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A theory of redox-mediated electron tunneling through an electrochemical two-center contact

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Abstract

The dependences of the tunnel current on the overpotential and bias voltage for a symmetric electrochemical contact involving two redox groups are calculated. The main physical situations involving various combinations of the strengths of the electronic coupling of the redox groups with each other and with the electrodes are considered in detail. The treatment is more rigorous and complete as compared with previous work. In particular, totally adiabatic transitions are discussed and the potential distribution in the tunnel gap is taken into account. It is shown that the system under consideration manifests negative differential resistance and rectification. A new effect is predicted in the current/overpotential dependence, namely the appearance of two maxima. The experimental data of (Tran *et al* 2006 *Faraday Discuss.* **131** 197) are addressed. It is concluded that they are compatible with the assumption on a strong screening of the electric potential within the tunnel gap.

1. Introduction

Tunnel contacts with a two-center molecule confined in the tunneling gap have been attracting the attention of researchers since the publication of the paper by Aviram and Ratner [1] where it was shown qualitatively that in a vacuum system the current/voltage characteristics can be asymmetric with respect to the sign of the bias voltage, thus demonstrating a sort of rectification. The effect is due to an asymmetric location of the energy levels of two molecular centers with respect to the Fermi levels of the source and drain electrodes. These energy levels come close to the resonance position under the application of a bias voltage of a certain sign, thus providing resonance electron tunneling, but they separate further for the other sign of the bias voltage, resulting in a negligible tunnel current. However this system in fact does not provide a real diode-like behavior. Although the energy levels are broadened due to the interaction with the metal electrodes the overlap of these broadened levels at first increases with the increase of the bias voltage, but then it reaches a maximum and decreases, resulting in a decrease of the tunnel current.

In this respect the electrochemical redox-mediated contacts are often considered to be better candidates for transistor-like elements. In particular, detailed theoretical [2–9] and experimental [10–20] studies of these contacts showed that they can demonstrate diode-like features, negative differential resistance, amplification of the current etc. Considerable attention was paid to the study of two-center electrochemical contacts [21–24]. In general the behavior of these contacts is similar to that with a single redox group. However the presence of two redox centers suggests a larger number of physical situations. Some of them were described in [24–26]. Although these works shed considerable light on the problem, a consistent theory able to describe the experimental data is still a challenge for researchers. Non-adiabatic sequential transitions were mainly considered in [24, 25]. The calculations of tunneling through the resonance states of the molecular groups at the electrodes [26] resulted in a maximum of the current as a function of the bias voltage, in contrast to an increase of the current up to a constant value obtained in similar calculations in [21]. The main experimental results of [22] are a sigmoidal curve for the current/bias voltage characteristics and a maximum of the current as a function of the overpotential in the neighborhood of the equilibrium electrode potential. The aim of the present

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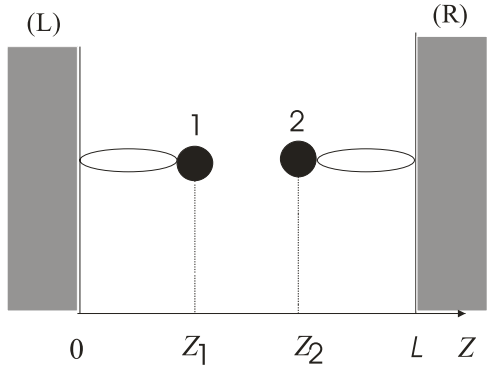


Figure 1. A scheme of the bridged electrochemical contact with two redox centers.

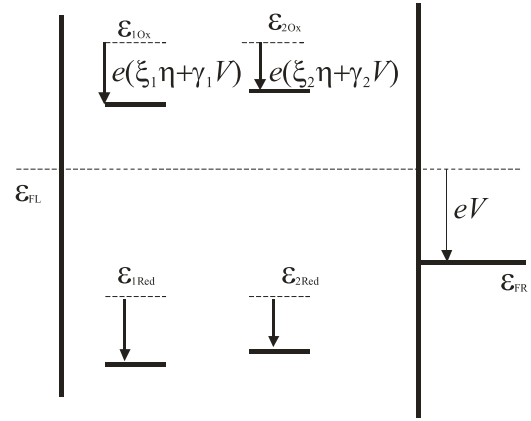


Figure 2. An energy scheme of the contact.

article is to study various physical mechanisms of electron transfer in such systems. These mechanisms involve the cases of weak interaction of the redox groups with each other and with the electrodes (totally non-adiabatic limit), weak interaction of the redox groups with each other (non-adiabatic transitions) and their strong interaction with the electrodes (adiabatic transitions), and other combinations of interactions. Some limiting cases discussed in previous publications will be treated in more detail, in particular with due account of the potential distribution in the tunneling gap. In addition other physical situations will be considered, in particular totally adiabatic transitions. We hope that analysis of various theoretical predictions will allow us to draw conclusions about the mechanism which operates under the experimental conditions of [21, 22].

