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Electron-electron correlations in molecular tunnel junctions: A diagrammatic approach

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In this work, the systematic studies of the effect of electron correlations in a bridge of a tunneling junction on transport properties is presented while the leads' electrons are considered to be noninteracting. A diagrammatic technique with respect to the Coulomb interaction is developed for various nonequilibrium bridge Green's functions. Dyson equations on a Keldysh contour for different Keldysh functions is derived. It is shown exactly that the structure of the Dyson equation Keldysh functions of the bridge molecule is the same as for a gas-phase bridge molecule where the zero order nonequilibrium Green's functions are modified by the interaction with the leads' electrons. These Green's functions contain nonvanishing imaginary parts that depend on the interaction between leads' and bridge electrons. As an example, the nonequilibrium bridge Green's functions in the random phase approximation are found where both direct and exchange terms are taken into account.

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I. INTRODUCTION

The proliferation of experimental techniques in molecular electronics[1,2] requires the further development of sophisticated computational methods to perform predictive calculations of conduction properties. There are several methodologies to find the electric current: the tight binding approximation,[3–5] density functional theory (DFT),[6–8] electron propagator methods[9–11] or many-body electron scattering approach,[12–14] the ionization potentials, and the electron affinities should be calculated rather than orbital energies in order to find electric current. The tight-binding approximation is an empirical method where electron correlation interaction is not included. In the latter two theories electron correlation is considered but in different ways. DFT employs an exchange potential to include exchange interaction into the calculation scheme. Such exchange potentials are functionals of an electron density that are chosen to fit experimental data, whereas electron propagator methods do not contain any adjustable parameters, functions, or functionals. The electron propagator approach has been widely used for quantum calculations of different molecular electronic properties.[15–20] It has been unambiguously proved that this method provides reliable results and is able to explain experimental data and predict novel properties.[21–27] Another approach based on the generalization of Hedin's screened potential expansion[28] to nonequilibrium Green's functions was proposed by Mukamel and co-workers[29] where closed hierarchy of equations was derived for Green's function, self-energy, screened potential, and vertex function in a Liouville space.

In this work, to include electron correlation effects, we employ the Green's function diagrammatic technique for molecular tunneling systems. Predictive calculations of transport properties of molecular devices may be improved by incorporation of electron propagator methodology.

In tunneling junctions, the molecular bridge electrons interact with electrons from the leads, and therefore the electronic levels of the molecular subsystem are modified by this interaction. Even if this interaction is small, there is finite dissipation resulting in the broadening of molecular levels. In the case of an isolated molecule, however, the imaginary part of the molecular Green's functions is infinitesimally small. Thus, the methodology of the calculations of the electronic levels of a bridge subsystem in a molecular tunneling junction should be reconsidered. The most systematic approach in many-body theory is a diagrammatic expansion with respect to the perturbation. In a many electron system this perturbation is usually the Coulomb interaction. In the case of tunneling junctions there are two interactions: (a) the interaction between the lead electrons and the electrons in the bridge and (b) the Coulomb interaction within the bridge (in this work we consider that the leads' electrons are noninteracting). Hence, we consider these two interactions as perturbations. For noninteracting lead electrons the expression for electric current was obtained in Refs. 30 and 31.

$$J = \frac{ie}{2\hbar}\int \frac{d\omega}{2\pi} Tr\{(\Gamma^L - \Gamma^R)\mathbf{G}^< + (f_L - f_R)(\mathbf{G}^r - \mathbf{G}^a)\}. \quad (1)$$

Here, $\Gamma^{L,R}_{n_1,n_2}(\omega)$ are line-broadening matrices defined as follows:

$$\Gamma^{L,R}_{n_1,n_2}(\omega) = \pi\sum_k [V_{L,R}(k,n_1)V^*_{L,R}(k,n_2) + c\,.\,c.]\delta(\omega - \varepsilon^{L,R}_k). \quad (2)$$

In Eq. (1) $\mathbf{G}^<$, $\mathbf{G}^r$, and $\mathbf{G}^a$ are nonequilibrium Green's functions of the bridge where the interaction between the bridge and leads' electrons is included into the Green's functions. f_L and f_R are Fermi-functions of the left and right leads, respectively. $V_{L,R}(k,n_1)$ is the matrix element of the interaction between the electrons of the left (right) lead and the bridge electrons. To determine the electric current, it is necessary to find Keldysh functions of the bridge molecule. These Green's functions are modified by the interactions with the leads electrons.

The main goal of this research is to find nonequilibrium bridge Green's functions by developing a diagrammatic approach. In particular, we derive the Dyson equations for bridge Keldysh functions that are modified by the interaction with the tunneling junction. The formalism of Feynman diagrams for noninteracting and interacting bridge electrons is developed. We show that the Dyson equations for bridge nonequilibrium Green's functions has the same structure as the Dyson equations for equilibrium Green's functions (with no interaction with the leads), however, the zeroth Green's functions are modified by the interaction with the lead electrons. As an example we consider the nonequilibrium bridge Green's function in the random phase approximation (RPA) where both direct and exchange terms are taken into account.

