Theoretical and Mathematical Physics, **194**(2): 236–251 (2018)

NONEQUILIBRIUM GREEN'S FUNCTIONS IN THE ATOMIC REPRESENTATION AND THE PROBLEM OF QUANTUM TRANSPORT OF ELECTRONS THROUGH SYSTEMS WITH INTERNAL DEGREES OF FREEDOM

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We develop the theory of quantum transport of electrons through systems with strong correlations between fermionic and internal spin degrees of freedom. The atomic representation for the Hamiltonian of a device and nonequilibrium Green's functions constructed using the Hubbard operators allow overcoming difficulties in the perturbation theory encountered in the traditional approach because of a larger number of bare scattering amplitudes. Representing the matrix elements of effective interactions as a superposition of terms each of which is split in matrix indices, we obtain a simple method for solving systems of very many equations for nonequilibrium Green's functions in the atomic representation. As a result, we obtain an expression describing the electron currents in a device one of whose sites is in tunnel coupling with the left contact and the other, with the right contact. We derive closed kinetic equations for the occupation numbers under conditions where the electron flow leads to significant renormalization of them.

Keywords: nonequilibrium Green's functions, Keldysh contour, atomic representation, kinetic equation, inelastic scattering

DOI: 10.1134/S0040577918020046

1. Introduction

When solving the problem of the electric current flow through atomic-scale systems (we call such systems devices in what follows), a situation is often encountered where the device has its own (intrinsic) degrees of freedom that do not directly participate in the charge transport processes [1]. Nevertheless, the presence of such additional subsystems interacting with the subsystem of charge degrees of freedom can, for example, influence the volt–ampere characteristics of the device because the resulting spectrum of fermionic excitations is modified. This is very important for applications because it opens wide possibilities for controlling the electron transport by the action of external fields (e.g., a magnetic field) on the internal, not only fermionic, degrees of freedom [2], [3].

As an example, we can consider a device with a subsystem of magnetic impurity ions. The processes of electron injection into the device, just as the processes of electron ejection from the device, are then

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This research was supported by the Russian Foundation for Basic Research, Government of Krasnoyarsk Territory, Krasnoyarsk Region Science and Technology Support Fund (Grant Nos. 16-02-00073, 16-42-243056, 16-42-242036, and 17-42-240441) and in part (S. V. A.) by the Program for Governmental Support for Young Scientists and Candidates of Science (Grant No. MK-1398.2017.2).

Translated from Teoreticheskaya i Matematicheskaya Fizika, Vol. 194, No. 2, pp. 277–294, February, 2018. Original article submitted May 2, 2017; revised May 22, 2017.

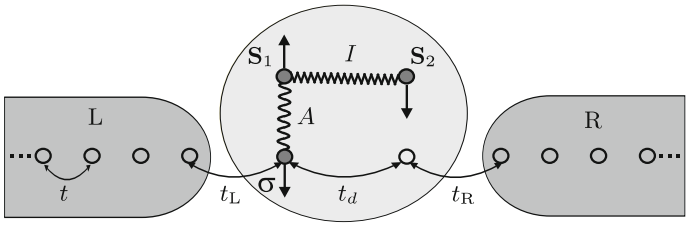

Fig. 1. Model of a device with two sites and two impurity spins: the left contact ($t_{\rm L}$) is coupled by tunneling to the first site of the device, and the right contact ($t_{\rm R}$), to the second site. An electron entering the device site (the first site in the figure) correlates with the impurity spin through an (s–$d(f)$)-exchange coupling.

accompanied by perturbations of the subsystem of impurity spins due to the (s–$d(f)$)-exchange interaction between the impurity spins and electrons in the device [4]. The correlation arising between the fermionic and spin degrees of freedom leads to a dependence of the energy spectrum of the device on the external magnetic field, which is significant for transport phenomena and thus determines a mechanism that allows a purposeful control of the transport characteristics of the device.

Unfortunately, calculating the volt–ampere characteristics of devices with internal degrees of freedom is significantly more difficult because the Hamiltonian taking the coupling between subsystems into account is off-diagonal in the usual representation of fermion and boson operators of secondary quantization. As a result, the perturbation series becomes much more complicated because of very many bare scattering amplitudes. At the same time, it is often insufficient to restrict the theory only to lower orders because it is also necessary to consider the effects of multiple scattering of electrons accompanying the processes of electron injection and ejection. Hence, a situation arises where it is necessary to sum an infinite perturbation series, but this series can be very cumbersome because of the numerous scattering potentials.

The processes of the device transition to excited states are also important. Such transitions are induced by the interaction of transported electrons with the charge and spin degrees of freedom of the device. As a result, the tunnel current flow can redistribute the populations of the energy states of the device. In this case, the final distribution of the device energy level population can significantly differ from the initial equilibrium distribution [5].

Here, we overcome the difficulties listed above by constructing nonequilibrium functions in the atomic representation. Introducing the Hubbard operators, we can represent the Hamiltonian of the device in diagonal form. Therefore, only the tunneling operator written in the atomic representation plays the role of the perturbation used to construct the diagram series. Such an approach allows describing the effects of multiple scattering of electrons and obtaining an expression for the current and a system of kinetic equations for the occupation numbers.

2. Hamiltonian systems

We consider the tunneling transport of electrons through the device shown in Fig. 1. The tunnel coupling to the left contact of the device is realized such that in the tunneling, an electron from the contact enters the first site in the state with the energy $\xi_{d\sigma}$. The tunnel coupling to the right contact is similar with the only difference that the second site of the device participates in the tunneling process. A specific feature of the device considered here is that it contains a subsystem of two localized spins. This corresponds to the simplest model situation that can reflect the dependence of the transport characteristics of the device on the interaction in its magnetic subsystem. The magnetic ions can be introduced in the device, for example, by adsorbing impurities in the domain between the contacts. Another possibility arises in the case where

the device structure is formed on the basis of a pair of transient ions with unfilled d or f shells.

A Heisenberg exchange interaction occurs between two localized spins of the device. For definiteness, we assume that this interaction is antiferromagnetic. According to the above, in the case where there are no electrons in the device, the ground state of the device is associated with the spin singlet, and the triplet term corresponding to three magnetic states is distinguished from the singlet term by the value of the exchange energy I.

Because of the $(s{-}d(f))$-exchange interaction, the spin state of each electron entering a site from a contact is strongly correlated with the state of one of the localized spins. As a result, the magnetic state of the device can qualitatively change in the process of electron tunneling into the device from a contact. This occurs because the parameter of the $(s{-}d(f))$-exchange coupling is, as a rule, significantly greater than the integral of the Heisenberg interaction. Breaking the singlet state of two localized spins then becomes energetically favorable because the localized spin strongly correlates with the spin of the incoming fermion. In the language of magnetic terms of the spin dimer, we can say that there is an excitation of triplet states. This means that the processes of electron transport through the device are accompanied by excitations of magnetic degrees of freedom. In other words, the electron transport in this case is significantly influenced by the process of inelastic electron scattering on internal (magnetic) degrees of freedom of the device.

We use the method of nonequilibrium Green's functions to take the influence of inelastic electron scattering processes on the characteristics of electron transport through the described device into account. The developed technique is novel because nonequilibrium functions are introduced in the atomic representation. We must use this representation and correspondingly pass to nonequilibrium Green's functions constructed on the Hubbard operators because there are internal degrees of freedom of the device. In this case, we succeed in formulating a perturbation theory such that only the tunneling processes determine the scattering matrix on the Keldysh contour. If the usual representation of secondary quantization were used, we would need to use very many bare vertices and a very cumbersome mathematical apparatus.