The paper is organized as follows. The totally non-adiabatic limit is considered in section 2. The adiabatic transitions at the electrodes with the non-adiabatic electron exchange between the redox groups in the limit of small width of the electron energy levels are analyzed in section 3. The non-adiabatic transitions at the electrodes with the adiabatic electron exchange between the redox groups are considered in section 4. Section 5 involves the case of the totally adiabatic transitions. Discussions of the results of calculations and the concluding remarks are given in sections 6 and 7.

2. The model and the totally non-adiabatic limit (weak interaction of the redox groups with the electrodes and weak interaction between the groups)

The system under consideration consists of two plane metallic electrodes separated by a distance L in the electrolyte solution. Keeping in mind the system of [21, 22], we will restrict ourselves to the discussion of symmetric contacts, i.e. the electrodes are assumed to be made of the same metal. Two identical redox groups are placed in sequence symmetrically between the electrodes (figure 1). The redox groups may belong to one molecule or to two different molecules attached to the electrodes.

When the current through each electrode is zero (at equilibrium), the electrochemical potentials of both electrodes, μ_L and μ_R (or the Fermi levels, ε_{FL} and ε_{FR}), coincide and the equilibrium positions of the electron energy levels of the

oxidized and reduced forms of the redox groups are located symmetrically with respect to the Fermi levels (figure 2). The corresponding electrode potential φ_0 is the equilibrium potential. In general it may differ from the redox potential of the bridge groups [27]. The positions of the electron energy levels of the redox groups can be shifted by the variation of the electrode potentials. Two potentials may be varied independently in these systems, namely the overpotential η and bias voltage V . They will be defined as follows: $\eta = \varphi_0 - \varphi_L$ and $eV = \mu_L - \mu_R$ where φ_L is the electrode potential of the left electrode. Note that the cathode overpotential will be used throughout the paper.

In the totally non-adiabatic limit the kinetic equations method can be used for the calculation of the tunnel current. Under steady-state conditions the current through any cross section of the contact is the same. Therefore we may write the expression for the current, e.g., as follows:

$$j = e [C_{1Red}k_{12}C_{2Ox} - C_{2Red}k_{21}C_{1Ox}] \quad (1)$$

where k_{12} and k_{21} are the rate constants for the electron transfer between the groups 1 and 2, C_{1Red} and C_{2Red} are average occupations of the electron energy levels ε_1 and ε_2 , $C_{1Ox} = 1 - C_{1Red}$ and $C_{2Ox} = 1 - C_{2Red}$.

Average occupations are determined by the steady-state balance conditions [24]

$$k_{L1}(1 - C_{1Red}) + k_{21}C_{2Red}(1 - C_{1Red}) = k_{1L}C_{1Red} + k_{12}C_{1Red}(1 - C_{2Red}) \quad (2)$$

$$k_{2R}C_{2Red} + k_{21}C_{2Red}(1 - C_{1Red}) = k_{R2}(1 - C_{2Red}) + k_{12}C_{1Red}(1 - C_{2Red}) \quad (3)$$

where k_{L1} , k_{1L} , k_{R2} and k_{2R} are the rate constants for the electron exchange between the electrodes and corresponding redox centers. General expressions for the rate constants are given in appendix A. It should be noted that they take into account the fact that the electron energy levels in the metals are degenerate due to the existence of the electron spin (see [28]). It should also be noted that the average occupations are uniquely determined from the steady-state balance conditions in the case where the rate constants are independent of the average occupations. This means, in

particular, that the energy U_{12} of the Coulomb repulsion between electrons occupying the valence orbitals of groups 1 and 2 is neglected. This is a reasonable assumption in the case of small electron hybridization between the redox groups. In contrast, it is assumed that the Coulomb interactions U_{11} and U_{22} between the electrons which occupy the same valence orbital are infinitely large.

The rate constants and average occupations of the redox groups depend on the bias voltage and overpotential. In order to find these dependences we consider a narrow tunneling gap and neglect the influence of the bridge group on the potential distribution within the gap. Then as was shown in [29] the potential distribution may be described in this case within the framework of linear electrostatics even at large potentials ($\varphi > kT/e$) in view of the compensation of various effects. In planar geometry the potential distribution has the form

$$\Psi(z) = \gamma(z)[\varphi_L - \varphi_L^{\text{pzc}}] + \gamma(L-z)[\varphi_R - \varphi_R^{\text{pzc}}] \quad (4)$$

where pzc means the potential of zero charge (the potential where the charge of the electrode is zero) and

$$\begin{aligned} \gamma(z) &= \frac{\exp(z/L_D) - \exp(-z/L_D)}{\exp(L/L_D) - \exp(-L/L_D)} \\ &= \sinh(z/L_D) / \sinh(L/L_D). \end{aligned} \quad (5)$$

Here L_D is the Debye length in the electrolyte solution.