II. KELDYSH FUNCTIONS FOR NONINTERACTING BRIDGE ELECTRONS: THE DIAGRAMMATIC APPROACH

The Hamiltonian that describes a tunnel junction is given by the following expression:

$$\hat{H} = \hat{H}_L + \hat{H}_R + \hat{H}_M + \sum_{k,n} \{[V_L(k,n) c_k^\dagger d_n + \text{H.c.}] + [V_R(k,n) b_k^\dagger d_n + \text{H.c.}]\}, \tag{3}$$

where only in the bridge Hamiltonian, $\hat{H}_M$, we have included Coulomb interaction between the electrons:

$$\hat{H}_L = \sum_k \varepsilon_k^L c_k^\dagger c_k,$$

$$\hat{H}_R = \sum_k \varepsilon_k^R b_k^\dagger b_k,$$

$$\hat{H}_M = \sum_n \varepsilon_n d_k^\dagger d_n + \frac{1}{2} \sum_{n_1,n_2,n_3,n_4} V^{(0)}_{n_1,n_2,n_4,n_3} d^\dagger_{n_1} d^\dagger_{n_2} d_{n_3} d_{n_4}. \tag{4}$$

Here, c_k and $c_k^\dagger$ are annihilation and creation Fermi operators for the left lead electrons, b_k, $b_k^\dagger$ are the same but for the right lead electrons, and d_n, $d_n^\dagger$ are creation and annihilation operators for the bridge electrons. In Eq. (3), $V_{L,R}(k,n)$ denotes the tunneling matrix element between the kth electronic state of the left (or right) lead and the nth bridge electronic state. In Eq. (4) $V^{(0)}_{n_1,n_2,n_4,n_3}$ is a Coulomb integral in the bridge. ε_k^L, ε_k^R, and ε_n stand for the single electron orbital electronic energies in the left lead, the right lead, and the bridge, respectively.

A. Uncorrelated electrons

To understand the diagrammatic approach which is introduced below, we first determine the nonequilibrium Green's functions for uncorrelated electrons in the leads and the bridge on the Keldysh contour employing a diagrammatic expansion rather than the equation of motion.[30,31] For such a system the Hamiltonian is given by:

$$\hat{H}_0 = \sum_k \varepsilon_k^L c_k^\dagger c_k + \sum_k \varepsilon_k^R b_k^\dagger b_k + \sum_n \varepsilon_n d_k^\dagger d_n. \tag{5}$$

In this subsection we calculate the Keldysh functions for the electrons in the bridge. Nonequilibrium Green's functions between the bridge, and left lead, and left-lead-bridge electrons are defined in the following way:

$$i\tilde{G}_{nm}(t-t') = \langle \tilde{T} d_n(t) d_m^\dagger(t') \rangle, \tag{6}$$

$$i g^L_{kk'}(t-t') = \langle \tilde{T} c_k(t) c^\dagger_{k'}(t') \rangle, \tag{7}$$

$$i g^R_{kk'}(t-t') = \langle \tilde{T} b_k(t) b^\dagger_{k'}(t') \rangle, \tag{8}$$

$$i\tilde{G}_{nk}(t-t') = \langle \tilde{T} d_n(t) c_k^\dagger(t') \rangle. \tag{9}$$

The Keldysh functions for the right electrode should be defined in the same manner. In Eqs. (6)–(9) we use time ordering $\tilde{T}$ on the Keldysh contour.[31,32]

In the interaction representation, the bridge Keldysh functions are presented as follows:

$$i\tilde{G}^{(0)}_{nm}(t-t') = \langle \tilde{T} \tilde{d}_n(t) \tilde{d}_m^\dagger(t') \hat{S}_c \rangle, \tag{10}$$

where S_c is a scattering matrix[31–37] with the time ordering on the Keldysh contour c:

$$\hat{S}_c = \tilde{T} \exp\left[-i \int_c dt_1 \hat{H}_{\text{int}}(t_1) \right] = \sum_{l=0}^{\infty} \frac{(-i)^l}{l!} \int_c dt_1 \ldots \int_c dt_l \tilde{T} \hat{H}_{\text{int}}(t_1) \ldots \hat{H}_{\text{int}}(t_l). \tag{11}$$

Here, the operators for $\hat{H}_{\text{int}}(t)$ are taken in the interaction representation:

$$\tilde{d}_n(t) = e^{i\hat{H}_0 t} d_n e^{-i\hat{H}_0 t},$$

$$\tilde{c}_k(t) = e^{i\hat{H}_0 t} c_k e^{-i\hat{H}_0 t},$$

$$\tilde{b}_k(t) = e^{i\hat{H}_0 t} b_k e^{-i\hat{H}_0 t}. \tag{12}$$

In Eq. (11), $\hat{H}_{\text{int}}$ in the interaction representation is defined as the interaction between the lead and bridge electrons:

$$\hat{H}_{\text{int}}(t) = \sum_{k,n} \{[V_L(k,n) \tilde{c}_k^\dagger(t) \tilde{d}_n(t) + \text{H.c.}] + [V_R(k,n) \tilde{b}_k^\dagger(t) \tilde{d}_n(t) + \text{H.c.}]\}. \tag{13}$$