The Hamiltonian of the system, which describes the left and right contacts and the device located between them and implements the quantum transport, can be written as

$$\widehat{H} = \widehat{H}_0 + \widehat{T} + \widehat{V}, \tag{1}$$

where the operator

$$\widehat{H}_0 = \widehat{H}_{\rm L} + \widehat{H}_{\rm R} + \widehat{H}_{\rm D}$$

describes the noninteracting subsystems of the left and right metal contacts

$$\widehat{H}_{\rm L} = \sum_{k\sigma} \xi_{{\rm L}k\sigma} c^+_{k\sigma} c_{k\sigma}, \qquad \widehat{H}_{\rm R} = \sum_{p\sigma} \xi_{{\rm R}p\sigma} d^+_{p\sigma} d_{p\sigma} \tag{2}$$

and the device, which in our case is represented by the Hamiltonian

$$\widehat{H}_{\rm D} = \sum_{l=1}^{2} \left\{ \sum_{\sigma} \xi_{d\sigma} a^+_{l\sigma} a_{l\sigma} + U n_{l\uparrow} n_{l\downarrow} \right\} + t_d \sum_{\sigma} (a^+_{1\sigma} a_{2\sigma} + a^+_{2\sigma} a_{1\sigma}) + U_{12} n_1 n_2 +$$

$$+ \sum_{l=1}^{2} \{ A(\boldsymbol{\sigma}_l \mathbf{S}_l) - g\mu_{\rm B} H S^z_l \} + I(\mathbf{S}_1 \mathbf{S}_2). \tag{3}$$

The existence of the tunnel coupling between the left contact and the device and between the right contact and the device is taken into account by the operator $\widehat{T}$ as

$$\widehat{T} = \sum_{k\sigma} t_{{\rm L}k} c^+_{k\sigma} a_{1\sigma} + \sum_{p\sigma} t_{{\rm R}p} d^+_{p\sigma} a_{2\sigma} + {\rm H.c.} = \widehat{T}_{\rm L} + \widehat{T}_{\rm R} + {\rm H.c.} \tag{4}$$

The origin of the operator $\widehat{V}$ is related to the potential difference applied to the system, which induces a current in the system. Because the potential is constant at each of the contacts and on the device, we relate the potential reference point to the left contact to obtain

$$\widehat{V} = \sum_{l=1}^{2} \sum_{\sigma} \frac{eV}{2} a_{l\sigma}^{+} a_{l\sigma} + \sum_{p\sigma} eV d_{p\sigma}^{+} d_{p\sigma}. \tag{5}$$

In the above expressions, we used the following notation: $c_{k\sigma}$ and $d_{p\sigma}$ are the electron annihilation operators at the respective left and right contacts with their corresponding wave vectors k and p and the spin projection σ; $\xi_{\mathrm{L}k\sigma} = \varepsilon_{\mathrm{L}k} - g_e\mu_{\mathrm{B}}H\sigma - \mu$ and $\xi_{\mathrm{R}p\sigma} = \varepsilon_{\mathrm{R}p} - \sigma g_e\mu_{\mathrm{B}}H - \mu$ are the one-electron energies at the respective left and right contacts referenced to the level of the chemical potential μ with the energy splitting according to the electron spin projection $\sigma = \pm 1/2$ in the magnetic field taken into account; g_e is the electron g-factor at the contacts; and μ_{B} is the Bohr magneton. We further assume that the contacts are single-band paramagnetic metals. The parameters contained in the Hamiltonian of the device have the following physical meanings: $\xi_{d\sigma} = \varepsilon_d - g_e\mu_{\mathrm{B}}H\sigma - \mu$ is the electron energy referenced to the chemical potential and depending on spin at one of the device sites in the external magnetic field H; ε_d is the bare one-electron energy; $n_{l\sigma} = a_{l\sigma}^{+} a_{l\sigma}$ is the operator of the number of electrons at the device site with the index l and the spin projection σ; $a_{l\sigma}^{+}$ and $a_{l\sigma}$ are the electron creation and annihilation operators in the device at the site l with the spin projection σ; the parameter U characterizes the Hubbard repulsion of two electrons at the same site with opposite spin projections; and $n_l = n_{l\uparrow} + n_{l\downarrow}$ is the operator of the total number of electrons at the device site with number l. The parameter U_{12} determines the intensity of Coulomb interaction between electrons located at the first and second sites of the device. The magnetic field action on the energy structure of the subsystem of localized spins with effective g-factors is described by the next to the last term in Hamiltonian (3). The relation between the spin degree of freedom of the transported electron and the localized spins of the device, which is implemented by the $(s{-}d(f))$-exchange coupling mechanism, is characterized by the parameter A. Here, $\mathbf{S}_l$ is the vector operator of the device localized spin, and $\boldsymbol{\sigma}_l$ is the vector operator of the transported electron spin. As is known, the scalar product $\boldsymbol{\sigma}\mathbf{S}$ contains operator terms taking the spin flip processes into account when the projection of impurity spins and electrons change simultaneously.

3. Tunnel current of electrons and nonequilibrium averages

We can obtain an expression for the current J flowing through the device based on the well-known relation between its value and the charge variation per unit time at the left contact, $J = e\dot{\widehat{N}}_{\mathrm{L}}$ ($\widehat{N}_{\mathrm{L}} = \sum_{k\sigma} c_{k\sigma}^{+} c_{k\sigma}$). After simple transformations, we obtain

$$J = \frac{-ie}{\hbar} \langle [\widehat{N}_{\mathrm{L}}, \widehat{T}_{\mathrm{L}}] \rangle, \tag{6}$$

where the symbol of averaging in the right-hand side contains the commutator of the electron number operator at the left contact with the operator of tunneling between the left contact and the device. As usual, e denotes the absolute value of the electron charge. The averaging is performed with the density matrix $\rho(t)$ [6],[7] satisfying the equation

$$i\hbar \frac{\partial \rho(t)}{\partial t} = [\widehat{H}, \rho(t)]. \tag{7}$$

We use the expressions for $\widehat{N}_{\mathrm{L}}$ and $\widehat{T}_{\mathrm{L}}$ to obtain

$$J = \frac{-iet_{\mathrm{L}}}{\hbar} \sum_{\sigma} [\langle c_{1\sigma}^{+} a_{1\sigma} \rangle - \langle a_{1\sigma}^{+} c_{1\sigma} \rangle]. \tag{8}$$

To calculate the averages in this expression, we commonly use nonequilibrium Green's functions because of the potential difference inducing an electron flow and thus leading to a nonequilibrium problem. The nonequilibrium Green's functions can be calculated in the perturbation theory framework.

To construct the perturbation theory where only the tunnel coupling between the contacts and the device formally plays the role of perturbation and the operator $\widehat{H}_0$ acts as the zero Hamiltonian, we perform two transformations.

The first transformation is related to the transition to the density matrix $\rho_v(t)$ [8] such that

$$\rho(t) = \widehat{U}_v^+ \rho_v(t) \widehat{U}_v, \qquad \widehat{U}_v = e^{it\widehat{V}/\hbar}. \tag{9}$$

The equation of motion for $\rho_v(t)$

$$i\hbar \frac{\partial \rho_v(t)}{\partial t} = [\widehat{H}_v(t), \rho_v(t)] \tag{10}$$

contains the Hamiltonian $\widehat{H}_v(t) = \widehat{H}_0 + \widehat{T}_v(t)$, where the tunneling operator

$$\hat{T_v}(t) = \sum_{k\sigma} t_{\mathrm{L}k}(t) c_{k\sigma}^+ a_{1\sigma} + \sum_{p\sigma} t_{\mathrm{R}p}(t) d_{p\sigma}^+ a_{2\sigma} + \mathrm{H.c.} \tag{11}$$

has an explicit time dependence determined by the functions

$$t_{\mathrm{L}k}(t) = t_{\mathrm{L}k} e^{-iteV/2\hbar}, \qquad t_{\mathrm{R}p}(t) = t_{\mathrm{R}p} e^{iteV/2\hbar}.$$

We must therefore use nonequilibrium Green's functions.

