A theory of molecular transistor based on the two-center electrochemical bridged tunneling contact

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ABSTRACT

It is shown that the two-center bridged tunneling contact in the serial configuration based on the donor–acceptor single redox molecule immersed in the electrolyte solution at the ambient conditions (i.e., room temperature and condensed matter environment) demonstrates pronounced transistor-like features for certain sets of the physical parameters of the system. Electrons at the redox centers of the bridge molecule are coupled strongly to the classical phonon modes of the condensed matter environment and Debye screening of the electric field is taken into account. The case of the non-adiabatic tunneling of electrons between the centers and between the centers and electrodes is considered and the limit of the infinite Coulomb repulsion between electrons occupying the same center is used. The regions of the physical parameters where both strong rectification and strong amplification (over three orders of magnitude) take place for all positive (or negative) values of the bias voltage are revealed and the transistor-like current/bias voltage characteristics are calculated.

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1. Introduction

The increasing interest in study of the single-molecule bridge-mediated tunneling contacts is connected with their possible applications in molecular electronics [1,2]. One of the most exciting applications is the use of these contacts as molecular transistors [1–3] (earlier the similar problem of single-electron devices based on the mesoscopic structures was considered in literature (see, e.g., the review article [4])). A key feature for this application is rectification in the current/bias voltage relation (the diode-like behavior). Different models of rectification were suggested and rectification has indeed been observed in a number of molecular junctions (see Refs. [2,5–7] and references therein). The most experimental studies were carried out for systems having many molecules or molecular wires. However, the single-molecule diodes were also experimentally realized [8,9].

A well-known model of rectification of the tunnel current by a two-center molecule confined in the tunneling gap was suggested by Aviram and Ratner [10] in 1974. It implies that the filled energy level of one of the center (donor) and the empty one of the other center (acceptor) cross, e.g., at the certain positive value of the bias voltage V and move apart at negative values of V. As a result, the tunnel current is large in the region $V > 0$ and negligibly small at the negative bias so that the current/bias voltage dependence is asymmetric. Since 1974, the tunnel current/bias voltage dependences were calculated for a number of molecular junctions using different theoretical methods and rectification was predicted (see, e.g., the recent papers [8,11–17] and references therein). In these works rectification was obtained for the non-symmetric bridge molecules [8,12,15–17] or for a single-level bridge molecule in the asymmetric tunneling contact [11,13,14]. It has also been shown that rectification emerges for a single-level bridge molecule in the in situ symmetric tunneling contacts when Debye screening is taken into account [18,19].

Rectification ratio R obtained in works cited above was found to be rather small. For example, rectification obtained in [8,16,17] has a nature of the type proposed in [10] but R is not large due to the large number of the energy levels of the centers which participate in the electron tunneling and cross both at positive and negative values of V (see, e.g., Fig. 8 of [8]).

The methods used in Refs. [8,12,15–17] for the calculations of the tunnel current are rather complicated (e.g., the non-equilibrium Green's function density functional theory is used in [8,16,17]) and molecules under consideration have the complex structures. On the other hand, the simplest configuration consisting of two quantum dots where each of them has only single electron energy level was considered in [20] within the non-equilibrium two-center Anderson model. It was shown that, for the serial double-site junction and asymmetry positions of the bare energy levels ε_{10} and ε_{20} of the quantum dots, the current/bias voltage dependence has some similarities to that for the experimentally realized single-molecular diode [8].

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Two-terminal devices were mainly addressed in [5–17]. However, in order the single-molecule tunneling contact can operate as molecular transistor, it should exhibit not only rectification but also amplification of the tunnel current so that the three-terminal single-molecular devices are of importance [2]. Three-terminal single-molecule transistors were experimentally realized both at low [21–24] and room temperatures [25–29] (in situ single-molecule tunneling contact). Most theoretical works in molecular transistors have been focused in three-terminal molecular devices where the gating mechanism was electrostatic [15,30–35] (e.g., the gate voltage is introduced simply as a capacitor field created by two charging disks at a certain distance from each other), both electrostatic and conformational [36] or both electrostatic and chemical [37]. Amplification obtained in [15,30–34,36,37] was no more than an order of magnitude. On the other hand, the electrochemical gating permits to obtain the change of the tunnel current over three orders of magnitude for the electroactive molecules which undergo reversible redox reactions [26,28].

Therefore, in contrast to Refs. [15,30–37], we study in the present paper the redox-mediated tunneling contacts in the condensed matter environment operating at room temperature (in situ systems) which can be considered as better candidates for the creation of the molecular scale electronics [2,28,38–41]. The notion "redox-mediated contact" means that each center of the bridge molecule has two quasi-stable states with the empty electron level (oxidized state) and occupied one (reduced state). A crucial factor for the use of in situ systems as the elements of molecular electronics is the possibility of the independent variations of two potential drops: the bias voltage V between the electrodes and the electrode potential φ of one of the electrodes relative to the third reference electrode (or overpotential η) as the gate voltage [38,42,43]. Another crucial factor which distinguishes in situ systems from the vacuum tunneling contacts is the strong interaction of the valence electrons of the bridge molecule with the classical phonons of the condensed matter environment. When the environment is the electrolyte solution, the Debye screening effect should be also taken into account.

