1238)G(32)\\ &-\frac{i}{2}\int d(234567)V(1234)G(36)\\ &\times G(45)\Gamma(5678)G(72)\end{aligned} \tag{36}$$

and

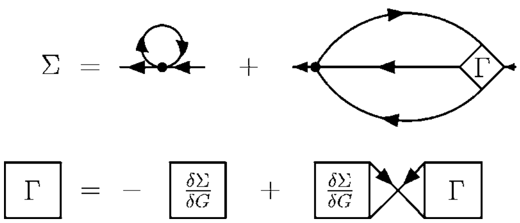

FIG. 4. Graphical display of the equations that relate the self-energy Σ to the vertex Γ.

$$\Gamma(1234) = -\frac{\delta\Sigma(14)}{\delta G(32)} + \int d(5678)\frac{\delta\Sigma(14)}{\delta G(65)}G(67)G(85)\Gamma(7238). \tag{37}$$

Equations (36) and (37), which are pictorially displayed in Fig. 4, represent a self-consistent set of equations that generate the perturbation series for the self-energy $\Sigma[G,V]$ in terms of the Green function and the interaction V. For instance, if one starts by taking $\Gamma=0$ in Eq. (36), then from Eq. (37) one obtains an improved four-point vertex Γ which inserted in Eq. (36) leads to an improved self-energy. It should be noted that at a correlated level the simultaneous solution of these equations is in general computationally demanding.[44] Moreover the self-consistent vertex and self-energy are not related by a Ward-identity[37,46] although the response functions calculated from the nonequilibrium Green function in external fields still satisfy the f sum rule.[45,46] However, as explained in the introduction, our aim is to obtain total energies. This can be done without solving the computationally demanding Eqs. (36) and (37) by using approximate Green functions and four-point vertices in the variational functional that we will construct in the next section.

IV. CONSTRUCTION OF A VARIATIONAL FUNCTIONAL

In this section we will construct a variational energy or action functional of the dressed Green function G and the renormalized four-point vertex Γ. The main reason for investigating such a functional is to obtain in a simple way contributions to the total energy that correspond to the infinite summation of ladder-type diagrams. Such diagrams correspond to an infinite number of terms in the Φ or Ψ-functional. In the new variables G and Γ we have a corresponding functional $\Xi[G,\Gamma]$. In order to derive the Ξ-functional, which we will denote as the De Dominicis functional,[29–32,47] we start with the action functional

$$iY[u,V] = -\ln \mathrm{Tr}\{U[u,V](t_0 - i\beta, t_0)\}, \tag{38}$$

which we will regard as a functional of u and V, where we defined

$$\begin{aligned}\hat{U}[u,V](t_0 - i\beta, t_0) = T_C \exp\Big(&-i\int dt\hat{H}_0(t) \\ &- i\int d1\int d2\,\hat{\psi}^\dagger(\mathbf{x}_1)u(12)\hat{\psi}(\mathbf{x}_2) \\ &- \frac{i}{4}\int d(1234)V(1234) \\ &\times \hat{\psi}^\dagger(\mathbf{x}_1)\hat{\psi}^\dagger(\mathbf{x}_2)\hat{\psi}(\mathbf{x}_3)\hat{\psi}(\mathbf{x}_4)\Big).\end{aligned} \tag{39}$$

Here $V(1234)$ is a general time-dependent two-body interaction which we require to have the following symmetry properties:

$$V(1234) = -V(2134) = -V(1243) = V(2143). \tag{40}$$

This will guarantee that the Feynman rules of the Hugenholtz diagram method are satisfied. Eventually, when we have derived our equations, we will set V equal to expression V_0 of Eq. (32). To give precise meaning to expression (39) we again have to specify how the time ordering is defined when we expand the exponent. This is done in Appendix B where we show that

$$i\frac{\delta Y}{\delta u(21)} = G(12), \tag{41}$$

$$i\frac{\delta Y}{\delta V(4321)} = -\frac{i}{4}G_2(1234). \tag{42}$$

In Appendix B it is further demonstrated that these one- and two-particle Green functions, even in the presence of time nonlocal fields, are related by the first equation of motion of the Martin-Schwinger hierarchy. By a Legendre transform we can now construct a functional of G and G_2,

$$F[G,G_2] = iY[u[G,G_2],V[G,G_2]] - \int d(12)u(21)G(12) + \frac{i}{4}\int d(1234)V(4321)G_2(1234), \tag{43}$$

where we now regard u and V as functionals of G and G_2. This functional satisfies

$$\frac{\delta F}{\delta G(12)} = -u(21), \tag{44}$$

$$\frac{\delta F}{\delta G_2(1234)} = \frac{i}{4}V(4321). \tag{45}$$

Therefore the functional

$$iY[G,G_2] = F[G,G_2] + \int d(12)u(21)G(12) - \frac{i}{4}\int d(1234)V(4321)G_2(1234) \tag{46}$$

for *fixed* u and V is a stationary functional of G and G_2, i.e.,

$$i\frac{\delta Y}{\delta G(12)} = 0, \tag{47}$$

$$i\frac{\delta Y}{\delta G_2(1234)} = 0, \tag{48}$$

where we will eventually be interested in the case $u=0$ and $V=V_0$. We can now modify the functional $Y[G,G_2]$ such that, rather than the two-particle Green function, we can use the renormalized four-point vertex Γ as a basic variable. For this purpose we use Eq. (35) which is displayed pictorially in Fig. 3 and which gives $G_2[G,\Gamma]$ as an explicit functional of G and Γ. We then define the functional

$$H[G,\Gamma] = F[G,G_2[G,\Gamma]], \tag{49}$$

which is a functional of the Green function G and the four-point vertex Γ. Then for fixed Γ we have

$$\begin{aligned}\frac{\delta H}{\delta G(12)} &= \frac{\delta F}{\delta G(12)} + \int d(3456)\frac{\delta F}{\delta G_2(3456)}\frac{\delta G_2(3456)}{\delta G(12)}\\ &= -u(21) - \Sigma(21) - \tilde{\Sigma}_C(21),\end{aligned} \tag{50}$$

where we defined

$$\Sigma(12) = \Sigma^{HF}(12) + \Sigma_C(12), \tag{51}$$

$$\Sigma^{HF}(14) = -i\int d(23)V(1234)G(32), \tag{52}$$

$$\begin{aligned}\Sigma_C(18) = -\frac{i}{2}\int d(234567)V(1234)G(36)\\ \times G(45)\Gamma(5678)G(72),\end{aligned} \tag{53}$$

$$\begin{aligned}\tilde{\Sigma}_C(18) = -\frac{i}{2}\int d(234567)\Gamma(1234)G(36)\\ \times G(45)V(5678)G(72).\end{aligned} \tag{54}$$

From Eq. (36) we recognize these terms as self-energy diagrams. They are displayed graphically in Fig. 5. We recognize the first term in Eq. (52) for $V=V_0$ as the Hartree-Fock part of the self-energy. The second part Σ_C of Eq. (53) involving the four-point vertex Γ describes the time-nonlocal correlation part of the self-energy. The third part $\tilde{\Sigma}_C$ in Eq. (54) is the adjoint correlation part of the self-energy. As mentioned earlier we can show from the Kubo-Martin-Schwinger boundary conditions for a system initially in thermodynamic equilibrium that $\tilde{\Sigma}_C(12)=\Sigma_C(12)$. However, in the following we will keep the tilde on the self-energy to keep track of the origin of this term. For fixed G we can also calculate the derivative with respect to Γ for which we have

$$\frac{\delta H}{\delta \Gamma(1234)} = \int d(5678)\frac{\delta F}{\delta G_2(5678)}\frac{\delta G_2(5678)}{\delta \Gamma(1234)} = \frac{i}{4}\tilde{V}(4321), \tag{55}$$

where we defined

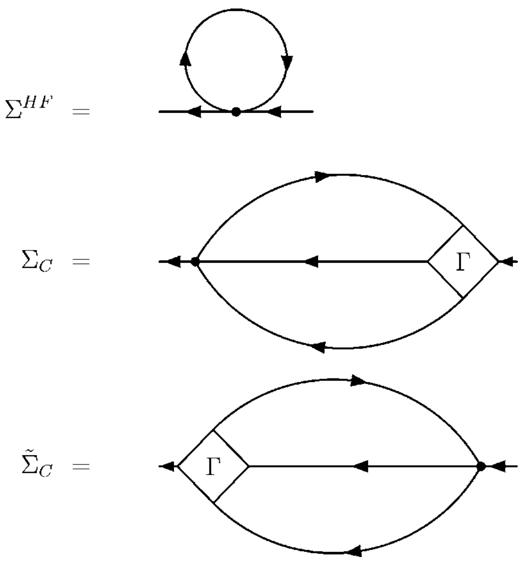

FIG. 5. Graphical display of the self-energy terms. The small dot denotes the bare vertex V and the big square denotes the full four-point vertex Γ.

$$\tilde{V}(1234) = \int d(5678)G(15)G(26)V(5678)G(73)G(84), \tag{56}$$

which is simply a bare vertex dressed with two ingoing and two outgoing dressed Green function lines. Using the functional H we can now regard the expression iY of Eq. (46) as a functional of G and Γ, i.e.,

$$\begin{aligned}iY[G,\Gamma] = H[G,\Gamma] + \int d(12)u(21)G(12)\\ -\frac{i}{4}\int d(1234)V(4321)G_2[G,\Gamma](1234),\end{aligned} \tag{57}$$

which is a stationary functional of G and Γ for fixed u and V. We have thus achieved our first goal and expressed the action iY as functional of G and Γ. Our next step is to specify the functional H in more detail. The variations in H are given by the expression

$$\begin{aligned}\delta H &= \int d(12)[-u(21) - \Sigma(21) - \tilde{\Sigma}_C(21)]\delta G(12)\\ &\quad + \frac{i}{4}\int d(1234)\tilde{V}(4321)\delta\Gamma(1234)\\ &= \int d(12)[G^{-1}(21) - G_0^{-1}(21) - \tilde{\Sigma}_C(21)]\delta G(12)\\ &\quad + \frac{i}{4}\int d(1234)\tilde{V}(4321)\delta\Gamma(1234),\end{aligned} \tag{58}$$

and hence we see that it is convenient to split up H as follows:

$$H[G,\Gamma] = -\operatorname{tr}\{\ln(-G^{-1})\} - \operatorname{tr}\{G_0^{-1}(G-G_0)\} - \Xi[G,\Gamma]. \tag{59}$$

This equation defines a new functional $\Xi[G,\Gamma]$ which will be the central object for the rest of the paper. In Eq. (59) we further defined the trace tr (not to be confused with the thermodynamic trace Tr) as

$$\operatorname{tr} A = \int d1 A(1,1^+), \tag{60}$$

where 1^+ denotes that time t_1 is approached from above on the contour. The definition of the Ξ-functional in Eq. (59) is convenient because then we have

$$\frac{\delta H}{\delta G(12)} = G^{-1}(21) - G_0^{-1}(21) - \frac{\delta \Xi}{\delta G(12)}, \tag{61}$$

$$\frac{\delta H}{\delta \Gamma(1234)} = -\frac{\delta \Xi}{\delta \Gamma(1234)}, \tag{62}$$

and therefore from Eq. (58) we see that the functional $\Xi[G,\Gamma]$ satisfies the equations

$$\frac{\delta \Xi}{\delta \Gamma(1234)} = -\frac{i}{4}\tilde{V}(4321), \tag{63}$$

$$\frac{\delta \Xi}{\delta G(12)} = \tilde{\Sigma}_C(21). \tag{64}$$

The functional Ξ is therefore directly related to the correlation part of the self-energy. To describe the correlations in the system it is therefore necessary to further study the structure of the Ξ-functional, which we will do in detail in the next section.

