KINETIC EQUATIONS FOR OPEN QUANTUM SYSTEM IN THE OCCUPATION NUMBER REPRESENTATION

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Master equation for density matrix of an open many–particle system is derived in the occupation number representation. The Born approximation with respect to system–bath interaction is utilized and the fast relaxation within the system is assumed to be fulfiled. The reduction of a linear master equation to a nonlinear set of kinetic equations for one–particle distribution functions is carried out at the condition of strong particle–particle interaction. As an example, the procedure of derivation of kinetic equations for description of electron transfer through specific molecular nanostructures like molecular wires is demonstrated with taking into consideration the strong Coulomb repulsion between the transferred electrons.
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1. INTRODUCTION

Correct and the most complete description of evolution of an open quantum system (QS) to its equilibrium state occurs with the nonequilibrium density matrix method [1,2]. The method brings to a Generalized Master Equation (GME) for density matrix of the QS, $\sigma(t)$. In Born approximation with respect to interaction H_{int} between the QS and the bath, the GME reads (cf. e.g. Refs. [3–5]

$$\dot{\sigma}(t) = -\frac{i}{\hbar}\left[H_0, \sigma(t)\right] - \frac{1}{\hbar^2}\int_0^t d\tau \left\langle e^{-i(H_0+H_B)\tau/\hbar} \right.$$
$$\left. \times \left[H_{int}^{-\tau}, \left[H_{int}, \rho_B \sigma(t-\tau)\right]\right]e^{i(H_0+H_B)\tau/\hbar}\right\rangle. \quad (1)$$

Here

$$\langle A \rangle = Tr\rho_B A, \quad A^\tau \equiv \exp\left[-i(H_0+H_B)\tau/\hbar\right]$$
$$\times A\exp\left[i(H_0+H_B)\tau/\hbar\right], \quad (2)$$

where H_0 is the QS Hamiltonian, and $\rho_B = \exp(-H_B/k_BT)/Tr_B\left[\exp(-H_B/k_BT)\right]$ is the equilibrium density matrix of heat bath. In GME (1), one takes $\langle H_{int} \rangle = 0$. If it is not the case, then the substitutions $H_0 \to H_0 + \langle H_{int}\rangle$ and $H_{int} \to H_{int} - \langle H_{int}\rangle$ have to be performed.

Integro–differential operator equation (1) represents a non–Markovian form of GME. Let τ_{ev} be the characteristic time of evolution process which exceeds strongly the characteristic time τ_d that specifies the kernel's decrease in the integral-containing part of Eq. (1). Therefore, in line with general principles of the reduction of non-Markovian equation to the Markovian one [1,4] one can extend the upper integration limit in Eq. (1) up to ∞, putting simultaneously $\sigma(t-\tau) \cong \sigma(t)$. Such a substitution reduces an integro–differential GME (1) to a pure differential GME. Below we shall utilize a tetradic form of differential GME (the Redfield's equation [3–5]),

$$\sigma_{nm}(t) = i\omega_{nm}\sigma_{nm}(t) - \frac{i}{\hbar}\sum_r \left(V_{nr}\sigma_{rm}(t) - V_{rm}\sigma_{nr}(t)\right)$$
$$- \sum_{n'm'}\Gamma_{nm}^{n'm'}\sigma_{n'm'}(t), \quad (3)$$

which is valid for elements $\sigma_{nm}(t) = \langle n|\sigma(t)|m\rangle$ of the QS density matrix. Here, the manifold $\{|n\rangle\}$ relates to a complete set of QS basic functions so that

$$H_0 = \sum_n E(n)|n\rangle\langle n| + \sum_{nn'} V_{nn'}\left(1 - \delta_{nn'}\right)|n\rangle\langle n'|, \quad (4)$$

$$H_{int} = \sum_{nn'}\hat{F}_{nn'}|n\rangle\langle n'|. \quad (5)$$

In Eq. (4), $E(n)$ is the QS energy in state $|n\rangle$ whereas $V_{nn'} = V_{n'n}^* = \langle n|H_0|n'\rangle$ is the transition matrix element between different states. Operator $\hat{F}_{nn'} = \hat{F}_{n'n}^* = \langle n|H_{int}|n'\rangle$ characterizes the coupling between the QS and the heat bath. Quantities $V_{nn'}$, and $\hat{F}_{nn'}$ specify the dynamic and relaxation transitions in the QS.

