Kinetic rectification of charge transmission through a single molecule

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Based on the nonequilibrium density matrix method the kinetic description of electron transmission through a single molecule with delocalized molecular orbitals is accomplished. Analytic expressions for the sequential (hopping) component and the direct (tunnel) component of the current are derived and analyzed for the particular case where the transmission proceeds through a single molecular orbital. It is shown that the population of the orbital by the transferred electrons leads to the formation of two transmission channels. One channel is related to electron transmission through the molecule in a state without an extra (transferred) electron. The other channel accounts for electron transmission with the participation of the singly reduced state of the molecule. Because the absence of an extra electron or the presence of one or two extra electrons is determined by inelastic electron hopping processes, even the direct (tunnel) current through the molecule is controlled by inelastic processes. These processes lead to a specific kinetic rectification effect, including a regime with negative differential resistance, for the tunneling component of the current, provided that the hopping rates between the molecule and the left electrode strongly differ from the hopping rates related to the right electrode.

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I. INTRODUCTION

During recent years substantial progress has been achieved in the experimental and theoretical investigation of electron transmission through individual molecules and molecular wires (see Refs. 1–8). Typically, electron transmission is described in a model where the molecule, embedded between two leads, acts as a dynamic scattering system. The inter-electrode current is caused by elastic tunneling and can be computed in the framework of the Landauer theory.[8–11] Recent improvement of this approach also account for inelastic tunneling processes by including the coupling of molecular electron vibrational states to bath vibrations.[12,13] The coupling not only leads to the broadening of the electron vibrational levels but also is responsible for the appearance of vibrational sidebands in the resonant transmission. The scattering approach assumes a direct transmission of an electron (or hole) from one electrode to another. However, there exists an additional sequential (hopping) mechanism of electron transfer[14–21] where the transmitted electron is captured by the molecule. Usually it is supposed that the direct (coherent) and the sequential (incoherent) mechanism of electron transfer give an additive contribution to the total interelectrode current. Generally, it is not the case.[21] The problem appears thus to describe the current formation in the framework of unified approach. This approach has to be beyond scattering theory. (For instance, it is shown[22] that off-resonant inelastic tunneling cannot be adequately described in the framework of Landauer theory.)

At present, two theoretical approaches are derived for a correct description of electron transfer processes in the molecules. The first one is based on Keldysh formalism and uses a nonequilibrium Green function method. This formalism has been successfully applied to describe a phonon-assisted tunneling through a single bridge level,[23,24] as well as for the line shape and linewidths observed in recent inelastic electron tunnel spectroscopy experiments.[24,25] The second theoretical approach is based on the nonequilibrium density matrix method. The method allows one to carry out a unified description of transmission processes reducing a general master equation for a density matrix of the reference system to the set of coupled kinetic (generally nonlinear) equations for electronic populations of the electrode's band levels and the molecular levels. The results of a unified description of electron transmission through a molecule (molecular wire) demonstrate that the tunnel and the sequential mechanisms of electron transfer give an additive contribution to the current if the population of the molecule by extra (transferred) electrons remains small.[21,26] Otherwise the Coulomb interaction between the transferred electrons essentially influences the charge transmission. Over 15 years ago, this effect was already described for mesoscopic two-barrier structures including single-level quantum dots (cf., e.g., Refs. 27 and 28). But the effect also appears in single molecules and molecular wires.[29–35]

The goal of the present paper is to demonstrate that it is the forward and backward hopping processes, modified by the Coulomb interaction between the transmitted electrons, which control the single-electron current formation in a typical device arrangement like "lead-molecule-lead" depicted in Fig. 1. Such a control takes place via the formation of specific transmission channels which are related to the number of extra electrons captured by the molecule in the course of electron transmission. The effect becomes particularly pronounced if the molecule is coupled asymmetrically to the leads which in turn gives rise to a kinetic rectification effect. The latter results in strongly asymmetric current-voltage characteristics, including regimes with negative differential
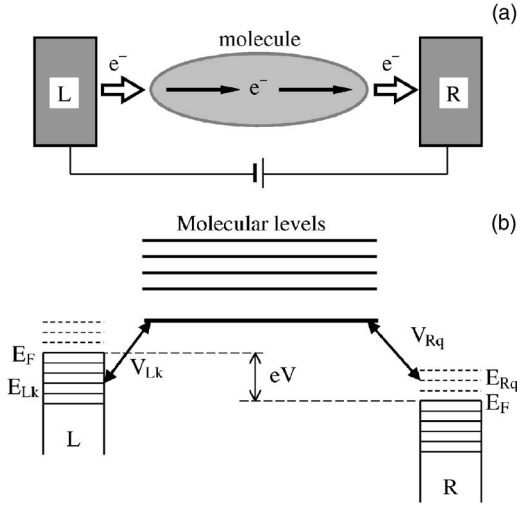
FIG. 1. Single molecule embedded between two nanoelectrodes, i.e., lead (L)-molecule-lead (R) (LMR) system. (a) Scheme of the charge transmission process. (b) Coupling of a single molecular orbital [lowest unoccupied molecular orbital (LUMO) level] to the band states of the left (right) electrode characterized by the quantity $V_{L\mathbf{k}}$ ($V_{R\mathbf{k}}$) (vibrational levels have been omitted).

resistance. A detail analysis of this effect will be given for the case where the main transmission pathway is offered by a single molecular orbital. The analytic results are derived with the use of a unified approach based on the nonequilibrium density matrix method.

II. MODEL AND BASIC EQUATIONS

The following considerations are based on our recent kinetic description of electron transmission through extended molecular orbitals of a single molecule or molecular wire.[21,26] We will restrict the description to those cases where the exchange interaction among the extra electrons is small enough that a discrimination between different total spin state of the extra electrons does not become necessary. Moreover, the neutral molecule is assumed to be in a zero-spin state, and magnetic properties of the electrodes should be of minor importance. It is also assumed that the sequential route of an electron transfer occurs against fast vibrational relaxation so that one can introduce the population probabilities for the molecular level.

A. Nonlinear kinetic equations for single-electron distributions

If the exchange interaction is of less importance the spin states of a particular system are exclusively defined by the spin projections of individual electrons. Therefore, each multielectron state $|a\rangle$ of the reference transfer system lead (L)-molecule-lead (R) (LMR system) can be characterized by a specific set of occupation numbers $\{N\}=\{\dots,N_{j\sigma_j},\dots\}$ where the symbols $j=r\mathbf{k}$ and $j=\mu$ describe the state of an electron with wave vector $\mathbf{k}$ in the conduction band of the rth ($r=L,R$) lead and the μth molecular orbital (MO), respectively. The spin projection of the jth single-electron state is denoted by $\sigma_j=+1/2,-1/2$ ($\uparrow,\downarrow$). Along with the occupa-

tion numbers $N_{j\sigma_j}=0,1$ one may introduce the distribution functions $P(N_{j\sigma_j},t)$, each of which defines the probabilities $P_{j\sigma_j}(t)=P(1_{j\sigma_j},t)$ and $1-P_{j\sigma_j}(t)=P(0_{j\sigma_j},t)$ that an electron with spin projection σ_j does, or does not, populate a single-electron state j, respectively. In the problem under consideration we need to calculate the current

$$I = e\dot{N}_L, \tag{1}$$

where $e<0$ denotes the electron charge and $\dot{N}_L$ $(=-\dot{N}_R)$ is the time derivative of the electron number of the left (right) lead. Since

$$N_L(t) = \sum_{\mathbf{k}\sigma_{\mathbf{k}}} P_{L\mathbf{k}\sigma_{\mathbf{k}}}(t), \tag{2}$$

one has to determine the time derivative of the single-electron state distribution $P_{j\sigma_j}(t)$ at $j=L\mathbf{k}$.

Generally, each $P_{j\sigma_j}(t)$ is obtained in using the definitions

$$P_{j\sigma_j}(t) = \sum_{N_{j\sigma_j}=0,1} N_{j\sigma_j} P(N_{j\sigma_j},t) \tag{3}$$

and

$$P(N_{j\sigma_j},t) = \sum_{\{N\}\neq N_{j\sigma_j}} \mathcal{P}_{\{N\}}(t), \tag{4}$$

where $\mathcal{P}_{\{N\}}(t)$ is the multielectron distribution function of the total LMR system. This function satisfies the set of balance-like equations[26]

$$\dot{\mathcal{P}}_{\{N\}}(t) = \sum_{\{N'\}} [K_{\{N'\}\to\{N\}}\mathcal{P}_{\{N'\}}(t) - K_{\{N\}\to\{N'\}}\mathcal{P}_{\{N\}}(t)]. \tag{5}$$

The transfer rate $K_{\{N\}\to\{N'\}}$ characterizes the transition from a multielectron state

$$|a\rangle \equiv |\{N\}\rangle = \prod_{\mathbf{k}\sigma_{\mathbf{k}}} |N_{L\mathbf{k}\sigma_{\mathbf{k}}}\rangle \prod_{\mathbf{q}\sigma_{\mathbf{q}}} |N_{R\mathbf{q}\sigma_{\mathbf{q}}}\rangle \prod_{\mu\sigma_\mu} |N_{\mu\sigma_\mu}\rangle$$

to a multielectron state

$$|b\rangle \equiv |\{N'\}\rangle = \prod_{\mathbf{k}\sigma_{\mathbf{k}}} |N'_{L\mathbf{k}\sigma_{\mathbf{k}}}\rangle \prod_{\mathbf{q}\sigma_{\mathbf{q}}} |N'_{R\mathbf{q}\sigma_{\mathbf{q}}}\rangle \prod_{\mu\sigma_\mu} |N'_{\mu\sigma_\mu}\rangle$$

of the LMR system. Provided that the LMR states are given as a product of single-electron states, the many-particle population $\mathcal{P}_a(t)$ can be also expressed as a product of single-particle populations. Noting this fact, summing up both parts of Eq. (5) with respect to the complete set of initial ($\{N\}$) and final ($\{N'\}$) occupation numbers, and using the definitions (3) and (4) along with the normalization condition

$$\sum_{N_{j\sigma_j}=0,1} P(N_{j\sigma_j},t) = 1, \tag{6}$$

we arrive at the following set of nonlinear kinetic equations for the single-electron populations:[21,26]

$$\dot{P}_{j\sigma_j}(t) = \sum_{\{N\}} \sum_{\{N'\}} \prod_{\mathbf{k}\sigma_{\mathbf{k}}} \prod_{\mathbf{q}\sigma_{\mathbf{q}}} \prod_{\mu\sigma_\mu} N_{j\sigma_j}[K_{\{N'\}\rightarrow\{N\}} P(N'_{L\mathbf{k}\sigma_{\mathbf{k}}},t)$$

$$\times P(N'_{R\mathbf{q}\sigma_{\mathbf{q}}},t) P(N'_{\mu\sigma_\mu},t) - K_{\{N\}\rightarrow\{N'\}}$$

$$\times P(N_{L\mathbf{k}\sigma_{\mathbf{k}}},t) P(N_{R\mathbf{q}\sigma_{\mathbf{q}}},t) P(N_{\mu\sigma_\mu},t)]. \tag{7}$$

These basic nonlinear kinetic equations (for the detailed derivation of this set of nonlinear kinetic equations see Refs. 21 and 26) are used in the following to derive an analytic expression for the current with the account of the Coulomb interaction between different transferred electrons.