The second transformation is the transition to the interaction representation

$$\rho_v(t) = \widehat{U}_0^+ \rho_{\mathrm{I}}(t) \widehat{U}_0, \qquad \widehat{U}_0 = e^{it\widehat{H}_0/\hbar}. \tag{12}$$

In this representation, the expression for the current becomes

$$J = \frac{-ie}{\hbar} \sum_{k\sigma} [t_{\mathrm{L}k}(t) \langle c_{k\sigma}^+(t) a_{1\sigma}(t) \rangle_{\mathrm{I}} - t_{\mathrm{L}k}^*(t) \langle a_{1\sigma}^+(t) c_{k\sigma}(t) \rangle_{\mathrm{I}}], \tag{13}$$

where the subscript I on the angle brackets means that the average is calculated with the density matrix satisfying the equation

$$i\hbar \frac{\partial \rho_{\mathrm{I}}(t)}{\partial t} = [\widehat{T}_{\mathrm{I}}(t), \rho_{\mathrm{I}}(t)]. \tag{14}$$

Here, the tunneling operator is written in the interaction representation

$$\widehat{T}_{\mathrm{I}}(t) = \sum_{k\sigma} t_{\mathrm{L}k}(t) c_{k\sigma}^+(t) a_{1\sigma}(t) + \sum_{p\sigma} t_{\mathrm{R}p}(t) d_{p\sigma}^+(t) a_{2\sigma}(t) + \mathrm{H.c.} \tag{15}$$

In this representation, the time dependence of the secondary quantization operators is determined as usual. The explicit time dependence for the contact operators

$$c_{k\sigma}(t) = \widehat{U}_0^+ c_{k\sigma} \widehat{U}_0 = c_{k\sigma} e^{-it\xi_{\mathrm{L}k\sigma}/\hbar}$$

is well known in this case. But obtaining the explicit time dependence for the device operators in the interaction representation $a_{1\sigma}(t) = \widehat{U}_0^+ a_{1\sigma} \widehat{U}_0$ for the considered system is a more complicated problem. This hinders the development of the perturbation theory where the fermion operators would be used. The

strategy for overcoming this difficulty is related to introducing the atomic representation for the device Hamiltonian (see below).

In the final stage of obtaining an expression for the current containing only averages calculated with the density matrix ρ_0 describing the device and the ensemble of the contacts that do not mutually interact, we introduce the evolution operator $S(t,-\infty)$, which allows obtaining the relation between $\rho_{\rm I}(t)$ and ρ_0:

$$\rho_{\rm I}(t) = S(t,-\infty)\rho_0 S^+(t,-\infty), \qquad \rho_0 = \rho_{\rm I}(-\infty). \tag{16}$$

Because the operator $S(t,-\infty)$ satisfies the equation

$$i\hbar\frac{\partial S(t,-\infty)}{\partial t} = \widehat{T}_{\rm I}(t)S(t,-\infty), \tag{17}$$

it can be expressed in terms of a T-ordered exponential,

$$S(t,-\infty) = T_t \exp\biggl(-\frac{i}{\hbar}\int_{-\infty}^{t}\widehat{T}_{\rm I}(t)\,dt\biggr). \tag{18}$$

The operator $S(t,-\infty)$ is a solution of the problem posed above because

$$\langle c^+_{k\sigma}(t)a_{1\sigma}(t)\rangle_{\rm I} = \langle S^+(t,-\infty)c^+_{k\sigma}(t)a_{1\sigma}(t)S(t,-\infty)\rangle_0. \tag{19}$$

Substituting the unit operator $S^{-1}(\infty,-\infty)S(\infty,-\infty)$ in the average in the right-hand side of this equation, we obtain

$$\langle c^+_{k\sigma}(t)a_{1\sigma}(t)\rangle_{\rm I} = \langle S^{-1}(\infty,-\infty)S(\infty,t)c^+_{k\sigma}(t)a_{1\sigma}(t)S(t,-\infty)\rangle_0. \tag{20}$$

Using the Keldysh contour C [7], [9]–[11] allows writing the considered averages in a form convenient for calculations,

$$\langle c^+_{k\sigma}(t)a_{1\sigma}(t)\rangle_{\rm I} = \langle T_C c^+_{k\sigma}(t)a_{1\sigma}(t)S_C\rangle_0, \tag{21}$$

where T_C is the operator of chronological ordering with respect to time on the Keldysh contour C and the scattering matrix

$$S_C = T_C \exp\biggl(-\frac{i}{\hbar}\int_C \widehat{T}_{\rm I}(t)\,dt\biggr) \tag{22}$$

is determined in terms of the tunneling operator, where the range of the time argument belongs to the same contour.

4. Atomic representation for the operators of the device

A significant specific feature of the considered problem is related to the device structure described by the Hamiltonian $\widehat{H}_{\rm D}$. It follows from its definition that an electron entering the device interacts with both the charge and spin degrees of freedom. The presence of a great many distinct bare scattering amplitudes results in not only a significant complication of the perturbation series but also the problem of calculating the explicit form of the fermion and spin operators in the interaction representation. This is related to the nonequidistant structure of the fermion (or spin) excitation spectrum of the operator $\widehat{H}_{\rm D}$. Using the diagram technique directly in terms of the secondary quantization operators is therefore impossible because the Wick theorem does not hold for the averages of the product of such operators.

To overcome this difficulty, we must construct the atomic representation and write the Hamiltonian of the device and the tunneling operator in this representation. For this, we introduce functions $|\Psi_n\rangle$ satisfying the Schrödinger equation for the device

$$\widehat{H}_{\rm D}|\Psi_n\rangle = E_n|\Psi_n\rangle, \quad n = 1,2,\ldots,N_{\rm D}. \tag{23}$$

The set of functions $|\Psi_1\rangle, |\Psi_1\rangle, \ldots, |\Psi_{N_\mathrm{D}}\rangle$ can be treated as a basis in the Hilbert space corresponding to the device, where the operators act. We introduce the Hubbard operators [12], [13]

$$X^{nm} = |\Psi_n\rangle\langle\Psi_m|, \quad n, m = 1, 2, \ldots, N_\mathrm{D}, \tag{24}$$

acting in the Hilbert space of the device. In particular, the action of these operators on the basis states is determined by $X^{nm}|\Psi_p\rangle = \delta_{mp}|\Psi_n\rangle$.

The first advantage of this representation is that the transition to it takes the Hamiltonian H_D to the diagonal form,

$$H_\mathrm{D} = \sum_{n=1}^{N_\mathrm{D}} E_n X^{nn}. \tag{25}$$

The second important specific feature of the atomic representation is that the explicit form of the Hubbard operators in the interaction representation $X^{nm}(t) = U_0(t)X^{nm}U_0^+(t)$ can easily be calculated. In this case, we have the usual time dependence according to the exponential law [12]

$$X^{nm}(t) = e^{i(E_n - E_m)t}X^{nm} \equiv e^{i\alpha E t}X^{nm}.$$

Here, we use a notation that is convenient below: E is understood as an N_D-dimensional vector (E_1, $E_2, \ldots, E_{N_\mathrm{D}}$), and α is treated as an N_D-dimensional vector whose ith component is the difference of two Kronecker symbols $\alpha_i(n, m) = \delta_{in} - \delta_{im}$. We then have the scalar product $\alpha E = E_n - E_m$ if $\alpha = \alpha_i(n, m)$, i.e., if α corresponds to the transition between the states Ψ_m and Ψ_n.

The simplicity of the time dependence of the Hubbard operators in the interaction representation obviously allows constructing a perturbation theory using the diagram technique for the Hubbard operators because the Wick theorem holds for them.

Introducing the matrix elements of the electron annihilation operators with the spin projection σ at the first and second sites

$$\gamma_{1\sigma}(nm) = \langle\Psi_n|a_{1\sigma}|\Psi_m\rangle, \qquad \gamma_{2\sigma}(nm) = \langle\Psi_n|a_{2\sigma}|\Psi_m\rangle, \tag{26}$$

we can express the fermion operators in terms of the Hubbard operators in a compact form:

$$a_{1\sigma} = \sum_\alpha \gamma_{1\sigma}(\alpha)X^\alpha, \qquad a_{2\sigma} = \sum_\alpha \gamma_{2\sigma}(\alpha)X^\alpha, \qquad \alpha \equiv \alpha(nm). \tag{27}$$

For brevity, we here write the summation over the index α bearing in mind summation over the pair of indices n and m of the atomic states of the device.