Eq. (3) is a basic one for derivation of kinetic equations describing an evolution process in different type of open QS. Two first terms in the right part of Eq. (3) describe a pure dynamic behavior of the QS ($\omega_{nm} \equiv \left[E(n) - E(m)\right]/\hbar$ is the transition frequency) while the third term is responsible for a nonequilibrium process which is characterized by a relaxation supermatrix

$$\Gamma_{nm}^{n'm'} = \frac{1}{\hbar^2}\sum_r\int_0^\infty d\tau\left\{\delta_{mm'}\left\langle\hat{F}_{nr}\hat{F}_{rn'}^\tau\right\rangle e^{i\omega_{mr}\tau}\right.$$
$$+ \delta_{nn'}\left\langle\hat{F}_{m'r}^\tau\hat{F}_{rm}\right\rangle e^{i\omega_{rn}\tau}$$
$$\left. - \left\langle\hat{F}_{n'n}^\tau\hat{F}_{nn'}\right\rangle e^{i\omega_{m'n}\tau} - \left\langle\hat{F}_{m'm}^\tau\hat{F}_{nn'}\right\rangle e^{i\omega_{mn'}\tau}\right\}. \quad (6)$$

(Strongly, the form (6) is valid at small value of $V_{nn'}$ and if $E(n) \approx E(n')$ [5,6]).

2. NONLINEAR FORM OF KINETIC EQUATION

The further specification of kinetic equations is dictated by the relation between the pure dynamic and relaxation processes in the QS. We restrict ourselves by consideration of transfer processes in a condensed matter where the bath vibrational levels imitate a quasi continuous spectrum. In this case, the transition

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5

probabilities coincide with those found in the framework of Fermi Golden Rule (i.e. at small couplings $V_{nn'}$ and if $E(n) \approx E(n')$ [6]). As a result, the basic set of equations (3) is transformed to a separate set of equations for diagonal elements $\sigma_{nn}(t)$ only. The set reads as

$$\dot{\sigma}_{nn}(t) = -\sum_{n'} R_{nn'}\left(\sigma_{nn}(t) - \sigma_{n'n'}(t)\right) \tag{7}$$

where quantity

$$R_{nn'} = R_{n'n} = \frac{2\pi}{\hbar}\left|V_{nn'}\right|^2 \delta\left(E(n) - E(n')\right) \tag{8}$$

specifies the transition probability between the QS states $|n\rangle$ and $|n'\rangle$. It is very important that each QS state has a complex structure with a manifold of substates, $\{\alpha\}$. Just a relaxation within such a manifold (caused by interaction with a heat bath) is responsible for appearance of the irreversibility of a common evolution process in open QS. Let, for instance, manifold $\{\alpha\}$ relate to vibrational substates of electronic term j so that $|n\rangle = |j\alpha\rangle$ and thus $E(n) = E_{j\alpha}$ is the energy of the α-th substate of site j while $V_{nn'} = V_{j\alpha j'\alpha'}$ is the coupling between the vibrational substates of terms j and j'. Fast relaxation between the vibrational substates of each term brings (for a short characteristic time τ_{rel}) to a Boltzmann distribution within the vibrational manifold. As far as the population of each state is defined by diagonal element $\sigma_{nn}(t) = \sigma_{j\alpha j\alpha}(t)$ the ratio

$$\sigma_{j\alpha j\alpha}(t)/\sigma_{j\alpha' j\alpha'}(t) = \exp\left[-\left(E_{j\alpha} - E_{j\alpha'}\right)/k_B T\right] \tag{9}$$

is satisfied at any time $t \gg \tau_{rel}$. [In Eq. (9), k_B and T are the Boltzmann constant and the temperature, respectively.] Therefore, if inter–term transitions occur with the characteristic time $\tau_{tr} \gg \tau_{rel}$, one can utilize a property (9) without any limitations. In particular, the property (9) allows us to transform Eq. (7) to Pauli–like equation

$$\dot{P}_j(t) = -\sum_{j'}\left[\kappa_{j\to j'}P_j(t) - \kappa_{j'\to j}P_{j'}(t)\right] \tag{10}$$

for integral term populations $P_j(t) = \sum_{\alpha}\sigma_{j\alpha j\alpha}(t)$. Quantities

$$\kappa_{j\to j'} = \frac{2\pi}{\hbar}\sum_{\alpha\alpha'}\left|V_{j\alpha j'\alpha'}\right|^2 W\left(E_{j\alpha}\right)\delta\left(E_{j\alpha} - E_{j'\alpha'}\right) \tag{11}$$

with

$$W\left(E_{j\alpha}\right) = \exp\left(-E_{j\alpha}/k_B T\right)\Big/\sum_{\alpha'}\exp\left(-E_{j\alpha'}/k_B T\right) \tag{12}$$

being the distribution function for the j-th term, are the inter–term transfer rates.