The rate constants in equations (2) and (3) to a considerable extent are determined by the corresponding free energies of transitions ΔF [27, 28]:

$$\begin{aligned} \Delta F_{L1} = F_1 - F_L &= \varepsilon_1 - \varepsilon_{FL} + \Delta F_{\text{sol}}^{(1)} + e[\varphi_L - \varphi_s] \\ &- e[\psi(z_1; \varphi_L - \varphi_L^{\text{pzc}}, \varphi_R - \varphi_R^{\text{pzc}}) - \varphi_s] \end{aligned} \quad (6)$$

$$\begin{aligned} \Delta F_{2R} = \varepsilon_{FR} - \varepsilon_2 - \Delta F_{\text{sol}}^{(2)} &- e[\varphi_R - \varphi_s] \\ &+ e[\psi(z_2; \varphi_L - \varphi_L^{\text{pzc}}, \varphi_R - \varphi_R^{\text{pzc}}) - \varphi_s] \end{aligned} \quad (7)$$

$$\begin{aligned} \Delta F_{12} = F_2 - F_1 = \varepsilon_2 - \varepsilon_1 + \Delta F_{\text{sol}}^{(2)} - \Delta F_{\text{sol}}^{(1)} &- e[\psi(z_2; \varphi_L - \varphi_L^{\text{pzc}}, \varphi_R - \varphi_R^{\text{pzc}}) - \varphi_s] \\ &+ e[\psi(z_1; \varphi_L - \varphi_L^{\text{pzc}}, \varphi_R - \varphi_R^{\text{pzc}}) - \varphi_s] \end{aligned} \quad (8)$$

where the Fermi energies ε_{FL} and ε_{FR} are counted from $-e\varphi_L$ and $-e\varphi_R$ respectively (φ_L and φ_R are Galvani potentials of the corresponding electrodes), ε_1 and ε_2 are the electron energies in the redox groups counted from $-e\varphi_s$. Here φ_s is the potential in the bulk of the solution which will be taken to be zero in what follows. $\Delta F_{\text{sol}}^{(i)}$ is the difference of the solvation free energies of the i th redox group in the reduced and oxidized states and $\psi(z_j; \varphi_L - \varphi_L^{\text{pzc}}, \varphi_R - \varphi_R^{\text{pzc}})$ is the potential at the site of the location z_j of the j th redox group. The latter depends on the Galvani potentials φ_L and φ_R and on the zero-charge potentials of the electrodes φ_L^{pzc} and φ_R^{pzc} .

In terms of the overpotential and bias voltage the free energies of transitions take the form [27]

$$\Delta F_{12} = F_2 - F_1 = e \left\{ [\xi_1 \eta + \gamma(z_1) V] - [\xi_2 \eta + \gamma(z_2) V] \right\} \quad (9)$$

$$\Delta F_{L1} = F_1 - F_L = -e [\xi_1 \eta + \gamma(z_1) V] + k_B T \ln 2 \quad (10)$$

$$\Delta F_{2R} = F_R - F_2 = e \left\{ \xi_2 \eta - [1 - \gamma(z_2)] V \right\} - k_B T \ln 2 \quad (11)$$

where

$$\xi_i = 1 - \gamma(z_k) - \gamma(L - z_k); \quad i = 1, 2. \quad (12)$$

Here z_1 and z_2 are the coordinates of the location of the groups 1 and 2 respectively. It follows from equation (5) that $\gamma(z_2) = \gamma(L - z_1)$ and $\gamma(z_1) = \gamma(L - z_2)$. Therefore we have

$$\xi_1 = \xi_2 = \xi = 1 - \gamma(z_1) - \gamma(z_2) = 1 - \gamma(z_1) - \gamma(L - z_1) \quad (13)$$

and

$$\Delta F_{12} = e [\gamma(z_1) - \gamma(z_2)] V = e [\gamma(z_1) - \gamma(L - z_1)] V, \quad (14)$$

i.e. the latter is independent of the overpotential.

The solution of equations (2) and (3) gives

$$C_{2\text{Red}} = \frac{k_{12} C_{1\text{Red}} + k_{R2}}{k_{2R} + k_{21} (1 - C_{1\text{Red}}) + k_{12} C_{1\text{Red}} + k_{R2}} \quad (15)$$

$$C_{1\text{Red}} = \frac{\sqrt{b^2 + 4ad} - b}{2a}. \quad (16)$$

It can be shown that $0 < C_{i\text{Red}} < 1$, as it should be. The expressions for the rate constants and the quantities a , b and d are given in appendix A.

Equations (1), (15) and (16) allow calculating the current as a function of the overpotential and bias voltage at arbitrary values of physical parameters. It is clear however that when the rate constants for the electron exchange between the redox groups and electrodes are sufficiently large, the equilibrium at the electrodes will exist also at non-zero current. A simpler expression for the current can be obtained in this case. In this limit the rate determining step is the electron transfer between groups 1 and 2. The overpotential dependence of the current is determined in this case by that of the average occupations $C_{1\text{Red}}$ and $C_{2\text{Red}}$. The latter can be found from the equilibrium equations as follows:

$$C_{1\text{Red}} = \frac{k_{L1}}{k_{L1} + k_{1L}} = \frac{1}{1 + \exp\left(-\frac{e\xi\eta + e\gamma(z_1)V}{k_B T}\right)} \quad (17)$$

$$C_{2\text{Red}} = \frac{k_{R2}}{k_{R2} + k_{2R}} = \frac{1}{1 + \exp\left(-\frac{e\xi\eta - e[1 - \gamma(z_2)]V}{k_B T}\right)}. \quad (18)$$