For simplicity, we consider only the left lead. The generalization to two leads is straightforward. Since the interaction has an odd number of each operators c and d [see Eq. (3)], the Taylor expansion in the S matrix in Eq. (11) contains only even terms, the nonequilibrium bridge Green's function yields:

$$i\tilde{G}^{(0)}_{nm}(t-t') = \langle \tilde{T} \tilde{d}_n(t) \tilde{d}_m^\dagger(t') \hat{S}_c \rangle = \sum_{l=0}^{\infty} \frac{(-1)^l}{(2l)!} \sum_{k_1,n_1} \cdots \sum_{k_{2l},n_{2l}} \int_c dt_1 \cdots \int_c dt_{2l} \times \langle \tilde{T} \tilde{d}_n(t) \tilde{d}_m^\dagger(t') [V_L(k_1,n_1) \tilde{c}^\dagger_{k_1}(t_1) \tilde{d}_{n_1}(t_1) + \text{H.c.}] \ldots [V_L(k_{2l},n_{2l}) \tilde{c}^\dagger_{k_{2l}}(t_{2l}) \tilde{d}_{n_{2l}}(t_{2l}) + \text{H.c.}] \rangle. \tag{14}$$

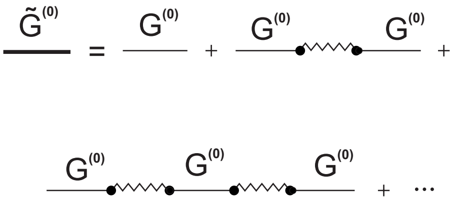

FIG. 1. Diagrammatic representation of Dyson Eq. (16). A solid line denotes the zeroth bridge Keldysh function, a waged line stands for a linear combination of the zeroth lead Keldysh functions determined by Eq. (17), and a dot represents a tunneling transition

It is apparent that different types of electrons should be averaged separately. According to Wick's theorem,[32,34–36] the averages of the multiple products of the operators in Eq. (14) can be decoupled into the product of Green's functions (paired operators). To find a Dyson equation, we regroup the infinite sums in the following manner:

$$\begin{aligned} i\tilde{G}^{(0)}_{nm}(t-t') &= \sum_{l=0}^{\infty}\frac{(-1)^l}{(2l)!}\sum_{k_{2l-1},n_{2l-1}}\sum_{k_{2l},n_{2l}}\int_c dt_{2l-1}\int_c dt_{2l}\langle\tilde{T}\tilde{d}_n(t)\tilde{d}^{\dagger}_{n_{2l}}(t_{2l})\rangle \\ &\quad\times[V_L(k_{2l},n_{2l})V_L^*(k_{2l-1},n_{2l-1})\langle\tilde{T}\tilde{c}_{k_{2l}}(t_{2l})\tilde{c}^{\dagger}_{k_{2l-1}}(t_{2l-1})\rangle] \\ &\quad\times[\ldots], \end{aligned} \tag{15}$$

where the rest of the series is presented in the brackets. Due to the symmetry of the integrand in the T-exponent series, t_{2l} and t_{2l-1} can be chosen $2l(2l-1)/2$ times. Therefore, the expression in the brackets is in fact the exact Green's function for the bridge electrons, $i\tilde{G}^{(0)}_{n_2m}(t_2-t')$. Thus, one obtains the following Dyson equation for the bridge Keldysh function:

$$\begin{aligned} \tilde{G}^{(0)}_{nm}(t-t') &= G^{(0)}_{nm}(t-t') + \sum_{n_1,n_2}\int_c dt_1\int_c dt_2 G^{(0)}_{nn_1}(t-t_1) \\ &\quad\times\Sigma^{(0)}_{n_1n_2}(t_1-t_2)\tilde{G}^{(0)}_{n_2m}(t_2-t'), \end{aligned} \tag{16}$$

where the self-energy matrix is defined in the following manner:

$$\begin{aligned} \Sigma^{(0)}_{n_1,n_2}(t_1-t_2) &= \sum_{k_1,k_2}\{[V_L(k_1,n_1)g^L_{k_1k_2}(t_1-t_2)V_L^*(n_2,k_2)] \\ &\quad+[V_R(k_1,n_1)g^R_{k_1k_2}(t_1-t_2)V_R^*(n_2,k_2)]\}. \end{aligned} \tag{17}$$

In Eq. (17) the generalization to two leads has been made. Here the left and right lead Keldysh functions are defined by Eqs. (7) and (8). The Dyson Eq. (16) is diagrammatically presented for noninteracting electrons in Fig. 1.

In this figure a solid line represents the zeroth bridge Keldysh function, $G^{(0)r}(t-t')$, and a waged line defines a linear combination of zeroth lead Keldysh functions determined by Eq. (17): $\Sigma_{k_1,k_2}V_L(k_1,n_1)g^L_{k_1k_2}(t_1-t_2)V_L^*(n_2,k_2)$. The dot is interaction, V, that has been included into the definition of a wage line. The graph describes a perturbation series with respect to $|V|^2$.