Rate equations (11) describe a linear one–particle transfer. However, if particle–particle correlations are important these linear equations do not reflect an actual situation. One of important examples is a distant electron transfer (ET) in molecular nanostructures like molecular wires [5,7-9]. Just in such mesoscopic systems, a Coulombic interaction between the transferred electrons is shown to form the specific nonlinear intramolecular currents [10,11].

The main goal of the present work is to derive kinetic equations for description of ET in the condition of strong electron–electron correlation. We restrict ourselves by the systems where ET occurs on the background of fast relaxation within the set of sublevels belonging each site of electron localization. It means that one can start from a general set of linear equations (7) where now the $|n\rangle$ specifies many–particle electronic states of the whole QS. Below we shall utilize the occupation number representation where

$$|n\rangle = \left|\{N\}\right\rangle = \prod_{\lambda}\left|N_{\lambda}\right\rangle \tag{13}$$

and thus manifold $\{N\}$ fixes electron occupation numbers $N_{\lambda} = 0,1$ for each single–electron state λ. The structure of many–particle state allows us to introduce the following form for diagonal elements of density matrix,

$$\sigma_{nn}(t) = \sigma_{\{N\}\{N\}}(t) = \prod_{\lambda}P_{N_{\lambda}}(t). \tag{14}$$

Here, quantity $P_{N_{\lambda}}(t) = \sigma_{N_{\lambda}N_{\lambda}}(t)$ satisfies the normalization condition,

$$\sum_{N_{\lambda}}P_{N_{\lambda}}(t) = 1, \tag{15}$$

and determines the occupancy of the λ-th QS state, $P_{\lambda}(t)$, via relations

$$P_{\lambda}(t) = \sum_{N_{\lambda}}N_{\lambda}P_{N_{\lambda}}(t) = \sum_{N_{\lambda}}\left(1 - N_{\lambda}\right)P_{1-N_{\lambda}}(t) \tag{16}$$

and

$$1 - P_{\lambda}(t) = \sum_{N_{\lambda}}\left(1 - N_{\lambda}\right)P_{N_{\lambda}}(t) = \sum_{N_{\lambda}}N_{\lambda}P_{1-N_{\lambda}}(t). \tag{17}$$

The structure of many–particle density matrix, Eq. (14) supposes the derivation of self–consistent set of equations for one–particle functions $P_{N_{\lambda}}(t)$ or that is the same, distribution functions $P_{\lambda}(t) = P_{1\lambda}(t) = = 1 - P_{0\lambda}(t)$. To derive the corresponding set of equations we substitute form (14) in Eq. (7) which now reads as

$$\frac{d}{dt}\prod_{\lambda}P_{N_{\lambda}}(t) = -\frac{2\pi}{\hbar}\sum_{\{N'\}}\left|V_{\{N'\}\{N\}}\right|^2\left[\prod_{\lambda}P_{N_{\lambda}}(t)\right.$$
$$\left. - \prod_{\lambda}P_{N'_{\lambda}}(t)\right]\delta\left(E(\{N'\}) - E(\{N\})\right) \tag{18}$$

Here,

$$E(\{N\}) = \sum_{\lambda}E_{\lambda}N_{\lambda} + U(\{N\}) \tag{19}$$

is the QS energy with taking into consideration an interaction between the particles (term $U(\{N\})$). Quantity $V_{\{N'\}\{N\}} = \left\langle\{N'\}\left|\hat{V}_{tr}\right|\{N\}\right\rangle$ is the matrix element between many–particle QS states with $\hat{V}_{tr}$ being the transfer operator. Linear form (18) generates automatically nonlinear kinetic equations for one–particle distribution functions. Actually, let one multiply

Eq. (18) by the N_ξ and then sum over all occupation numbers N_λ. With utilization of Eqs. (15)–(17) one derives $\sum_{N_\lambda(\lambda\neq\xi)}\sum_{N_\xi}N_\xi P_{N_\xi}(t)\prod_{\lambda\neq\xi}P_{N_\lambda}(t) = P_\xi(t)$ and thus

$$\dot{P}_\xi(t) = -\frac{2\pi}{\hbar}\sum_{\{N\}\{N'\}}\left|V_{\{N'\}\{N\}}\right|^2 N_\xi\left[\prod_\lambda P_{N_\lambda}(t)\right.$$
$$\left.-\prod_\lambda P_{N'_\lambda}(t)\right]\delta\left(E(\{N'\}) - E(\{N\})\right) \qquad (20)$$

This nonlinear equation written for one–particle occupancies $P_\xi(t)$ is the main result of the present work. Note that form (24) works in conditions of fast relaxation in QS. The further specification of Eq. (24) is dictated by concrete transfer process.