The contribution of the Coulomb interaction to the overall energy of an LMR system strongly depends on the number of electrons captured by the molecule. Therefore, the character of the nonlinearity present in the kinetic equations (7) is also determined by the number of captured electrons. It is reflected in a specific behavior of the rate $K_{\{N\}\rightarrow\{N'\}}$ on the occupation numbers. It has been shown[26] that just these extra electrons are responsible for the formation of different transmission channels. One of them dominates the transmission within the voltage region $[0, V_{res}]$, where V_{res} is the voltage at which the resonant transmission through the lowest unoccupied or highest occupied molecular orbital (LUMO or HOMO) becomes possible. This channel corresponds to a pure single-electron transmission through the neutral molecule (without extra electrons). The probability for the electrons to be transmitted through a neutral molecule is proportional to the nonlinearity factor[16,20,26]

$$W_0(t) = \prod_{\mu\sigma_\mu} [1 - P_{\mu\sigma_\mu}(t)]. \tag{8}$$

This factor indicates that the efficiency of charge transfer through the neutral molecule decreases when the population $P_{\mu\sigma_\mu}(t)$ of any μth MO increases.

B. Kinetic equations for the transmission through an isolated molecular level

In what follows we consider the current formation caused by a combined transmission through the neutral and singly charged molecule. This circumvents the restriction $|V| \leq V_{res}$ and thus includes a region where the voltage bias $|V|$ exceeds V_{res}. Now, apart from expression (8) the additional nonlinearity factors determine the transmission process. To understand such a complex process in more detail let us restrict the transmission process through the LUMO level only (Fig. 1) by supposing that all other unoccupied levels are positioned far away from Fermi level. Consequently, at given voltages, these levels provide a less important contribution to the total current. Note, that the given description of charge transmission through a single MO is only important for an understanding of all those quantities responsible for the transmission.[6,7,23,24,32] In the present paper, we will show analytically in which way the Coulomb interaction and the kinetic processes control the formation of the current caused by a direct (elastic) lead-lead and an indirect (inelastic) electron transmission. To this end, we will use the following electron vibrational Hamiltonian of the LMR system

$$H_{LMR} = H_{LR} + H_M + H_{LR-M}. \tag{9}$$
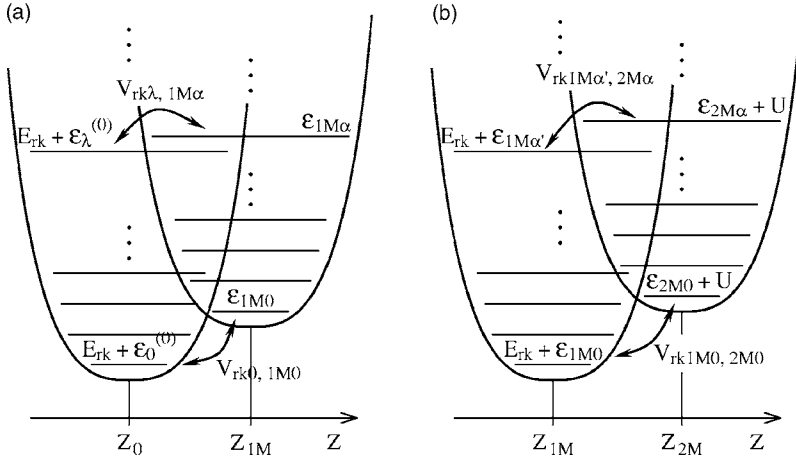
The first term on the right-hand side

$$H_{LR} = \sum_{r=L,R} \sum_{\mathbf{k},\sigma} E_{r\mathbf{k}} a^\dagger_{r\mathbf{k}\sigma} a_{r\mathbf{k}\sigma} \tag{10}$$

is the standard electronic Hamiltonian of the leads with $E_{r\mathbf{k}}$ being the energy of an electron in the conduction band of the rth electrode. In the absence of any magnetic interactions this energy is independent of the electron spin $\sigma = \pm 1/2$. Electron creation and electron annihilation operators are denoted by $a^\dagger_{r\mathbf{k}\sigma}$ and $a_{r\mathbf{k}\sigma}$, respectively. The second term in Eq. (9) refers to the molecular Hamiltonian. Its concrete form is determined by the number of molecular levels, as well as the number of extra electrons occupying these levels. In the present paper, we study the formation of the direct (tunnel) as well as the sequential (hopping) current component at the presence of the Coulomb interaction between the transferred electrons. To achieve a clear understanding of such a process, the transmission through a single isolated molecular level M is considered only. (In our case, the M is associated with the LUMO level.) In the occupation number space, the electronic eigenstates of the molecular Hamiltonian are written as $|N_{M\uparrow} N_{M\downarrow}\rangle$ where $N_{M\sigma}$ gives the number (1 or 0) of an extra electron occupying the MO M with spin σ. Introducing related electron creation ($a^\dagger_{M\sigma}$) and annihilation ($a_{M\sigma}$) operators we obtain for the molecular Hamiltonian

$$H_M = \sum_\lambda \varepsilon^{(0)}_\lambda |\chi_\lambda\rangle\langle\chi_\lambda| \otimes |0_{M\uparrow}\rangle\langle 0_{M\uparrow}| \otimes |0_{M\downarrow}\rangle\langle 0_{M\downarrow}|$$

$$+ \sum_{\sigma\alpha} \mathcal{E}_{1M\alpha} |\chi_{1M\alpha}\rangle\langle\chi_{1M\alpha}| \otimes |0_{M-\sigma}\rangle\langle 0_{M-\sigma}| \otimes a^\dagger_{M\sigma} a_{M\sigma}$$

$$+ \sum_\alpha (\mathcal{E}_{2M\alpha} + U)|\chi_{2M\alpha}\rangle\langle\chi_{2M\alpha}| \otimes a^\dagger_{M\uparrow} a_{M\uparrow} a^\dagger_{M\downarrow} a_{M\downarrow}. \tag{11}$$

This Hamiltonian is diagonal with respect to the occupation number states $|N_{M\uparrow} N_{M\downarrow}\rangle$. The eigenvalues define the energies of the molecular electron vibrational states. In the case of a neutral ("empty") molecule ($N_{M\uparrow}=0$, $N_{M\downarrow}=0$) the energies $\varepsilon^{(0)}_\lambda$ give the position of the vibrational levels of the molecular ground state (neutral state). (Note that $\lambda=0,1,2,\dots$.) If a single extra electron occupies the molecule ($N_{M\uparrow}=1$, $N_{M\downarrow}=0$ or $N_{M\uparrow}=0$, $N_{M\downarrow}=1$) the respective electron vibration energies are given by $\mathcal{E}_{1M\alpha}$ with α ($=0,1,2,\dots$) counting the vibrational levels. The energies for a doubly charged molecule ($N_{M\uparrow}=1$, $N_{M\downarrow}=1$) are denoted by $\mathcal{E}_{2M\alpha}+U$. Here, the Hubbard parameter U has been included to account for the Coulomb interaction among two extra electrons. The vibrational eigenstates of the neutral, as well as of the singly, and doubly charged molecule are denoted by $|\chi_\lambda\rangle$, $|\chi_{1M\alpha}\rangle$ and $|\chi_{2M\alpha}\rangle$, respectively. Figure 2 shows the mutual position of these vibrational levels which are originated by a single reaction coordinate Z.

Each eigenvalue related to a singly ($s=1$) and doubly ($s=2$) occupied molecule contains an imaginary part

FIG. 2. Relative position of potential energy surfaces referring to the neutral (empty) and singly charged molecule (a) as well as to the singly charged molecule and the molecule with two extra electrons (b). The nuclear displacement ζ relates to the reaction coordinate Z. $E_{r\mathbf{k}}$ denotes the electron energy at lead r, $\varepsilon_{sM\alpha} = \varepsilon_{sM\alpha}(0) + s\eta eV$ is the energetic position of the αth electron vibration level at nonzero voltage V for a singly ($s=1$) and doubly ($s=2$) charged molecule [$\varepsilon_{sM\alpha}(0)$ gives the position at zero voltage]. The quantities $V_{r\mathbf{k}\lambda,1M\alpha}$ and $V_{r\mathbf{k}1M\alpha',2M\alpha}$ characterize the coupling between LMR electron vibrational states.

$$\mathcal{E}_{sM\alpha} = \varepsilon_{sM\alpha} - i\Gamma_{sM\alpha}/2. \tag{12}$$

In the imaginary part,

$$\Gamma_{sM\alpha} = 2\gamma_{sM\alpha} + (\Gamma_{sM\alpha}^{(L)} + \Gamma_{sM\alpha}^{(R)})(\delta_{s,1} + 2\delta_{s,2}), \tag{13}$$

the contribution $\gamma_{sM\alpha}$ determines the broadening of a MO (with s captured electrons) caused by the interaction of the molecular electron vibrational states with the bath modes. The quantities $\Gamma_{sM\alpha}^{(L)}$ and $\Gamma_{sM\alpha}^{(R)}$ are given by the imaginary parts of those self-energies which result from the interaction of the molecule with the left (L) and the right (R) electrode.[4,24,36,37] In the case under consideration we set ($r = L, R$)

$$\Gamma_{1M\alpha}^{(r)} = \sum_{\lambda} \Gamma_{\lambda 1M\alpha}^{(r)}(\varepsilon_{1M\alpha} - \varepsilon_{\lambda}^{(0)}),$$

$$\Gamma_{\lambda 1M\alpha}^{(r)}(E) = 2\pi \sum_{\mathbf{k}} |V_{r\mathbf{k}\lambda,1M\alpha}|^2 \delta(E_{r\mathbf{k}} - E) \tag{14}$$

and

$$\Gamma_{2M\alpha}^{(r)} = \sum_{\alpha'} \Gamma_{1M\alpha'2M\alpha}^{(r)}(\varepsilon_{2M\alpha} + U - \varepsilon_{1M\alpha'}),$$

$$\Gamma_{1M\alpha'2M\alpha}^{(r)}(E) = 2\pi \sum_{\mathbf{k}} |V_{r\mathbf{k}1M\alpha',2M\alpha}|^2 \delta(E_{r\mathbf{k}} - E). \tag{15}$$