B. Renormalized zeroth Green's functions

The nonequilibrium zeroth Green's functions are determined by the Dyson equations Eqs. (16) and (17) on the Keldysh contour. The standard way to solve these equations is to perform a Fourier transform and then solve the algebraic matrix equations for the Green's functions. For the Keldysh functions this procedure cannot be implemented in a straightforward way because of two time lines. Thus, we should find the Fourier transform for each Keldysh function after applying the Langreth's mapping procedure.[31,38] In particular for $\tilde{G}^{(0)<}_{nm}(t-t')$, the Dyson equation is given by

$$\begin{aligned} \tilde{G}^{(0)<}_{nm}(t-t') &= G^{(0)<}_{nm}(t-t') + \sum_{n_1,n_2}\int_{t_0}^{t} dt_1\int_{t_0}^{t} dt_2 G^{(0)r}_{nn_1}(t-t_1) \\ &\quad\times\Sigma^{(0)<}_{n_1n_2}(t_1-t_2)\tilde{G}^{(0)a}_{n_2m}(t_2-t') \\ &\quad+\sum_{n_1,n_2}\int_{t_0}^{t} dt_1\int_{t_0}^{t} dt_2 G^{(0)<}_{nn_1}(t-t_1) \\ &\quad\times\Sigma^{(0)a}_{n_1n_2}(t_1-t_2)\tilde{G}^{(0)a}_{n_2m}(t_2-t') \\ &\quad+\sum_{n_1,n_2}\int_{t_0}^{t} dt_1\int_{t_0}^{t} dt_2 G^{(0)r}_{nn_1}(t-t_1) \\ &\quad\times\Sigma^{(0)r}_{n_1n_2}(t_1-t_2)\tilde{G}^{(0)<}_{n_2m}(t_2-t'). \end{aligned} \tag{18}$$

For $\tilde{G}^{(0)a}_{nm}(t-t')$ we obtain the following Dyson equation:

$$\begin{aligned} \tilde{G}^{(0)a}_{nm}(t-t') &= G^{(0)a}_{nm}(t-t') + \sum_{n_1,n_2}\int_{t_0}^{t} dt_1\int_{t_0}^{t} dt_2\tilde{G}^{(0)a}_{nn_1}(t-t_1) \\ &\quad\times\Sigma^{(0)a}_{n_1n_2}(t_1-t_2)G^{(0)a}_{n_2m}(t_2-t'). \end{aligned} \tag{19}$$

Thus, the Fourier transform of Eqs. (18) and (19) in a matrix form (here we omit n,m for simplicity) yields, respectively:

$$\begin{aligned} \tilde{G}^{(0)<}(\omega) &= G^{(0)<}(\omega) + G^{(0)<}(\omega)\Sigma^{(0)<}(\omega)\tilde{G}^{(0)a}(\omega) \\ &\quad+G^{(0)<}(\omega)\Sigma^{(0)a}(\omega)\tilde{G}^{(0)a}(\omega) \\ &\quad+G^{(0)r}(\omega)\Sigma^{(0)r}(\omega)\tilde{G}^{(0)<}(\omega), \end{aligned} \tag{20}$$

and

$$\tilde{G}^{(0)a}(\omega) = G^{(0)a}(\omega) + \tilde{G}^{(0)a}(\omega)\Sigma^{(0)a}(\omega)G^{(0)a}(\omega). \tag{21}$$

From the second equation we find that

$$\tilde{G}^{(0)<}(\omega) = G^{(0)a}(\omega)[\hat{1}-\Sigma^{(0)a}(\omega)G^{(0)a}(\omega)]^{-1}. \tag{22}$$

Using this equation, we obtain the matrix solution of Eq. (20)

$$\begin{aligned} \tilde{G}^{(0)<}(\omega) &= [\hat{1}-G^{(0)r}(\omega)\Sigma^{(0)r}(\omega)]^{-1} \\ &\quad\times[G^{(0)<}(\omega)+G^{(0)r}(\omega)\Sigma^{(0)<}(\omega)G^{(0)a}(\omega)] \\ &\quad\times[\hat{1}-\Sigma^{(0)a}(\omega)G^{(0)a}(\omega)]^{-1}. \end{aligned} \tag{23}$$

To solve Eqs. (22) and (23), we should find $\Sigma^{(0)<}(\omega)$, $\Sigma^{(0)a}(\omega)$, and $\Sigma^{(0)r}(\omega)$ from Eq. (17). Thus,

$$\Sigma^{<}_{n_1,n_2}(t_1-t_2)=\sum_{k_1,k_2}\{[V_L(k_1,n_1)g^{L<}_{k_1k_2}(t_1-t_2)V_L^*(n_2,k_2)] + [V_R(k_1,n_1)g^{R<}_{k_1k_2}(t_1-t_2)V_R^*(n_2,k_2)]\}. \tag{24}$$

For noninteracting electrons $g^{L,R<}_{k_1k_2}(\omega)$ is known[32]

$$g^{L,R<}_{k_1k_2}(\omega)=2i\pi f_{L,R}(\omega)\delta_{k_1k_2}\delta(\omega-\varepsilon^{L,R}_{k_1}), \tag{25}$$

where

$$g^{L,R<}_{k_1k_2}(\omega)=\int_{-\infty}^{\infty}dte^{i\omega t}g^{L,R<}_{k_1k_2}(t). \tag{26}$$

Is a Fourier transform of the Green's function. In the noninteracting electron gas approximation:

$$\Sigma^{<}_{n_1,n_2}(\omega)=i[f_L(\omega)\Gamma^L_{n_1,n_2}(\omega)+f_R(\omega)\Gamma^R_{n_1,n_2}(\omega)]. \tag{27}$$

Here $\Gamma^{L,R}_{n_1,n_2}(\omega)$ are line-broadening matrices defined as follows:

$$\Gamma^{L,R}_{n_1,n_2}(\omega)=2\pi\sum_k[V_{L,R}(k,n_1)V^*_{L,R}(n_2,k)]\delta(\omega-\varepsilon^{L,R}_k). \tag{28}$$

In this definition Γ is always positive.