At small values of the bias voltage ($eV \ll E_{12}$, where E_{12} is the medium reorganization energy) the rate constant k_{12} is approximately equal to

$$k_{12} \approx k_{12}^0 \exp\left\{-\frac{e[\gamma(z_1) - \gamma(z_2)]V}{2k_B T}\right\} \quad (19)$$

where

$$k_{12}^0 = k_0 \exp\left(-\frac{E_{12}}{4k_B T}\right) \quad (20)$$

and k_0 is the pre-exponential factor.

Using equations (19) and (20) in equation (1) we get

$$j \approx ek_0 e^{-\frac{E_{12}}{4k_B T}} \frac{\text{sh} \frac{eV}{2k_B T}}{2 \text{ch} \frac{e\xi\eta + e\gamma(z_1)V}{2k_B T} \text{ch} \frac{e\xi\eta - e[1 - \gamma(z_2)]V}{2k_B T}}. \quad (21)$$

It may be easily seen that at fixed value of V the current/overpotential dependence has a maximum at η_{\max} equal to

$$\eta_{\max} = \frac{1}{2}V. \quad (22)$$

Unlike the case considered in [21], the width of the current/overpotential maximum is independent of the medium reorganization energy. The width equals $2kT \ln\{\text{ch}\frac{e\mu V}{kT} + 2 + [(\text{ch}\frac{e\mu V}{kT} + 2)^2 - 1]^{1/2}\}/(e\xi)$ and increases from $2kT \ln(3 + 8^{1/2})/(e\xi) \approx 3.5kT/(e\xi)$ for $e\mu V/kT \ll 1$ to $2 \mu V$ for $e\mu V/kT \gg 1$ where $\mu = 0.5[1 + \gamma(z_1) - \gamma(z_2)]$.

3. Strong interaction of the redox groups with the electrodes and weak interaction between the groups

If the interaction of the redox groups with the electrodes is strong, the reactions of the electron exchange at each electrode are adiabatic. At the same time the interactions of the redox groups with each other may be either weak or strong. If the electron interaction V_{12} between the redox groups is much smaller than or of the order of $k_B T$, the electron states of the redox groups represent a sort of resonance at corresponding electrodes with the densities of electron states

$$\rho_{M_i}(\varepsilon) = \frac{1}{\pi} \frac{\Delta_{M_i}}{(\varepsilon - \varepsilon_i)^2 + \Delta_{M_i}^2}; \quad i = 1, 2; \quad (23)$$

M1 = L, M2 = R

where ε_i is the position of the resonance and Δ_{M_i} is the width of the resonance determined by the interaction of the redox group with the corresponding electrode. For the sake of simplicity we accept a spinless approximation in this section. Generalization to account for the electron spin is straightforward.

The positions of these resonances ε_i depend on the coordinates of vibrational modes q_k . For the sake of simplicity we shall assume that the electron state of each redox group interacts with different independent effective vibrational modes, q_1 and q_2 . If the widths of these resonances are small as compared to the energy window between the Fermi levels $eV \gg k_B T$, the contribution to the current due to the overlap of the tails of the distributions of the electron density of states may be neglected, and the whole process may be considered as a sequential stepwise transition with adiabatic or non-adiabatic electron transfer between the redox groups. This approach was used in [24]. If however the widths of the resonances are sufficiently large, the electric current may be considered as a result of direct tunneling between these resonances:

$$j = eT_{12} \frac{\Delta_{L1} \Delta_{R2}}{Z_1 Z_2} \frac{1}{\pi^2} \int dq_1 dq_2 \exp \left\{ -\frac{U_1(q_1) + U_2(q_2)}{k_B T} \right\} \times \int d\varepsilon [f_L(\varepsilon) - f_R(\varepsilon)] \times \frac{1}{\left\{ [\varepsilon - \varepsilon_1(q_1)]^2 + \Delta_{L1}^2 \right\} \left\{ [\varepsilon - \varepsilon_2(q_2)]^2 + \Delta_{R2}^2 \right\}}$$

where $T_{12} = \frac{2\pi}{\hbar} |V_{12}|^2$ is the transmission probability, Z_i are the normalization factors for the configuration integrals over

coordinates of vibrational modes q_i , f_L and f_R are the Fermi distribution functions for the left and the right electrodes, and $U_i(q_k)$ are the free energy surfaces for the vibrational modes.

Unlike the approach of [21], equation (24) describes tunneling between individual energy levels rather than between the redox groups characterized by some average occupations. In this respect equation (24) is closer to the approach used in [26]. It differs however from the latter in the fact that this equation takes into account both reduced and oxidized states of the redox groups whereas only a reduced state of the group 1 and an oxidized state of the group 2 was considered in [26]. In our case this is manifested in the double-well shape of the free energy surfaces. In addition we take into account the potential dependence of the positions of the two resonances which, in its turn, affects strongly the dependence of the tunnel current on the bias voltage.