Note that in Eq. (59) we could also have written $\ln(G^{-1})$ rather than $\ln(-G^{-1})$. These terms differ only by a (possibly infinite) constant and depend on the definition of the branch cut of the logarithm. However, the particular definition here reduces properly to the grand potential of the noninteracting system when the interactions are switched off.[10] The final De Dominicis functional (for $u=0$) is thus given from Eqs. (57) and (59) by

$$iY[G,\Gamma] = -\operatorname{tr}\{\ln(-G^{-1})\} - \operatorname{tr}\{G_0^{-1}(G-G_0)\} - \Xi[G,\Gamma] - \frac{i}{4}\int d(1234)V_0(1234)G_2[G,\Gamma](4321). \tag{65}$$

We can check that in the absence of interactions we have $iY = -\operatorname{tr}\ln\{-G_0^{-1}\}$, which yields the grand potential of the noninteracting system, as we will discuss in more detail later. Let us now check the variational property. The derivatives of iY with respect to G and Γ are given by

$$i\frac{\delta Y}{\delta \Gamma(1234)} = \frac{i}{4}[\tilde{V}(4321) - \tilde{V}_0(4321)], \tag{66}$$

$$i\frac{\delta Y}{\delta G(12)} = G^{-1}(21) - G_0^{-1}(21) - \tilde{\Sigma}_C(21;V) + \Sigma(21;V_0) + \tilde{\Sigma}_C(21;V_0), \tag{67}$$

where we used that

$$-\frac{i}{4}\frac{\delta}{\delta G(56)}\int d(1234)V_0(1234)G_2[G,\Gamma](4321) = \Sigma(65;V_0) + \tilde{\Sigma}_C(65;V_0). \tag{68}$$

The variational equations that are obtained by putting the derivatives (66) and (67) equal to zero are obviously solved for the G and Γ that self-consistently solve the equations

$$G^{-1} = G_0^{-1} - \Sigma[G,\Gamma], \tag{69}$$

$$\tilde{V}_0 = \tilde{V}[G,\Gamma], \tag{70}$$

where Σ is calculated from Eqs. (52) and (53). Therefore the functional $Y[G,\Gamma]$ is stationary whenever the Dyson equation is obeyed and whenever the electron-electron interaction expanded in G and Γ is equal to the specified interaction V_0. Equation (65) for the variational functional $Y[G,\Gamma]$ is the first basic result of this work. However, before it can be used in actual calculations we have, among others, to specify the specific structure of the functional $\Xi[G,\Gamma]$. We will show that for several infinite series of diagrammatic terms contributing to this functional we can find explicit expressions in terms of G and Γ. To do this we first have to study the functional $\tilde{V}[G,\Gamma]$ of Eq. (70). This is the topic of the next section.

V. STRUCTURE OF THE Ξ FUNCTIONAL

In this section we analyze in more detail the diagrammatic structure of the four-point vertex Γ and the functional $\tilde{V}[G,\Gamma]$ of Eq. (70) which will allow us to obtain more explicit expressions for the functional Ξ. These quantities can be directly obtained from a diagrammatic expansion of the two-particle Green function. If we express the diagrams in terms of the fully dressed Green function G we only need to consider diagrams that do not contain any self-energy insertions. Since different authors use different definitions and drawing conventions for the two-particle Green function, it is important to be clear about them. We strictly follow the sign, loop rule, and drawing conventions of Ref. 41 with the small difference that we use Hugenholtz diagrams.[25–28] For clarity our Feynman rules are given in Appendix C. In Fig. 6 we show the first and second order Hugenholtz diagrams in terms of the fully dressed Green function G that contribute to the two-particle Green function G_2. We see that we can write Γ as a sum of four classes of diagrams. There are three classes of the form (ab,cd) which denote diagrams which by removal of two internal Green function lines can separate the diagram into two parts, one part being connected to the external points ab and one part being connected to points cd. The class (12, 34) contains diagrams of the particle-particle type, such as the diagram in Fig. 6(d), and will be denoted by

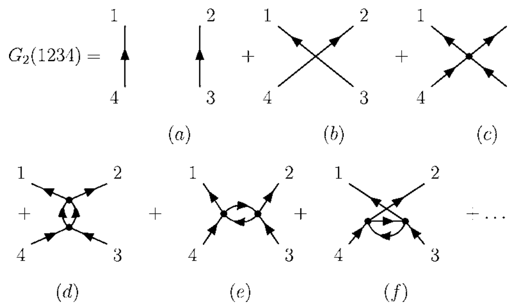

FIG. 6. Expansion of the two-particle Green function G_2 in terms of the full G. The dot denotes the bare vertex V.

Γ_{pp}. There are two classes of particle-hole type, namely (14, 32) and (13, 24) which will be denoted by Γ^A_{ph} and Γ^B_{ph}. Examples of diagrams of these types are Figs. 6(e) and 6(f). The remaining diagrams which do not fall into one of these classes are denoted by Γ_0 [such as Fig. 6(c)]. We can therefore write

$$\Gamma(1234) = \Gamma_{pp}(1234) + \Gamma^A_{ph}(1234) + \Gamma^B_{ph}(1234) + \Gamma_0(1234). \tag{71}$$

The simplest diagram in class Γ_0 is simply the bare vertex $iV(1234)$ [i.e., Fig. 6(c) the factor i follows from the Feynman rules in Appendix C]. Since this diagram is special we separate it off from Γ_0 and define the remaining diagrams Γ'_0 by the equation

$$\Gamma_0(1234) = \Gamma'_0(1234) + iV(1234). \tag{72}$$

Using Eq. (72) we can then write

$$-iV(1234) = \Gamma_{pp}(1234) + \Gamma^A_{ph}(1234) + \Gamma^B_{ph}(1234) + \Gamma'_0(1234) - \Gamma(1234). \tag{73}$$

We will now first show how all the terms on the right-hand side of this equation can be constructed as a functional of Γ. When we have done this we can insert this functional into Eq. (63) and perform the integration with respect to Γ and thereby construct our desired functional $\Xi[G,\Gamma]$.

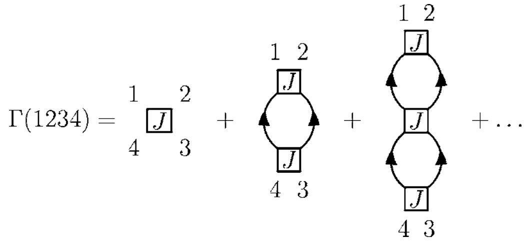

FIG. 7. Expression of Γ in terms of J blocks.

Let us start with the particle-particle diagrams Γ_{pp}. The contribution of all diagrams for Γ_{pp} can be written as sums of blocks of diagrams J connected with two parallel Green function lines (see Fig. 7). Each of these blocks J contains diagrams which cannot disconnect points (12) and (34) by cutting two Green function lines [such blocks are called simple with respect to Eqs. (12) and (34) in the terminology of De Dominicis] and therefore each J block does not contain diagrams of the type Γ_{pp}. We thus have

$$J(1234) = \Gamma(1234) - \Gamma_{pp}(1234). \tag{74}$$

We introduce a convenient matrix notation

$$\langle 12|J|34\rangle = J(1234), \tag{75}$$

$$\langle 12|GG|34\rangle = G(13)G(24). \tag{76}$$

Within this notation we can, for instance, conveniently write $C=AB$ instead of

$$C(1234) = \langle 12|AB|34\rangle = \int d(56)\langle 12|A|56\rangle\langle 56|B|34\rangle = \int d(56)A(1256)B(5634). \tag{77}$$

If we use this notation, then from the Feynman rules in Appendix C one can readily convince oneself that in matrix notation we simply have

$$\Gamma = J + \Gamma_{pp} = J + \frac{1}{2}JGGJ + \left(\frac{1}{2}\right)^2 JGGJGGJ + \dots = J + \frac{1}{2}JGG\Gamma, \tag{78}$$

where for every pair of Green function lines we have to add a factor of $\frac{1}{2}$ (see Refs. 26–28 and 47). This follows because for any diagram contributing to J, the diagram with outgoing lines interchanged leads to the same diagram for Γ (for the simple diagram iV in J it follows from Feynman rule 5 in Appendix C). Relation (78) allows us to express Γ_{pp} in terms of Γ. We have

$$J = \Gamma\left(1 + \frac{1}{2}GG\Gamma\right)^{-1}. \tag{79}$$

In combination with Eq. (74) this then gives

$$\Gamma_{pp} = \Gamma - \Gamma\left(1 + \frac{1}{2}GG\Gamma\right)^{-1}, \tag{80}$$

which expresses Γ_{pp} in terms of Γ. Let us now do the same for the particle-hole diagrams. Since

$$\Gamma^B_{ph}(1234) = -\Gamma^A_{ph}(2134), \tag{81}$$

we only need to construct Γ^A_{ph} as a functional of Γ. For the particle-hole diagrams Γ^A_{ph} we can follow a similar reasoning as for Γ_{pp} and we first write Γ in terms of repeated blocks I given by

$$I(1234) = \Gamma(1234) - \Gamma^A_{ph}(1234). \tag{82}$$

The expression for Γ in terms of I is displayed in Fig. 8. If we use the notation

$$\langle 41|\bar{I}|23\rangle = I(1234), \tag{83}$$

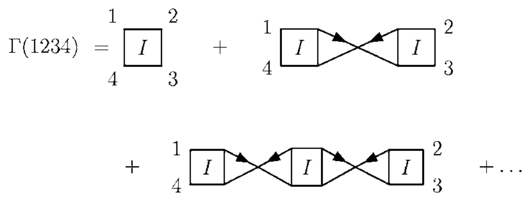

FIG. 8. Expression of Γ in terms of I blocks.