To find $\Sigma^{(0)a}(\omega)$, and $\Sigma^{(0)r}(\omega)$ we employ Eq. (17) where

$$\Sigma^{(0)a}_{n_1,n_2}(t_1-t_2)=\sum_{k_1,k_2}\{[V_L(k_1,n_1)g^{La}_{k_1k_2}(t_1-t_2)V_L^*(n_2,k_2)] + [V_R(k_1,n_1)g^{Ra}_{k_1k_2}(t_1-t_2)V_R^*(n_2,k_2)]\}. \tag{29}$$

The retarded Green's function can be easily found from the following relation:

$$\tilde{G}^r(\omega)=[\tilde{G}^a(\omega)]^\dagger. \tag{30}$$

In the case of noninteracting electrons

$$g^{L,Rr,a}_{k_1k_2}(\omega)=\frac{\delta_{k_1k_2}}{\omega-\varepsilon^{L,R}_k\pm i\delta}\quad(\delta\to+0). \tag{31}$$

Consequently,

$$\Sigma^{a}_{n_1,n_2}(\omega)=\sum_k\left\{\left[\frac{V_L(k,n_1)V_L^*(n_2,k)}{\omega-\varepsilon^L_k-i\delta}\right]+\left[\frac{V_R(k,n_1)V_R^*(n_2,k)}{\omega-\varepsilon^R_k-i\delta}\right]\right\}. \tag{32}$$

Equations (27) and (32) coincide with the similar equations obtained by Meir and Wingreen in Refs. 30 and 31 by making use of the equation-of-motion approach.

Now that the self-energy operators are known, the zeroth Keldysh functions can be easily obtained from Eqs. (22) and (23):

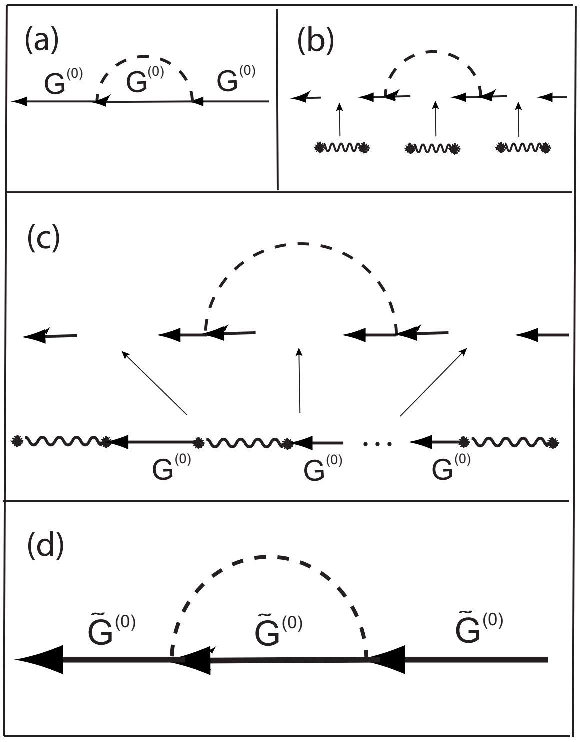

FIG. 2. Diagrammatic representation of the first order Hartree-Fock exchange diagram: (a) no interaction with the leads is included, (b) the interaction with the leads is considered in the second order with respect to V^2 for each $G^{(0)}$, (c) the interaction with the lead electrons is considered in all orders to V^2, and (d) the diagram (c) is presented according to Dyson Eq. (16) where the zeroth Green's functions, $G^{(0)}$, have been substituted by the renormalized zeroth Green's functions, $\tilde{G}^{(0)}$.

$$\tilde{G}^{(0)<}_{nm}(\omega)=i\sum_{l_1,l_2}(f_L(\omega)\Gamma^L_{l_1,l_2}+f_R(\omega)\Gamma^R_{l_1,l_2})\times\frac{(\omega-\varepsilon_m+i\delta)(\omega-\varepsilon_n+i\delta)}{(\omega-\varepsilon_{l_1}-i\delta)(\omega-\varepsilon_{l_2}-i\delta)}\times\left(\omega-\tilde{\varepsilon}_{ml_1}(\omega)+i\frac{\Gamma_{ml_1}(\omega)}{2}\right)^{-1}\times\left(\omega-\tilde{\varepsilon}_{l_2n}(\omega)-i\frac{\Gamma_{l_2n}(\omega)}{2}\right)^{-1}, \tag{33}$$

and

$$\tilde{G}^{(0)r,a}_{nm}(\omega)=\frac{\omega-\varepsilon_m\pm i\delta}{\omega-\varepsilon_n\pm i\delta}\left(\omega-\tilde{\varepsilon}_{mn}(\omega)\pm i\frac{\Gamma_{mn}}{2}\right)^{-1}. \tag{34}$$

In Eqs. (33) and (34), we have assumed that V is finite introducing the following definitions:

$$\tilde{\varepsilon}_{mn}\equiv\varepsilon_m+P\sum_k\frac{V^L_{mk}V^{L*}_{kn}}{\omega-\varepsilon^L_k}+P\sum_k\frac{V^R_{mk}V^{R*}_{kn}}{\omega-\varepsilon^R_k},$$

$$\Gamma_{mn}(\omega)=\Gamma^L_{mm}(\omega)+\Gamma^R_{mm}(\omega). \tag{35}$$

The presented derivation of Eqs. (33) and (34) is exact.