When the atomic representation is used, the tunneling operator contained in the scattering matrix takes a form convenient for constructing a perturbation theory explicitly containing the operators of the transition between atomic states,

$$\widehat{T}_\mathrm{I}(t) = \sum_{k\sigma,\alpha} t_{\mathrm{L}k}(t)\gamma_{1\sigma}(\alpha)c_{k\sigma}^+(t)X^\alpha(t) + \sum_{p\sigma,\alpha} t_{\mathrm{R}p}(t)\gamma_{2\sigma}(\alpha)d_{p\sigma}^+(t)X^\alpha(t) + \mathrm{H.c.} \tag{28}$$

For the device under study, the total number of states $|\Psi_m\rangle$, $m = 1, 2, \ldots, N_\mathrm{D}$, is 64. In the strong correlation regime, the Hubbard repulsion parameter U and the intersite Coulomb interaction U_{12} are significantly greater than the values of the other energy parameters of the system. This allows restricting our consideration only to the states of the device containing at most one transported electron. There are 20 such states.

To describe such states, we introduce the creation operators $f_{1\sigma}^+$ and $f_{2\sigma}^+$ and the annihilation operators $f_{1\sigma}$ and $f_{2\sigma}$ of localized fermions with the spin projection σ at the first and second sites of the device. The sector of the Hilbert space of the Hamiltonian of the device not containing transported electrons then corresponds to the states of the dimer system. The singlet state of the device can be written as

$$|1\rangle = \frac{1}{\sqrt{2}}(f_{1\uparrow}^+ f_{2\downarrow}^+ - f_{1\downarrow}^+ f_{2\uparrow}^+)|0\rangle, \qquad E_1 = -\frac{3I}{4}, \tag{29}$$

where $|0\rangle$ is the vacuum state. The three triplet states of this sector are

$$|2\rangle = \frac{1}{\sqrt{2}}(f_{1\uparrow}^+ f_{2\downarrow}^+ + f_{1\downarrow}^+ f_{2\uparrow}^+)|0\rangle, \qquad |3\rangle = f_{1\uparrow}^+ f_{2\uparrow}^+|0\rangle, \qquad |4\rangle = f_{1\downarrow}^+ f_{2\downarrow}^+|0\rangle \tag{30}$$

and have the energy $E_2 = I/4$. In the set of 16 states of the one-electron sector, eight states correspond to even and odd states with the total spin $S_t = 3/2$. We write four even states in a form that allows calculating the representation parameters simply,

$$|5\rangle = \frac{a_{1\uparrow}^+ + a_{2\uparrow}^+}{\sqrt{2}}|3\rangle, \qquad |6\rangle = \frac{\hat{S}_t^-}{\sqrt{3}}|5\rangle, \qquad |7\rangle = \frac{\hat{S}_t^+}{\sqrt{3}}|8\rangle, \qquad |8\rangle = \frac{a_{1\downarrow}^+ + a_{2\downarrow}^+}{\sqrt{2}}|4\rangle, \tag{31}$$

where

$$\hat{S}_t^- = \sum_{j=1}^{2}(f_{j\downarrow}^+ f_{j\uparrow} + a_{j\downarrow}^+ a_{j\uparrow}), \qquad \hat{S}_t^+ = \sum_{j=1}^{2}(f_{j\uparrow}^+ f_{j\downarrow} + a_{j\uparrow}^+ a_{j\downarrow}).$$

The four odd states with $S_t = 3/2$ are

$$|9\rangle = \frac{a_{1\uparrow}^+ - a_{2\uparrow}^+}{\sqrt{2}}|3\rangle, \qquad |10\rangle = \frac{\hat{S}_t^-}{\sqrt{3}}|9\rangle, \qquad |11\rangle = \frac{\hat{S}_t^+}{\sqrt{3}}|12\rangle, \qquad |12\rangle = \frac{a_{1\downarrow}^+ - a_{2\downarrow}^+}{\sqrt{2}}|4\rangle. \tag{32}$$

According to the summation rule for angular momenta in quantum mechanics, there are doublet terms in the set of one-electron states of the device. We write two even (g) and two odd (u) states with the spin projection of the total spin $S_t^z = 1/2$, which correspond to the even and odd doublet terms, in the form

$$\begin{aligned}
\left|\frac{1}{2},\frac{1}{2}\right\rangle_{\pm}^{g} &= \sum_{\sigma} C_{g\sigma}^{\pm}(f_{1\sigma}^+ f_{2\bar{\sigma}}^+ a_{1\uparrow}^+ + f_{1\bar{\sigma}}^+ f_{2\sigma}^+ a_{2\uparrow}^+)|0\rangle + C_{gg}^{\pm}(a_{1\downarrow}^+ + a_{2\downarrow}^+)f_{1\uparrow}^+ f_{2\uparrow}^+|0\rangle, \\
\left|\frac{1}{2},\frac{1}{2}\right\rangle_{\pm}^{u} &= \sum_{\sigma} C_{u\sigma}^{\pm}(f_{1\sigma}^+ f_{2\bar{\sigma}}^+ a_{1\uparrow}^+ - f_{1\bar{\sigma}}^+ f_{2\sigma}^+ a_{2\uparrow}^+)|0\rangle + C_{uu}^{\pm}(a_{1\downarrow}^+ - a_{2\downarrow}^+)f_{1\uparrow}^+ f_{2\uparrow}^+|0\rangle.
\end{aligned} \tag{33}$$

The remaining eight states are then labeled as

$$|13\rangle = \left|\frac{1}{2},\frac{1}{2}\right\rangle_{+}^{g}, \qquad |14\rangle = \hat{S}_t^-|13\rangle, \qquad |15\rangle = \left|\frac{1}{2},\frac{1}{2}\right\rangle_{-}^{g}, \qquad |16\rangle = \hat{S}_t^-|15\rangle,$$

$$|17\rangle = \left|\frac{1}{2},\frac{1}{2}\right\rangle_{+}^{u}, \qquad |18\rangle = \hat{S}_t^-|17\rangle, \qquad |19\rangle = \left|\frac{1}{2},\frac{1}{2}\right\rangle_{-}^{u}, \qquad |20\rangle = \hat{S}_t^-|19\rangle.$$

To write expressions (33), we use the notation

$$\begin{aligned}
C_{g\uparrow}^{\pm} &= \pm\frac{1}{\sqrt{2}}\frac{b_g^{\pm}}{Z_g^{\pm}}, \qquad C_{g\downarrow}^{\pm} = \frac{1}{\sqrt{2}}\frac{a_g^{\pm}}{Z_g^{\pm}}, \qquad C_{gg}^{\pm} = \pm\frac{1}{\sqrt{2}}\frac{c_g^{\pm}}{Z_g^{\pm}}, \\
C_{u\uparrow}^{\pm} &= \pm\frac{1}{\sqrt{2}}\frac{b_u^{\pm}}{Z_u^{\pm}}, \qquad C_{u\downarrow}^{\pm} = \frac{1}{\sqrt{2}}\frac{a_u^{\pm}}{Z_u^{\pm}}, \qquad C_{uu}^{\pm} = \pm\frac{1}{\sqrt{2}}\frac{c_u^{\pm}}{Z_u^{\pm}}, \\
Z_g^{\pm} &= \sqrt{(a_g^{\pm})^2 + (b_g^{\pm})^2 + (c_g^{\pm})^2}, \qquad Z_u^{\pm} = \sqrt{(a_u^{\pm})^2 + (b_u^{\pm})^2 + (c_u^{\pm})^2},
\end{aligned}$$

where

$$a_g^{\pm} = (\nu_g \mp A)(\nu_g \mp I \mp 2t_d), \qquad b_g^{\pm} = (I + 2t_d)(\nu_g \mp I \mp 2t_d), \qquad c_g^{\pm} = A(\nu_g \mp A),$$

$$a_u^{\pm} = (\nu_u \mp A)(\nu_u \mp I \pm 2t_d), \qquad b_u^{\pm} = (I - 2t_d)(\nu_u \mp I \pm 2t_d), \qquad c_u^{\pm} = A(\nu_u \mp A),$$

$$\nu_g = \sqrt{(A - I - 2t_d)^2 + A(I + 2t_d)}, \qquad \nu_u = \sqrt{(A - I + 2t_d)^2 + A(I - 2t_d)}.$$

