



# Giant switch-on and switch-off currents in device “electrode–molecule–electrode”

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## ABSTRACT

The transient current formation in a device “electrode–single molecule–electrode” is studied theoretically. It is demonstrated that a giant transient current is formed if the two transfer couplings of the molecule to the electrodes differ strongly and if the applied voltage is instantaneously switched on or off. This behavior is mainly caused by a recharge of the molecule due to nonequilibrium electron hopping processes from or into the electrodes.

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## 1. Introduction

During the last decade numerous experimental data have been reported demonstrating nonlinear current–voltage ( $I$ – $V$ ) characteristics of single molecules and molecular wires [1–6]. Rectification properties and memory effects in single organic molecules could be observed [7–9], and negative differential conductance with in a single molecule were measured [10]. The type of molecule–electrode coupling, the energetic position of the molecular orbitals (MOs) relative to the Fermi-levels of the electrodes, the molecular DOS, the conformational mobility of the molecule, etc. could be identified as the main factors determining actual  $I$ – $V$  characteristics [11–15]. If the applied voltage  $V$  does not exceed a resonant voltage  $V_{\text{res}}^1$  the current formation mainly results from tunneling of charges between the electrodes. Now, the transmission process takes place via a virtual population of the MOs by the transferred electrons/holes. The tunneling pathway results from a distant superexchange electrode–electrode coupling [16–18]. If the applied voltage exceeds the resonant one the charge transmission becomes much more involved. The transferred electrons

are able to occupy empty and half-filled MOs and, thus, tunneling and hopping pathways contribute to the charge transmission [18–20]. An important observation of these studies is that even in the case where the hopping current component is small compared to the tunneling one, inelastic transition processes strongly control both types of current. This control is achieved via a real population of the MOs by the transferred electrons, i.e. by a molecular recharge [21,22]. Thus, in the resonant regime of charge transmission inter-electrode tunneling proceeds against the background of an alternating molecular charge state. The latter is completely determined by the electrode–molecule hopping rates as well as the intra-molecular charge transfer rates.

Despite the fact that the steady state  $I$ – $V$  characteristics of single molecules give a rather detail information on the physical mechanisms of current formation in the system “left electrode–molecule–right electrode” (LMR-device) the study of electron transmission under the influence of  $ac$ -fields allows us to open new perspectives for the charge control through single molecules and molecular wires (see e.g. recent papers [23–27]). Be also aware of another important problem which refers to the clarification of the possible mechanisms of nonstationary (transient) current formation in LMR-devices just after the switch-on and switch-off of an inter-electrode voltage. For example, transient currents appear when a molecular device executes signal transformation operations. In this case, it becomes necessary to know the characteristic time (times) of the current to reach its steady state value. In the present communication, we show that the transient current may remarkably exceed the steady state current. This effect

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<sup>1</sup> Resonant voltage corresponds to such voltage bias  $V = V_{\text{res}}$  at which the energies of electron at the Fermi-level and at the MO become equal in value so that an isoenergetic electrode–molecule electron jump occurs in the LMR-device. Each  $V_{\text{res}} = V_{\text{res}}^{(rV)}$  is determined from the condition that the gap  $\Delta E_{rV}(V)$  (cf. Fig. 1 and Eq. (4)) associated with the specific charge transmission route  $rV$ , vanishes.

is shown to be completely determined by charge hopping between the molecule and the electrodes. The transient current achieves its largest values if the resonant regime of charge transmission has been realized.

## 2. Model and basic expressions for the current components

To study the mechanism of transient current formation we use a model of LMR-device where among all MOs only a single frontier MO contributes to the charge transmission. Therefore, it is supposed that the frontier MO is energetically well separated from all other MOs. [For example, the lowest unoccupied MO may serve as a frontier MO.] In a chosen voltage region, all MOs except the frontier MO only weakly contribute to the current formation. Moreover, we assume that the electron–vibrational coupling is weak compared to the molecule–electrode couplings. As a consequence, the latter couplings mainly determine the broadening of the frontier MO energy levels. Therefore, any effect of the electron–vibrational coupling is neglected in the following (these effects only become important when concentrating on the fine structure of  $I$ – $V$  curves, see e.g. [21,22,28–30]). We also assume nonmagnetic electrodes, the absence of a magnetic field, and a zero-spin state for the neutral molecule. Molecular charging is caused by inelastic electron transmission through the molecule. Bearing in mind the noted simplifications one is able to use the electronic LMR-device Hamiltonian  $H_{\text{LMR}}$  in the well-known Anderson's form [31]. In the case of a single frontier MO, it reads