In the next section we show that the Green's functions (33) and (34) become the zeroth Green's functions in diagrammatic expansion if the Coulomb interaction is considered between the bridge electrons.

III. NONEQUILIBRIUM GREEN'S FUNCTIONS FOR INTERACTING BRIDGE ELECTRONS

In this section we include electron-electron interaction into the bridge Hamiltonian. Thus, the bridge Hamiltonian yields:

$$\hat{H}_M = \sum_n \varepsilon_n d_k^\dagger d_n + \frac{1}{2} \sum_{n_1,n_2,n_3,n_4} V^{(c)}_{n_1,n_2,n_4,n_3} d^\dagger_{n_1} d^\dagger_{n_2} d_{n_3} d_{n_4}, \tag{36}$$

where $V^{(c)}_{n_1,n_2,n_4,n_3}$ represents a Coulomb four center integral. For simplicity we assume that there is only one (left) electrode. The generalization to two electrodes is straightforward and will be done at the end. As in the case of noninteracting electrons, we present Keldysh functions described in the same manner as in Eq. (10):

$$iG_{nm}(t-t') = \langle \tilde{T}\tilde{d}_n(t)\tilde{d}^\dagger_m(t')\hat{S}_C \rangle . \tag{37}$$

Here, S_c is a scattering matrix given by Eq. (11). All the operators are taken in the interaction representation described by Eq. (12). The interaction Hamiltonian includes now both tunneling and Coulomb terms:

$$\hat{H}_{\mathrm{int}}(t) = \sum_{k,n} [V_L(k,n)\tilde{c}^\dagger_k(t)\tilde{d}_n(t) + \mathrm{H.c.}] + \frac{1}{2} \sum_{n_1,n_2,n_3,n_4} V^{(c)}_{n_1,n_2,n_4,n_3} \tilde{d}^\dagger_{n_1} \tilde{d}^\dagger_{n_2} \tilde{d}_{n_3} \tilde{d}_{n_4}. \tag{38}$$

Thus, a diagrammatic expansion in the interaction representation can be presented as follows:

$$\begin{aligned} i\tilde{G}^{(0)}_{nm}(t-t') = \langle \tilde{T}\tilde{d}_n(t)\tilde{d}^\dagger_m(t')\hat{S}_C \rangle = \sum_{l=0}^{\infty} \frac{(-1)^i}{(l)!} \int_c dt_1 \ldots \int_c dt_l \Big\langle \tilde{T}\tilde{d}_n(t)\tilde{d}^\dagger_m(t') \Big[\sum_{k_1,n_1} V_L(k_1,n_1)\tilde{c}^\dagger_{k_1}(t_1)\tilde{d}_{n_1}(t_1) + \mathrm{H.c.} \\ + \frac{1}{2} \sum_{n_1,n_2,n_3,n_4} V^{(c)}_{n_1,n_2,n_4,n_3} d^\dagger_{n_1}(t_1) d^\dagger_{n_2}(t_1) d_{n_3}(t_1) d_{n_4}(t_1) \Big] \cdots \Big[\sum_{k_l,n_l} V_L(k_l,n_l)\tilde{c}^\dagger_{k_l}(t_l)\tilde{d}_{n_l}(t_l) + \mathrm{H.c.} \\ + \frac{1}{2} \sum_{n_1,n_2,n_3,n_4} V^{(c)}_{n_1,n_2,n_4,n_3} d^\dagger_{n_1}(t_l) d^\dagger_{n_2}(t_l) d_{n_3}(t_l) d_{n_4}(t_l) \Big] \Big\rangle . \end{aligned} \tag{39}$$

In Eq. (39) all terms, even and odd, are included into the expansion. As a particular case we consider a first order exchange Hartree-Fock diagram is depicted in Fig. 2(a). The exchange diagram (a) is given by the following equation:

$$\begin{aligned} G^{(1)}_{kl}(t-t') &= (-i)^3 \sum_{n_1 n^2 n^3 n^4} V_{n_1 n_2 n_{3_3} n_4} \int_c dt_1 \tilde{G}_{kn_1}(t-t_1)^{(0)} \tilde{G}^{(0)}_{n_3 n_2}(t_1 - t_1^+) \tilde{G}^{(0)}_{n_4 l}(t_1 - t') \\ &= (-i)^3 \sum_n V_{knnl} \int_c dt_1 \tilde{G}_{kk}(t-t_1)^{(0)} \tilde{G}^{(0)}_{nn}(t_1 - t_1^+) \tilde{G}^{(0)}_{ll}(t_1 - t') . \end{aligned} \tag{40}$$