In the framework of the labeling of one-electron states introduced above, their energies then become

$$\begin{aligned} &E_{5(9)} = \xi_d + \frac{A+I}{4} \pm t_d, \qquad E_{13(15)} = \xi_d - \frac{A+I}{4} \pm \frac{\nu_g}{2}, \\ &E_{17(19)} = \xi_d - \frac{A+I}{4} \pm \frac{\nu_u}{2}. \end{aligned} \tag{34}$$

Taking the explicit form of the basis functions of the device into account, we can easily show that the parameters of the representation of the operator $a_{1\uparrow}$ in terms of the Hubbard operators are

$$\begin{aligned} &\gamma_{1\uparrow}(3,5) = \gamma_{1\uparrow}(3,9) = \frac{1}{\sqrt{2}}, && \gamma_{1\uparrow}(2,6) = \gamma_{1\uparrow}(2,10) = \frac{1}{\sqrt{3}}, \\ &\gamma_{1\uparrow}(4,7) = \gamma_{1\uparrow}(4,11) = \frac{1}{\sqrt{6}}, && \gamma_{1\uparrow}(1,13(15)) = \frac{C_{g\uparrow}^{+(-)} - C_{g\downarrow}^{+(-)}}{\sqrt{2}}, \\ &\gamma_{1\uparrow}(1,17(19)) = \frac{C_{u\uparrow}^{+(-)} - C_{u\downarrow}^{+(-)}}{\sqrt{2}}, && \gamma_{1\uparrow}(2,13(15)) = -\frac{C_{gg}^{+(-)}}{\sqrt{2}}, \\ &\gamma_{1\uparrow}(2,17(19)) = \frac{C_{uu}^{+(-)}}{\sqrt{2}}, && \gamma_{1\uparrow}(4,14(16)) = \sqrt{2}\gamma_{1\uparrow}(2,13(15)), \\ &\gamma_{1\uparrow}(4,18(20)) = \sqrt{2}\gamma_{1\uparrow}(2,17(19)). \end{aligned} \tag{35}$$

For the considered device, we have $|\gamma_{2\uparrow}(\alpha)| = |\gamma_{1\uparrow}(\alpha)|$ and $\gamma_{2\uparrow}(\alpha) = -\gamma_{1\uparrow}(\alpha)$ for half the transitions. Below, we use these properties of the representation parameters to determine the current and to derive the kinetic equations. The parameters $\gamma_{1,2\downarrow}(\alpha)$ are calculated similarly.

5. Nonequilibrium Green's functions, spectral functions of the device, and spectral functions of the tunnel coupling

If the Hubbard operators are used, then the expression for the current in the atomic representation becomes

$$J = \left(\frac{-ie}{\hbar}\right) \sum_{k\sigma,\alpha} \gamma_{1\sigma}(\alpha) \big[t_{\mathrm{L}k}(t) \langle c_{1\sigma}^{+}(t) X^{\alpha}(t) \rangle_{\mathrm{I}} - t_{\mathrm{L}k}^{*}(t) \langle X^{-\alpha}(t) c_{1\sigma}(t) \rangle_{\mathrm{I}} \big], \tag{36}$$

which permits using the perturbation theory in diagram form. For this, we introduce nonequilibrium Green's functions constructed on the fermion and Hubbard operators and the functions containing the product of the fermion and Hubbard operators,

$$\begin{aligned} G_{\mathrm{L}k\sigma}^{ab}(\tau,\tau') &= -i\langle T_C c_{k\sigma}(\tau_a) c_{k\sigma}^{+}(\tau_b') \rangle_0, \\ D_{\alpha,\beta}^{ab}(\tau,\tau') &= -i\langle T_C X^{\alpha}(\tau_a) X^{-\beta}(\tau_b') S_C \rangle_0, \\ R_{k\sigma,\alpha}^{ab}(\tau,\tau') &= -i\langle T_C c_{k\sigma}(\tau_a) X^{-\alpha}(\tau_b') S_C \rangle_0, \\ R_{\alpha,k\sigma}^{ab}(\tau,\tau') &= -i\langle T_C X^{\alpha}(\tau_a) c_{k\sigma}^{+}(\tau_b') S_C \rangle_0, \end{aligned} \tag{37}$$

where each of the superscripts a and b can take one of the two values + or −. The first index a is associated with the time τ_a for the first operator contained in the average which is ordered in the sense of Keldysh. This means that for $a = +$ or −, the operator $c_{k\sigma}(\tau_a)$ or $X^{\alpha}(\tau_a)$ in the interaction representation is taken at the time τ on the respective lower or upper branch of the Keldysh contour. Similarly, for $b = +$ or −, the operator $X^{-\alpha}(\tau'_b)$ or $c^{+}_{k\sigma}(\tau'_b)$ is taken at the time τ' on the respective lower or upper branch of the Keldysh contour.

The Green's functions given by (37) allow writing the expression for the current in a form convenient for applying perturbation theory

$$J = \left(\frac{e}{\hbar}\right)\sum_{k\sigma,\alpha} t_{\mathrm{L}k}\gamma_{1\sigma}(\alpha)\big\{e^{ieVt/2}R^{++}_{\mathrm{L}k\sigma,\alpha}(t,t+\delta) - e^{-ieVt/2}R^{++}_{\alpha,\mathrm{L}k\sigma}(t,t+\delta)\big\}, \quad \delta \to +0. \tag{38}$$

An analysis of the diagram series arising in the expansion of the scattering matrix S_C in (37) shows that the Green's functions $R^{++}_{\mathrm{L}k\sigma,\alpha}(t,t')$ and $R^{++}_{\alpha,\mathrm{L}k\sigma}(t,t')$ can be written as integral convolutions of the nonequilibrium Green's functions for the left contact with the nonequilibrium Green's functions for the device written in the atomic representation:

$$\begin{aligned}
R^{++}_{\mathrm{L}k\sigma,\alpha}(t,t') &= \sum_{\beta} t_{\mathrm{L}k}\gamma_{1\sigma}(\beta)\times \\
&\quad\times\int_{-\infty}^{+\infty} d\tau\{G^{++}_{\mathrm{L}k\sigma}(t-\tau)D^{++}_{\alpha\beta}(\tau-t') - G^{+-}_{\mathrm{L}k\sigma}(t-\tau)D^{-+}_{\alpha\beta}(\tau-t')\}e^{-ieV\tau/2\hbar}, \\
R^{++}_{\alpha,\mathrm{L}k\sigma}(t,t') &= \sum_{\beta} t_{\mathrm{L}k}\gamma_{1\sigma}(\beta)\times \\
&\quad\times\int_{-\infty}^{+\infty} d\tau\{D^{++}_{\alpha\beta}(t-\tau)G^{++}_{\mathrm{L}k\sigma}(\tau-t') - D^{+-}_{\alpha\beta}(t-\tau)G^{-+}_{\mathrm{L}k\sigma}(\tau-t')\}e^{+ieV\tau/2\hbar}.
\end{aligned} \tag{39}$$

Applying the Fourier transform for the nonequilibrium functions

$$\begin{aligned}
G^{ab}_{\mathrm{L}k\sigma}(\tau-\tau') &= \int \frac{d\omega}{2\pi}\, e^{-i\omega(\tau-\tau')}G^{ab}_{\mathrm{L}k\sigma}(\omega), \\
D^{ab}_{\alpha\beta}(\tau-\tau') &= \int \frac{d\omega}{2\pi}\, e^{-i\omega(\tau-\tau')}D^{ab}_{\alpha\beta}(\omega),
\end{aligned} \tag{40}$$

we see that the current can be expressed in terms of the spectral functions of the system as

$$J = \left(\frac{e}{h}\right)\sum_{\sigma}\int_{-\infty}^{+\infty} d\omega[M^{-+}_{1\sigma}(\omega)W^{+-}_{1\sigma}(\omega) - M^{+-}_{1\sigma}(\omega)W^{-+}_{1\sigma}(\omega)], \tag{41}$$

for which we use the following definitions.