Assuming linear dependence of the electron energy levels on the vibrational coordinates

$$\varepsilon_i(q_i) = \varepsilon_i^0 - \hbar\omega g_i q_i \quad (25)$$

and introducing new variables

$$Q_i = \hbar\omega g_i q_i \quad (26)$$

we write U_i in the form

$$U_i(Q_i) = \frac{1}{4E_{ri}} Q_i^2 - \frac{1}{2} Q_i - \frac{1}{\pi} \left\{ \left(\varepsilon_{FM_i} - \varepsilon_i^0 + e\xi\eta + e\gamma(z_i) \times V + Q_i \right) \arctan \frac{\varepsilon_{FM_i} - \varepsilon_i^0 + e\xi\eta + e\gamma(z_i)V + Q_i}{\Delta_{M_i}} - \frac{\Delta_{M_i}}{2} \ln \frac{(\varepsilon_{FM_i} - \varepsilon_i^0 + e\xi\eta + e\gamma(z_i)V + Q_i)^2 + \Delta_{M_i}^2}{(\varepsilon_{FM_i} - \varepsilon_i^0 + e\xi\eta + e\gamma(z_i)V)^2 + \Delta_{M_i}^2} \right\} \quad (27)$$

where M1 = L, M2 = R, $E_{ri} = \hbar\omega g_i^2/2$ are the reorganization energies of vibrational modes, the Fermi distribution functions were replaced by the stepwise functions and a term independent of the coordinates Q_i is omitted. Equations (24)–(27) allow calculating the dependence of the current on the bias voltage and overpotential with due account of equation (13) and the following relationships:

$$\varepsilon_i^0 - \varepsilon_{FL} = E_{ri} - e\xi\eta - e\gamma(z_i)V \quad (28)$$

$$\varepsilon_2^0 - \varepsilon_{FR} = E_{r2} - e\xi\eta + e(1 - \gamma(z_2))V.$$

It should be emphasized that tunneling occurs from the occupied states of the left resonance to the free states of the right one.

4. Strong interaction between the redox groups and weak interaction of the groups with the electrodes

When the redox groups are linked to the electrodes via long chain molecules one may assume that the interaction of these groups with the electrodes is weak. At the same time the interaction between the groups can be strong in view of their proximity to each other. This physical situation may be

realistic for the experimental setup of [22]. Depending on the nature of the redox groups one may distinguish several possible cases as concerns the occupation of these groups by the electrons. Even each individual group may have in principle more than one valence energy level. However, keeping in mind the experimental system of [22], we will assume that each group considered separately has only one valence level. Moreover we will assume that in view of the proximity of two groups only one electron may be located in the pair of redox groups. This is a limit of very large Coulomb interactions U_{12} , U_{11} and U_{22} between the electrons. It implies that the spin of the electrons has no influence on the energy of one-electron states of the system and the spinless approximation is applicable for the calculation of one-electron energy levels of the complex consisting of two groups. The corresponding spinless Hamiltonian describing this complex with due account of its interaction with molecular environment has the form

$$H = H_{12} + H_{\text{ph}}(p_k, q_k) + H_{\text{int}}(n_i, q_k) \quad (29)$$

$$H_{12} = \varepsilon_1^0 n_1 + \varepsilon_2^0 n_2 + V_{12} c_1^\dagger c_2 + V_{12}^* c_2^\dagger c_1 \quad (30)$$

where c_i^\dagger , c_i are the creation and annihilation operators for the valence orbital $|i\rangle$ of the i th redox group having the energy ε_i^0 (see the first line in equation (28)), $n_i = c_i^\dagger c_i$ is the occupation number operator, H_{ph} is the Hamiltonian of the molecular environment (phonons) with p_k and q_k as the dimensionless momenta and coordinates of slow vibrational modes, and H_{int} describes the interaction of two subsystems (see appendix B).

In the case of strong interaction of the redox groups the eigenvalues

$$\begin{aligned} E_{\text{I}}^0 &= \left\{ \varepsilon_1^0 + \varepsilon_2^0 - \left[(\varepsilon_1^0 - \varepsilon_2^0)^2 + 4 |V_{12}|^2 \right]^{1/2} \right\} / 2; \\ E_{\text{II}}^0 &= \left\{ \varepsilon_1^0 + \varepsilon_2^0 + \left[(\varepsilon_1^0 - \varepsilon_2^0)^2 + 4 |V_{12}|^2 \right]^{1/2} \right\} / 2, \end{aligned} \quad (31)$$

and valence orbitals

$$|\text{I}\rangle = \cos \theta |1\rangle + \sin \theta |2\rangle; \quad |\text{II}\rangle = -\sin \theta |1\rangle + \cos \theta |2\rangle, \quad (32)$$

are more appropriate for the description of the electron states of the complex, where

$$\cos \theta = \frac{\left\{ \left[(\varepsilon_1^0 - \varepsilon_2^0)^2 + 4 |V_{12}|^2 \right]^{1/2} - (\varepsilon_1^0 - \varepsilon_2^0) \right\}}{2^{1/2} \left[(\varepsilon_1^0 - \varepsilon_2^0)^2 + 4 |V_{12}|^2 \right]^{1/2}}. \quad (33)$$

Then the average occupation numbers $\langle n_1 \rangle$ and $\langle n_2 \rangle$ of the redox groups in the ground (bonding) state of the redox complex equal $\cos^2 \theta$ and $\sin^2 \theta$, respectively.