The quantity $V_{r\mathbf{k}\lambda,1M\alpha}$ is the matrix element characterizing single-electron transfer, with an electron preliminary occupying the αth vibrational sublevel of a given MO and having the energy $\varepsilon_{1M\alpha}$. It hops to the $\mathbf{k}$th band level of the rth electrode (with energy $E_{r\mathbf{k}}$). Within the transition the molecule in the neutral state moves into the λth vibrational sublevel with energy $\varepsilon_{\lambda}^{(0)}$. The other matrix element $V_{r\mathbf{k}1M\alpha',2M\alpha}$ describes single-electron transfer from the αth molecular electron vibrational level (with energy $\varepsilon_{2M\alpha}$) related to a doubly charged molecule (cf. Fig. 2). The transferred electron arrives at the $\mathbf{k}$th band level of the rth electrode while the molecule (with only a single extra electron) changes into the α'th electron-vibrational level with energy $\varepsilon_{1M\alpha'}$. The related transfer operator reads

$$V_{LR\text{-}M} = \sum_{r=L,R} \sum_{\mathbf{k}\sigma} \left(\sum_{\lambda\alpha} V_{r\mathbf{k}\lambda,1M\alpha} a_{r\mathbf{k}\sigma}^{\dagger} a_{M\sigma} \otimes |0_{M-\sigma}\rangle\langle 0_{M-\sigma}| \right.$$
$$\otimes |\chi_{\lambda}\rangle\langle\chi_{1M\alpha}| + \sum_{\alpha\alpha'} V_{r\mathbf{k}1M\alpha',2M\alpha} a_{r\mathbf{k}\sigma}^{\dagger} a_{M\sigma}$$
$$\left. \otimes |1_{M-\sigma}\rangle\langle 1_{M-\sigma}| \otimes |\chi_{1M\alpha'}\rangle\langle\chi_{2M\alpha}| + \text{H.c.} \right). \tag{16}$$

It is responsible for single-electron transitions between the molecule and the leads and covers all charged states of the molecule described so far.

We are now in a position to specify the kinetic equations describing electron transfer in the LMR system with a single MO. Since both electrodes are considered as macroscopic systems and in the absence of a magnetic field as well as for nonmagnetic electrodes it becomes possible to set (see also Ref. 21) $P_{r\mathbf{k}\uparrow}(t) = P_{r\mathbf{k}\downarrow}(t) \simeq f_r(E_{r\mathbf{k}} - eV_r)$ on the right-hand side of set (7). Here,

$$f_r(\epsilon) = \{\exp[(\epsilon - E_{rF})/k_B T] + 1\}^{-1} \tag{17}$$

is the Fermi distribution of the rth electrode (E_{rF} denotes the respective Fermi level). Below, to be specific, we suppose that the left lead stays at zero voltage; thus $V_L = 0$, $V_R = V$. Furthermore, we put $E_{LF} = E_{RF} = E_F$.

The analysis of the charge transmission is based on the solution of a closed set of kinetic equations for the single-electron distribution functions $P_{L\mathbf{k}\sigma_{\mathbf{k}}}(t)$, $P_{R\mathbf{q}\sigma_{\mathbf{q}}}(t)$, and $P_{M\sigma_M}(t)$. These kinetic equations follow from a general set of nonlinear kinetic equations (7) after specifying the form of each transfer rate $K_{\{N\}\to\{N'\}}$. This can be done by using the general expression for the $K_{\{N\}\to\{N'\}}$ [see Eq. (36) of Ref. 26], as well as upon use of Eqs. (10), (11), and (16). It yields

$$\dot{P}_{L\mathbf{k}\uparrow}(t) = -[K_{L\mathbf{k}\to M}W_0(t) - K_{M\to L\mathbf{k}}W_{M0}(t)]$$
$$- [K_{L\mathbf{k}\to M}(U)W_{0M}(t) - K_{M\to L\mathbf{k}}(U)W_{MM}(t)]$$
$$- \sum_{\mathbf{q}} \{(K_{L\mathbf{k}\to R\mathbf{q}} - K_{R\mathbf{q}\to L\mathbf{k}})W_0(t) + [K_{L\mathbf{k}\to R\mathbf{q}}(U)$$
$$- K_{R\mathbf{q}\to L\mathbf{k}}(U)][W_{0M}(t) + W_{M0}(t)]\} \tag{18}$$

and

$$\dot{P}_{M\uparrow}(t) = - \sum_{r=L,R} \sum_{\mathbf{k}} \{[K_{M\to r\mathbf{k}}W_{M0}(t) - K_{r\mathbf{k}\to M}W_0(t)]$$
$$+ [K_{M\to r\mathbf{k}}(U)W_{MM}(t) - K_{r\mathbf{k}\to M}(U)W_{0M}(t)]\}. \tag{19}$$

The nonlinear equations governing the remaining populations $P_{L\mathbf{k}\downarrow}(t)$, $P_{R\mathbf{q}\uparrow}(t)$, $P_{R\mathbf{q}\downarrow}(t)$, and $P_{M\downarrow}(t)$ have a similar form. They directly follow from the respective nonlinear equations (18) and (19) by introducing some simple changes in the notation. The partial rate constants in Eqs. (18) and (19) assume a form which is similar to those derived in Ref. 26 [cf. Eqs. (A24) and (A29)]. Therefore, we quote the final expressions for the transfer rates only [see Eqs. (23)–(26), (29), and (30)]. The nonlinearity of the kinetic equations (18) and (19) is caused by the following four nonlinearity factors:

$$W_0(t) = [1 - P_{M\uparrow}(t)][1 - P_{M\downarrow}(t)],$$

$$W_{M0}(t) = P_{M\uparrow}(t)[1 - P_{M\downarrow}(t)],$$

$$W_{0M}(t) = [1 - P_{M\uparrow}(t)]P_{M\downarrow}(t), \quad W_{MM}(t) = P_{M\uparrow}(t)P_{M\downarrow}(t). \tag{20}$$

Each factor defines the probability to find the MO in a specific charging state. The first factor is identical to that is given by Eq. (8).

The kinetic equations (18) and (19) can be simplified somewhat by using the fact that in the absence of a magnetic field the relation $P_{M\uparrow}(t) = P_{M\downarrow}(t) \equiv P(t)$ is valid. Thus, using Eqs. (2), (18), and (20) one arrives at

$$\dot{N}_L(t) = - 2\{\chi_L[1 - P(t)]^2 - \chi_{-L}P(t)[1 - P(t)]\}$$
$$- 2\{\chi_L(U)P(t)[1 - P(t)] - \chi_{-L}(U)P^2(t)\}$$
$$- 2\{Q_{LR}[1 - P(t)]^2 + 2Q_{LR}(U)P(t)[1 - P(t)]\}. \tag{21}$$

It follows from relation (1) and Eq. (21) that the current is not only defined by respective transfer rates but as well by the level populations $[1 - P(t)]^2$, $P(t)[1 - P(t)]$, and $P^2(t)$. The kinetic equation for a single-electron distribution $P(t)$ follows from Eq. (19), and reads

$$\dot{P}(t) = - \{(\chi_{-L} + \chi_{-R})P(t)[1 - P(t)] - (\chi_L + \chi_R)[1 - P(t)]^2\}$$
$$- \{[\chi_{-L}(U) + \chi_{-R}(U)]P^2(t)$$
$$- [\chi_L(U) + \chi_R(U)]P(t)[1 - P(t)]\}. \tag{22}$$

In Eqs. (21) and (22) the integral transfer rates

$$\chi_L = \frac{2\pi}{\hbar} \sum_{\alpha\lambda\mathbf{k}} |V_{L\mathbf{k}\lambda,1M\alpha}|^2 f_L(E_{L\mathbf{k}})W(\varepsilon_\lambda^{(0)})L(E_{L\mathbf{k}} + \varepsilon_\lambda^{(0)} - \varepsilon_{1M\alpha}),$$

$$\chi_L(U) = \frac{2\pi}{\hbar} \sum_{\alpha\alpha'\mathbf{k}} |V_{L\mathbf{k}1M\alpha,2M\alpha'}|^2 f_L(E_{L\mathbf{k}})W(\varepsilon_{1M\alpha})$$
$$\times L(E_{L\mathbf{k}} + \varepsilon_{1M\alpha} - \varepsilon_{2M\alpha'} - U) \tag{23}$$

and

$$\chi_R = \frac{2\pi}{\hbar} \sum_{\alpha\lambda\mathbf{q}} |V_{R\mathbf{q}\lambda,1M\alpha}|^2 f_R(E_{R\mathbf{q}} - eV)W(\varepsilon_\lambda^{(0)})$$
$$\times L(E_{R\mathbf{q}} + \varepsilon_\lambda^{(0)} - \varepsilon_{1M\alpha}),$$

$$\chi_R(U) = \frac{2\pi}{\hbar} \sum_{\alpha\alpha'\mathbf{q}} |V_{R\mathbf{q}1M\alpha,2M\alpha'}|^2 f_R(E_{R\mathbf{q}} - eV)W(\varepsilon_{1M\alpha})$$
$$\times L(E_{R\mathbf{q}} + \varepsilon_{1M\alpha} - \varepsilon_{2M\alpha'} - U) \tag{24}$$

describe transitions of an electron from the singly occupied molecular level to the leads (rates χ_L and χ_R), or from the doubly occupied molecular level [rates $\chi_L(U)$ and $\chi_R(U)$]. The integral transfer rates

$$\chi_{-L} = \frac{2\pi}{\hbar} \sum_{\alpha\lambda\mathbf{k}} |V_{L\mathbf{k}\lambda,1M\alpha}|^2 [1 - f_L(E_{L\mathbf{k}})]W(\varepsilon_{1M\alpha})$$
$$\times L(E_{L\mathbf{k}} + \varepsilon_\lambda^{(0)} - \varepsilon_{1M\alpha}),$$