$$H_{\text{LMR}} = \sum_{r=L,R} \sum_{\mathbf{k},\sigma} [E_{r\mathbf{k}} a_{r\mathbf{k}\sigma}^{\dagger} a_{r\mathbf{k}\sigma} + V_{r\mathbf{k}} c_{\sigma}^{\dagger} a_{r\mathbf{k}\sigma} + V_{r\mathbf{k}}^* a_{r\mathbf{k}\sigma}^{\dagger} c_{\sigma}] + \sum_{\sigma} [\varepsilon(V) + U c_{-\sigma}^{\dagger} c_{-\sigma}] c_{\sigma}^{\dagger} c_{\sigma}, \quad (1)$$

where  $E_{r\mathbf{k}}$  is the energy of a conduction band electron with wave vector  $\mathbf{k}$  and spin projection  $\sigma$  belonging to the  $r$ th electrode. In contrast,  $\varepsilon(V)$  is the energy of an extra electron occupying the frontier MO. Related electron creation and annihilation operators are denoted by  $a_{r\mathbf{k}\sigma}^{\dagger}$ ,  $c_{\sigma}^{\dagger}$  and  $a_{r\mathbf{k}\sigma}$ ,  $c_{\sigma}$ , respectively. Coulomb repulsion between two electrons in the frontier MO is characterized by the Hubbard parameter  $U$ . The quantity  $V_{r\mathbf{k}}$  describes the coupling between the frontier MO and the  $\mathbf{k}$ th state of an electron in the  $r$ th electrode. Note that a Hamiltonian like that of Eq. (1) has been applied in various studies on electron transmission through an isolated level of a quantum dot or a single molecule (see, e.g. Refs. [32–37]).

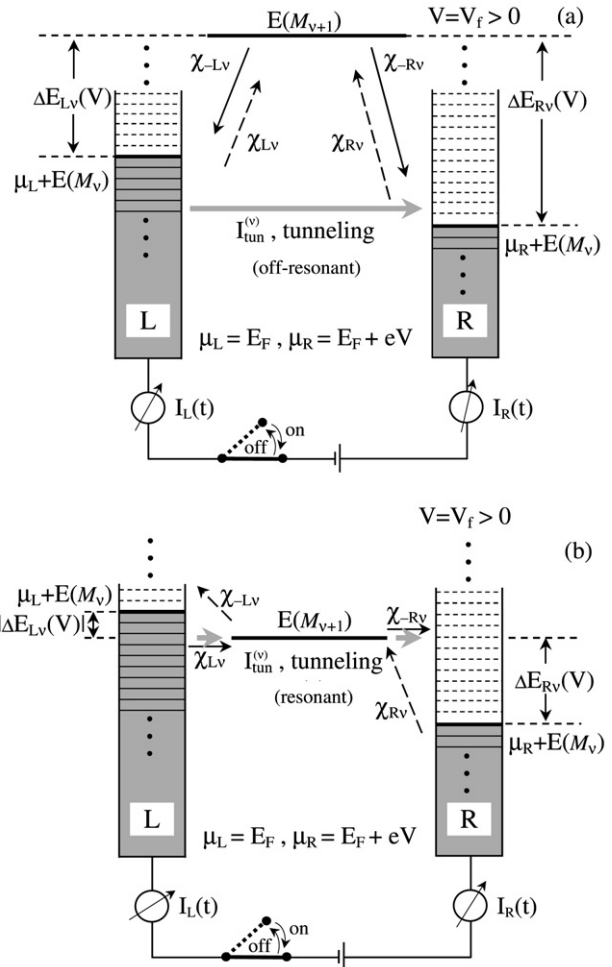
It follows from the Hamiltonian (1) that in the absent of molecule–electrode coupling a proper energy of the molecule in its  $\nu$ th charge state reads

$$E(M_{\nu}) = \nu\varepsilon(V) + \frac{\nu(\nu-1)}{2}U \quad (\nu = 0, 1, 2). \quad (2)$$