If we turn on the interaction with the leads as shown in Fig. 2(b), the tunneling self energy terms can be inserted into a zeroth Green's function by breaking the solid line. In the same manner all orders of V^2 can be included into the zeroth Green's function as depicted in Fig. 2(c). According to Eq. (16), such insertions are the renormalized zeroth Green's functions shown in Fig. 2(d). Thus, for any order diagram, the lead-bridge interaction retains the topological structure of a graph in the same manner as for noninteracting case where the ordinary zeroth Green's functions are substituted by the renormalized zeroth Green's functions described by Eqs. (33) and (34). The rigorous proof of this is almost the same as for noninteracting electrons presented in a previous section and is based on the essential property of a T product, $\tilde{T}A(t_1)A(t_2) = \tilde{T}A(t_2)A(t_1)$ independent of the order of operators. Indeed, by grouping the operators $\tilde{T}\tilde{d}(t_1)\tilde{d}(t_2)$ in the product (39), the order of the time sequence becomes irrelevant. This feature is crucial to break up a zeroth order line and substitute it by a renormalized zero order keldysh function. Hence, the Dyson equation for nonequilibrium Green's function yields;

$$G(t-t') = \tilde{G}^{(0)}(t-t') + \int_c dt_1 \int_c dt_2 \tilde{G}^{(0)}(t-t_1) \times \Sigma(t_1 - t_2) G(t_2 - t'), \tag{41}$$

where self-energy operator $\Sigma(t)$ includes all possible diagrams with respect to the Coulomb interaction taken with the renormalized zeroth Keldysh functions. The approach presented above is valid if the Coulomb interaction is consid-

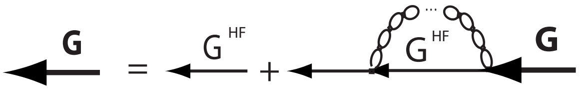

FIG. 3. Hugenlotz diagrammatic representation of Dyson Eq. (49) in the RPA. The chain line represents the polarization operator $\Pi(t-t')$ (Refs. 35 and 36).

ered between the bridge electrons, while lead elections are still nonintersecting. For the calculation of nonequlibrium Green's functions such a change is essential because now the zeroth Green's functions have finite imaginary parts as described by Eqs. (33) and (34). Thus, various quantum chemical schemes for Green's functions calculations have to be modified. As an example of such modification we consider a bridge molecule in the RPA.

IV. NONEQUILIBRIUM BRIDGE GREEN'S FUNCTIONS IN THE RANDOM PHASE APPROXIMATION

In this section, we present the formalism and derive the integral equations for the bridge nonequilibrium Green's functions in the RPA.

For further study of the nonequilibrium bridge functions in the RPA, it is useful to prove a statement where Hartree-Fock nonequilibrium Green's functions are considered as zero order Green's functions. Such renormalization results in the omission of first order self-energy operator from the diagrammatic expansion of the Green's functions with respect to the Coulomb interaction. As a first step, we introduce an inverse operator on a Keldysh contour:

$$\int_c dt_1 \hat{A}^{-1}(t-t_1)\hat{A}(t_1-t') = \delta(t-t'), \qquad (42)$$

where all times are taken on the Keldysh contour c. For simplicity we omit the integration symbol and the integral of the operator product is presented as the product of the operators:

$$\hat{A}\hat{B} \equiv \int_c dt_1 \hat{A}(t-t_1)\hat{B}(t_1-t'). \qquad (43)$$

We have previously proved that the Dyson equation for nonequilibrium bridge Green's functions has the same topological structure as the equilibrium Green's function where the zeroth Green's functions, $G^{(0)}$ are substituted by the renormalized zeroth Green's functions, $\tilde{G}^{(0)}$ [see integral Eq. (41)]:

$$\hat{G} = \hat{\tilde{G}}^{(0)} + \hat{\tilde{G}}^{(0)}\hat{\Sigma}\hat{G}. \qquad (44)$$

In addition, we introduce the Hartree-Fock Keldysh function satisfied by the following nonlinear Dyson equation:

$$\hat{G}^{\mathrm{HF}} = \hat{\tilde{G}}^{(0)} + \hat{\tilde{G}}^{(0)}\hat{\Sigma}^{\mathrm{HF}}\hat{G}^{\mathrm{HF}}, \qquad (45)$$

where

$$\Sigma^{\mathrm{HF}}_{mn} = i\sum_k \{mk|V^c|nk\}\tilde{G}_k(t-t^+). \qquad (46)$$

Here the four-center Coulomb integral is defined as follows:

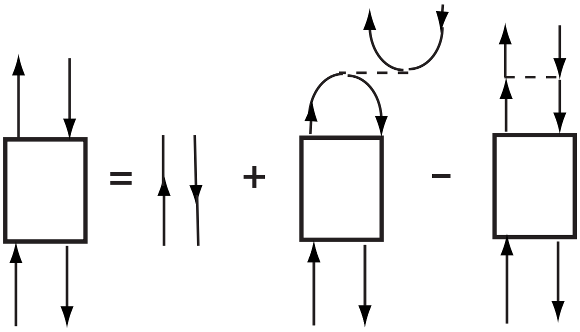

FIG. 4. Diagrammatic representation of Dyson Eq. (49) for the polarization operator Π in the RPA (Refs. 35 and 36).

$$\{mk|V^c|kn\} \equiv \langle mk|V^c|nk\rangle - \langle mk|V^c|kn\rangle. \qquad (47)$$

Both Dyson Eqs. (44) and (46) can be presented in the following equivalent forms:

$$\hat{G}^{-1} = (\hat{\tilde{G}}^{(0)})^{-1} - \hat{\Sigma},$$

$$(\hat{G}^{\mathrm{HF}})^{-1} = (\hat{\tilde{G}}^{(0)})^{-1} - \hat{\Sigma}^{\mathrm{HF}}. \qquad (48)$$

Subtracting the second equation from the first one and applying the simple algebraic transformations, we obtain the following Dyson equation for the Keldysh functions:

$$\hat{G} = \hat{\tilde{G}}^{(\mathrm{HF})} + \hat{\tilde{G}}^{(\mathrm{HF})}(\hat{\Sigma} - \hat{\Sigma}^{\mathrm{HF}})\hat{G}. \qquad (49)$$

Thus, the zero order Green's functions are presented by the Hartree-Fock Green's functions, and the self energy operator is given by all possible diagrams started from the second order. In this research we consider the self-energy operator in the RPA:[35,36]

$$\Sigma^{\mathrm{RPA}} = \hat{\Sigma} - \hat{\Sigma}^{\mathrm{HF}}. \qquad (50)$$

The Dyson equation for the Keldysh function in the RPA is graphically depicted in Fig. 3 (Ref. 35) in term of the Hugenholtz diagrams.