The left- and right-sided spectral functions $W^{ab}_{1\sigma}(\omega)$ and $W^{ab}_{2\sigma}(\omega)$ of the device are expressed in terms of atomic functions as

$$W^{ab}_{1\sigma}(\omega) = \sum_{\alpha\beta}\gamma_{1\sigma}(\alpha)\gamma_{1\sigma}(\beta)D^{ab}_{\alpha\beta}(\omega), \qquad W^{ab}_{2\sigma}(\omega) = \sum_{\alpha\beta}\gamma_{2\sigma}(\alpha)\gamma_{2\sigma}(\beta)D^{ab}_{\alpha\beta}(\omega). \tag{42}$$

The names of the introduced functions are related to the representation parameters for the electron annihilation operator at a site participating in the tunnel coupling with the respective left or the right contact.

Moreover, we also introduce the left- and right-sided spectral functions of the tunnel coupling between the contacts and the device

$$M_{1\sigma}^{ab}(\omega)=\sum_k t_{\mathrm{L}k}^2 G_{\mathrm{L}k\sigma}^{ab}\left(\omega+\frac{eV}{2\hbar}\right),\qquad M_{2\sigma}^{ab}(\omega)=\sum_p t_{\mathrm{R}p}^2 G_{\mathrm{R}p\sigma}^{ab}\left(\omega-\frac{eV}{2\hbar}\right),\tag{43}$$

where $G_{\mathrm{L}k\sigma}^{ab}$ and $G_{\mathrm{R}p\sigma}^{ab}$ are the nonequilibrium Green's functions of the left and right contacts. Then,

$$G_{\mathrm{L}k\sigma}^{++}(\omega)=\frac{n_{\mathrm{L}k\sigma}}{\omega-\xi_{\mathrm{L}k\sigma}-i\delta}+\frac{1-n_{\mathrm{L}k\sigma}}{\omega-\xi_{\mathrm{L}k\sigma}+i\delta},$$

$$G_{\mathrm{L}k\sigma}^{--}(\omega)=-\frac{n_{\mathrm{L}k\sigma}}{\omega-\xi_{\mathrm{L}k\sigma}+i\delta}-\frac{1-n_{\mathrm{L}k\sigma}}{\omega-\xi_{\mathrm{L}k\sigma}-i\delta},$$

$$G_{\mathrm{L}k\sigma}^{+-}(\omega)=2\pi i n_{\mathrm{L}k\sigma}\delta(\omega-\xi_{\mathrm{L}k\sigma}),\qquad G_{\mathrm{L}k\sigma}^{-+}(\omega)=2\pi i(n_{\mathrm{L}k\sigma}-1)\delta(\omega-\xi_{\mathrm{L}k\sigma}),$$

where

$$n_{\mathrm{L}k\sigma}=\{1+e^{(\varepsilon_{\mathrm{L}k\sigma}-\mu)/T}\}^{-1}.$$

The functions $G_{\mathrm{R}p\sigma}^{ab}$ are defined similarly with the only difference that instead of the index L of the left contact, we must use the index R of the right contact.

Formula (41) reduces the problem of calculating the tunnel current to the problem of calculating the spectral functions $W_{1\sigma}^{+-}(\omega)$ and $W_{1\sigma}^{-+}(\omega)$ of the device. We note that the sums over α and β contained in these functions correspond to taking the contributions to the current from the processes related to the transitions between the states $\Psi_1,\Psi_2,\ldots,\Psi_{N_{\mathrm{D}}}$ of the device into account.

6. Effective interactions of the device in the atomic representation

Calculating the spectral functions $W_{1\sigma}^{ab}$ and $W_{2\sigma}^{ab}$ of the device is related to solving a system of equations for the nonequilibrium Green's functions $D_{\alpha\beta}^{ab}$. Obtaining such a system is significantly simplified if we take into account that the terms of the perturbation series for $D_{\alpha\beta}^{ab}(\tau-\tau')$ are nonzero only if the number of the tunneling operator entries in the average is even. In this case, because H_0 is additive with respect to the subsystems of the contacts and the device, the averages of the fermion operators and of the Hubbard operators can be calculated independently. This allows explicitly calculating the averages of the fermion operators in each order of the perturbation theory. We then have a renormalized series that allows obtaining a more precise representation for the nonequilibrium Green's functions $D_{\alpha\beta}^{ab}$ in the form

$$D_{\alpha\beta}^{ab}(\tau-\tau')=-i\langle T_C X^{\alpha}(\tau_a)X^{-\beta}(\tau_b')\widetilde{S}_C\rangle_0.\tag{44}$$

Here, the renormalized scattering matrix

$$\widetilde{S}_C=T_C\exp\Big\{-i\int_C d\tau_1\int_C d\tau_2\sum_{\alpha\beta}\widetilde{V}_{\alpha\beta}(\tau_1-\tau_2)X^{-\alpha}(\tau_1)X^{\beta}(\tau_2)\Big\}\tag{45}$$

is determined in terms of the effective interaction, which depends on the difference between the time arguments on the Keldysh contour. Matrix elements of the effective interaction are expressed in terms of characteristics of the contacts and strengths of the tunnel couplings of the device with the left and right contacts:

$$\widetilde{V}_{\alpha\beta}(\tau_1-\tau_2)=\sum_{k\sigma}\gamma_{1\sigma}(\alpha)\gamma_{1\sigma}(\beta)t_{\mathrm{L}k}^2 e^{ieV(\tau_1-\tau_2)/2}G_{\mathrm{L}k\sigma}(\tau_1-\tau_2)+$$

$$+\sum_{p\sigma}\gamma_{2\sigma}(\alpha)\gamma_{2\sigma}(\beta)t_{\mathrm{R}p}^2 e^{-ieV(\tau_1-\tau_2)/2}G_{\mathrm{R}p\sigma}(\tau_1-\tau_2).\tag{46}$$

The obtained representation for $D^{ab}_{\alpha\beta}(\tau-\tau')$ together with the explicit expressions for $\widetilde{S}_C$ and $\widetilde{V}_{\alpha\beta}(\tau_1-\tau_2)$ allows determining the nonequilibrium functions of the device using only the diagram technique for the Hubbard operators, where the time dependence of the operators is determined on the Keldysh contour.

7. System of equations for the nonequilibrium Green's functions of the device

To take the transition of electrons from the contact to the device and conversely into account in all perturbation orders, we use the loopless approximation well known in the theory of strongly correlated systems. Its specific character in the theory of nonequilibrium functions $D^{ab}_{\alpha\beta}(\omega)$ is determined by the following two factors. The first factor is the time dependence of the effective interaction, which is manifested in the frequency dependence of the interaction matrix elements. The second factor is that the time evolution of the operators occurs on the Keldysh contour C. This complicates the structure of the equations written in the frequency representation.