$$\langle 12|\widehat{GG}|34\rangle = G(31)G(24), \tag{84}$$

where in the first term we defined a new matrix $\bar{I}$ by a cyclic permutation of the indices, then (again using the Feynman rules of Appendix C) we have in matrix notation

$$\bar{\Gamma} = \bar{I} + \bar{\Gamma}^A_{ph} = \bar{I} - I\widehat{GG}\bar{I} + I\widehat{GG}I\widehat{GG}\bar{I} - \ \dots \ = \bar{I} - I\widehat{GG}\bar{\Gamma}, \tag{85}$$

where the alternating signs in Eq. (85) are related to Feynman rule 4 in Appendix C. As a remark we note that from Eqs. (85) and (37) we see that there is a simple relation between I and the self-energy:

$$I(1234) = -\frac{\delta\Sigma(14)}{\delta G(32)}. \tag{86}$$

One can indeed check, by iterating Eqs. (36) and (37), that the term $\delta\Sigma/\delta G$ only yields diagrams that contribute to I. We can now express $\bar{\Gamma}^A_{ph}$ in terms of $\bar{\Gamma}$. We have

$$\bar{I} = \bar{\Gamma}(1 - \widehat{GG}\bar{\Gamma})^{-1}, \tag{87}$$

which gives

$$\bar{\Gamma}^A_{ph} = \bar{\Gamma} - \bar{\Gamma}(1 - \widehat{GG}\bar{\Gamma})^{-1}. \tag{88}$$

Before discussing the last set of diagrams Γ'_0 let us see if we can integrate the functionals Γ_{pp} and Γ^A_{ph} that we obtained so far. To do this we first make a general remark about functional derivatives. We consider a given four-point function $a[\Gamma](1234)$ that we want to integrate with respect to Γ to obtain a functional A, i.e.,

$$\delta A = \int d(1234) a[\Gamma](1234)\delta\Gamma(1234). \tag{89}$$

In our case we want to do this for $a[\Gamma]$ being Γ_{pp}, Γ^A_{ph}, Γ^B_{ph}, and Γ'_0. Because $\delta\Gamma$ has the symmetry property of Eq. (40) this can also be written as

$$\delta A = \frac{1}{4}\int d(1234)[a(1234) - a(2134) + a(3412) - a(1243)]\delta\Gamma(1234). \tag{90}$$

Therefore any part of a which is symmetric in the indices (12) and (34) [or antisymmetric with respect to the interchange of pair (12) and pair (34)] will not contribute to this variation. Therefore only certain (anti)symmetric parts of a are uniquely determined as functional derivatives. This does not pose a problem if the functional a we want to integrate already has the same symmetry as Γ. This applies for instance to Γ_{pp} and Γ'_0. However, the function $\Gamma^A_{ph}(1234)$ is not antisymmetric in the indices (12) and (34). However, the combination

$$\Gamma^A_{ph}(1234) - \Gamma^A_{ph}(2134) = \Gamma^A_{ph}(1234) + \Gamma^B_{ph}(1234) \tag{91}$$

has this property and therefore

$$2\int d(1234)\Gamma^A_{ph}(1234)\delta\Gamma(1234) = \int d(1234)[\Gamma^A_{ph}(1234) + \Gamma^B_{ph}(1234)]\delta\Gamma(1234). \tag{92}$$

We can therefore obtain $\Gamma^A_{ph}+\Gamma^B_{ph}$ as a functional derivative by formally integrating Γ^A_{ph} and multiplying the resulting functional by 2. With this in mind we can now address the integration of $\tilde{V}$ in the right-hand side of Eq. (63) with respect to Γ. Using Eq. (73) we can write

$$-i\tilde{V}(1234) = \tilde{\Gamma}_{pp}(1234) + \tilde{\Gamma}^A_{ph}(1234) + \tilde{\Gamma}^B_{ph}(1234) + \tilde{\Gamma}'_0(1234) - \tilde{\Gamma}(1234), \tag{93}$$

where the expressions with the tilde are defined as in Eq. (56). Let us start by integrating $\tilde{\Gamma}_{pp}$ with respect to Γ. Using Eq. (80) and taking into account the factor 1/4 in Eq. (63), we have

$$\begin{aligned}\frac{1}{4}\tilde{\Gamma}_{pp} &= \frac{1}{4}GG\Gamma_{pp}GG = \frac{1}{4}GG\Gamma\left[1 - \left(1 + \frac{1}{2}GG\Gamma\right)^{-1}\right]GG \\ &= \frac{1}{4}GG\Gamma GG - \frac{1}{2}\left[1 - \left(1 + \frac{1}{2}GG\Gamma\right)^{-1}\right]GG \\ &= \frac{\delta L_{pp}[G,\Gamma]}{\delta\Gamma},\end{aligned} \tag{94}$$

where we defined

$$L_{pp}[G,\Gamma] = \frac{1}{8}\,\mathrm{tr}\{GG\Gamma GG\Gamma\} - \frac{1}{2}\,\mathrm{tr}\{GG\Gamma\} + \mathrm{tr}\left\{\ln\left(1 + \frac{1}{2}GG\Gamma\right)\right\}. \tag{95}$$

In this expression the trace tr (not to be confused with the thermodynamic trace Tr) for two-particle functions is defined as

$$\mathrm{tr}\{A\} = \int d(12)\langle 12|A|12\rangle. \tag{96}$$

The diagrammatic expansion of the functional L_{pp} is displayed in the upper part of Fig. 9. Let us now consider the particle-hole diagrams. Since

$$\mathrm{tr}\{\widehat{GG}\bar{\Gamma}^A_{ph}\widehat{GG}\delta\bar{\Gamma}\} = \mathrm{tr}\{\tilde{\Gamma}^A_{ph}\delta\Gamma\}, \tag{97}$$

it is sufficient to integrate $\widehat{GG}\bar{\Gamma}^A_{ph}\widehat{GG}$ with respect to $\bar{\Gamma}$. We have, using Eq. (88),

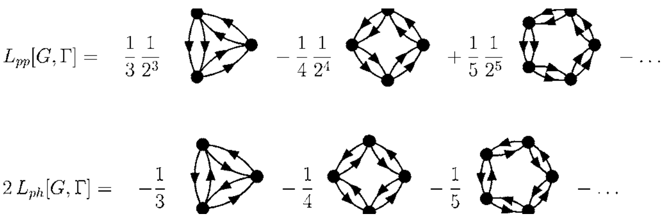

FIG. 9. Expansion of the functionals L_{pp} and L_{ph} in diagrams. The four-point vertex Γ is denoted with a big black dot.

$$\frac{1}{4}\tilde{\bar{\Gamma}}^A_{ph} = \frac{1}{4}\widehat{GG}\bar{\Gamma}^A_{ph}\widehat{GG} = \frac{1}{4}\widehat{GG}\bar{\Gamma}[1-(1-\widehat{GG}\bar{\Gamma})^{-1}]\widehat{GG}$$
$$= \frac{1}{4}\widehat{GG}\bar{\Gamma}^A_{ph}\widehat{GG} + \frac{1}{4}[1-(1-\widehat{GG}\bar{\Gamma})^{-1}]\widehat{GG}$$
$$= \frac{1}{2}\frac{\delta L_{ph}[G,\Gamma]}{\delta\bar{\Gamma}}, \tag{98}$$

where we defined the functional

$$L_{ph}[G,\Gamma] = \frac{1}{4}\,\mathrm{tr}\{\widehat{GG}\bar{\Gamma}\widehat{GG}\bar{\Gamma}\} + \frac{1}{2}\,\mathrm{tr}\{\widehat{GG}\bar{\Gamma}\}$$
$$+ \frac{1}{2}\,\mathrm{tr}\{\ln(1-\widehat{GG}\bar{\Gamma})\}. \tag{99}$$

The diagrammatic expansion of the functional L_{ph} is displayed in the lower part of Fig. 9. Now since

$$\mathrm{tr}\{(\tilde{\Gamma}^A_{ph}+\tilde{\Gamma}^B_{ph})\delta\Gamma\} = 2\,\mathrm{tr}\{\tilde{\Gamma}^A_{ph}\delta\Gamma\} = 2\,\mathrm{tr}\{\widehat{GG}\bar{\Gamma}^A_{ph}\widehat{GG}\delta\bar{\Gamma}\}, \tag{100}$$

we obtain

$$\frac{1}{4}(\tilde{\Gamma}^A_{ph}+\tilde{\Gamma}^B_{ph}) = \frac{\delta L_{ph}[G,\Gamma]}{\delta\Gamma}. \tag{101}$$

We now collect our results and define

$$L[G,\Gamma] = L_{pp}[G,\Gamma] + L_{ph}[G,\Gamma] - \frac{1}{8}\,\mathrm{tr}\{GG\Gamma GG\Gamma\}. \tag{102}$$

This functional L has the property

$$\frac{\delta L}{\delta\Gamma} = \frac{1}{4}(\tilde{\Gamma}_{pp}+\tilde{\Gamma}^A_{ph}+\tilde{\Gamma}^B_{ph}-\tilde{\Gamma}). \tag{103}$$

Using this functional we can now split up the functional Ξ further as

$$\Xi[G,\Gamma] = L[G,\Gamma] + L'[G,\Gamma]. \tag{104}$$

This defines a new functional $L'[G,\Gamma]$. Then from Eq. (63) we see that if we differentiate both sides of Eq. (104) with respect to Γ we obtain

$$\frac{\delta\Xi}{\delta\Gamma} = -\frac{i}{4}\tilde{V} = \frac{1}{4}(\tilde{\Gamma}_{pp}+\tilde{\Gamma}^A_{ph}+\tilde{\Gamma}^B_{ph}-\tilde{\Gamma}) + \frac{\delta L'}{\delta\Gamma}. \tag{105}$$

