Chemical Physics 459 (2015) 155–171

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

Effect of the band structure of the electrodes on the non-adiabatic electron tunneling through a one-level redox molecule

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ARTICLE INFO

Article history:
Received 16 June 2015
In final form 7 August 2015
Available online 29 August 2015

Keywords:
Molecular transistor
Bridged tunneling contact
Redox molecule
Strong electron–phonon coupling
Non-adiabatic electron tunneling
Band structure effects

ABSTRACT

Effect of the band structure of the electrodes having the relatively narrow density of states on the non-adiabatic electron tunneling (the weak tunneling limit) through a one-level redox molecule is considered. The differential conductance, amplification and rectification of the tunnel current are studied and calculated. It is shown that, for some narrow-band electrodes, the dependences of these tunnel current characteristics on the bias voltage differs essentially from those both for the vacuum tunneling contacts and the electrochemical tunneling contacts based on the wide-band electrodes. It is also shown that the band structure effects are of importance and can lead to a number of peculiarities in amplification and rectification of the tunnel current including the possibility to obtain the larger amplification and rectification as compared with those for the in situ tunneling contacts having the wide-band electrodes.

1. Introduction

The experimental and theoretical study of the single-molecule tunneling contacts is of large importance due to their possible application in the molecular electronics since they display such diode and transistor-like properties as rectification and amplification of the tunnel current [1–4]. Perspective candidates for this purpose are the redox-mediated tunneling contacts [2,5,6] (see also references cited in [7]) which can operate in the condensed matter environment (in particular, the electrolyte solution) at room temperature (in situ systems). The term "redox molecule" (RM) means that the bridge molecule has two quasi-stable states with the empty electron level (the oxidized state) and occupied one (the reduced state) (see Fig. 1). The oxidized and reduced states can be transformed to each other due to the thermal fluctuations of the phonon modes of the condensed media (or the intramolecular modes in the case of the vacuum tunneling contacts). The important property of the redox-mediated tunneling contacts operating in the electrolyte solution is the possibility of the independent variation of two potential drops: the bias voltage between two working electrodes and the electrode potential φ (or overpotential η) of one of the working electrodes relative to the third reference electrode which play the role of the gate electrode. A simplest particular case of these systems is the one-level RM when the single-electron energy level spacing in the RM is sufficiently large so that only one valence level can be taken into account. The theoretical study of amplification and rectification of the tunnel current in the one-level electrochemical bridged tunneling contacts was mainly performed for the case of the non-adiabatic electron tunneling (the weak tunneling limit) within the wide-band approximation [8,9,7]. It was shown that the electron tunneling through the RM valence level depends strongly on the thermal fluctuations of the vibrational modes of the condensed media (the strength of the RM valence level–phonon coupling is characterized by the solvent reorganization free energy E_r (the polaron shift)), the overpotential η, Debye screening of the electric potential in the tunneling gap and the energy U of the Coulomb repulsion between two electrons occupying the RM valence level.

However, the electrodes having the narrow partly filled d-bands are often used in the electrochemical tunneling contacts (see, e.g., Refs. [10,11] were the platinum electrode is employed). One may also expect the appearance of the new types of the electrodes having the single narrow band arising due to some cover layers. Therefore, it is of importance to extend the theory of the bridged electrochemical tunneling contacts to the case of the electrodes having arbitrary electronic energy bands and, especially, to the case of the narrow-band electrodes since one may expect the appearance of some new characteristic features in the diode and transistor-like properties of these contacts. Indeed, it is known [12–16] that, for the vacuum tunneling contacts, the negative differential resistance (NDR) can be obtained in the cases of the electron tunneling between the electrodes having the relatively narrow density of states (DOS) contribution to the total DOS. Such cases can include the electron tunneling between the localized

http://dx.doi.org/10.1016/j.chemphys.2015.08.015
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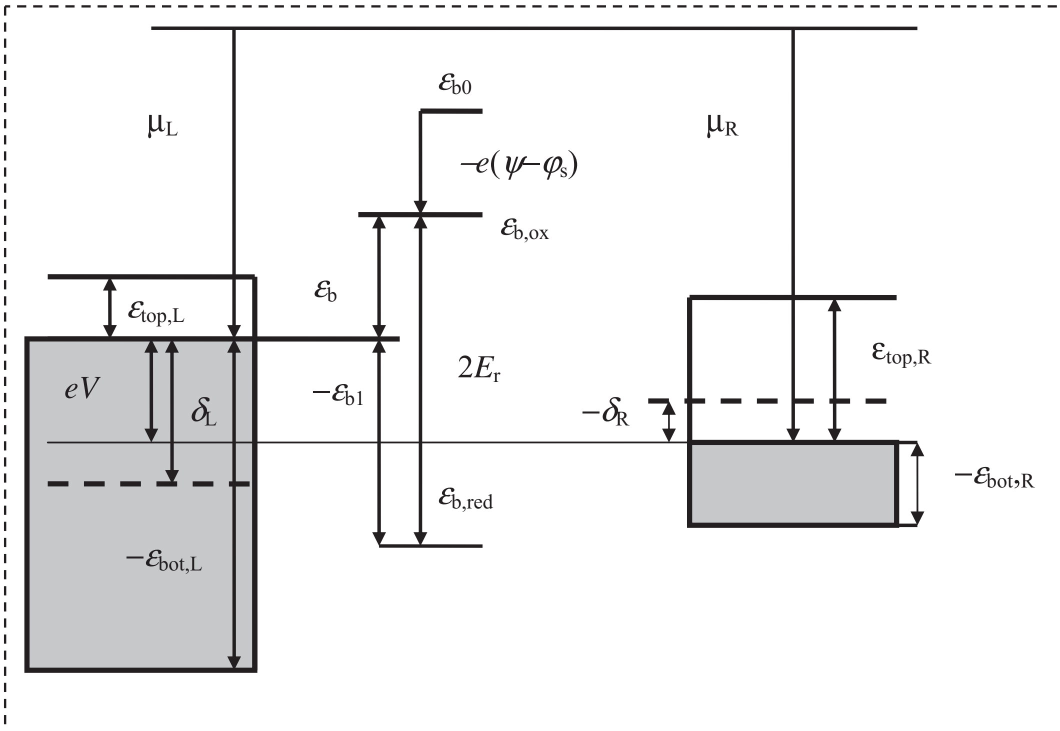