The RPA self-energy operator can be presented in the following manner:[35,36]

$$\Sigma^{\mathrm{RPA}}_{\mu\nu} = \sum_{\beta,\delta,\lambda}\sum_{\alpha,\gamma,\kappa}\{\mu\delta|V^c|\beta\lambda\}\Pi_{\alpha\beta;\gamma\delta}G^{\mathrm{HF}}_{\lambda\kappa}\{\alpha\kappa|V^c|\gamma\nu\}. \qquad (51)$$

Here, the polarization operator is defined in Fig. 4: Figure 4 describes an integral equation for a one particle-one-hole polarization operator that includes both direct (the first part) and exchange (the second part) terms. Usually an exchange term is small in metals and always disregarded.[35] For molecules, however, (or other finite Fermi systems) this term should be included. According to Fig. 4, we can write the following set of integral equations for the polarization operator:

$$\Pi_{aA|\alpha,\beta}(t-t') = G^{\mathrm{HF}}_{\alpha a}(t-t')G^{\mathrm{HF}}_{A\beta}(t'-t) + \sum_{bdBC}\int_c dt_1\{aC|V^c|Ad\}G^{\mathrm{HF}}_{db}(t-t_1)G^{\mathrm{HF}}_{BC}(t_1-t)\Pi_{bB;\alpha\beta}(t_1-t')$$
$$+ \sum_{bdBC}\int_c dt_1\{ad|V^c|AC\}G^{\mathrm{HF}}_{db}(t_1-t)G^{\mathrm{HF}}_{BC}(t-t_1)\Pi_{Bb;\alpha\beta}(t_1-t'),$$

$$\Pi_{Aa|\alpha,\beta}(t-t') = G^{\mathrm{HF}}_{A\alpha}(t'-t)G^{\mathrm{HF}}_{a\beta}(t-t') + \sum_{bdBC}\int_c dt_1\{AC|V^c|ad\}G^{\mathrm{HF}}_{db}(t-t_1)G^{\mathrm{HF}}_{BC}(t_1-t)$$
$$\times\Pi_{bB;\alpha\beta}(t_1-t')\sum_{bdBC}\int_c dt_1\{Ad|V^c|aC\}G^{\mathrm{HF}}_{db}(t_1-t)G^{\mathrm{HF}}_{BC}(t-t_1)\Pi_{Bb;\alpha\beta}(t_1-t') \qquad (52)$$

Here, we have introduced the following notation: small Greek letters, $\alpha,\beta,\ldots$, denote both electronic (occupied) and hole (unoccupied) states, small letters $a,b,c\ldots$, denote only electronic states, and large letters, $A,B,C,\ldots$, denote only hole states. We also distinguish the polarization operators, $\Pi_{aA|\alpha,\beta}(t-t')$ and $\Pi_{Aa|\alpha,\beta}(t-t')$. The second sum in each equation represents the exchange term in Fig. 4. Equations (52) are written on the Keldysh contour. Finally different nonequilibrium functions can be found my making use of Langreth's projection methodology.[38] Here, we do not present tedious integral equations for each Keldysh polarization operator because we do not intend to perform numerical calculations for nonequilibrium Green's functions in this work.

V. CONCLUSIONS

In this research, we have studied the effect of electron correlations in a bridge (while lead electrons remain uncorrelated) on transport properties in molecular tunnel junctions. To determine nonequilibrium Green's functions, we have proposed a diagrammatic technique on a Keldysh time contour. First we have considered a system of noninteracting electrons in both leads and the bridge. We have derived the Dyson equation for renormalized zeroth Keldysh functions [see Eqs. (16) and (17)]. These equations have been solved and the Keldysh functions have been obtained in the energy representation of Eqs. (33) and (34) where the renormalized energies and their imaginary parts are given by Eq. (35). We have presented the procedure for diagrammatic expansion for Keldysh functions where both tunneling and Coulomb interactions have been considered as perturbations. After some regrouping of the terms, we have found that the zeroth Green's functions can be renormalized to the functions given by Eqs. (33) and (34). Moreover, all diagrams have represented the familiar diagrammatic expansion with respect to the Coulomb interaction only. Thus, it has become possible to write the exact Dyson equation with the renormalized zeroth Green's functions with finite imaginary parts. As an example, we have studied a bridge molecule in the random phase approximation. Within the RPA we have derived the equations for the nonequilibrium Green's functions where both direct and indirect terms have been considered in one particle-one hole, $1p-1h$, channel (1p-1h). Now that the nonequilibrium Green's functions are found, one is able to determine electric current according to the Wingreen and Meir's formula (1).[30,31]

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