We therefore see by comparing to Eq. (73) that the functional L' must satisfy

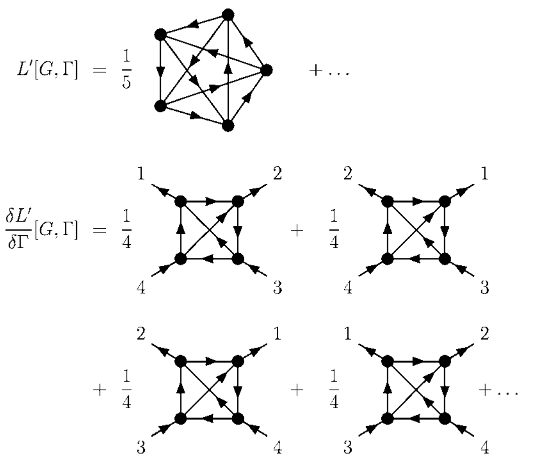

FIG. 10. The first term in the expansion of the L' functional and its functional derivative with respect to Γ. For clarity in drawing the diagrams for $\delta L'/\delta\Gamma$ we interchanged the end-point labels rather than making the outgoing lines cross.

$$\frac{1}{4}\tilde{\Gamma}'_0 = \frac{\delta L'[G,\Gamma]}{\delta\Gamma}. \tag{106}$$

This functional cannot be written out explicitly, but since Γ'_0 is well-defined diagrammatically the functional L' does have a diagrammatic expansion. The first term in this expansion is displayed in Fig. 10 together with its functional derivative. Note that the derivative yields four diagrams in accordance with Eq. (90). We can further consider the functional derivative of the functional $\Xi[G,\Gamma]$ with respect to G. According to Eq. (64) this yields self-energy diagrams, as is also seen from the diagrammatic expansion of Ξ. The G derivatives of L_{pp}, L_{ph}, and L' lead to correlation self-energy diagrams $\Sigma_{C,pp}[G,\Gamma]$, $\Sigma_{C,ph}[G,\Gamma]$, and $\Sigma'_C[G,\Gamma]$ in terms of G and Γ that fall into different topological classes.

We now again collect our results and find from Eq. (65) that the final De Dominicis functional (for $u=0$) is given by

$$iY[G,\Gamma] = -\,\mathrm{tr}\{\ln(-G^{-1})\} - \mathrm{tr}\{G_0^{-1}(G-G_0)\} - L[G,\Gamma]$$
$$- L'[G,\Gamma] - \frac{i}{4}\mathrm{tr}\{V_0G_2[G,\Gamma]\}. \tag{107}$$

We finally write the functional in a different form using the Dyson equation of Eq. (33)

$$iY[G,\Gamma] = -\,\mathrm{tr}\{\ln(\Sigma - G_0^{-1})\} - \mathrm{tr}\{\Sigma G\} - L[G,\Gamma] - L'[G,\Gamma]$$
$$- \frac{i}{4}\mathrm{tr}\{V_0G_2[G,\Gamma]\}. \tag{108}$$

We can readily check the variationally property of this functional. We then find that

$$i\delta Y = -\,\mathrm{tr}\{[(\Sigma-G_0^{-1})^{-1}+G]\delta\Sigma\} - \mathrm{tr}\{[\Sigma(V)-\Sigma(V_0)+\tilde{\Sigma}_C(V)$$
$$-\tilde{\Sigma}_C(V_0)]\delta G\} + \frac{i}{4}\mathrm{tr}\{(\tilde{V}-\tilde{V}_0)\delta\Gamma\} = 0, \tag{109}$$

whenever $V[G,\Gamma]=V_0$ for a self-consistent solution of the Dyson equation. The variational functional (108) together with the variational property (109) is the central result of this work. In the next sections we will investigate the practical evaluation of this functional. It is important to note that although the functionals in Eqs. (107) and (108) are equivalent when evaluated on the fully self-consistent G and Γ obtained from the Dyson equation and $V[G,\Gamma]=V_0$, this is not true anymore when evaluated at approximate G and Γ. In accordance with Ref. 5 the functional forms in Eqs. (107) and (108) will be denoted as the Klein-form and Luttinger-Ward-form of the functional Y. It was demonstrated in the Φ formalism that the Luttinger-Ward form of the functional is more stable (has a smaller second derivative) when used for the calculation of total energies.[8] We will therefore use in the following the Luttinger-Ward form of the functional.

VI. Ξ DERIVABLE THEORIES ARE CONSERVING

In this section we will show that any approximate Ξ-functional leads to a corresponding Φ-functional. Since we know from the work of Baym[37] that any Φ-derivable theory is conserving it follows that also Ξ-derivable theories are conserving, i.e., they respect the macroscopic conservation laws, such a momentum, energy, and particle number conservation and related constraints such as the virial theorem.[7] Consider any approximate Ξ-functional. Then from the variational equation

$$\frac{\delta\,\Xi[G,\Gamma]}{\delta\Gamma} = -\frac{i}{4}\tilde{V}_0 \tag{110}$$

we can construct $\Gamma[G,V_0]$ as a functional of G and the bare interaction V_0 (some examples of this procedure are given in the next section). With the functional $\Gamma[G,V_0]$ defined in this way we define the following Φ-functional,

$$\Phi[G,V_0] = -\Xi[G,\Gamma[G,V_0]] - \frac{i}{4}\mathrm{tr}\{V_0 G_2[G,\Gamma[G,V_0]]\} \tag{111}$$

and the action functional

$$iY[G,V_0] = -\mathrm{tr}\{\ln(\Sigma - G_0^{-1})\} - \mathrm{tr}\{\Sigma G\} + \Phi[G,V_0], \tag{112}$$

where in this expression self-energy $\Sigma[G,\Gamma[G,V_0]]$ must also be regarded as a functional of G and V_0. From the definition of Φ it then follows directly that

$$\delta\Phi = -\mathrm{tr}\{\tilde{\Sigma}_C\delta G\} + \frac{i}{4}\mathrm{tr}\{\tilde{V}_0\delta\,\Gamma\} + \mathrm{tr}\{(\Sigma + \tilde{\Sigma}_C)\delta G\} - \frac{i}{4}\mathrm{tr}\{\tilde{V}_0\delta\Gamma\} = \mathrm{tr}\{\Sigma\,\delta G\}. \tag{113}$$

We therefore obtain the result

$$\frac{\delta\Phi}{\delta G(12)} = \Sigma(21). \tag{114}$$

We further have that the functional $Y[G,V_0]$ of Eq. (112) is stationary when

$$0 = -\mathrm{tr}\{[(\Sigma - G_0^{-1})^{-1} + G]\delta\Sigma\} - \mathrm{tr}\left\{\left(\Sigma - \frac{\delta\Phi}{\delta G}\right)\delta G\right\}, \tag{115}$$

i.e., whenever the Dyson equation is obeyed for a Φ-derivable self-energy. On the basis of the work of Baym[37] we can therefore conclude that Ξ-derivable theories are conserving.

VII. APPROXIMATIONS USING THE Ξ FUNCTIONAL

A. Practical use of the variational property

After having discussed the general properties of the functional $Y[G,\Gamma]$ we will discuss its use in the calculation of total energies. For a given approximation to $\Xi[G,\Gamma]$ the stationary point of the functional Y corresponds to an approximation for the self-energy and the four-point vertex obtained from a solution of the Dyson equation and of an equation of Bethe-Salpeter type, both of which need to be solved to self-consistency. The solution of these equations for general electronic systems is computationally very expensive or impossible. However, if we are only interested in total energies, then we can use the variational property of Y and save greatly in computational cost as the full self-consistency step can then be skipped. To illustrate this we let G and Γ be self-consistent solutions to the variational equations and we let $\tilde{G}$ and $\tilde{\Gamma}$ be approximations to G and Γ. Then we have that

$$Y[\tilde{G},\tilde{\Gamma}] = Y[G,\Gamma] + \frac{1}{2}\mathrm{tr}\left\{\frac{\delta^2 Y}{\delta G\delta G}\Delta G\Delta G\right\} + \mathrm{tr}\left\{\frac{\delta^2 Y}{\delta G\delta\Gamma}\Delta G\Delta\Gamma\right\} + \frac{1}{2}\mathrm{tr}\left\{\frac{\delta^2 Y}{\delta\Gamma\delta\Gamma}\Delta\Gamma\Delta\Gamma\right\} + \cdots, \tag{116}$$

where $\Delta G=\tilde{G}-G$ and $\Delta\Gamma=\tilde{\Gamma}-\Gamma$ are the deviations from the Green function and four-point vertex to the self-consistent ones. We see that the error we make in Y is only of second order in ΔG and $\Delta\Gamma$. We may therefore obtain rather accurate energies from rather crude inputs. These expectations were indeed borne out by our earlier calculations within the Φ formalism on atoms and molecules.[8] Obviously the actual error we make also depends on how large the second derivatives of functional Y are. For this reason the Klein and Luttinger-Ward forms of the functional perform differently. In fact, experience within the Φ-functional formalism has shown that the Luttinger-Ward is more stable than the Klein functional with respect to changes of the input Green function.[8]

B. Approximate Ξ-functionals

In the following we study some approximate schemes using the Ξ functional in order to illustrate the formalism discussed in the preceding sections. We restrict ourselves here to the two most simplest examples, the self-consistent second order approximation and the self-consistent T-matrix approximation. A more advanced approximation, also involving the particle-hole diagrams, is discussed in the section on the practical evaluation of the Ξ-functional.