$$\chi_{-L}(U) = \frac{2\pi}{\hbar} \sum_{\alpha\alpha'\mathbf{k}} |V_{L\mathbf{k}1M\alpha,2M\alpha'}|^2 [1 - f_L(E_{L\mathbf{k}})]W(\varepsilon_{2M\alpha'})$$
$$\times L(E_{L\mathbf{k}} + \varepsilon_{1M\alpha} - \varepsilon_{2M\alpha'} - U) \tag{25}$$

and

$$\chi_{-R} = \frac{2\pi}{\hbar} \sum_{\alpha\lambda\mathbf{q}} |V_{R\mathbf{q}\lambda,1M\alpha}|^2 [1 - f_R(E_{L\mathbf{k}} - eV)]W(\varepsilon_{1M\alpha})$$
$$\times L(E_{R\mathbf{q}} + \varepsilon_\lambda^{(0)} - \varepsilon_{1M\alpha}),$$

$$\chi_{-R}(U) = \frac{2\pi}{\hbar} \sum_{\alpha\alpha'\mathbf{q}} |V_{R\mathbf{q}1M\alpha,2M\alpha'}|^2 [1 - f_R(E_{R\mathbf{q}})]W(\varepsilon_{2M\alpha'})$$
$$\times L(E_{R\mathbf{q}} + \varepsilon_{1M\alpha} - \varepsilon_{2M\alpha'} - U) \tag{26}$$

characterize the reverse processes, where a single electron moves from the corresponding lead into the empty (rates χ_{-L} and χ_{-R}), or singly occupied [rates $\chi_{-L}(U)$ and $\chi_{-R}(U)$] MO, respectively. In the expressions (23)–(26), the Lorentzians $L(E_a - E_b) = (2/\pi)\{(\Gamma_a + \Gamma_b)/[(E_a - E_b)^2 + (\Gamma_a + \Gamma_b)^2/4]\}$ include the broadenings Γ_a and Γ_b of the involved molecular electron vibrational levels. These broadenings are defined by Eq. (13). The distribution function

$$W(\varepsilon_\lambda^{(0)}) = Z_0^{-1} e^{-(\varepsilon_\lambda^{(0)} - \varepsilon_0^{(0)})/k_B T}, \quad Z_0 = \sum_\alpha e^{-(\varepsilon_\lambda^{(0)} - \varepsilon_0^{(0)})/k_B T}, \tag{27}$$

specifies the probability to find an neutral (empty) molecule in the λth vibrational state. Similar distribution functions

$$W(\varepsilon_{sM\alpha}) = Z_s^{-1} e^{-(\varepsilon_{sM\alpha} - \varepsilon_{sM0})/k_B T}, \quad Z_s = \sum_\alpha e^{-(\varepsilon_{sM\alpha} - \varepsilon_{sM0})/k_B T} \tag{28}$$

describe the state with a single extra electron ($s=1$) or with two extra electrons ($s=2$) occupying the MO. Note that the quantities $\varepsilon_\lambda^{(0)}$ and ε_{sM0} denote the lowest vibrational levels of corresponding molecular level.

In Eq. (21), the quantity $Q_{LR}=K_{L\to R}-K_{R\to L}$ is the net charge flow from the left lead to the right lead if the molecule does not contain an extra electron. Similarly, the flow through a singly charge molecule is $Q_{LR}(U)=K_{L\to R}(U)-K_{R\to L}(U)$. The charge flows are given by the respective lead-lead integral transfer rates $K_{L(R)\to R(L)}$ and $K_{L(R)\to R(L)}(U)$. If an electron moves from the left to the right lead, the noted rates are given by the expressions

$$K_{L\to R} = \frac{2\pi}{\hbar} \sum_{\lambda\lambda'} \sum_{\mathbf{kq}} \left| \sum_{\alpha} \frac{V^*_{L\mathbf{k}\lambda,1M\alpha} V_{R\mathbf{q}\lambda',1M\alpha}}{E_{L\mathbf{k}} + \varepsilon_\lambda^{(0)} - \mathcal{E}_{1M\alpha}} \right|^2$$
$$\times f_L(E_{L\mathbf{k}})[1 - f_R(E_{R\mathbf{q}} - eV)]W(\varepsilon_\lambda^{(0)})$$
$$\times L(E_{L\mathbf{k}} + \varepsilon_\lambda^{(0)} - E_{R\mathbf{q}} - \varepsilon_{\lambda'}^{(0)}) \qquad (29)$$

and

$$K_{L\to R}(U) = \frac{2\pi}{\hbar} \sum_{\alpha\alpha'\beta} \sum_{\mathbf{kq}} \left| \sum_{\alpha'} \frac{V^*_{L\mathbf{k}1M\alpha,2M\alpha'} V_{R\mathbf{q}1M\beta,2M\alpha'}}{E_{L\mathbf{k}} + \varepsilon_{1M\alpha} - \mathcal{E}_{2M\alpha'} - U} \right|^2$$
$$\times f_L(E_{L\mathbf{k}})[1 - f_R(E_{R\mathbf{q}} - eV)]W(\varepsilon_{1M\alpha})$$
$$\times L(E_{L\mathbf{k}} + \varepsilon_{1M\alpha} - E_{R\mathbf{q}} - \varepsilon_{1M\beta}). \qquad (30)$$

Similar expressions are valid for the integral transfer rates $K_{R\to L}$ and $K_{R\to L}(U)$ which characterize the motion of an electron from the right lead to the left lead. Note that both rates $K_{L(R)\to R(L)}$ and $K_{L(R)\to R(L)}(U)$ describe a coherent lead-lead electron transmission process. In the expressions (29) and (30) the quantities $\mathcal{E}_{1M\alpha}$ and $\mathcal{E}_{2M\alpha}$ are the molecular electron vibrational energies corresponding the case where either a single extra electron or two extra electrons occupy the same MO. These energies contain imaginary parts ($\Gamma_{1M\alpha}/2$ or $\Gamma_{2M\alpha}/2$) caused by the interaction with the bath and the leads [cf. Eq. (13)].

Setting $\dot{P}(t)=0$ and denoting by P the stationary occupancy of a molecular level by a single extra electron with a definite spin projection one obtains the solution of Eq. (22) as

$$P = \frac{S}{1+S},$$

$$S = \frac{1}{2A(U)}\{\sqrt{[A - B(U)]^2 + 4BA(U)} - [A - B(U)]\},$$
$$(31)$$

where we have introduced the set of abbreviations

$$A = \hbar(\chi_{-L} + \chi_{-R}), \quad B = \hbar(\chi_L + \chi_R),$$

$$A(U) = \hbar[\chi_{-L}(U) + \chi_{-R}(U)], \quad B(U) = \hbar[\chi_L(U) + \chi_R(U)].$$
$$(32)$$

III. CURRENT THROUGH DIRECT AND SEQUENTIAL TRANSMISSION PATHWAYS

Based on Eqs. (1), (21), and (31) we will analyze hereafter the stationary current-voltage (I-V) characteristics of a single molecule. Note, that the integral transfer rates characterizing the electron transmission in a LMR system include different vibrational-assisted transition pathways. This allows one to study vibrational-assisted transmission in the presence of Coulomb interactions between the transferred electrons. Recent studies on vibrational-assisted single-electron transmission (done for such conditions where the Coulomb corrections are less important) highlighted the particular nature of the vibronic states involved in the transfer process.[12,13,23,24] In the present paper, however, we will exclusively concentrate on the influence of Coulomb interactions on the kinetics of current formation. In order to do this, a somewhat simplified description is carried out by replacing the Lorentzians in the transfer rates (23)–(26), (29), and (30) by corresponding δ functions. This translates, for example, the rates (23) into

$$\chi_L = \frac{1}{\hbar} \sum_{\lambda\alpha} W(\varepsilon_\lambda^{(0)}) f_L(E) \Gamma^{(L)}_{\lambda 1M\alpha}(E) \quad (E = \varepsilon_{1M\alpha} - \varepsilon_\lambda^{(0)}),$$

$$\chi_L(U) = \frac{1}{\hbar} \sum_{\alpha\alpha'} W(\varepsilon_{1M\alpha'}) f_L(E) \Gamma^{(L)}_{1M\alpha'2M\alpha}(E)$$
$$(E = \varepsilon_{2M\alpha} + U - \varepsilon_{1M\alpha'}). \qquad (33)$$

A further simplification can be introduced by applying the Condon approximation resulting in $V_{r\mathbf{k}\lambda,1M\alpha}=V_{r\mathbf{k}}\langle\chi_\lambda|\chi_{1\alpha}\rangle$ and $V_{r\mathbf{k}1M\alpha',2M\alpha}=V_{1r\mathbf{k}}\langle\chi_{1\alpha'}|\chi_{2\alpha}\rangle$. $V_{r\mathbf{k}}$ and $V_{1r\mathbf{k}}$ are the couplings between the lowest electron vibrational molecular levels and the $\mathbf{k}$th band level of the rth electrode when the molecule is singly or doubly occupied by the extra electrons (cf. Fig. 1). Using the definition of the broadenings given in Eqs. (14) and (15) one obtains $\Gamma^{(L)}_{1M\alpha}(E)=\Sigma_\lambda \Gamma_L(E)\langle\chi_\lambda|\chi_{1\alpha}\rangle^2$ where $\Gamma_L(E)=2\pi\Sigma_\mathbf{k}|V_{r\mathbf{k}}|^2\delta(E_{L\mathbf{k}}-E)$ $(E=\varepsilon_{1M\alpha}-\varepsilon_\lambda^{(0)})$ is the standard form for the broadening caused by the interaction with a macroscopic electrode. It is a well established fact that for a wide conduction band $\Gamma_L(E)$ [as well as the $\Gamma_R(E)$] are independent of E.[3,6,10,38] Thus, setting $\Gamma_L(\varepsilon_{1M\alpha}-\varepsilon_\lambda^{(0)})\approx\Gamma_L$ and taking into account the property $\Sigma_\lambda\langle\chi_\lambda|\chi_\alpha\rangle^2=1$ one realizes that in the wideband approximation, $\Gamma^{(L)}_{\lambda 1M\alpha}(E)\approx\Gamma_L$, becomes independent of the vibrational molecular states. Accordingly, we obtain

$$\chi_L \approx (1/\hbar)\Gamma_L\mathcal{F}_L^{(ine)},$$

$$\mathcal{F}_L^{(ine)} \equiv \sum_{\lambda\alpha} W(\varepsilon_\lambda^{(0)})\langle\chi_\lambda|\chi_{1\alpha}\rangle^2 f_L(\varepsilon_{1M\alpha} - \varepsilon_\lambda^{(0)}). \qquad (34)$$