3. KINETIC EQUATION FOR SHORT MOLECULAR WIRE

As an example we consider the ET through a short molecular wire where interaction between the transferred electrons is so large that no more than one transferred electron be captured by the wire in the course of ET across the wire [11]. Let $E_{m\mu}$ and $E^0_{m\mu}$ be the energies of the -th vibrational state when the transferred electron does or does not occupy the m-th wire unit while $E_{s\mathbf{k}}$ is the electron energy when an electron (with the wave vector $\mathbf{k}$) occupies the conduction band of the left ($=$L) or the right ($=$R) microelectrodes. Linear wire of units is assumed to contact with the corresponding electrodes via their terminal units $m = 1$ and $m = M$. No any magnetic interactions are supposed to be in the system "electrode L–Wire–electrode R" (LWR–system). With omitting the spin identification we operate with two type of single–electron states, $\lambda = s\mathbf{k}$ and $\lambda = m\mu$. Thus, just the occupation numbers $N_{s\mathbf{k}} = 0,1$ and $N_m = \sum_\mu N_{m\mu} = 0,1$ along with the electronic occupancies $P_{s\mathbf{k}}(t)$ and $P_m(t) = \sum_\mu P_{m\mu}(t)$ exhibit as the main quantum and statistical characteristics of an electron in the LWR–system. Electron energy (19) of this system has a form

$$E(\{N\}) = \sum_\mathbf{k}E_{L\mathbf{k}}N_{L\mathbf{k}} + \sum_m\left[E_{m\mu}N_m + E^0_{m\mu}(1-N_m)\right]$$
$$+\sum_\mathbf{q}E_{R\mathbf{q}}N_{R\mathbf{q}} + U(\{N\}). \qquad (21)$$

This value depends strongly on the number of electrons captured by the wire units (via the numbers $N_m = 0,1$), and a Coulomb repulsion between the transferring electrons (via term $U(\{N\})$).

Single–electron transitions are caused by the transition operator

$$V_{tr} = \sum_{\lambda,\lambda'}T_{\lambda\lambda'}a^+_\lambda a_{\lambda'} \qquad (22)$$

where a^+_λ and a_λ are electron creation and electron annihilation operators with respect to a single electron state λ while $T_{\lambda\lambda'}$ is the corresponding transition matrix element. Let one derive kinetic equation for the occupancy $P_{L\mathbf{k}}(t)$. In this case, only single–electron

states $\lambda,\lambda' = L\mathbf{k},l\mu_1$ participate in the ET process. E.g. the ET occurs between the -th vibrational level of site $m = 1$ and the $\mathbf{k}$-th band state. The corresponding coupling reads $T_{\lambda\lambda'} = V_{L\mathbf{k}}\langle\mu'_1|\mu_1\rangle$. [We employ a Condon approximation, when matrix elements $V_{n\nu_n m\mu_m}$ are factorized to the form where is the pure electronic coupling while is the overlap integral between the vibrational functions]. Therefore,

$$V_{\{N'\}\{N\}} = \left[V_{L\mathbf{k}}N_{L\mathbf{k}}(1-N_1) + V^*_{L\mathbf{k}}N'_{L\mathbf{k}}(1-N'_1)\right]\langle\mu'_1|\mu_1\rangle$$
$$\times\delta_{N'_1,1-N_1}\delta_{N'_{L\mathbf{k}},1-N_{L\mathbf{k}}}$$
$$\times\prod_{\mathbf{k}'\neq\mathbf{k}}\delta_{N'_{L\mathbf{k}'},N_{L\mathbf{k}}}\prod_{j\neq1}\delta_{N'_j,N_j}\prod_\mathbf{q}\delta_{N'_{R\mathbf{q}},N_{R\mathbf{q}}} \qquad (23)$$