The very simplest nontrivial approximation to the we can make to the Ξ-functional is to take $L_{pp}=L_{ph}=L'=0$. This yields the functional

$$iY_2[G,\Gamma] = -\mathrm{tr}\{\ln(\Sigma - G_0^{-1})\} - \mathrm{tr}\{\Sigma G\} + \frac{1}{8}\mathrm{tr}\{GG\Gamma GG\Gamma\} - \frac{i}{4}\mathrm{tr}\{V_0 G_2[G,\Gamma]\} \tag{117}$$

which we will denote by Y_2 since it only involves second order diagrams. The variational equations yield

$$G^{-1} = G_0^{-1} - \Sigma[G,\Gamma], \tag{118}$$

$$0 = \frac{1}{4}\tilde{\Gamma} - \frac{i}{4}\tilde{V}_0, \tag{119}$$

which simply implies that $\Gamma = iV_0$ and that

$$\Sigma[G,V_0](11') = -i\int d(23)V_0(1231')G(32) + \frac{1}{2}\int d(234567)V_0(1234)G(36)G(45) \times V_0(5671')G(72). \tag{120}$$

This amounts to a self-consistent solution of the Dyson equation with only second order diagrams. A fully self-consistent solution of these equations for molecules was recently carried out by us.[7] One of the next simplest approximations is obtained by taking $L'=L_{ph}=0$ which yields the functional

$$iY_{pp}[G,\Gamma] = -\mathrm{tr}\{\ln(\Sigma - G_0^{-1})\} - \mathrm{tr}\{\Sigma G\} - L_{pp}[G,\Gamma] + \frac{1}{8}\mathrm{tr}\{GG\Gamma GG\Gamma\} - \frac{i}{4}\mathrm{tr}\{V_0 G_2[G,\Gamma]\}. \tag{121}$$

The variational equations correspond to

$$G^{-1} = G_0^{-1} - \Sigma[G,\Gamma] \tag{122}$$

$$0 = -\frac{\delta L_{pp}}{\delta\Gamma} + \frac{1}{4}\tilde{\Gamma} - \frac{i}{4}\tilde{V}_0, \tag{123}$$

where Σ is calculated from Eqs. (52) and (53). The second variational, Eq. (124), corresponds to

$$iV_0 = \Gamma\left(1 + \frac{1}{2}GG\Gamma\right)^{-1}. \tag{124}$$

This equation can be inverted to give

$$\Gamma = (iV_0)\left(1 - \frac{1}{2}GG(iV_0)\right)^{-1}, \tag{125}$$

and expresses the renormalized four-point vertex as a sum of particle-particle (direct and exchange) ladder diagrams in terms of the bare potential V_0. The corresponding self-energy is then readily obtained from Eqs. (52) and (53) by inserting the Γ of Eq. (125) in Eq. (53). This approximation is equivalent to the self-consistent T-matrix approximation. It is clear that the set of approximations can be made more and more advanced by using more sophisticated approximations for the Ξ-functional. In the following sections we will discuss the numerical evaluation of iY. We will then, among other things, consider an approximate four-point vertex obtained from the T-matrix approximation as an approximate input for the evaluation of the energy functional iY at a more sophisticated level of perturbation theory.

VIII. PRACTICAL EVALUATION OF THE FUNCTIONAL

A. Evaluation of the traces

In this section we discuss how to evaluate the functional $Y[G,\Gamma]$ in actual applications. Our goal is to evaluate Y for an equilibrium system in which case all two-time quantities depend on relative time variables on the vertical stretch of the Keldysh contour. In that case it is convenient to go over to a Matsubara representation (we use the notation of Kadanoff and Baym[48])

$$A(t-t') = \frac{i}{\beta}\sum_z e^{-iz(t-t')}A(z), \tag{126}$$

$$A(z) = \int_0^{-i\beta} dt A(t-t')e^{iz(t-t')}, \tag{127}$$

where the times are imaginary ($t=-i\tau$ for $0 \leqslant \tau \leqslant \beta$) and where $z=in\pi/\beta$ are the Matsubara frequencies which run over even or odd integers n depending on whether A is a bosonic or fermionic function. In this way the equation of motion for the Green function simply attains the form

$$[z - h(\mathbf{x}_1)]G(\mathbf{x}_1\mathbf{x}_2,z) = \delta(\mathbf{x}_1,\mathbf{x}_2) + \int d\mathbf{x}_3\Sigma(\mathbf{x}_1\mathbf{x}_3,z)G(\mathbf{x}_3\mathbf{x}_2,z). \tag{128}$$

For the traces of two-point functions we have the expression

$$\mathrm{tr}\,A = \int_0^{-i\beta} dt d\mathbf{x} A(1,1^+) = \lim_{\eta\to 0^+}\sum_z \int d\mathbf{x} e^{\eta z}A(\mathbf{x},\mathbf{x},z). \tag{129}$$

For the various traces in the functional Y it is further convenient to introduce a one-particle basis, such that we can write

$$A(\mathbf{x}_1,\mathbf{x}_2,z) = \sum_{ij} A_{ij}(z)\varphi_i(\mathbf{x}_1)\varphi_j^*(\mathbf{x}_2). \tag{130}$$

Then we have, for instance, that

$$\mathrm{tr}\,AB = \lim_{\eta\to 0^+}\sum_{ij,z} e^{\eta z}A_{ij}(z)B_{ji}(z). \tag{131}$$

If we choose the orbitals to be eigenfunctions of the one-particle Hamiltonian h,

$$h(\mathbf{x})\varphi_i(\mathbf{x}) = e_i\varphi_i(\mathbf{x}), \tag{132}$$

then the equation of motion of the Green function attains the form

$$(z-e_i)G_{ij}(z)=\delta_{ij}+\sum_k \Sigma_{ik}(z)G_{kj}(z) \tag{133}$$

and we see immediately that the noninteracting Green function G_0 is given by

$$G_{0,ij}(z)=\frac{\delta_{ij}}{z-e_i}. \tag{134}$$

Consequently the grand potential for the noninteracting system is given by $\Omega_0=iY_0/\beta$ where[10,28,49]

$$\begin{aligned}\Omega_0&=-\frac{1}{\beta}\mathrm{tr}\ \ln\{-G_0^{-1}\}=-\frac{1}{\beta}\lim_{\eta\to 0^+}\sum_i\sum_z e^{\eta z}\ln(e_i-z)\\&=-\frac{1}{\beta}\sum_i \ln(1+e^{-\beta e_i}).\end{aligned} \tag{135}$$

In the zero-temperature limit $\beta\to\infty$ this simply gives

$$\lim_{\beta\to\infty}\Omega_0=\sum_{i=1}^N e_i, \tag{136}$$

where the sum runs over the N occupied electron orbitals. Note that the chemical potential μ is included in h such that $e_i=\epsilon_i-\mu$ where ϵ_i are the eigenvalues of the one-body part of the Hamiltonian.

As a next step we will discuss how to evaluate the functional on an approximate Green function $\tilde G$ and an approximate vertex $\tilde\Gamma$. The input Green function will in practice not be a fully interacting Green function but rather one obtained from a local density approximation or from a Hartree-Fock approximation. With approximate inputs $\tilde G$ and $\tilde\Gamma$ the first term in Eq. (109) can be written in a computationally convenient form as[5]

$$\begin{aligned}&-\mathrm{tr}\ \ln\{\Sigma[\tilde G,\tilde\Gamma]-G_0^{-1}\}\\&\quad=-\mathrm{tr}\{\ln(-\bar G^{-1})\}-\mathrm{tr}\{\ln(1-\bar G\Sigma_C[\tilde G,\tilde\Gamma])\},\end{aligned} \tag{137}$$

where we defined

$$\Sigma_C[\tilde G,\tilde\Gamma]=\Sigma[\tilde G,\tilde\Gamma]-\Sigma^{HF}[\tilde G] \tag{138}$$

and the Green function $\bar G$ from the Dyson equation

$$\bar G=G_0+G_0\Sigma^{HF}[\tilde G]\bar G. \tag{139}$$

The Green function $\bar G$ therefore presents the first iteration towards the Hartree-Fock Green function starting from $\tilde G$. Therefore $\bar G=G^{HF}$ when we take $\tilde G=G^{HF}$ as an input Green function. The term Σ_C represents the correlation part of the self-energy evaluated at an approximate $\tilde G$ and $\tilde\Gamma$. The reason for introducing $\bar G$ is that by doing this we have in the last term of Eq. (137) eliminated a static part of the self-energy, which makes this term well defined without a convergence factor and also makes it decay much faster for large frequencies, which is computationally advantageous as was shown in Ref. 5. The first term in Eq. (137) can be evaluated analytically to give

$$i\bar Y_0=-\mathrm{tr}\{\ln(-\bar G^{-1})\}=-\sum_i \ln(1+e^{-\beta\bar e_i}), \tag{140}$$

where $\bar e_i=\bar\epsilon_i-\mu$ and $\bar\epsilon_i$ are the eigenvalues the Hartree-Fock equations with a nonlocal self-energy $\Sigma^{HF}[\tilde G]$. In practice (for instance for LDA input Green functions) these eigenvalues are close to the true Hartree-Fock eigenvalues. Now the functional $Y[\tilde G,\tilde\Gamma]$ can be written as

$$\begin{aligned}iY[\tilde G,\tilde\Gamma]&=i\bar Y_0-\mathrm{tr}\{\ln(1-\bar G\Sigma_C[\tilde G,\tilde\Gamma])\}-\mathrm{tr}\{\Sigma[\tilde G,\tilde\Gamma]\tilde G\}\\&\quad-L[\tilde G,\tilde\Gamma]-L'[\tilde G,\tilde\Gamma]-\frac{i}{4}\mathrm{tr}\{V_0G_2[\tilde G,\tilde\Gamma]\}.\end{aligned} \tag{141}$$

The second term can be evaluated by diagonalization of $\bar G\Sigma_C$ since for a matrix $A(z)$ we have

$$\mathrm{tr}\{\ln(1-A)\}=\lim_{\eta\to 0^+}\sum_{z,i}e^{\eta z}\ln[1-\lambda_i(z)], \tag{142}$$

where $\lambda_i(z)$ are the eigenvalues of $A(z)$. This completes one part of the evaluation of the functional Y.

B. Evaluation of the $L'=0$ functional

Let us now discuss the evaluation of the $L[G,\Gamma]$ and $L'[G,\Gamma]$ functionals. The evaluation of even the lowest order term of the L' functional will be computationally very difficult in practice. The first term in the expansion of L' is the pentagon of Fig. 10 containing five four-point vertices Γ. Since every four-point vertex depends on four space-time coordinates the pentagon is (apart from the spin summations) formally an 80-dimensional integral. Fortunately, even the approximation $L'=0$ represents a very sophisticated many-body approximation. We will therefore in the following concentrate on this case and consider the evaluation of the functional

$$\begin{aligned}iY[G,\Gamma]&=i\bar Y_0-\mathrm{tr}\{\ln(1-\bar G\Sigma_C[G,\Gamma])\}-\mathrm{tr}\{\Sigma G\}-L[G,\Gamma]\\&\quad-\frac{i}{4}\mathrm{tr}\{V_0G_2[G,\Gamma]\}.\end{aligned} \tag{143}$$

The evaluation of the first terms in this expression has been discussed in the preceding subsection and we will therefore concentrate on evaluation of $L[G,\Gamma]$. In this term the trace is taken over two-particle functions and its evaluation will therefore be slightly different from the case discussed above.