In a similar way one derives

$$\chi_L(U) \approx (1/\hbar)\Gamma_L(U)\mathcal{F}_L^{(ine)}(U),$$

$$\mathcal{F}_L^{(ine)}(U) \equiv \sum_{\alpha\alpha'} W(\varepsilon_{1\alpha})\langle\chi_{1\alpha}|\chi_{2\alpha'}\rangle^2 f_L(\varepsilon_{2M\alpha'} + U - \varepsilon_{1M\alpha}).$$
$$(35)$$

The rates χ_R and $\chi_R(U)$ are again given by Eqs. (34) and (35) but with the replacement Γ_L, $\Gamma_L(U)$, and $f_L(E)$ by Γ_R, $\Gamma_R(U)$, and $f_R(E-eV)$, respectively. The expressions $\mathcal{F}_L^{(ine)}$, $\mathcal{F}_R^{(ine)}$,
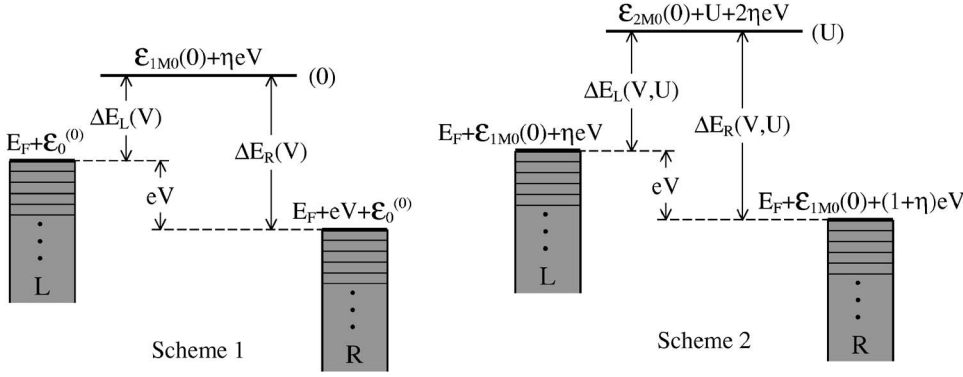
FIG. 3. Energy gaps in the LMR system for the singly charged molecule (scheme 1) and the molecule with two extra electrons (scheme 2). [In the framework of the Hubbard model one may set $\varepsilon_{2M0}(0)=2\varepsilon_{1M0}(0)$.]

$\mathcal{F}_L^{(ine)}(U)$, and $\mathcal{F}_R^{(ine)}(U)$ include the temperature and cause the voltage dependence of the respective transfer rates. They also control the vibrational-assisted inelastic component of the current. The backward hopping transfer rates are expressed through respective direct transfer rates as ($s=L,R$)

$$\chi_{-s} = e^{\Delta E_s(V)/k_B T}\chi_s, \quad \chi_{-s}(U) = e^{\Delta E_s(V,U)/k_B T}\chi_s(U). \quad (36)$$

The $\Delta E_L(V)=\Delta E_1^{(0)}+\eta eV$, $\Delta E_R(V)=\Delta E_1^{(0)}-(1-\eta)eV$, and $\Delta E_L(V,U)=\Delta E_2^{(0)}+U+\eta eV$, $\Delta E_R(V,U)=\Delta E_2^{(0)}+U-(1-\eta)eV$ are the gaps between the LMR electronic energy levels and respective Fermi levels. These LMR levels differ from one other by the number of electrons occupying the MO. η denotes the voltage division factor (see below). The quantities $\Delta E_1^{(0)}=\varepsilon_{1M0}(0)-\varepsilon_0^{(0)}-E_F$ and $\Delta E_2^{(0)}+U=\varepsilon_{2M0}(0)-\varepsilon_{1M0}(0)+U-E_F$ denote the zero-voltage gaps. In the framework of a Hubbard model one has to set $\varepsilon_{2M0}(0)=2\varepsilon_{1M0}(0)$. It means that the energy difference $\varepsilon_{1M0}(0)-\varepsilon_0^{(0)}$ coincides with $\varepsilon_{2M0}(0)-\varepsilon_{1M0}(0)$ and thus $\Delta E_1^{(0)}=\Delta E_2^{(0)}\equiv\Delta E(0)$. Therefore, the noted gaps can be represented in the form (cf. Fig. 3)

$$\Delta E_L(V) = \Delta E_L(V,U=0), \quad \Delta E_L(V,U) = \Delta E(0) + U + \eta eV,$$

$$\Delta E_R(V) = \Delta E_R(V,U=0),$$

$$\Delta E_R(V,U) = \Delta E(0) + U - (1-\eta)eV. \quad (37)$$

The energy gaps depend on the voltage division factor $\eta^{3,6,38}$ which controls (through the applied voltage V) the shift of delocalized molecular levels.

Now, using the above given expressions for the transfer rates as well as Eqs. (1), (2), and (21) we arrive at the following formula for the stationary current:

$$I = I_{ine} + I_{dir}. \quad (38)$$

The inelastic current component reads

$$I_{ine} = I_0 2\pi\{\Gamma_L\mathcal{F}_L^{(ine)}[(1-P)^2 - e^{\Delta E_L(V)/k_B T}P(1-P)]$$
$$+ \Gamma_L(U)\mathcal{F}_L^{(ine)}(U)[P(1-P) - e^{\Delta E_L(V,U)/k_B T}P^2]\}, \quad (39)$$

and the current component associated with a direct electron tunneling between the electrodes takes the form (note the introduction of elementary current unit $I_0 \equiv 2|e|/h \approx 80~\mu A$):

$$I_{dir} = 2I_0\left(\frac{\Gamma_L\Gamma_R}{\Gamma_L+\Gamma_R}\mathcal{F}(1-P)^2\right.$$
$$\left. + 2\frac{\Gamma_L(U)\Gamma_R(U)}{\Gamma_L(U)+\Gamma_R(U)}\mathcal{F}(U)P(1-P)\right). \quad (40)$$

The prefactors

$$\mathcal{F} = \sum_{\lambda\alpha} W(\varepsilon_\lambda^{(0)})\langle\chi_\lambda|\chi_{1\alpha}\rangle^4$$
$$\times\left[\arctan\left(\frac{2\Delta\epsilon_{R\lambda\alpha}}{\Gamma_L+\Gamma_R}\right) - \arctan\left(\frac{2\Delta\epsilon_{L\lambda\alpha}}{\Gamma_L+\Gamma_R}\right)\right] \quad (41)$$

and

$$\mathcal{F}(U) = \sum_{\alpha\alpha'} W(\varepsilon_{1M\alpha})\langle\chi_{1\alpha}|\chi_{2\alpha'}\rangle^4$$
$$\times\left[\arctan\left(\frac{2\Delta\epsilon_{R\alpha\alpha'}(U)}{\Gamma_L+\Gamma_R}\right) - \arctan\left(\frac{2\Delta\epsilon_{L\alpha\alpha'}}{\Gamma_L+\Gamma_R}\right)\right] \quad (42)$$

include the temperature and voltage dependence of the respective direct current components. The quantities

$$\Delta\epsilon_{r\lambda\alpha} = \Delta E_r(V) + (\varepsilon_{1M\alpha}-\varepsilon_{1M0}) - (\varepsilon_\lambda^{(0)}-\varepsilon_0^{(0)}),$$

$$\Delta\epsilon_{r\alpha\alpha'}(U) = \Delta E_r(V,U) + (\varepsilon_{2M\alpha'}-\varepsilon_{2M0}) - (\varepsilon_{1M\alpha}-\varepsilon_{1M0}) \quad (43)$$

are the energy gaps between the electron vibrational molecular energies and the Fermi level of the rth electrode [cf. Eq. (37) for electronic energy gaps].

IV. RESULTS AND DISCUSSION

Equations (38)–(40) together with Eq. (31) enables us to analyze the electron transfer through a molecule for such a case that the charge transmission takes place through a single isolated level. This transmission is controlled by the Coulomb interaction between the extra electrons occupying the same MO as well as by kinetic processes. Those are not only responsible for a delivery of electrons from one lead to another but also for the population of the molecule by the transferred electrons. The prefactors $\mathcal{F}_{L(R)}^{(ine)}$ and $\mathcal{F}_{L(R)}^{(ine)}(U)$ [cf. Eqs. (34) and (35)], as well as $\mathcal{F}$ and $\mathcal{F}(U)$ [cf. Eqs. (41) and
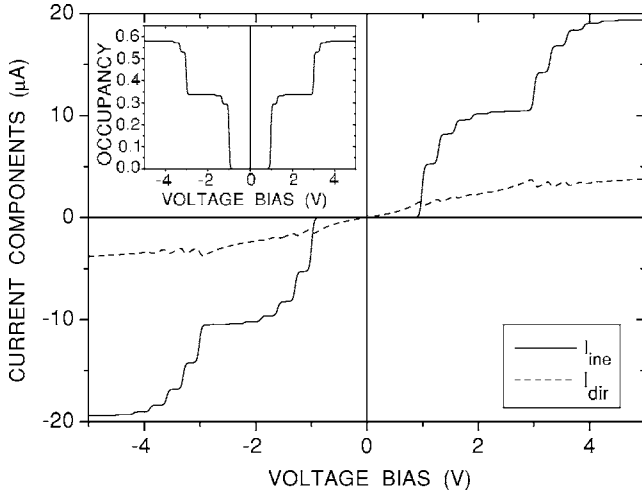
FIG. 4. Electron vibrational fine structure of the symmetric *I-V* characteristics related to the inclusion of a single molecular orbital. Each current component is controlled by the level populations. The small steps (for the inelastic component, solid line) and the small peaks (for the direct component, dashed line) fix the position of the resonances related to the electron vibrational levels. [The calculations are based on Eqs. (39), (40), and (31) with $k_B T = 0.01$ eV, $\hbar\omega_0 = 0.15$ eV, $\eta = 0.5$, $\zeta = 1.8$, $\Delta E(0) = 0.5$ eV, $U = 1$ eV, $\Gamma_L(0) = \Gamma_R(0) = 0.15$ eV, $\Gamma_L(U) = \Gamma_R(U) = 0.25$ eV.]