and thus

$$\dot{P}_{L\mathbf{k}}(t) = -\frac{2\pi}{\hbar}\left|V_{L\mathbf{k}}\right|^2\sum_{N_{L\mathbf{k}}}\sum_{N_{R\mathbf{q}}}\sum_{N_{m\mu_m}}\sum_{N_1}\sum_{\mu_1\mu'_1}\langle\mu_1|\mu'_1\rangle^2$$
$$\times N_{L\mathbf{k}}(1-N_1)\delta\left(E(\{N\}) - E(\{N'\})\right)$$
$$\times\left[P_{N_{L\mathbf{k}}}(t)P_{N_1\mu_1}(t) - P_{1-N_{L\mathbf{k}}}(t)P_{1-N_1\mu_1}(t)\right]$$
$$\times\prod_{m\neq1}P_{N_m\mu_m}(t)\prod_\mathbf{q}P_{N_{R\mathbf{q}}}(t). \qquad (24)$$

Now we take into consideration the fact of fast relaxation within electronic terms. It has been already noted that such a relaxation brings to important ratio (9) between the partial site occupancies. Similar ratio exists for the occupancies $P_{N_{m\mu}}(t)$. It reads $P_{N_{m\mu}}(t)/P_{N_{m\mu'}}(t) =$
$= \exp\left[-\left(E_{m\mu} - E_{m\mu'}\right)N_m/k_\mathrm{B}T - \left(E^0_{m\mu_0} - E^0_{m\mu_0}\right)(1-N_j)/k_\mathrm{B}T\right]$
and thus expresses the vibration occupancies $P_{N_{m\mu}}(t)$ via the integral occupancies $P_{N_m}(t)$ as

$$P_{N_{m\mu}}(t) = P_{N_m}(t)\left[W\left(E_{m\mu}\right)\delta_{N_m,1} + W\left(E^0_{m\mu}\right)\delta_{N_m,0}\right] \qquad (25)$$

where Gibbs distribution functions for electronic terms are defined by Eq. (12). Now, bearing in mind a weak dependence of Coulombic repulsion on vibrational states μ we can sum a right part of Eq. (24) over all vibrational states μ_m (except μ_1 and μ'_1). With normalization conditions $\sum_{\mu_m}W(E_{m\mu}) = 1$ and $\sum_{\mu_m}W(E^0_{m\mu}) = 1$ it yields

$$\dot{P}_{L\mathbf{k}}(t) = -\frac{2\pi}{\hbar}\left|V_{L\mathbf{k}}\right|^2\sum_{N_{L\mathbf{k}}}\sum_{N_{R\mathbf{q}}}\sum_{N_m}\sum_{N_1}\sum_{\mu_1\mu'_1}\langle\mu_1|\mu'_1\rangle^2$$
$$\times N_{L\mathbf{k}}(1-N_1)\left[W\left(E_{1\mu_1}\right)\delta_{N_1,1} + W\left(E^0_{1\mu'_1}\right)\delta_{N_1,0}\right]$$
$$\times\left(P_{N_{L\mathbf{k}}}(t)P_{N_1}(t) - P_{1-N_{L\mathbf{k}}}(t)P_{1-N_1}(t)\right)$$
$$\times\prod_{m\neq1}P_{N_m}(t)\prod_\mathbf{q}P_{N_{R\mathbf{q}}}(t)\,\delta\left(E(\{N\}) - E(\{N'\})\right). \qquad (26)$$

Note now that for a short molecular wire under consideration, the repulsion of transferring electrons is assumed to be too strong to allow the appearance of more then one transferring electron within the wire. Physically, this fact indicates that energy conservation law, $E(\{N\}) = E(\{N'\})$, containing in δ–function of Eq. (26), is assumed to be fulfilled if only a single hopping electron is captured by the wire in the course of ET, i.e. at conditions $\sum_{m=1}^N N_m \leq 1$ and $\sum_{m=1}^N N'_m \leq 1$. Just these conditions one has to take into consideration when the summation over occupation numbers is carried out. To specify this circumstance, we introduce the