As our approximate Γ we will take the sum of all particle-particle and exchange ladders in terms of V_0 for which we will eventually take the zero-frequency limit. This is the approximate T matrix used in Ref. 23. This approximate Γ we will denote as $\tilde\Gamma$. This approximate Γ will be expressed in terms of our approximate Green function which we will denote with $\tilde G$. Then from Eq. (78) we have

$$\tilde\Gamma=iV_0+\frac{i}{2}V_0\tilde G\tilde G\tilde\Gamma. \tag{144}$$

If we write

$$V_0(1234) = \delta(t_1,t_2)\,\delta(t_1,t_4)\,\delta(t_2,t_3)\,V_0(\mathbf{x}_1\mathbf{x}_2\mathbf{x}_3\mathbf{x}_4) \quad (145)$$

with $V_0(\mathbf{x}_1\mathbf{x}_2\mathbf{x}_3\mathbf{x}_4)$ explicitly given in Eq. (23), we see that we can write

$$\widetilde{\Gamma}(1234) = \delta(t_1,t_2)\,\delta(t_3,t_4)\,\gamma(\mathbf{x}_1\mathbf{x}_2\mathbf{x}_3\mathbf{x}_4;t_1t_3). \quad (146)$$

If we further expand γ in a basis as

$$\gamma(\mathbf{x}_1\mathbf{x}_2\mathbf{x}_3\mathbf{x}_4;t_1t_3) = \sum_{ijkl} \gamma_{ijkl}(t_1t_3)\,\varphi_i^*(\mathbf{x}_1)\,\varphi_j^*(\mathbf{x}_2)\,\varphi_k(\mathbf{x}_3)\,\varphi_l(\mathbf{x}_4) \quad (147)$$

then from Eq. (144) we see that γ satisfies

$$\gamma_{ijkl}(t_1t_3) = i\,\delta(t_1,t_3)\,V_{0,ijkl} + \frac{i}{2}\sum_{pqrs}\int_0^{-i\beta} dt_2\, V_{0,ijpq} \times \widetilde{G}_{qr}(t_1,t_2)\widetilde{G}_{ps}(t_1,t_2)\,\gamma_{rskl}(t_2t_3), \quad (148)$$

which in frequency space attains the form

$$\gamma_{ijkl}(z) = iV_{0,ijkl} - \frac{1}{2\beta}\sum_{z_1}\sum_{pqrs} V_{0,ijpq} \times \widetilde{G}_{qr}(z_1)\widetilde{G}_{ps}(z-z_1)\,\gamma_{rskl}(z) \quad (149)$$

(note that for γ we have to sum over the even Matsubara frequencies). For simple approximate Green functions $\widetilde{G}$ of Hartree-Fock or local density type the frequency sum over z_1 is readily evaluated. We are now ready to evaluate the functionals $L_{pp}[\widetilde{G},\widetilde{\Gamma}]$ and $L_{ph}[\widetilde{G},\widetilde{\Gamma}]$. They are given by the expressions

$$L_{pp} = \mathrm{tr}\{\ln(1+A)\} - \mathrm{tr}\{A\} + \tfrac{1}{2}\mathrm{tr}\{A^2\}, \quad (150)$$

$$L_{ph} = \tfrac{1}{2}\mathrm{tr}\{\ln(1-B)\} + \tfrac{1}{2}\mathrm{tr}\{B\} + \tfrac{1}{4}\mathrm{tr}\{B^2\}, \quad (151)$$

where $A = GG\Gamma$ and $B = \widehat{\mathrm{GG}}\bar{\Gamma}$. Therefore in order to calculate L_{pp} and L_{ph} we have to diagonalize A and B in a two-particle basis. Let us start by the calculation of A. We have for our approximate $\widetilde{\Gamma}$ and $\widetilde{G}$,

$$A_{ijkl}(t_1t_2t_3t_4) = \delta(t_3,t_4)\sum_{pq}\int_0^{-i\beta} dt_5\,\widetilde{G}_{ip}(t_1,t_5) \times \widetilde{G}_{jq}(t_2,t_5)\,\gamma_{pqkl}(t_5t_3). \quad (152)$$

Because of the equal-time δ function in Eq. (152) we find that

$$\begin{aligned}\mathrm{tr}\{A^n\} &= \int d(11'\ldots nn')\langle 11'|A|22'\rangle \cdots \langle nn'|A|11'\rangle \\ &= \sum_{p_1\cdots p_n}\int_0^{-i\beta} d(t_1\ldots t_n)\bar{A}_{p_1p_2}(t_1,t_2)\ldots\bar{A}_{p_np_1}(t_n,t_1) \\ &= \lim_{\eta\to 0^+}\sum_z e^{\eta z}\bar{A}_{p_1p_2}(z)\ldots\bar{A}_{p_np_1}(z), \end{aligned} \quad (153)$$

where $p_k = (i_kj_k)$ are multi-indices and where we defined

$$\bar{A}_{ijkl}(t_1t_3) = \sum_{pq}\int_0^{-i\beta} dt_5\,\widetilde{G}_{ip}(t_1,t_5)\widetilde{G}_{jq}(t_1,t_5)\,\gamma_{pqkl}(t_5t_3), \quad (154)$$

which in frequency space attains the form

$$\bar{A}_{ijkl}(z) = \frac{i}{\beta}\sum_{z_1,pq}\widetilde{G}_{ip}(z_1)\widetilde{G}_{jq}(z-z_1)\,\gamma_{pqkl}(z). \quad (155)$$

From diagonalization of $\bar{A}_{pq}(z)$ where $p=(ij)$ and $q=(kl)$ we then immediately obtain

$$L_{pp}[\widetilde{G},\widetilde{\Gamma}] = \sum_{z,p}\left(\ln[1+\lambda_p(z)] - \lambda_p(z) + \frac{1}{2}\lambda_p^2(z)\right), \quad (156)$$

where $\lambda_p(z)$ are the eigenvalues of $\bar{A}(z)$. Let us finally concentrate on the evaluation of B. This expression is given by

$$B_{ijkl}(t_1t_2t_3t_4) = \sum_{pq}\widetilde{G}_{qi}(t_4,t_1)\widetilde{G}_{jp}(t_2,t_3)\,\gamma_{pklq}(t_3t_4). \quad (157)$$

This expression depends on three relative times which makes it awkward to evaluate the logarithm. We therefore follow Ref. 23 and replace in frequency space $\gamma_{ijkl}(z)$ by its zero-frequency limit $\gamma_{ijkl}(0)$,

$$\gamma_{ijkl}(t_3t_4) = \gamma_{ijkl}(0)\,\delta\,(t_3,t_4) \quad (158)$$

such that

$$B_{ijkl}(t_1t_2t_3t_4) = \delta(t_3t_4)\sum_{pq}\widetilde{G}_{qi}(t_4,t_1)\widetilde{G}_{jp}(t_2,t_3)\,\gamma_{pklq}(0). \quad (159)$$

Then, similarly as for the quantity A we have

$$\mathrm{tr}\{B^n\} = \lim_{\eta\to 0^+}\sum_z e^{\eta z}\bar{B}_{p_1p_2}(z)\ldots\bar{B}_{p_np_1}(z), \quad (160)$$

where

$$\bar{B}_{ijkl}(z) = \frac{i}{\beta}\sum_{z_1,pq}\widetilde{G}_{qi}(z_1)\widetilde{G}_{jp}(z_1+z)\,\gamma_{pklq}(0). \quad (161)$$

Now $\bar{B}(z)$ is readily diagonalized with respect to its two-particle indices to give

$$L_{ph}[\widetilde{G},\widetilde{\Gamma}] = \sum_{z,p}\left(\frac{1}{2}\ln[1-\hat{\lambda}_p(z)] + \frac{1}{2}\hat{\lambda}_p(z) + \frac{1}{4}\hat{\lambda}_p^2(z)\right), \quad (162)$$

where $\hat{\lambda}_p(z)$ are the eigenvalues of $\bar{B}(z)$. The full functional $L[\widetilde{G},\widetilde{\Gamma}]$ is then constructed as

$$L[\widetilde{G},\widetilde{\Gamma}] = L_{pp}[\widetilde{G},\widetilde{\Gamma}] + L_{ph}[\widetilde{G},\widetilde{\Gamma}] - \frac{1}{8}\mathrm{tr}\{A^2\}, \quad (163)$$

where the last term is easily found by summing the squares of the eigenvalues of A and performing a frequency sum. It finally remains to calculate an explicit expression for $\Sigma[\widetilde{G},\widetilde{\Gamma}]$ and to evaluate the last term in Eq. (143). The self-energy is readily calculated from Eqs. (52) and (53) to be

$$\Sigma_{ij}(z) = \Sigma_{ij}^{HF} + \Sigma_{ij,C}(z), \tag{164}$$

where

$$\Sigma_{ij}^{HF} = \frac{1}{\beta} \lim_{\eta \to 0^+} \sum_z V_{0,ipqj} \widetilde{G}_{qp}(z) \tag{165}$$

and

$$\Sigma_{ij,C}(z) = \frac{i}{2\beta} \sum_{z_1,z_2} \sum_{pqrstu} V_{0,ipqr} \widetilde{G}_{rs}(z_1) \widetilde{G}_{qt}(z_2) \times \widetilde{G}_{up}(z_1 + z_2 - z) \gamma_{stuj}(0). \tag{166}$$

This expression is, of course, considerably simplified when we use a diagonal input Green function. This finally concludes the discussion on the practical evaluation of the functional.

In summary: evaluation of the functional Y in practice therefore essentially involves the diagonalization of the one-particle matrix $A(z)$ of Eq. (142) and the diagonalization of the matrices $\bar{A}(z)$ and $\bar{B}(z)$ of Eqs. (154) and (161) in a two-particle basis followed by a frequency summation. This is, for instance within the DMFT approach used by Katsnelson and Lichtenstein,[23] a numerically quite feasible procedure.

IX. CONCLUSIONS

In this work we studied variational functionals of the Green function and the renormalized four-point vertex in order to calculate total energies for strongly correlated systems. The variational functionals were derived by Legendre transform techniques starting from an expression of the action (or grand potential) defined on the Keldysh contour. The structure of the functionals was further analyzed by means of diagrammatic techniques. We finally gave a detailed discussion of the practical use and evaluation of these for different approximate functionals. Future applications along the lines described are intended.

Finally we comment on further applications of the variational functionals. It was found that within the Φ and the Ψ formalism could be successfully used to derive expressions for response functions within time-dependent density-functional theory (TDDFT).[38] This was done by inserting approximate Green functions $G[v]$, coming from a noninteracting system with a local potential v, into the variational functionals. Then the potentials were optimized by requiring that $\delta Y / \delta v = 0$. Due to the one-to-one correspondence between the density and the potential (as follows from the time-dependent generalization of the Hohenberg-Kohn theorem[2]) this then implies that we are optimizing a time-dependent density functional. The optimized potentials are then to be interpreted as Kohn-Sham potentials. In this way one obtains a density functional for every diagrammatic expression from the Φ or Ψ-functional. A similar procedure can now be carried out for the Ξ-functional.