We use the Keldysh contour to write the first system of equations for the nonequilibrium Green's functions $D^{+-}_{\alpha\beta}(\omega)$ and $D^{--}_{\alpha\beta}(\omega)$ in the atomic representation:

$$\begin{aligned} D^{+-}_{\alpha\beta}(\omega) &= \sum_{\nu} D_{\alpha}(\omega)[\widetilde{V}^{++}_{\alpha\nu}(\omega)D^{+-}_{\nu\beta}(\omega) - \widetilde{V}^{+-}_{\alpha\nu}(\omega)D^{--}_{\nu\beta}(\omega)], \\ D^{--}_{\alpha\beta}(\omega) &= -\delta_{\alpha\beta}D_{\alpha}(\omega) - \sum_{\nu} D_{\alpha}(\omega)[\widetilde{V}^{--}_{\alpha\nu}(\omega)D^{--}_{\nu\beta}(\omega) - \widetilde{V}^{-+}_{\alpha\nu}(\omega)D^{+-}_{\nu\beta}(\omega)]. \end{aligned} \tag{47}$$

The second system of equations for $D^{-+}_{\alpha\beta}(\omega)$ and $D^{++}_{\alpha\beta}(\omega)$ is obtained similarly and can be written as

$$\begin{aligned} D^{-+}_{\alpha\beta}(\omega) &= \sum_{\nu} D_{\alpha}(\omega)[\widetilde{V}^{-+}_{\alpha\nu}(\omega)D^{++}_{\nu\beta}(\omega) - \widetilde{V}^{--}_{\alpha\nu}(\omega)D^{-+}_{\nu\beta}(\omega)], \\ D^{++}_{\alpha\beta}(\omega) &= \delta_{\alpha\beta}D_{\alpha}(\omega) + \sum_{\nu} D_{\alpha}(\omega)[\widetilde{V}^{++}_{\alpha\nu}(\omega)D^{++}_{\nu\beta}(\omega) - \widetilde{V}^{+-}_{\alpha\nu}(\omega)D^{-+}_{\nu\beta}(\omega)]. \end{aligned} \tag{48}$$

To obtain these equations, we use the nonequilibrium bare device functions

$$\begin{aligned} D^{++}_{0\alpha}(\omega) &= \frac{N_n}{\omega+\alpha E+i\delta} + \frac{N_m}{\omega+\alpha E-i\delta}, \qquad D^{+-}_{0\alpha}(\omega) = 2\pi i N_m\delta(\omega+\alpha E), \\ D^{--}_{0\alpha}(\omega) &= -\frac{N_n}{\omega+\alpha E-i\delta} - \frac{N_m}{\omega+\alpha E+i\delta}, \qquad D^{-+}_{0\alpha}(\omega) = -2\pi i N_n\delta(\omega+\alpha E). \end{aligned} \tag{49}$$

Moreover, we introduce the propagator $D_{\alpha}(\omega) = b(\alpha)/[\omega+\alpha E]$, where the terminal factor is $b(\alpha) = N_n+N_m$ for $\alpha = \alpha(n,m)$. This factor is determined by the sum of the occupation numbers $N_n = \langle X^{nn}\rangle$ and $N_m = \langle X^{mm}\rangle$ of the device states $|\Psi_n\rangle$ and $|\Psi_m\rangle$ between which the transition is initiated. The Fourier transform of the interaction matrix element $\widetilde{V}^{ab}_{\alpha\beta}(\omega)$ is

$$\widetilde{V}^{ab}_{\alpha\beta}(t-t') = \int \frac{d\omega}{2\pi} e^{-i\omega(t-t')}\widetilde{V}^{ab}_{\alpha\beta}(\omega), \tag{50}$$

as previously for the Green's functions.

8. Calculation of the spectral functions of the device

The solution of system of equations (47) and (48) is significantly simplified if we take into account that the interaction matrix elements $\widetilde{V}^{ab}_{\alpha\beta}(\omega)$ can be written as a sum of four terms each of which splits into the indices α and β:

$$\widetilde{V}^{ab}_{\alpha\beta}(\omega) = \sum_{j=1}^{2}\sum_{\sigma} \gamma_{j\sigma}(\alpha)\gamma_{j\sigma}(\beta)M^{ab}_{j\sigma}(\omega). \tag{51}$$

The interaction strength of each of the four terms in this case is determined by the representation parameters and by the values of left- and right-sided spectral characteristics (43) of the tunnel couplings of the device.

The splitting factor allows introducing the linear combinations

$$\Phi^{ab}_{j\sigma\beta}(\omega) = \sum_{\nu} \gamma_{j\sigma}(\nu) D^{ab}_{\nu\beta}(\omega) \tag{52}$$

and obtaining closed systems of equations for them. For the four combinations $\Phi^{+-}_{1\sigma\beta}(\omega)$, $\Phi^{--}_{1\sigma\beta}(\omega)$, $\Phi^{+-}_{2\sigma\beta}(\omega)$, and $\Phi^{--}_{2\sigma\beta}(\omega)$ introduced above, system (47) then allows easily obtaining a system of four equations, which we write in the matrix form for brevity,

$$\hat{\Lambda}_{\sigma}(\omega) \cdot \Pi^{(1)}_{\sigma\beta}(\omega) = -\Upsilon^{(1)}_{\sigma\beta}(\omega). \tag{53}$$

Here, the four-dimensional vector $\Pi^{(1)}_{\sigma\beta}(\omega)$ comprises the four combinations introduced above,

$$\widetilde{\Pi}^{(1)}_{\sigma\beta}(\omega) = \left[\Phi^{--}_{1\sigma\beta}(\omega), \quad \Phi^{--}_{2\sigma\beta}(\omega), \quad \Phi^{+-}_{1\sigma\beta}(\omega), \quad \Phi^{+-}_{2\sigma\beta}(\omega)\right], \tag{54}$$

and the dynamical matrix $\hat{\Lambda}_{\sigma}(\omega)$ is

$$\begin{bmatrix} 1 + L^{\sigma}_{11}(\omega) M^{--}_{1\sigma}(\omega) & L^{\sigma}_{12}(\omega) M^{--}_{2\sigma}(\omega) & -L^{\sigma}_{11}(\omega) M^{-+}_{1\sigma}(\omega) & -L^{\sigma}_{12}(\omega) M^{-+}_{2\sigma}(\omega) \\ L^{\sigma}_{12}(\omega) M^{--}_{1\sigma}(\omega) & 1 + L^{\sigma}_{11}(\omega) M^{--}_{2\sigma}(\omega) & -L^{\sigma}_{12}(\omega) M^{-+}_{1\sigma}(\omega) & -L^{\sigma}_{11}(\omega) M^{-+}_{2\sigma}(\omega) \\ L^{\sigma}_{11}(\omega) M^{+-}_{1\sigma}(\omega) & L^{\sigma}_{12}(\omega) M^{+-}_{2\sigma}(\omega) & 1 - L^{\sigma}_{11}(\omega) M^{++}_{1\sigma}(\omega) & -L^{\sigma}_{12}(\omega) M^{++}_{2\sigma}(\omega) \\ L^{\sigma}_{12}(\omega) M^{+-}_{1\sigma}(\omega) & L^{\sigma}_{11}(\omega) M^{+-}_{2\sigma}(\omega) & -L^{\sigma}_{12}(\omega) M^{++}_{1\sigma}(\omega) & 1 - L^{\sigma}_{11}(\omega) M^{++}_{2\sigma}(\omega) \end{bmatrix},$$

where we introduce the functions

$$L^{\sigma}_{ij}(\omega) = \sum_{\alpha} \gamma_{i\sigma}(\alpha) \gamma_{j\sigma}(\alpha) D_{\alpha}(\omega).$$

The right-hand side of matrix equation (53) contains the vector $\Upsilon^{(1)}_{\sigma\beta}(\omega)$ such that

$$\tilde{\Upsilon}^{(1)}_{\sigma\beta}(\omega) = \left[\gamma_{1\sigma}(\beta), \quad \gamma_{2\sigma}(\beta), \quad 0, \quad 0\right] \cdot D_{\beta}(\omega). \tag{55}$$

It follows from the above equations that

$$\Phi^{+-}_{1\sigma\beta}(\omega) = \frac{\gamma_{2\sigma}(\beta)\Delta^{23}_{\sigma}(\omega) - \gamma_{1\sigma}(\beta)\Delta^{13}_{\sigma}(\omega)}{\Delta_{\sigma}(\omega)} D_{\beta}(\omega), \tag{56}$$

where $\Delta_{\sigma}(\omega) = \det(\Lambda_{\sigma}(\omega))$ and $\Delta^{nm}_{\sigma}(\omega)$ is the third-order determinant obtained from $\Delta_{\sigma}(\omega)$ by deleting the nth row and mth column. We use the definition of the left-sided spectral function of the device to obtain the solution of it:

$$W^{+-}_{1\sigma\beta}(\omega) = \sum_{\beta} \gamma_{1\sigma}(\beta) \Phi^{+-}_{1\sigma\beta}(\omega) = \frac{L^{\sigma}_{12}(\omega)\Delta^{23}_{\sigma}(\omega) - L^{\sigma}_{11}(\omega)(\beta)\Delta^{13}_{\sigma}(\omega)}{\Delta_{\sigma}(\omega)}. \tag{57}$$