Separating the motion of the electrons and molecular environment with the use of the Born–Oppenheimer approximation we end up with the adiabatic free energy surfaces (AFES) $U_{\text{ad},m}(q_k)$ ($m = \text{I}, \text{II}$) for the ground and first excited electron states. In general the AFES of the ground state may have either two potential wells or a single one [30]. In the case of two potential wells the kinetic scheme for the calculation of the tunnel current involves a number of transitions between the

electrodes and various electron states of the redox complex, including both the ground state and the excited one. The normal coordinates and frequencies of vibrational modes are in general different for different electron states of the redox complex. This makes the calculation of the tunnel current rather onerous (see, e.g., [24] where only $U_{\text{ad},I}(q_k)$ was taken into account approximately).

The situation is simpler in the case when the AFES of the ground state has only one potential well. This takes place if $|V_{12}| > 0.5E_{12}$ where E_{12} is the reorganization energy for the electron transition between two redox groups (see appendix B). Spacing of the electron energy levels in this case is always large and the contribution of the excited (antibonding) state may be neglected as having the order of $\exp(-|V_{12}|/k_B T)$ with respect to the contribution of the ground state (we recall that in the limit $U_{12} \rightarrow \infty$ the redox groups can have only one electron which occupies the bonding or antibonding level). In this limit the problem is similar to that for a single redox group confined in the tunneling gap and the expression for the current has the form [28]

$$j = e \frac{k_{\text{LI}} k_{\text{IR}} - k_{\text{IL}} k_{\text{RI}}}{k_{\text{LI}} + k_{\text{IL}} + k_{\text{RI}} + k_{\text{IR}}} \quad (34)$$

It should be noted that although the bridge complex was treated within the spinless model, equation (34) takes into account the electron spin effect in the approximation of infinite Coulomb repulsion (see appendix A).

The calculation of the rate constants in general may still be rather complicated. We can use two approaches in this case. The first one is to start from the bridge group considered as the single bridge molecule having the bonding state $|\text{I}\rangle$ coupled to free phonon modes. Then the tunnel current is calculated using the usual rate constants for the non-adiabatic electron transitions between the electrodes and the valence level E_{I}^0 . Within the second approach the one-electron bridge molecule is characterized by the diabatic free energy surface which is obtained from the expression for $U_{\text{ad},I}(q_k)$ considered in the harmonic approximation near the single potential well. In this approach the phonon frequencies and the normal coordinates differ from those for the free phonons. Only the first approach is considered in what follows.

The rate constants in equation (34) depend on the free energies of transition $\Delta F_{\text{IL}} = \Delta F_{\text{IL}} + \varepsilon_1^0 - E_{\text{I}}^0 - \delta F_{\text{solv}}$ and $\Delta F_{\text{IR}} = \Delta F_{\text{IR}} + \varepsilon_2^0 - E_{\text{I}}^0 - \delta F_{\text{solv}}$ where $\delta F_{\text{solv}} = \Delta F_{\text{solvl}} - \Delta F_{\text{solv}}$. Here ΔF_{solvl} is the difference of the solvation free energies of the redox complex in the reduced and oxidized states and $\Delta F_{\text{solv}} = \Delta F_{\text{solvl}}^{(1)} = \Delta F_{\text{solvl}}^{(2)}$ for the symmetric contact. Using equations (10)–(13) and (31) one obtains that

$$\begin{aligned} \Delta F_{\text{IL}}^{(2)} &= e\xi\eta + [\gamma(z_1) + \gamma(z_2)]eV/2 \\ &+ \left\{ [\gamma(z_1) - \gamma(z_2)]^2 (eV)^2 + 4V_{12}^2 \right\}^{1/2} / 2 - \delta F_{\text{solv}} \end{aligned} \quad (35)$$

$$\begin{aligned} \Delta F_{\text{IR}}^{(2)} &= e\xi\eta + [\gamma(z_1) + \gamma(z_2) - 2]eV/2 \\ &+ \left\{ [\gamma(z_1) - \gamma(z_2)]^2 (eV)^2 + 4V_{12}^2 \right\}^{1/2} / 2 - \delta F_{\text{solv}} \end{aligned} \quad (36)$$