A further point of future investigation is concerned with finding the variationally most stable functional. It was already mentioned that the Klein and Luttinger-Ward (LW) forms of the functional lead to different results. The Luttinger-Ward form was found to be more stable. This is probably due to the fact that the second derivatives of the LW functional are smaller than those of the Klein functional. However, it is very well possible that one could derive a better functional that would make the second derivatives even smaller or make them vanish. In that case the errors we make would be only to third order in the deviation ΔG of the input Green to the true self-consistent one. This still remains an issue for future investigations. Finally we mention that work on implementation of the formalism discussed here is in progress.

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APPENDIX A: A GENERATING FUNCTIONAL FOR THE GREEN FUNCTION

In order to obtain the Green functions as variational derivatives we define[37] an evolution operator in terms of a time and space nonlocal potential $u(12)$,

$$\hat{U}[u](t_0 - i\beta, t_0) = T_C \exp\left(-i \int dt \hat{H}(t) - i \int d1 \int d2 \hat{\psi}^\dagger(\mathbf{x}_1) u(12) \hat{\psi}(\mathbf{x}_2) \right), \tag{A1}$$

where we used the compact notation $1 = (\mathbf{x}_1, t_1)$. Since we now have two times in the exponent this expression only has meaning if we define how the time ordering is specified if we expand this expression. It is defined as follows:

$$\hat{U}[u](t_0 - i\beta, t_0) \equiv \hat{U}[u=0](t_0 - i\beta, t_0) + \sum_{n=1}^{\infty} \frac{(-i)^n}{n!} \times \int d(11' \dots nn') u(1'1) \dots u(n'n) \times \langle T_C[\hat{\psi}_H^\dagger(1') \hat{\psi}_H(1) \dots \hat{\psi}_H^\dagger(n') \hat{\psi}_H(n)] \rangle, \tag{A2}$$

where the expectation values under the integral sign are averages [as in Eq. (8)] in the absence of the nonlocal field u. This definition agrees in the limit of a time-local potential, i.e., $u(12) = u(\mathbf{x}_1 t_1, \mathbf{x}_2 t_1) \delta(t_1^+, t_2)$, with an expression that can be derived directly from the time-dependent Schrödinger equation. We now define the functionals

$$Z[u] = \mathrm{Tr}\{U[u](t_0 - i\beta, t_0)\}, \tag{A3}$$

$$iY[u] = -\ln Z[u]. \tag{A4}$$

Then the one-particle Green function in the presence of the nonlocal field u is defined as

$$G_u(11') \equiv i\frac{\delta Y}{\delta u(1'1)} = -\frac{1}{Z[u]}\frac{\delta Z}{\delta u(1'1)}. \tag{A5}$$

When evaluated at $u=0$ the Green function reduces to the familiar one

$$G_{u=0}(11') = -i\langle T_C[\hat{\psi}_H^\dagger(1)\hat{\psi}(1')]\rangle. \tag{A6}$$

Let us note that one should be careful with dealing with time-nonlocal potentials. It would, for instance, be tempting to think that G_u would be given by the expression

$$G_u(11') = -i\frac{\mathrm{Tr}\{U[u](t_0 - i\beta, t_0)T_C[\hat{\psi}_H^\dagger(1')\hat{\psi}_H(1)]\}}{\mathrm{Tr}\{U[u](t_0 - i\beta, t_0)\}}, \tag{A7}$$

where the Heisenberg operators in the presence of u would be given by $\hat{O}_H = U[u](t_0,t)\hat{O}\hat{U}[u](t,t_0)$. However, this expression is *not* valid if u is nonlocal in time. For instance, when expanding Eqs. (A5) and (A7) in powers of u using Eq. (A2), one immediately sees that certain time orderings of the field operators in Eq. (A5) are absent in Eq. (A7). Similarly the evolution operator $\hat{U}[u](t,t')$ does not satisfy a simple equation of motion. However, we can still derive the equations of motion for G_u on the basis of the hierarchy equations of the n-body Green functions in the absence of the nonlocal field u, as we will show below.

More generally we can now define n-body Green functions $G_{n,u}$ from a repeated differentiation of $Z[u]$, i.e.,

$$\frac{1}{Z[u]}\frac{\delta^n Z}{\delta u(1'1)\ldots\delta u(n'n)} = \epsilon_n G_{n,u}(1\ldots n, 1'\ldots n'), \tag{A8}$$

where $\epsilon_n = (-1)^{n(n+1)/2}$. The prefactor ϵ_n results from reordering the operator product $\langle T_C[\hat{\psi}^\dagger(1')\hat{\psi}(1)\ldots\hat{\psi}^\dagger(n')\hat{\psi}(n)]\rangle$ to $\langle T_C[\hat{\psi}(1)\ldots\hat{\psi}(n)\hat{\psi}^\dagger(1')\ldots\hat{\psi}^\dagger(n')]\rangle$ as is easily verified by induction. One can readily check that for $u=0$, Eq. (A8) agrees with our previous definition of the n-body Green function of Eq. (19). From Eq. (A8) we further immediately obtain that

$$\begin{aligned}\frac{\delta G_u(14)}{\delta u(32)} &= \frac{\delta}{\delta u(32)}\left(-\frac{1}{Z[u]}\frac{\delta Z}{\delta u(41)}\right)\\ &= \frac{1}{Z^2}\frac{\delta Z}{\delta u(14)}\frac{\delta Z}{\delta u(32)} - \frac{1}{Z}\frac{\delta^2 Z}{\delta u(41)\delta u(32)}\\ &= G_u(14)G_u(23) - G_{2,u}(1234).\end{aligned} \tag{A9}$$

This is Eq. (27) used in Sec. III. As a next step we derive the hierarchy equations for the Green functions $G_{n,u}$. From Eq. (A8) we see that we can expand the functional $Z[u]$ as a Taylor series expansion in u as

$$Z[u] = Z[0]\sum_{n=0}^{\infty}\frac{\epsilon_n}{n!}\int d(11'\ldots nn') \times G_n(1\ldots n, 1'\ldots n')u(1'1)\ldots u(n'n), \tag{A10}$$

where the term with $n=0$ is just defined to be one. The Green functions G_n are the Green functions in the absence of the field u. The one-body and n-body Green functions can therefore be expressed in terms of the field-free Green functions using Eqs. (A5), (A8), and (A10). One obtains for G_u and $G_{2,u}$ the equations

$$\frac{Z[u]}{Z[0]}G_u(11') = G(11') - \sum_{n=2}^{\infty}\frac{\epsilon_n}{(n-1)!}\int d(22'\ldots nn') \times G_n(1\ldots n, 1'\ldots n')u(2'2)\ldots u(n'n), \tag{A11}$$

$$\begin{aligned}&\frac{Z[u]}{Z[0]}G_{2,u}(12;1'2')\\ &= G(12;1'2') - \sum_{n=3}^{\infty}\frac{\epsilon_n}{(n-2)!}\int d(33'\ldots nn')\\ &\quad\times G_n(1\ldots n, 1'\ldots n')u(3'3)\ldots u(n'n).\end{aligned} \tag{A12}$$

From these expressions we see that G_u and $G_{2,u}$ inherit the Kubo-Martin-Schwinger boundary conditions from the G_n. If we act with the operator $i\partial_{t_1} - h(1)$ on both sides of Eq. (A11) and use the Martin-Schwinger hierarchy equations (21) for the Green functions G_n in the absence of the u field together with Eq. (A12), we obtain, after slightly tedious but straightforward manipulations, the equation of motion for G_u,

$$\begin{aligned}[i\partial_{t_1} - h(1)]G_u(11') &= \delta(11') + \int d2\, u(12)G_u(21')\\ &\quad - i\int d\mathbf{x}\, v(\mathbf{x}_1,\mathbf{x})G_{2,u}(1,\mathbf{x}t_1,\mathbf{x}t_1^+,1').\end{aligned} \tag{A13}$$

By functional differentiation with respect to u we can generate equations of motion for the higher-order Green functions. To see this we first multiply Eq. (A13) by $Z[u]$ to obtain

$$\begin{aligned}[i\partial_{t_1} - h(1)](-i)\langle 11'\rangle &= \delta(11')Z[u] + \int d\bar{1}\, u(1\bar{1})(-i)\langle\bar{1}1'\rangle\\ &\quad - i\int d\mathbf{x}\, v(\mathbf{x}_1,\mathbf{x})(-i)^2\langle 1,\mathbf{x}t_1,\mathbf{x}t_1^+,1'\rangle,\end{aligned} \tag{A14}$$

where we introduced the simplified notation

$$\langle 1\ldots n; 1'\ldots n'\rangle = Z[u]G_{n,u}(1\ldots n, 1'\ldots n'). \tag{A15}$$

We use the convention that the primed variables are always associated with creation operators and that the unprimed variables are always associated with the annihilation operators. Taking the functional derivative of Eq. (A14) with respect to $u(2'2)$ then gives

$$\begin{aligned}[i\partial_{t_1} - h(1)](-i)^2\langle 11'2'2\rangle &= \delta(11')(-i)\langle 2'2\rangle + \delta(12')(-i)\langle 21'\rangle \\ &\quad + \int d\bar{1}u(1\bar{1})(-i)^2\langle \bar{1}1'2'2\rangle \\ &\quad - i\int d\mathbf{x}v(\mathbf{x}_1,\mathbf{x})(-i)^3\langle 1,\mathbf{x}t_1,\mathbf{x}t_1^+,1'2'2\rangle. \quad \text{(A16)}\end{aligned}$$

Reordering the indices and dividing by $Z[u]$ then gives

$$\begin{aligned}[i\partial_{t_1} - h(1)]G_{2,u}(121'2') &= -\delta(11')G_u(22') + \delta(12')G_u(21') \\ &\quad + \int d\bar{1}u(1\bar{1})G_{2,u}(\bar{1}21'2') \\ &\quad - i\int d\mathbf{x}v(\mathbf{x}_1,\mathbf{x})G_{3,u}(12,\mathbf{x}t_1,\mathbf{x}t_1^+,1'2'). \quad \text{(A17)}\end{aligned}$$

By continued differentiation we obtain the general hierarchy equations for $G_{n,u}$

$$\begin{aligned}&[i\partial_{t_1} - h(1)]G_{n,u}(1\ldots n,1'\ldots n') \\ &= \sum_{j=1}^{n}\delta(1j')(-1)^{n-j} \\ &\quad \times G_{n-1,u}(2\ldots n,1'\ldots j'-1,j'+1\ldots n') \\ &\quad + \int d\bar{1}u(1\bar{1})G_{n,u}(\bar{1}2\ldots n,1'\ldots n') \\ &\quad - i\int d\mathbf{x}v(\mathbf{x}_1,\mathbf{x})G_{n+1,u}(1\ldots n,\mathbf{x}t_1,\mathbf{x}t_1^+,1'\ldots n').\end{aligned}$$

(A18)

These equations are readily checked by induction if we multiply them by $Z[u]$ and take the functional derivative with respect to $u(n'+1,n+1)$. We have therefore established that Green functions $G_{n,u}$ satisfy an obvious generalization of the hierarchy equations. The relation (A18) is the main result of this Appendix and will be essential to the derivation in the next section. Note further that Eq. (A18) can be used to derive a Wick's theorem in the presence of the nonlocal field u. If we put $w=0$ we find that the noninteracting n-body Green functions $G_{n,u}$ satisfy Eq. (A18) if they are written as determinants in terms of G_u.