The increase of the tunnel current with the change of the gate voltage observed in [26,28] was attributed to an empty molecular state-mediated electron transfer [26,28]. This case can be considered theoretically as the electron tunneling through a one-level redox molecule. Rectification and amplification for these systems was studied in [19]. It was shown that rectification takes place only in the large E_r limit ($|eV|$, $|e\eta| < E_r$) where E_r is the reorganization energy of the classical phonon modes. As a result, the gate voltage can not be varied within the large interval in order to obtain large amplification along with large rectification. Moreover, the increase of the gate voltage leads to the increase of the tunnel current in some intervals of the bias voltage (amplification) but to the decrease of it in other intervals. Therefore, it may be concluded that the good molecular transistor can not be constructed based on the one-level redox molecule.

On the other hand, the electrochemical two-center tunneling contacts give more options for the creation of molecular transistors due to the larger number of parameters describing these systems. The first theoretical study of rectification by in situ two-center molecular contact was presented in [3]. However, only the large E_r limit and the case of the equal electronic energy levels of the centers ($\delta = \varepsilon_{10} - \varepsilon_{20} = 0$, where δ is the asymmetry of the energy levels.) with the neglect of the energy of the Coulomb repulsion U_{12} between electrons occupying different centers were considered in [3] within a rather approximate method. As a result, the rectification ratio obtained in [3] was small ($R = 1$–6). Fig. 7 of [3] also shows a small effect of amplification which takes place due to the increase of η. The same problem was studied in Ref. [44] using the exact solution for the spin-less model in the case when the presence of

the Fermi seas of the leads is ignored (see, e.g., the discussion of this solution in [45]). Therefore, only the reduced state of the center 1 and the oxidized state of the center 2 were taken into account. It was noted in [3,44] that, due to the separate control of two potential drops, the in situ system can be considered as a molecular transistor. Although a rather strong rectification behavior was obtained in [44] for large values of η (see Fig. 4 of [44]) the current/gate voltage dependencies were not studied explicitly. The in situ double-tunnel nanoscale switches were considered in [46] with due account of the two potential drops. A more rigorous treatment of the in situ two-center tunneling contacts was presented in [47] for different regimes of the electron tunneling for the spin-less model in the case $\delta = 0$. In particular, it was shown that a strong rectification effect takes place even at $\delta = 0$ for rather large values of η (see Fig. 20 of [47]). However, the detailed study of transistor-like properties of the in situ two-center tunneling contact was not performed in Ref. [47]. A consistent method for the calculation of the tunnel current through a redox-mediated two-center bridged contact for the case of the totally non-adiabatic electron transitions was presented in [48]. It was shown that amplification due to the electrochemical gating takes place and the position of the maximum of the tunnel current/overpotential curve depends on δ. Based on the method of Ref. [48], the effect of the Coulomb repulsion energy U_{12} on the tunnel current through the two-center redox molecule in the totally non-adiabatic (weak tunneling) limit in the case of the strong electron–phonon coupling was studied in [49].

Using the results of [49] we show that the redox-mediated two-center tunneling contact in the serial configuration immersed in the electrolyte solution at room temperature demonstrates pronounced transistor-like features for certain sets of the physical parameters of the system. Valence electrons at the one-level redox centers are coupled strongly to the classical phonon modes of the condensed matter environment and Debye screening of the electric field in the tunnel gap is taken into account. The limit of the infinite Coulomb repulsion between electrons occupying the same redox center is used. We consider rectification mechanisms similar to that suggested by Aviram and Ratner [10] and reveal the regions of the physical parameters of the system there both strong rectification and strong amplification take place. For the sake of clarity and in order to take into account the dynamic solvent effects, we study the simplest configuration consisting of two-center redox molecule where each center has only single electron energy level and specifically address the well-defined totally non-adiabatic limit. The electron transfer is here of sequential character with the intermediate electron localization at the valence orbitals of the redox centers after configurational fluctuations and full relaxation of the vibrational subsystem. It is important that the tunnel current depends exponentially on the gate voltage in this limit. It is also important that the use of this limit allows one to study the problem of rectification and amplification analytically based on rather simple expressions for the tunnel current. In contrast to Ref. [3], these expressions are valid for arbitrary values of E_r and are obtained using the proper method [48,49] of calculation of the occupation probabilities of the energy levels of the bridge molecule. It should be noted that the consideration of the totally adiabatic limit is very complicated because the adiabatic free energy surface for the classical phonon modes can not be defined in the general case [47]. We show that rectification and amplification can be tuned by variation of δ, z_i, L_D/L, E_r, k_0/k and U_{12}. Here $z_i = Z_i/L$ where Z_i, $i = 1, 2$, is the position of the ith redox center, L_D is the Debye screening length, L is the distance between the electrodes, k_0 and k are the characteristic rates of the electron tunneling between the centers and between the centers and electrodes, respectively. The range of the effective amplification is determined by the width of the corresponding current/gate voltage curve which depends essentially on the parameter k_0/k [49]. Large values of R and thousandfold