Fig. 1. The energy diagram of the redox-mediated tunneling contact. The upper line shows the energy $-e\varphi_s$ where φ_s is the potential in the bulk of solution. The chemical potentials μ_L and μ_R of the left and right electrodes are counted from the energy $-e\varphi_s$ and specify the positions of the corresponding Fermi levels. μ_L and μ_R are negative in this diagram. The bare electron energy level ε_{b0} of the valence orbital of the RM is shifted down (for the positive difference $\psi-\varphi_s$) to the level $\varepsilon_{b,ox}$. $\psi(z,\varphi_L,\varphi_R)$ is the potential at the position z of the RM which depends on the electrode potentials φ_L, φ_R and, therefore, on the bias voltage $V=(\mu_L-\mu_R)/e$ and the overpotential. $\varepsilon_{b,ox}$ and $\varepsilon_{b,red}$ are the energy levels of the valence electron of the RM in the oxidized and reduced states, respectively. The dashed lines show the centers of the energy bands of the electrodes. E_r is the solvent reorganization energy. The other symbols are explained in the text.

atomic-like sates [12], between the electrodes covered by the some layer which plays a role of the link group [13] or between the electrodes made from transition metals having the DOS with the strong d-band contribution near the Fermi level [14–16]. A physical meaning of the NDR in these cases is rather obvious [12–16]: when the bias voltage varies, the tunnel current decreases when the narrow DOSs of the electrodes move from each over. Since the position of the valence level depends on the bias voltage, the crucial role here plays a shift of the valence level out of the energy interval where the corresponding DOS is non-zero.

The account of the strong coupling of the electrons of the RM valence level to the phonon modes of the condensed matter environment introduce new important features both in the differential conductance/bias voltage characteristics and the effects of amplification and rectification of the tunnel current. In particular, the case of the electron tunneling between the atomic−like localized states is similar to that in the tunneling contact having two RM or the double−level RM. This system was studied in [17] also in the totally non-adiabatic limit and the regions of NDR were obtained. However, in contrast to the vacuum tunneling systems, the form of the differential conductance/bias voltage curves depends essentially on the reorganization free energy, overpotential and the Debye screening length. Although the results obtained in the present paper are valid for arbitrary electrodes with arbitrary covers having the narrow local DOS with respect to the RM valence state, we use here (for the sake of definiteness and as the specimen) the parameters of the d-band structure of the electrodes made from the transition metals having partly filled d-bands. In contrast to the works based the wide-band approximation, it allows us to study the new important problem concerning the dependence of the tunnel current characteristics not only on the bias voltage V, overpotential η, E_r and the Debye screening length but also on the electronic properties of the electrodes such as, for example, their bandwidths and the positions of the Fermi levels relative to the centers of their d-bands. We take here into account only the d-bands of the transition metals since the sticking d-states of the transition metal atom may couple stronger to the RM valence electron as compared with the sp-electrons of the electrode. In particular, this assumption is often made in the theory of hydrogen chemisorption on the transition metals [18]. For example, calculations of the interaction of the atomic hydrogen with the transition metal clusters [19] show that the d-states of some transition metals give the main contribution to this interaction. Even in the case when the coupling of the RM valence electrons to the sp-states of the transition metal is stronger than that with the d-states, the contribution of the sp-electrons to the total binding energy may be essentially smaller due to the larger value of the sp-bandwidth of the transition metal [20]. On the other hand, it was found in [21] that the d-states couple weakly to the RM in the case of the electron transfer through an alkanethiol monolayer. Nevertheless, for the sake of simplicity, we study in what follows only the current due to the tunneling of the d-electrons while the contribution of the sp-electrons of the electrodes to the total tunnel current will be considered as a background. We also neglect the contribution to the tunnel current arising from the electron tunneling through the RM from the sp-band to the d-band of different working electrodes.

The nature of the transition metals has a strong impact on different chemical and physical processes taking place on their surfaces. In particular, in Ref. [22] the dependence of the hydrogen chemisorption energy on the electronic properties of the transition metals was studied (a more complex model of hydrogen