APPENDIX B: THE EQUATION OF MOTION OF $G_{u,V}$

The main goal in this Appendix is to derive the equations of motion for the Green function in the presence of the a nonlocal one-body potential $u(12)$ and a nonlocal two-body potential $V(1234)$. As in Appendix A the main difficulty is caused by the fact that u and V are nonlocal in time. Our final result can be obtained with the help of Eq. (A18). Let $Z[u,V]$ be given by

$$Z[u,V] = \mathrm{Tr}\{\hat{U}[u,V](t_0 - i\beta,t_0)\} \quad \text{(B1)}$$

where

$$\begin{aligned}\hat{U}[u,V](t_0-i\beta,t_0) = T_C\exp\biggl(&-i\int dt\hat{H}_0(t) \\ &- i\int d1\int d2\hat{\psi}^\dagger(\mathbf{x}_1)u(12)\hat{\psi}(\mathbf{x}_2) \\ &- \frac{i}{4}\int d(1234)V(1234) \\ &\times \hat{\psi}^\dagger(\mathbf{x}_1)\hat{\psi}^\dagger(\mathbf{x}_2)\hat{\psi}(\mathbf{x}_3)\hat{\psi}(\mathbf{x}_4)\biggr). \quad \text{(B2)}\end{aligned}$$

Due to the multiple time integrals this expression has only meaning when we define how the time ordering is specified when we expand this expression. We define

$$\begin{aligned}\hat{U}[u,V](t_0-i\beta,t_0) \equiv \hat{U}[0,0](t_0-i\beta,t_0) + \sum_{n,m=1}^{\infty}\frac{(-i)^{n+m}}{n!m!4^m} \\ \times\int d(y_{\bar{1}}\ldots y_{\bar{n}})d(X_1\ldots X_m) \\ \times u_{\bar{1}}\ldots u_{\bar{n}}V_1\ldots V_m \\ \times T_C[\hat{y}_{\bar{1}}\ldots\hat{y}_{\bar{n}}\hat{X}_1\ldots\hat{X}_m], \quad \text{(B3)}\end{aligned}$$

where for the coordinates we introduced the short notation

$$y_{\bar{i}} = (\bar{i}',\bar{i}), \quad \text{(B4)}$$

$$X_i = ((2i-1)',(2i)',2i-1,2i) \quad \text{(B5)}$$

and we further defined

$$u_{\bar{i}} = u(y_i), \quad \text{(B6)}$$

$$\hat{y}_{\bar{i}} = \hat{\psi}_H^\dagger(\bar{i}')\hat{\psi}_H(\bar{i}), \quad \text{(B7)}$$

$$V_i = V(X_i), \quad \text{(B8)}$$

$$\hat{X}_i = \hat{\psi}_H^\dagger((2i-1)')\hat{\psi}_H^\dagger((2i)')\hat{\psi}_H(2i-1)\hat{\psi}_H(2i), \quad \text{(B9)}$$

where the Heisenberg representation of the operators is defined with respect to $\hat{H}_0$. We then define the n-particle Green function $G_{n,u,V}$ in the presence of the time-nonlocal fields u and V as

$$\epsilon_n G_{n,u,V}(1\ldots n;1'\ldots n') \equiv \frac{1}{Z[u,V]}\frac{\delta^n Z[u,V]}{\delta u(1'1)\ldots u(n'n)},$$

(B10)

where $\epsilon_n = (-1)^{n(n+1)/2}$. For $V=0$ this definition agrees with the definition (A8) in Appendix A in the absence of two-particle interactions. Now from Eq. (B3) one can readily derive that

$$\frac{\delta^k Z[u,V]}{\delta V_1\ldots\delta V_k} = \frac{(-i)^k}{4^k}\frac{\delta^{2k}Z[u,V]}{\delta u(1'1)\ldots u((2k)',2k)}. \quad \text{(B11)}$$

With this equation we find that we can express the Green functions equivalently as

$$G_{2n,u,V}(1\ldots 2n;1'\ldots(2n)')=\frac{4^n(-i)^n}{Z[u,V]}\frac{\delta^{k}Z[u,V]}{\delta V_1\ldots\delta V_n}, \tag{B12}$$

$$G_{2n+1,u,V}(\bar{1},1,\ldots 2n;\bar{1}',1'\ldots(2n)') = -\frac{4^n(-i)^n}{Z[u,V]}\frac{\delta^{2n+1}Z[u,V]}{\delta u_{\bar{1}}V_1\ldots V_n}. \tag{B13}$$

As a particular case we have

$$G_{u,V}(11')=-\frac{1}{Z[u,V]}\frac{\delta Z[u,V]}{\delta u(1'1)}, \tag{B14}$$

$$G_{2,u,V}(121'2')=-\frac{4i}{Z[u,V]}\frac{\delta Z[u,V]}{\delta V(1'2'12)}. \tag{B15}$$

These equations are two basic starting equations, Eqs. (41) and (42), of Sec. IV. It remains to show that they are related by an equation of motion. From Eqs. (B12) and (B13) we see that $Z[u,V]$ has the following Taylor expansion around $V=0$:

$$\frac{Z[u,V]}{Z[u,0]}=\sum_{n=0}^{\infty}\frac{i^n}{n!4^n}\int d(X_1\ldots X_n) \times G_{2n,u}(1\ldots 2n;1'\ldots 2n')V_1\ldots V_n, \tag{B16}$$

where we denote $G_{n,u}=G_{n,u,V=0}$. Similarly for $G_{u,V}$ we have from Eq. (B13) the Taylor series expansion

$$\frac{Z[u,V]}{Z[u,0]}G_{u,V}(\bar{1}\bar{1}')=G_u(\bar{1},\bar{1}')+\sum_{n=1}^{\infty}\frac{i^n}{n!4^n}\int d(X_1\ldots X_n) \times G_{2n+1,u}(\bar{1}1\ldots 2n;\bar{1}'1'\ldots 2n')V_1\ldots V_n \tag{B17}$$

and for the two-particle Green function from Eq. (B12),

$$\frac{Z[u,V]}{Z[u,0]}G_{2,u,V}(\bar{1}\bar{2},\bar{1}'\bar{2}') = G_{2,u}(\bar{1}\bar{2},\bar{1}'\bar{2}')-i\sum_{n=2}^{\infty}\frac{i^n}{4^{n-1}(n-1)!}\int d(X_1\ldots X_{n-1}) \times G_{2n,u}(\bar{1}\bar{2}12\ldots 2(n-1); \bar{1}'\bar{2}'1'2'\ldots 2(n-1)')V_1\ldots V_{n-1}. \tag{B18}$$

To obtain an equation of motion of $G_{u,V}$ we can use the hierarchy equations for $G_{n,u}$ of Eq. (A18) for $w=0$,

$$[i\partial_{t_1}-h(1)]G_{n,u}(1\ldots n,1'\ldots n') = \sum_{j=0}^{n-1}\delta(1j')(-1)^{n-j}G_{n-1,u}(2\ldots n,1'\ldots(j-1)', (j+1)'\ldots n')+\int d\bar{1}u(1\bar{1})G_{n,u}(\bar{1}2\ldots n,1'\ldots n'). \tag{B19}$$

If we act with $i\partial_{t_{\bar{1}}}-h(\bar{1})$ on both sides of Eq. (B17) and subsequently use Eqs. (B19), (B16), and (B18) we obtain

$$[i\partial_{t_{\bar{1}}}-h(\bar{1})]G_{u,V}(\bar{1}\bar{1}')=\delta(\bar{1}\bar{1}')+\int d2u(\bar{1}2)G_{u,V}(2\bar{1}') -\frac{i}{2}\int d(234)V(\bar{1}234)G_{2,u,V}(432\bar{1}'). \tag{B20}$$

This is the equation of motion for the Green function used in Sec. IV. Again by differentiating this equation with respect to u we obtain the hierarchy equations for the higher order Green functions $G_{n,u,V}$.

APPENDIX C: FEYNMAN RULES FOR THE TWO-PARTICLE GREEN FUNCTION

In this section we give a brief summary of the Feynman rules for the two-particle Green function G_2 within the Hugenholtz diagram technique.[25–28] The general structure of the two-particle Green function is as given in Fig. 3. The Green function $G_2(1234)$ is written with the points (1234) positioned clockwise on four corners of the diagram where corners 1 and 2 are connected to outgoing lines and corners 3 and 4 are connected to ingoing lines. If one expands the evolution operators in the definition of G_2 in powers of the interaction V one finds for the diagrams the following rules:

(1) Every Green function line (contraction according to Wick's theorem) gives a factor iG.

(2) Every vertex gives a factor $-iV$.

(3) Every closed loop of Green function lines gives a minus sign, i.e., we have a factor $(-1)^l$ where l is the number of closed loops. To find the number of loops one must replace the Hugenholtz vertex by the first term on the right-hand side of Fig. 2 (with the same labeling) and count the number of loops that appear in this way.

(4) A line starting at 3 and ending at 1 gives a minus sign, i.e., we have a factor $(-1)^{L_{13}}$ where $L_{13}=1$ when 1 and 3 are connected and zero otherwise. To determine the connectivity it is necessary that one again first replaces the Hugenholtz vertex by the first term on the right-hand side of Fig. 2 (see also Ref. 27).

(5) Two Green function lines (so-called equivalent lines) starting from a given vertex and ending both on the same vertex give a factor $\frac{1}{2}$, i.e., we have a factor 2^{-p} where p is the number of equivalent lines.

(6) There is a factor $(-i)^2$ from the definition of G_2.

From these rules we find that the overall prefactor of a G_2 diagram with n vertices is given by $i^n(-1)^{l+L_{13}}2^{-p}$. For example, Figs. 6(a)–6(f) have prefactors 1, −1, i, $-\frac{1}{2}$, 1, and −1, respectively.

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