(42)], show that a vibrational fine structure of the *I-V* characteristics should become observable at appreciable displacements among the different nuclear equilibrium configurations in the molecule (or/and at sufficiently large change of the vibrational frequencies). If such a displacement exists between the empty as well as the singly and doubly charged molecules (cf. Fig. 2), then the overlap integrals $\langle \chi_\lambda | \chi_{1\alpha} \rangle$ and $\langle \chi_{1\alpha} | \chi_{2\alpha'} \rangle$ between the different vibrational wave functions do not vanish even at $\lambda \neq \alpha$ and $\alpha \neq \alpha'$.

A. Case with symmetric contacts

Figure 4 displays the behavior of both current components for the case of symmetric contacts of the molecule, using $\eta = 1/2$, $\Gamma_L = \Gamma_R$, $\Gamma_L(U) = \Gamma_R(U)$, as well as for a relatively large nuclear displacement ζ. The quantity ζ determines the overlap integrals $\langle \chi_\lambda | \chi_{1\alpha} \rangle$ and $\langle \chi_{1\alpha} | \chi_{2\alpha'} \rangle$. For instance, $\langle \chi_0 | \chi_{1\alpha} \rangle^2 \approx \langle \chi_{10} | \chi_{2\alpha} \rangle^2 = (\zeta^2/2)^\alpha (1/\alpha!) \exp(-\zeta^2/2)$. For the sake of simplicity the displacement ζ as well as the frequency ω_0 of the single reaction coordinate are assumed to be independent of the electronic state of the molecule, as in the Holstein model.[39] The *I-V* characteristics are strongly nonlinear and contain steps, induced by the inelastic component, and peaks, stemming from the direct component. The steps and peaks appear at identical resonance voltages defined by the conditions $\Delta\epsilon_{r\lambda\alpha} = 0$ and $\Delta\epsilon_{r\alpha\alpha'}(U) = 0$. The resonance voltages completely coincide with those for a single-electron level occupancy [cf. the inset in Fig. 4]. This fact clearly demonstrates that the population of the molecule by the transferred electrons represents an important factor which controls the sequential and the direct transmission process. The first step and the first peak corresponds to the activation

of the phononless resonance transmission at $V = V_{Lr}(0)$ and $|V| = V_{Rr}(0)$, where

$$V_{\mathrm{L}r}(0) = \Delta E(0)/\eta |e|, \quad V_{Rr}(0) = \Delta E(0)/(1-\eta)|e|. \quad (44)$$

At a symmetric position of the molecule with respect to the leads the voltage division factor η equals 0.5 and thus choosing $\Delta E(0) = 0.5$ eV one obtains $V_{Lr}(0) = V_{Rr}(0) = 1$ V. The following steps and peaks correspond to the vibrational satellites. The transmission processes appearing at the resonance voltage (44) occur along the first transmission channel. Such a channel is formed if the molecule does not contain an extra electron and thus each transferring electron moves through the empty (i.e., neutral) molecule. If the voltage reaches $V = V_{Lr}(U)$ or $|V| = V_{Rr}(U)$ where

$$V_{\mathrm{L}r}(U) = [\Delta E(0) + U]/\eta |e|,$$

$$V_{Rr}(U) = [\Delta E(0) + U]/(1-\eta)|e|, \quad (45)$$

a new phononless resonant transmission process starts. It proceeds along the second transmission channel. This channel is formed when the molecule is reduced by a single extra electron. This electron is captured by the molecule in the course of electron transmission and, thus, each transferred electron interacts via Coulomb forces with the electron already captured. In the regions $V \gtrsim V_{Lr}(U) = 3$ V and $|V| > V_{Rr}(U) = 3$ V the steps and peaks are originated by the second transmission channel.[40]

The number of vibrational satellites, which define the fine structure of the current components through the steps and peaks, is determined by two parameters. The first parameter is the frequency of reaction coordinate ω_0 and the second one is the nuclear displacement ζ. In our case, the frequency is a rather large so that $\exp(-\hbar\omega_0/k_B T) \ll 1$. Therefore, even at room temperature, the factors (34), (35), (41), and (42) become temperature-independent quantities. It means that only the $T = 0$ (cold) vibrational satellite are represented in Fig. 4. Moreover, the parameter ζ controls the contribution of each current component to the total current (through the overlap integrals $\langle \chi_\lambda | \chi_{1\alpha} \rangle$ and $\langle \chi_{1\alpha} | \chi_{2\alpha'} \rangle$). Since the factors (34), (35), (41), and (42) include the overlap integrals in the second and fourth powers, respectively, the inelastic component exceeds the direct one. Therefore, at the given value $\zeta = 1.8$ the steps are more pronounced than the peaks. The direct current component exceeds the inelastic one only in the pre-resonant regions $V < V_{Lr}(0)$ and $|V| < V_{Rr}(0)$ since the latter is exclusively originated by thermal activation processes.

The influence of the parameter ζ on the current is depicted in Fig. 5, indicating an increase of the current with a decrease of the nuclear displacement. Moreover, the *I-V* characteristics attains less pronounced structures. At small nuclear displacements (cf. Fig. 6) the overlap integrals reduce to Kronecker symbols, $\langle \chi_\lambda | \chi_{1\alpha} \rangle \approx \delta_{\lambda,\alpha}$ and $\langle \chi_{1\alpha} | \chi_{2\alpha'} \rangle \approx \delta_{\alpha,\alpha'}$ what lets the vibrationless transmission dominate. Note, however, that basic structure in the *I-V* characteristics (the resonant switching among two transmission channels at 1 and 3 V) survives. Moreover, the resonant voltages (44) and (45) are fixed in a much more clear way for the case of vibrationless transmission. Below we will use this fact to
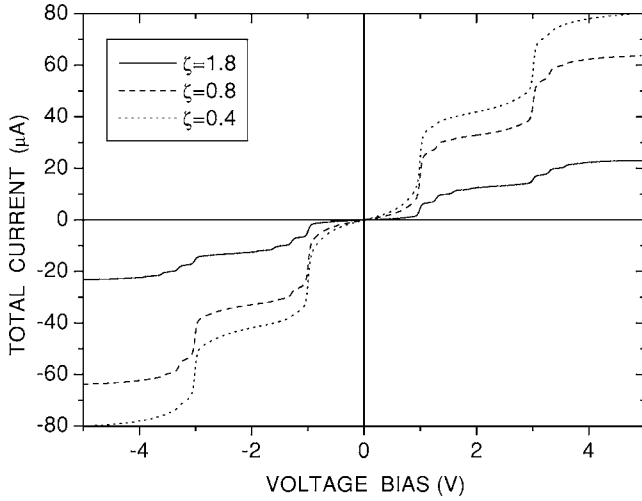
FIG. 5. Symmetric *I-V* characteristics related to the inclusion of a single molecular orbital. For a small nuclear displacement the electron vibrational fine structure of the total current vanishes and the current peculiarities (stepwise behavior) caused by the Coulomb interaction between the captured electrons are clearly displayed. [Calculations according to Eqs. (31) and (38)–(40). The parameters are the same as those of Fig. 4 except for the displacement ζ.]

demonstrate the importance of kinetic processes and the Coulomb interaction in the current formation.

Let us next consider such a somewhat approximate description in more detail. To this end, we set $\langle\chi_\lambda|\chi_{1\alpha}\rangle \approx \delta_{\lambda,\alpha}$ and $\langle\chi_{1\alpha}|\chi_{2\alpha'}\rangle \approx \delta_{\alpha,\alpha'}$, and use the Holstein model for the description of vibrational states. In the framework of this model the relations $\varepsilon_{1M\alpha}-\varepsilon_\alpha^{(0)}=\varepsilon_{1M0}-\varepsilon_0^{(0)}$ are valid for any vibrational state α. Therefore, the expressions (41) and (42) emerge as
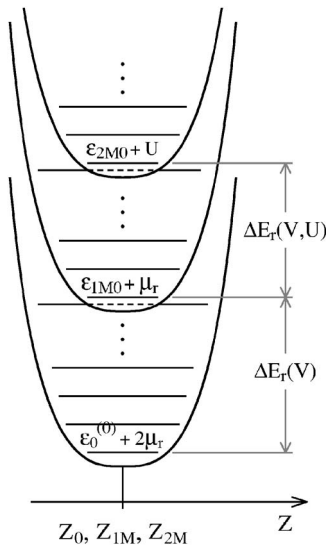

FIG. 6. Relative position of the potential energy surfaces for a small mutual displacement of nuclear equilibrium configuration. The peculiar case is considered where the extra electron comes from the Fermi level of the *r*th electrode so that $E_{r\mathbf{k}}=\mu_r$. The gaps between the lowest LMR energy levels are given by Eqs. (37) at $\mu_L=E_F$ and $\mu_R=E_F+eV$.

$$\mathcal{F}=\arctan\left(\frac{2\Delta E_R(V)}{\Gamma_L+\Gamma_R}\right)-\arctan\left(\frac{2\Delta E_L(V)}{\Gamma_L+\Gamma_R}\right),$$

$$\mathcal{F}(U)=\arctan\left(\frac{2\Delta E_R(V,U)}{\Gamma_L(U)+\Gamma_R(U)}\right)-\arctan\left(\frac{2\Delta E_L(V,U)}{\Gamma_L(U)+\Gamma_R(U)}\right).$$
(46)

Now, the direct interelectrode current is given by Eqs. (40) and (46). The factors $\mathcal{F}_{L(R)}^{(ine)}$ and $\mathcal{F}_{L(R)}^{(ine)}(U)$ are also simplified, leading to

$$\chi_r=\frac{1}{\hbar}\Gamma_r n(\Delta E_r(V)), \quad \chi_{-r}=\frac{1}{\hbar}\Gamma_r[1-n(\Delta E_r(V))],$$

$$\chi_r(U)=\frac{1}{\hbar}\Gamma_r(U)n(\Delta E_r(V,U)),$$

$$\chi_{-r}(U)=\frac{1}{\hbar}\Gamma_r(U)[1-n(\Delta E_r(V,U))],$$
(47)

where we introduced the distribution functions

$$n(\Delta E_r(V))=\{\exp[\Delta E_r(V)/k_BT]+1\}^{-1},$$

$$n(\Delta E_r(V,U))=\{\exp[\Delta E_r(V,U)/k_BT]+1\}^{-1}.$$
(48)