"repulsion multiplier" $Q_0 \equiv \prod_{m=1}^{N}(1 - N_m)$ which is equal 1 for empty wire (i.e. at $\sum_{m=1}^{N} N_m = 0$) and 0 if even one transferring electron occupies the wire (i.e. at $\sum_{m=1}^{N} N_m > 0$). The introduction of enables one to omit the Coulombic contributions $U(\{N\})$ and $U(\{N'\})$ in the energies involved in δ–function of Eq. (26). With substitution the $\delta\left(E(\{N\}) - E(\{N'\})\right)$ for the $Q_0 \delta\left(E_{a\mathbf{k}} + E_{1\mu'}^{0} - E_{1\mu}\right)$ and utilization of Eqs. (15-17) we reduce Eq. (26) to the following compact form

$$\dot{P}_{\text{L}\mathbf{k}}(t) = -\frac{2\pi}{\hbar}|V_{\text{L}\mathbf{k}}|^2 \sum_{\mu\mu'} \langle \mu | \mu' \rangle^2 \delta\left(E_{a\mathbf{k}} + E_{1\mu'}^{0} - E_{1\mu}\right)$$
$$\times \left[P_{\text{L}\mathbf{k}}(t)W\left(E_{1\mu'}^{0}\right)(1 - P_1(t)) - (1 - P_{\text{L}\mathbf{k}}(t))W\left(E_{1\mu}\right)P_1(t)\right]$$
$$\times \prod_{m\neq 1}^{N}(1 - P_m(t)) \qquad (27)$$

This equation defines automatically the variation in time of the number of electrons which are capable to be transferred through a molecular wire from electrode L to electrode R, i.e. the quantity $\dot{N}_{\text{L}}(t) = \sum_{\mathbf{k}} \dot{P}_{\text{L}\mathbf{k}}(t) = -\dot{N}_{\text{R}}(t)$. As far as $N_L(t)$ is the bulk characteristic, it varies slightly in the course of the ET through a molecular wire. It means that the $P_{\text{L}\mathbf{k}}(t)$ has a minor distinction from equilibrium Fermi distribution function

$$n(E_{\text{L}\mathbf{k}}) = \left\{\exp\left[(E_{\text{L}\mathbf{k}} - E_{\text{F}})/k_{\text{B}}T\right] + 1\right\}^{-1} \qquad (28)$$

where E_F is the Fermi energy of electrode. This let one put $P_{\text{L}\mathbf{k}}(t) \cong n(E_{\text{L}\mathbf{k}})$ in right part of Eq. (27) and thus

$$\dot{N}_{\text{L}}(t) = -\chi_{\text{L}}\prod_{m=1}^{N}(1 - P_m(t))$$
$$+ \chi_{-\text{L}}P_1(t)(1 - \delta_{m1})\prod_{m=2}^{N}(1 - P_m(t)). \qquad (29)$$

Rate constants χ_{L} and $\chi_{-\text{L}}$ follow from Eq. (27) at $P_{\text{L}\mathbf{k}}(t) \cong n(E_{\text{L}\mathbf{k}})$ and read as

$$\chi_{\text{L}} = \frac{2\pi}{\hbar}\sum_{\mathbf{k}\mu\mu'}|V_{\text{L}\mathbf{k}}|^2 \langle \mu | \mu' \rangle^2 n(E_{\text{L}\mathbf{k}})$$
$$\times W\left(E_{1\mu'}^{0}\right)\delta\left[(E_{1\mu} - E_{1\mu'}^{0}) - E_{\text{L}\mathbf{k}}\right], \qquad (30)$$

and

$$\chi_{-\text{L}} = \frac{2\pi}{\hbar}\sum_{\mathbf{k}\mu\mu'}|V_{\text{L}\mathbf{k}}|^2 \langle \mu | \mu' \rangle^2 [1 - n(E_{\text{L}\mathbf{k}})]$$
$$\times W\left(E_{1\mu}\right)\delta\left[(E_{1\mu} - E_{1\mu'}^{0}) - E_{\text{L}\mathbf{k}}\right]. \qquad (31)$$

Analogously, one can derive a complete set of equations for all site occupancies $P_m(t)$. For instance,

$$\dot{P}_1(t) = -(\chi_{-\text{L}} + g_1)P_1(t)\prod_{m=2}^{N}(1 - P_m(t))$$
$$+ \chi_{\text{L}}\prod_{m=1}^{N}(1 - P_m(t)) + r_2 P_2(t)\prod_{m\neq 2}^{N}(1 - P_m(t)). \qquad (32)$$

It is clearly seen from Eqs. (27) and (32) that just nonlinear factors $\prod_{m}(1 - P_m(t))$ caused by extremely strong Coulomb repulsion between the transferred electrons are responsible for possible blocking the ET process. Similar situation appears e.g. at resonant electron tunneling in semiconductor heterostructures [12].

In conclusion, we note that the approach proposed in the present paper gives possibility to derive different form of nonlinear kinetic equations for one–particle distribution functions if only the characteristic time of transfer process exceeds strongly the characteristic times of relaxation processes within electronic terms of the QS.

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