[Here, the symbol  $\nu$  is used to indicate neutral ( $\nu = 0$ ), singly charged ( $\nu = 1$ ) and doubly charged ( $\nu = 2$ ) states of the molecule.] Since in the model under consideration no more than two extra electrons can occupy a single frontier MO, only two different transmission gaps control the charge transfer. With respect to each electrode  $r$  ( $= L, R$ ), the gaps are determined as  $\Delta E_{r\nu}(V) = E(M_{\nu+1}) - (\mu_r + E(M_{\nu}))$ , cf. Fig. 1. For the sake of definiteness, we consider the case where the left electrode is fixed at zero voltage so that the chemical potentials of the electrodes are  $\mu_L = E_F$  and  $\mu_R = E_F + eV$ . At such conditions, the shift of the frontier MO energy against the applied voltage  $V$  is given as

$$\varepsilon(V) = \varepsilon(0) + \eta eV, \quad (3)$$

where  $\varepsilon(0)$  is the unbiased energy position of the frontier MO and  $\eta$  is the voltage division factor [3]. Thus, the voltage dependent shift of the transmission gaps reads



**Fig. 1.** Scheme of kinetic processes in LMR-device with a single frontier MO at off-resonant (a) and resonant (b) charge transmission. Just after an instantaneous voltage alteration, the currents  $I_L(t)$  and  $I_R(t)$  through respective electrodes become unequal. Coincidence of the currents occurs at  $t \gg \tau_{ET}$  where  $\tau_{ET}$  is the least characteristic time of the establishment of steady current in the device. Charge hopping processes are characterized by the contact electrode–molecule and molecule–electrode rate constants  $\chi_{r\nu}$  and  $\chi_{-r\nu}$ , respectively. These rates are responsible for a molecular recharge. Tunnel current  $I_{\text{tun}}^{(\nu)}$  determines a distant single-step electron jump between the electrodes. Symbol  $\nu$  ( $= 0, 1$ ) indicates the transmission routes associated with a charge state of the molecule. At  $V > 0$ , a resonant regime of current formation occurs when the transmission gap  $\Delta E_{L\nu}(V)$  becomes negative.

$$\Delta E_{L\nu}(V) = \Delta E(0) + \nu U + \eta eV,$$

$$\Delta E_{R\nu}(V) = \Delta E(0) + \nu U - (1 - \eta)eV \quad (\nu = 0, 1), \quad (4)$$

with  $\Delta E(0) = \varepsilon(0) - E_F$  being the single-electron unbiased gap. The gaps, Eq. (4) control the charge transmission for both the hopping and the tunnel pathway. Resonant regimes of charge transmission at a concrete molecular charge state  $\nu = 0$  (or  $\nu = 1$ ) occur if  $\Delta E_{L\nu}(V) \leq 0$  (at  $V > 0$ ) and  $\Delta E_{R\nu}(V) \leq 0$  (at  $V < 0$ ).

The current evolution which is of interest here represents a nonequilibrium kinetic process characterizing the adaptation of the current from a certain initial steady state value  $I_{\text{steady}}(V = V_i)$  to a final steady state value  $I_{\text{steady}}(V = V_f)$ . In the process of such an adaptation, the charge state of the molecule is changed. It is reflected in an alteration of the probabilities  $P(0, t)$ ,  $P(1, t) \equiv P(1, \sigma = +1/2, t) = P(1, \sigma = -1/2, t)$  and  $P(2, t)$  to involve, respectively, a neutral, a singly, and a doubly charged molecule in the charge transmission process. Physically, these probabilities define the occupation of the molecule by extra (transferred) electrons. Therefore, the evolution of the above mentioned probabilities (molecular charge occupancies) to their steady values appears

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