where $\Delta F_{\text{IL}}^{(2)} = \Delta F_{\text{IL}} + k_{\text{B}}T \ln 2$ and $\Delta F_{\text{IR}}^{(2)} = \Delta F_{\text{IR}} + k_{\text{B}}T \ln 2$. In view of the symmetry of the contact, $z_1 = L - z_2$, and the energy levels of the oxidized and reduced forms of the redox groups are located symmetrically with respect to Fermi levels so that equation (12) holds here too. It follows from equations (35) and (36) that $\Delta F_{\text{IL}}^{(2)} = \Delta F_{\text{IR}}^{(2)} = V_{12} - \delta F_{\text{solv}}$ when $V = \eta = 0$. Therefore the equilibrium potential should be redefined in this case: $e\varphi_0 \rightarrow e\varphi_0 + (V_{12} - \delta F_{\text{solv}})/\xi$. Then we have

$$\Delta F_{\text{IL}}^{(2)} = e\xi\eta + \frac{\cosh(\delta/2L_{\text{D}})}{\cosh(L/2L_{\text{D}})}eV/2 + A/2 - V_{12} \quad (37)$$

where $\delta = z_2 - z_1$ and

$$A = \left\{ \left[\frac{\sinh(\delta/2L_{\text{D}})}{\sinh(L/2L_{\text{D}})} \right]^2 (eV)^2 + 4V_{12}^2 \right\}^{1/2}. \quad (38)$$

The rate constants in equation (34) are obtained from equations (A.11)–(A.14) with the substitution of ΔF_{IL} for ΔF_{IL} , ΔF_{IR} for ΔF_{IR} , $k_{\text{L}}\langle n_1 \rangle$ for k_{L} , $k_{\text{R}}\langle n_2 \rangle$ for k_{R} , I_{IL} for I_{L} and I_{IR} for I_{R} , E_{r} for E_{L} and E_{R} . Here E_{r} is the solvent reorganization energy in the case when the redox complex is in the ground state. The expression for the tunneling current takes finally the form

$$\begin{aligned} j = j_{\text{max}} \frac{4V_{12}(I_{\text{IL}}I_{\text{IR}})^{1/2}}{A} \left(\frac{2k_{\text{B}}T}{\pi E_{\text{r}}} \right)^{1/2} \\ \times \left\{ \exp(-E_{\text{r}}/4k_{\text{B}}T) \sinh(eV/2k_{\text{B}}T) \exp \left\{ - \left[(\Delta F_{\text{IL}})^2 \right. \right. \right. \\ \left. \left. \left. + (\Delta F_{\text{IL}} - eV)^2 \right] / 8E_{\text{r}}k_{\text{B}}T \right\} \right\} \left\{ \exp(eV/4k_{\text{B}}T) \right. \\ \left. \times \cosh(a + e\eta_V/2k_{\text{B}}T) + \exp(-eV/4k_{\text{B}}T) \right. \\ \left. \times \cosh(a - e\eta_V/2k_{\text{B}}T) \right\}^{-1} \quad (39) \end{aligned}$$

where $j_{\text{max}} = ek(\pi E_{\text{r}}/k_{\text{B}}T)^{1/2}/4$ is the tunneling current for the spinless model at $z_1 = z_2$ and $|V| \rightarrow \infty$ (here $k_{\text{L}} = k_{\text{R}} = k$ for the symmetric contact), $e\eta_V = \Delta F_{\text{IL}}^{(2)} - eV/2$,

$$a = \frac{1}{2} \ln \left(\frac{I_{\text{IL}} \cos^2 \theta}{I_{\text{IR}} \sin^2 \theta} \right) - \frac{(\Delta F_{\text{IL}})^2}{8E_{\text{r}}k_{\text{B}}T} + \frac{(\Delta F_{\text{IL}} - eV)^2}{8E_{\text{r}}k_{\text{B}}T} \quad (40)$$

and equations (A.15) and (A.16) were used for the calculation of j_{max} . If $|V| \rightarrow \infty$, j tends to $j_{\text{lim}}(V) = 8j_{\text{max}}V_{12}^2/[A^2(\cos^2 \theta + 1)]$.

When AFES $U_{\text{ad},i}$ has only one potential well (adsorption state) we have $\langle n_1 \rangle \approx \langle n_2 \rangle \approx 1/2$ (see appendix B). The reorganization energy E_{r} can be estimated then as $\langle n_1 \rangle^2 E_{\text{L}} + \langle n_2 \rangle^2 E_{\text{R}} + 2\langle n_1 \rangle \langle n_2 \rangle E_{\text{mix}} = E_{12}$ where $E_{\text{L}} = E_{\text{R}} = E_{\text{mix}} = E_{12}$ (see appendix B).

The current of equation (39) has a maximum at some η_{max} which is a rather complicated function of V , V_{12} , δ/L and L_{D}/L . However if eV , $|\Delta F_{\text{IL}}| \ll E_{\text{r}}$, one obtains that the maximum is located at $\eta_V \approx 0$ so that equation (37) yields

$$\eta_{\text{max}} = \left\{ \left[1 - \frac{\cosh(\delta/2L_{\text{D}})}{\cosh(L/2L_{\text{D}})} \right] eV/2 - A/2 + V_{12} \right\} (e\xi)^{-1}. \quad (41)$$

The width of the curve $j(\eta)$ at half-maximum equals $4k_{\text{B}}T \operatorname{arccosh}(2)/e$ in this case.