Therefore, the inelastic current component (39) can be obtained as

$$I_{ine}=I_0 2\pi(\Gamma_L\{n(\Delta E_L(V))(1-P)^2-[1-n(\Delta E_L(V))]$$
$$\times P(1-P)\}+\Gamma_L(U)\{n(\Delta E_L(V,U))P(1-P)$$
$$-[1-n(\Delta E_L(V,U))]P^2\}).$$
(49)

Both the direct and the sequential current components [cf. Eqs. (40) and (49), respectively] include the transmission through two intermediate molecular states. The lowest intermediate state corresponds to a singly occupied molecule. In Fig. 3 (scheme 1), this state is denoted by the symbol (0) referring to the absence of the Coulomb interaction between the transferred electrons. Such a state is connected with the lead states via the couplings $V_{L\mathbf{k}}$ and $V_{R\mathbf{q}}$ (cf. Fig. 1). This results in level broadenings $\Gamma_L/2$ and $\Gamma_R/2$ which characterize the efficiency of the electron transfer through the first transmission channel. The other intermediate state corresponds to two extra electrons in the molecule, and the presence of the Coulomb interaction between these extra electrons has to be considered. In Fig. 3 (scheme 2) the second state is denoted by the symbol (U). Now, the molecule-lead couplings are $V_{1L\mathbf{k}}$ and $V_{1R\mathbf{q}}$ and the corresponding level broadenings are $\Gamma_L(U)/2$ and $\Gamma_R(U)/2$. The latter quantities characterize the efficiency of electron transfer through the second transmission channel. Generally, the couplings $V_{r\mathbf{k}}$ and $V_{1r\mathbf{k}}$ differ from each other. Therefore, the quantities Γ_r and $\Gamma_r(U)$ ($r=L,R$) do not coincide. The formation of the intermediate states strongly depends on inelastic processes in the LMR system. In our case the sequential electrode-molecule and molecule-electrode hopping processes provide a mechanism that leads to a population of the molecule by
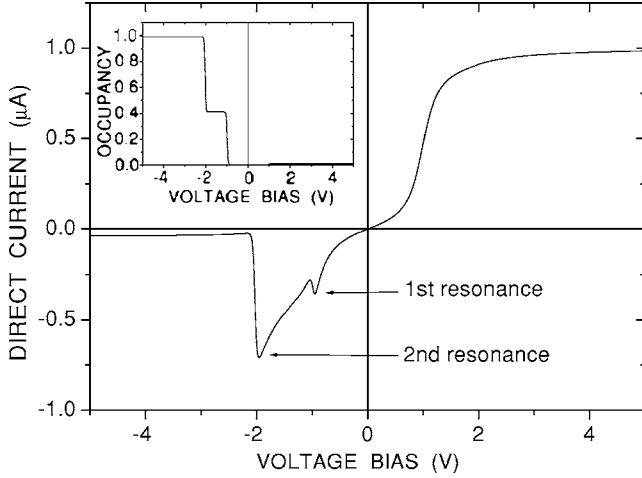
FIG. 7. Kinetic rectification of the current through a single molecular level. The current asymmetry results from different values of the level broadening. The performed calculations are according to the set of equations (31) and (40). The chosen parameters are the same as those in Fig. 4 except for $\zeta=0.01$, $\Gamma_L(0)=0.002$ eV, $\Gamma_R(0)=0.2$ eV, $\Gamma_L(U)=0.04$ eV, and $\Gamma_R(U)=0.4$ eV.

the transferred electrons. This fact is clearly reflected in the dependence of the single-electron distributions P on the hopping transfer rates $\chi_{r(-r)}$ and $\chi_{r(-r)}(U)$ [cf. Eqs. (31) and (32)].

B. Case with asymmetric contacts

In what follows we will analyze the importance of inelastic processes in regulating the direct current I_{dir}. The direct current component covers two contributions which are related to the tunneling transfer through the intermediate states discussed before and, thus, two different transmission channels contribute. In contrast to the sequential mechanism of current formation the direct transmission mechanism moves the electrons just from one lead to the other. Therefore, the molecular states only act as virtual states providing the coupling between the leads. It is important, however, to emphasize that the opening of each direct transmission channel strongly depends on the population of the molecule (charging state), i.e., on the probabilities $(1-P)^2$ and $P(1-P)$ to have the molecule without an extra electron and with a single extra electron, respectively. Because these probabilities are determined by inelastic hopping processes [cf. Eqs. (31) and (32)] the direct lead-lead transmission is also governed by inelastic processes. Figure 7 demonstrates this dependence at asymmetric molecule-lead couplings. The inset elucidates the role of inelastic processes in the formation of a single-electron level population.

Let us discuss the first mechanism of current formation for $V>0$. In the region $V<V_{Lr}(0)$, the gap $\Delta E_L(V)$ (cf. Fig. 3), scheme 1, is positive and, thus, the transmission occurs in the preresonance region. The main contribution to the direct component is related to the first transmission channel where the molecule mediates an electron transfer by remaining in its neutral, empty state. According to the condition $\Delta E_L(V) > 0$, the thermal population of the molecule by the trans-

ferred electrons is negligible. Actually, in Eq. (47), the distribution functions (48) are close to zero and, consequently, $A(0)\approx\Gamma_L+\Gamma_R$, $B(0)\approx0$, $A(U)\approx\Gamma_L(U)+\Gamma_R(U)$, $B(U)\approx0$.[41] It yields $P\approx0$. One can perceive that in the preresonant region $V<V_{Lr}(0)$ the direct current component is ruled by the first term on the right side of Eq. (40). In the voltage region $V>V_{Lr}(0)$ the gap $\Delta E_L(V)$ becomes negative. It means that an electron moves out of the left lead and enters the molecular level in a resonant manner. In the same way, it leaves the molecular level and arrives at an empty band level of the right lead. Since the stationary regime is studied, the probability for the transferred electron to be captured by the molecule is given by a relation between the rates ingoing and outgoing transfer [via the quantities (32)].

In the voltage region $V_{Lr}(U)\geqslant V>V_{Lr}(0)$, one may derive $A(0)\approx\Gamma_R$, $B(0)\approx\Gamma_L$, $A(U)\approx\Gamma_L(U)+\Gamma_R(U)$, $B(U)\approx0$. In the case under consideration, the asymmetry in the couplings of the molecule to the electrodes is determined by the relations $\Gamma_L/\Gamma_R=10^{-2}$, and $\Gamma_L(U)/\Gamma_R(U)=10^{-2}$. Therefore, in accordance with Eq. (31) one obtains $P\approx\Gamma_L/\Gamma_R=10^{-2}$. When $V\geqslant V_{Lr}(U)$, see in Eq. (44), then $\Delta E_L(V)<0$ and $\Delta E_L(V,U)<0$ (cf. Fig. 3). Now, the molecular levels covering a single or two electrons are in resonance with the band levels of the left electrode. This results in $A(0)\approx\Gamma_R$, $B(0)\approx\Gamma_L$, $A(U)\approx\Gamma_R(U)$, $B(U)\approx\Gamma_L(U)$. Again, it yields $P\approx\Gamma_L/\Gamma_R=10^{-2}$. Therefore, at $V\geqslant0$ the dependence of the direct current component on V is given by the expression

$$I_{dir}=I_0\frac{2\Gamma_L\Gamma_R}{\Gamma_L+\Gamma_R}\mathcal{F}\approx2I_0\Gamma_L\mathcal{F}. \tag{50}$$

Here, $\mathcal{F}$ is defined by Eq. (46), and the expression for I_{dir} shows that the direct current has not any particular structure at positive voltages.

The behavior changes for negative bias voltages. Although the voltage dependence of the current in the region $|V|<V_{Rr}(0)$ is similar to that for $V<V_{Lr}(0)$ (the value of the current increases with V), it changes just when the first resonant transmission is switched on. This resonant transmission involves the sequential transfer mechanism, and the molecular level is populated by the transferred electrons coming from the right electrode. Actually, in the region $V_{Rr}(U)\geqslant|V|>V_{Rr}(0)$ one may derive $A(0)\approx\Gamma_L$, $B(0)\approx\Gamma_R$, $A(U)\approx\Gamma_L(U)+\Gamma_R(U)$, $B(U)\approx0$. Therefore, $P\approx\sqrt{\Gamma_R}/[\sqrt{\Gamma_R}+\sqrt{\Gamma_R(U)}]\approx0.41$. The probability for a single-electron population becomes $P\approx0.41$, and a particular blocking of the first transmission channel takes place. But the presence of an extra electron at the molecular level opens the second transmission channel. The blocking of the first channel and the opening of the second channel are responsible for the first resonant peak in a direct current component. The increase of the direct current takes place up to $V=V_{Rr}(U)$ where a sudden current drop appears, constituting a pronounced regime with negative differential resistance. This is caused by the fact that both molecular levels, with one and two captured electrons (cf. Fig. 3) are in resonance with the filled band levels of the right electrode at $V\geqslant V_{Rr}(U)$. Therefore, $A(0)\approx\Gamma_L$, $B(0)\approx\Gamma_R$, $A(U)\approx\Gamma_L(U)$, $B(U)\approx\Gamma_R(U)$, and thus $P\approx\Gamma_R(U)/[\Gamma_L(U)+\Gamma_R(U)]\approx1$ while $1-P\approx\Gamma_L(U)/\Gamma_R(U)$

$\approx 10^{-2}$. This means that in the vicinity of the second resonant voltage $V = V_{Rr}(U)$ the current takes the value

$$I_{dir} = 4I_0[\Gamma_L(U)^2/\Gamma_R(U)]\mathcal{F}(U). \tag{51}$$

Comparing the current at $V>0$ and $V<0$ as depicted in Fig. 7 one notices a strong asymmetry in the *I-V* characteristics. Moreover, a pronounced rectification effect is observed for $|V|>2$ V, which originates via a regulation effect of inelastic kinetic processes on the tunnel transmission. These processes are responsible for population of the considered molecular level by the transferred electrons. The effect becomes particularly important at a resonant transmission and for those situations where the transfer rates responsible for the electron population of the molecule differ strongly from those controlling the escape of electrons.