The second system in (48) can be solved similarly. If we introduce the vectors

$$\begin{aligned} \widetilde{\Pi}^{(2)}_{\sigma\beta}(\omega) &= \left[\Phi^{-+}_{1\sigma\beta}(\omega), \quad \Phi^{-+}_{2\sigma\beta}(\omega), \quad \Phi^{++}_{1\sigma\beta}(\omega), \quad \Phi^{++}_{2\sigma\beta}(\omega)\right], \\ \tilde{\Upsilon}^{(2)}_{\sigma\beta}(\omega) &= \left[0, \quad 0, \quad \gamma_{1\sigma}(\beta), \quad \gamma_{2\sigma}(\beta)\right] \cdot D_{\beta}(\omega), \end{aligned} \tag{58}$$

then we obtain the equation

$$\hat{\Lambda}_{\sigma}(\omega) \cdot \Pi^{(2)}_{\sigma\beta}(\omega) = \Upsilon^{(2)}_{\sigma\beta}(\omega). \tag{59}$$

This implies that the sought spectral intensity is equal to

$$W^{-+}_{1\sigma\beta}(\omega) = \frac{L^{\sigma}_{11}(\omega)\Delta^{31}_{\sigma}(\omega) - L^{\sigma}_{12}(\omega)(\beta)\Delta^{41}_{\sigma}(\omega)}{\Delta_{\sigma}(\omega)}. \tag{60}$$

9. Current and kinetic equations for the occupation numbers

We use the solution obtained above and perform simple calculations to obtain the expression for the current

$$J = 4\frac{e}{h}\sum_{\sigma}\int_{-\infty}^{+\infty} d\omega \frac{[L_{12}^{\sigma}(\omega - eV/2)]^2}{\Delta_{\sigma}(\omega - eV/2)}\Gamma_1(\omega)\Gamma_2(\omega)[n_2(\omega - eV) - n_1(\omega)], \tag{61}$$

where

$$\Gamma_1(\omega) = \pi\sum_k t_{\mathrm{L}k}^2\delta(\omega - \xi_{\mathrm{L}k\sigma}), \qquad \Gamma_2(\omega) = \pi\sum_p t_{\mathrm{R}p}^2\delta(\omega - eV - \xi_{\mathrm{R}p\sigma}).$$

We further consider only the case of wide-band metal contacts $t_{\mathrm{L}}, t_{\mathrm{R}} \ll W$, where W is the contact bandwidth, which is frequently encountered in practice. For the dynamical matrix $\hat{\Lambda}_{\sigma}(\omega)$, we then obtain the expression

$$\Delta_{\sigma}(\omega) = \left[1 - \Gamma_1(\omega)\Gamma_2(\omega)\left([L_{11}^{\sigma}(\omega)]^2 - [L_{12}^{\sigma}(\omega)]^2\right)\right]^2 + \Gamma^2(\omega)[L_{11}^{\sigma}(\omega)]^2, \tag{62}$$

where $\Gamma(\omega) = \Gamma_1(\omega) + \Gamma_2(\omega)$.

We note that expression (61) satisfies obvious requirements. First, this is related to the current vanishing as soon as $t_{\mathrm{R}} = 0$ or $t_{\mathrm{L}} = 0$. A finer effect is that the current must be zero for the accepted geometry of the device if there is no coupling between the sites of the device, i.e., for $t_d = 0$. The parameter t_d does not appear explicitly in the expression for the current, but the dependence on it is manifested through the functions L_{11}^{σ} and L_{12}^{σ}. In the limit case $t_d = 0$, we obtain $L_{11}^{\sigma} \neq 0$ and $L_{12}^{\sigma} = 0$. The current therefore vanishes in this limit as it must. Moreover, if we pass to the situation with a single site at the center where the electron can be located, then $L_{11}^{\sigma} = L_{12}^{\sigma} \equiv L_{\sigma}$. As a result, expressions (61) and (62) take the form previously obtained in [14].

The functions in the expression for the current contain terminal factors, which are determined in terms of the occupation numbers N_m, $m = 1, 2, \ldots, N_{\mathrm{D}}$, of the states of the device. To obtain the kinetic equations that must be satisfied by the occupation numbers, we use the nonequilibrium functions $D_{\alpha\alpha}^{+-}(t - t')$ with different α. It follows from (37) that

$$D_{\alpha\alpha}^{+-}(t - t') = i\langle X^{-\alpha}(t')X^{\alpha}(t)\rangle = \int \frac{d\omega}{2\pi}e^{-i\omega(t-t')}D_{\alpha\alpha}^{+-}(\omega). \tag{63}$$

For $t = t'$, we then obtain

$$N_m \equiv \langle X^{mm}\rangle = \int \frac{d\omega}{2\pi i}D_{\alpha\alpha}^{+-}(\omega), \quad \alpha = \alpha(n, m). \tag{64}$$

As follows from (47), the function $D_{\alpha\beta}^{+-}(\omega)$ can be expressed in terms of the combinations $\Phi_{j\sigma\beta}^{+-}(\omega)$ and $\Phi_{j\sigma\beta}^{--}(\omega)$ introduced above. The solution for $\Phi_{1\sigma\beta}^{+-}(\omega)$ is given by formula (57). Using a similar technique, we can easily obtain the missing functions.

After simple but cumbersome calculations, we obtain the sought system of kinetic equations for the occupation numbers:

$$N_m = \sum_{\sigma}\int \frac{d\omega}{\pi}\gamma_{1\sigma}^2(\alpha)\frac{D_{\alpha}^2}{\Delta_{\sigma}}K_{\alpha}(\omega), \quad \alpha = \alpha(n, m), \tag{65}$$

where

$$K_{\alpha} = \Gamma_1 n_1 + \Gamma_2 n_2 + \Gamma_1\Gamma_2(\Gamma_1 n_2 + \Gamma_2 n_1)[L_{11}^{\sigma} - \Theta_{12}^{\sigma}(\alpha)L_{12}^{\sigma}]^2. \tag{66}$$

The dependence on ω is here omitted for brevity, and $\Theta_{12}^{\sigma}(\alpha) = \mathrm{sgn}[\gamma_{1\sigma}(\alpha)\gamma_{2\sigma}(\alpha)]$.

10. Conclusion

The development of the theory of quantum transport of electrons described above was motivated by the problem of a large number of bare scattering amplitudes in atomic-scale systems with internal degrees of freedom when they are described in the framework of usual secondary quantization operators.

We solved the problem by passing to the atomic representation for the Hamiltonian of the device and introducing the Hubbard operators. This allowed taking all interactions in the device into account exactly and representing its Hamiltonian in the diagonal form. In such an approach, the role of a perturbation is played only by the tunneling operator. It is significant that writing this operator in the atomic representation allows using the diagram technique for the Hubbard operators.

Another very important point is that the expression for the current can be written in terms of the universal spectral characteristics of the device, which are determined in terms of the nonequilibrium Green's functions in the atomic representation. For these functions, we obtain a system of equations with the scattering processes taken into account in all orders of the perturbation theory. Writing the matrix elements of the interaction in the split form allows solving this system by simple methods.

We considered the case where the left and right contacts are in tunnel coupling with different sites of the device, which is often encountered in practice. Such a geometry is required for analyzing the transport characteristics of a device with edge states. We showed that we can pass to the limit for the current when the coupling between ions in tunnel interaction with the contacts is broken inside the device.

For the problem geometry discussed above, the developed approach allowed deriving a closed system of kinetic equations for the occupation numbers. Because the Green's functions obtained with regard to the process of multiple electron scattering were used in this case, the obtained system of equations can be used in the case of strong renormalization of the occupation numbers due to the interaction between the transported electrons with internal spin degrees of freedom.

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