In the considered example only the case has been discussed where in the resonant region at $V>0$, the hopping rates $\chi_L = \Gamma_L/\hbar$ and $\chi_L(U) = \Gamma_L(U)/\hbar$ are much smaller than the rates $\chi_{-R} = \Gamma_R/\hbar$ and $\chi_{-R}(U) = \Gamma_R(U)/\hbar$. In such a situation, the molecule rapidly looses the transferred electrons; consequently, its population remains negligible for $V>0$. As a result, the direct tunnel current through the single molecular level is formed in line with standard scattering theory. In contrast, in the resonant region at $V<0$, the hopping rates $\chi_{-L} = \Gamma_L/\hbar$ and $\chi_{-L}(U) = \Gamma_L(U)/\hbar$ are much smaller than the hopping rates $\chi_R = \Gamma_R/\hbar$ and $\chi_R(U) = \Gamma_R(U)/\hbar$. Now, the transferred electrons dominantly populate the molecule and, as a result, the probability to find a molecule without extra electrons strongly decreases. This is the effect which explains the control of the tunnel current by inelastic transfer processes and allows to elucidate the kinetic rectification. Note that the effect holds true even for $\eta = 0.5$ where the standard scattering approach does not predict any rectification.

V. CONCLUSIONS

With this present work we investigated the influence of kinetic processes and the Coulomb interaction in the course of charge transmission through a single molecule that is embedded in between two electrodes. Equations (38)–(40) describe analytically the off-resonant as well as resonant currents mediated by an isolated molecular level. Note that the current component (39) is formed by a pure inelastic electron transfer through the molecule. At the same time, the current component (40) refers to a direct interelectrode electron transmission. This component is associated with a tunnel mechanism of electron transfer which, however, proceeds against the background of a kinetic population of the molecule by the transferred electrons. By use of analytical means we could elucidate that in preresonant voltage region both elastic (tunnel) and inelastic (hopping) mechanisms of off-resonant charge transmission work independently of one another. The off-resonant regime exists when a level is positioned sufficiently high above the Fermi level of the electrodes to avoid thermally activated population of the molecule by extra electrons. Such a situation is guaranteed in the preresonant voltage regions $0 \leq V < V_{Lr}(0)$ and $0 \leq |V|$

$< V_{Rr}(0)$ [Eq. (44)]. The first transmission channel is realized if the molecule does not contain any extra electron. Since the molecule remains neutral (it is empty), there does not appear interelectron Coulomb interaction, and a direct electron transmission from one electrode to the other can be described by the standard Landauer scattering theory. The situation changes drastically for $V \geq V_{Lr}(0)$ $[|V| \geq V_{Rr}(0)]$. At such voltages, a resonant charge transmission is switched on so that the activationless hopping transfer moves electrons from the electrodes into the molecule. The probability that a molecule remains empty becomes now less than 1 and is determined by $(1-P)^2$, where P denotes the single-electron population of the molecular level, Eq. (31). Therefore, the contribution to the current related to the first transmission channel strongly decreases. Note, however, that at the same time the second transmission channel caused by the singly reduced molecule is involved in the transfer process. If the molecule already contains a single extra electron the next transferred electron senses it via the Coulomb repulsion. The probability for the molecule to capture a single extra electron is $2P(1-P)$ (the prefactor 2 accounts for spin degeneracy). Since the population P is originated by inelastic hopping processes [cf. Eqs. (22), (31), and (32)], the direct (tunnel) electron transmission is also modified by inelastic transfer processes. It is important to emphasize that the extent of single-electron population strongly depends on the direction of the electron transfer process. If the outflow of an electron from the molecular level is much faster than the transfer from the electrode into the level, the molecule is unable to capture an electron and conserves its empty state even at resonant transmission conditions. In the reverse case, however, the stationary population P becomes large. This is possible for $V \geq V_{Lr}(U)$ $[|V| \geq V_{Rr}(U)]$ depending on the relation between the broadenings Γ_L, Γ_R, $\Gamma_L(U)$, and $\Gamma_R(U)$. The asymmetry in molecular population of the transferred electrons leads to the appearance of a specific kinetic rectification effect: this is manifested by a strongly asymmetric *I-V* characteristic which in addition also contains regions of negative differential resistance, Fig. 7. Thus, the hopping processes play an important role in resonant electron transfer (including the transfer along a tunnel route) via the kinetic population of the molecule by the transferred electrons, i.e., via a molecular recharge. At large nuclear displacements, the electron vibrational coupling leads to the formation a vibrational fine structure (Figs. 4 and 5). This, however, does not affect the formation of the two main transmission channels that dominantly regulate the current through the molecule.

Our analytic results has been derived for description of the current formed by a charge transmission through a single isolated molecular level. The results demonstrate the important role of inelastic kinetic processes as well as the role of the Coulomb interaction between the captured electrons in the transmission process; in particular, the formation of a kinetic rectification effect. This result can be tested and verified experimentally if one measures the conductivity of a single molecule with a well isolated conductive level. This level has to be positioned not too far from Fermi levels of the leads (about tenths of eV). One of the molecular candidates possessing such an isolated level could be associated with a

level belonging the metallic ion (as an example, Cu^{2+}) incorporated into a molecule. In this case, due to a large Coulomb interaction between the extra electrons occupying the level during the transmission, only the first transmission channel (the channel with the empty level) is involved in a transfer process and thus the *I-V* characteristic of the molecule has not to be too complex. To our knowledge, up to now the available experiments use molecules which possess more than one level participating in the transmission. Meanwhile, an in-depth analysis of basic transmission processes in a single molecule can be done by studying the simplest case of charge transfer through a single isolated molecular level.

[1] M. Reed, Proc. IEEE **87**, 652 (1999).

[2] R. M. Metzger, Acc. Chem. Res. **32**, 950 (1999).

[3] A. Nitzan, Annu. Rev. Phys. Chem. **52**, 681 (2001).

[4] P. Hänggi, M. Ratner, and S. Yaliraki, Chem. Phys. **281**, 111 (2002).

[5] A. Nitzan and M. A. Ratner, Science **300**, 1384 (2003).

[6] F. Zahid, M. Paulsson, and S. Datta, in *Advanced Semiconductors and Organic Nanotechniques*, edited by H. Morkos (Academic Press, New York, 2003), Chap. 2, p. 41.

[7] S. Datta, Nanotechnology **15**, S433 (2004).

[8] S. Kohler, J. Lehmann, and P. Hänggi, Phys. Rep. **406**, 379 (2005).

[9] Y. Meir and N. S. Wingreen, Phys. Rev. Lett. **68**, 2512 (1992).

[10] S. Datta, *Electronic Transport in Mesoscopic Systems* (Cambridge University Press, Cambridge, UK, 1995).

[11] C. Gonzales, Y. Simon-Monso, J. Batteas, M. Marquez, M. Ratner, and V. Mujica, J. Phys. Chem. B **108**, 181414 (2004).

[12] J. Lehmann, S. Kohler, V. May, and P. Hänggi, J. Chem. Phys. **121**, 2278 (2004).

[13] M. Cizek, M. Thoss, and W. Domcke, Phys. Rev. B **70**, 125406 (2004).

[14] E. G. Petrov, I. S. Tolokh, A. A. Demidenko, and V. V. Gorbach, Chem. Phys. **193**, 237 (1995).

[15] C. Kergueris, J.-P. Bourgoin, S. Palacin, D. Esteve, C. Urbina, M. Magoga, and C. Joachim, Phys. Rev. B **59**, 12505 (1999).

[16] E. G. Petrov and P. Hänggi, Phys. Rev. Lett. **86**, 2862 (2001).

[17] A. Nitzan, J. Phys. Chem. A **105**, 2677 (2001).

[18] J. Lehmann, G.-L. Ingold, and P. Hänggi, Chem. Phys. **281**, 199 (2001).

[19] A. M. Kuznetsov and J. Ulstrup, J. Chem. Phys. **116**, 2149 (2002).

[20] E. G. Petrov, V. May, and P. Hänggi, Chem. Phys. **281**, 211 (2002).

[21] E. G. Petrov, V. May, and P. Hänggi, Chem. Phys. **296**, 251 (2004).

[22] A. Mitra, I. Aleiner, and A. J. Millis, Phys. Rev. B **69**, 245302 (2004).

[23] S. Tikhodeev, M. Natario, K. Makoshi, T. Mii, and Y. Ueba, Surf. Sci. **493**, 63 (2001).

[24] M. Galperin, M. A. Ratner, and A. Nitzan, J. Chem. Phys. **121**, 11965 (2004).

[25] M. Galperin, M. A. Ratner, and A. Nitzan, Nano Lett. **4**, 1605 (2004).

[26] E. G. Petrov, V. May, and P. Hänggi, Chem. Phys. **319**, 380 (2005).

[27] W. Häusler, B. Kramer, and J. Masek, Z. Phys. B: Condens. Matter **85**, 435 (1991).

[28] A. L. Yeyati, A. Martin-Rodero, and F. Flores, Phys. Rev. Lett. **71**, 2991 (1993).

[29] V. Mujica, A. E. Roitberg, and M. A. Ratner, J. Chem. Phys. **112**, 6834 (2000).

[30] M. H. Hettler, H. Schoeller, and W. Wenzel, Europhys. Lett. **57**, 571 (2002).

[31] A. Nitzan, M. Galperin, G.-L. Ingold, and H. Grabert, J. Chem. Phys. **117**, 10837 (2002); S. Pleutin, H. Grabert, G.-L. Ingold, and A. Nitzan, *ibid.* **118**, 3756 (2003).

[32] V. Mujica, A. Nitzan, S. Dutta, M. Ratner, and C. P. Kubiak, J. Phys. Chem. B **107**, 91 (2003).

[33] S. K. Pati, J. Chem. Phys. **118**, 6529 (2003).

[34] P. Orellana and F. Claro, Phys. Rev. Lett. **90**, 178302 (2003).

[35] G. C. Liang, A. W. Ghosh, M. Paulsson, and S. Datta, Phys. Rev. B **69**, 115302 (2004).

[36] M. Galperin and A. Nitzan, Ann. N.Y. Acad. Sci. **1006**, 48 (2003).

[37] E. G. Petrov, Low Temp. Phys. **31**, 338 (2005).

[38] W. Tian, S. Datta, S. Hong, R. Reifenberger, J. I. Henderson, and C. P. Kubiak, J. Chem. Phys. **109**, 2874 (1998).

[39] T. Holstein, Ann. Phys. (N.Y.) **8**, 325 (1959).

[40] In region $V > V_{Lr}(U)$ $[|V| > V_{Rr}(U)]$, the phonon sidebands associated with the first transmission channel give a background contribution in the current.

[41] To derive the form of $A(0)$, $B(0)$, $A(U)$, and $B(U)$ we take into consideration the fact that at room temperature the Fermi distribution function [and thus the functions (48)] is well approximated by a step function. It thus allows us to express the rates $\chi_{s(-s)}$ from Eq. (47) through the corresponding width parameters Γ_s.