5. Totally adiabatic transitions

If the interactions both between the redox groups and between the redox groups and the electrodes are strong, the Born–Oppenheimer approximation can be used for the whole system involving the electrodes and the redox groups. Therefore, one can calculate values of the average electron occupation numbers of the valence orbital of the redox groups and the value of the tunneling current at fixed values of the energies $\varepsilon_1(q_k)$ and $\varepsilon_2(q_k)$. We start from the case when U_{11} and U_{22} are very large but the energy U_{12} is neglected. In contrast to the case considered in the previous section, this implies that two electrons may be located in the pair of redox groups. The spinless model can be applied in this case for the calculation not only for one-electron states (as in the previous section) but also for the many-electron properties of the whole electronic subsystem. Using the non-equilibrium Green function method as was done in [31] for the one-level bridge molecule one obtains that

$$\begin{aligned} \langle n_1 \rangle(q_k) &= \frac{1}{\pi} \\ &\times \int_{-\infty}^{\infty} \frac{\{\Delta_{\text{L}}f_{\text{L}}(\varepsilon)[(\varepsilon - \varepsilon_2(q_k))^2 + \Delta_{\text{R}}^2] + \Delta_{\text{R}}f_{\text{R}}(\varepsilon)|V_{12}|^2\} d\varepsilon}{Z(\varepsilon)} \quad (42) \end{aligned}$$

$$\begin{aligned} \langle n_2 \rangle(q_k) &= \frac{1}{\pi} \\ &\times \int_{-\infty}^{\infty} \frac{\{\Delta_{\text{R}}f_{\text{R}}(\varepsilon)[(\varepsilon - \varepsilon_1(q_k))^2 + \Delta_{\text{L}}^2] + \Delta_{\text{L}}f_{\text{L}}(\varepsilon)|V_{12}|^2\} d\varepsilon}{Z(\varepsilon)} \quad (43) \end{aligned}$$

$$j(q_k) = \frac{2e}{\pi\hbar} \Delta_{\text{L}}\Delta_{\text{R}}|V_{12}|^2 \int_{-\infty}^{\infty} \frac{[f_{\text{L}}(\varepsilon) - f_{\text{R}}(\varepsilon)]}{Z(\varepsilon)} d\varepsilon \quad (44)$$

where

$$\begin{aligned} Z(\varepsilon) &= (\varepsilon - \varepsilon_1(q_k))^2(\varepsilon - \varepsilon_2(q_k))^2 + (\varepsilon - \varepsilon_1(q_k))^2\Delta_{\text{R}}^2 \\ &+ (\varepsilon - \varepsilon_2(q_k))^2\Delta_{\text{L}}^2 - 2|V_{12}|^2(\varepsilon - \varepsilon_1(q_k))(\varepsilon - \varepsilon_2(q_k)) \\ &+ (\Delta_{\text{L}}\Delta_{\text{R}} + |V_{12}|^2)^2 \quad (45) \end{aligned}$$

and

$$\varepsilon_i(q_k) = \varepsilon_i^0 - \sum_k \gamma_{ik}q_k \quad (46)$$

where γ_{ik} are coupling constants. Equation (44) was also obtained in [26] with the use of the equilibrium Green function method.

As was shown in [31], the well defined value $E(q_k)$ of the lowest electronic energy exists at the steady state for the one-level bridge molecule. It was also shown that $\langle n_a \rangle(q_k) = \partial E(q_k)/\partial \varepsilon_a(q_k)$ where $\varepsilon_a(q_k)$ is the energy of the valence orbital and $\langle n_a \rangle(q_k)$ is its occupation number. Therefore, AFES $U_{\text{ad}}(q_k)$ can be defined for the total system so that the tunnel current can be calculated as the thermal Boltzmann average of $j(q_k)$ over AFES [31].

Generalizing the results of [32] to the two-level system, it can be shown that the expression for the effective force F_k acting on the k th phonon mode due to the interaction of phonons with the valence electrons has the form

$$F_k = \sum_i \gamma_{ik} \langle n_i \rangle. \quad (47)$$

If the coupling constants γ_{ik} have arbitrary values (i.e., γ_{1k} is not proportional to γ_{2k}), then it can be shown that AFES $U_{ad}(q_k)$ resulting in the forces F_k ($F_k = -\partial U_{ad}(q_k)/\partial q_k$) for the two-level system exists only in the case when the derivatives $\partial\langle n_1\rangle(q_k)/\partial\varepsilon_2(q_k)$ and $\partial\langle n_2\rangle(q_k)/\partial\varepsilon_1(q_k)$ are equal to each other. However, these derivatives are not equal in the general case for $V_{12} \neq 0$:

$$\frac{\partial\langle n_1\rangle(q_k)}{\partial\varepsilon_2} - \frac{\partial\langle n_2\rangle(q_k)}{\partial\varepsilon_1} = 4\Delta_L\Delta_R|V_{12}|^2 \times \int_{-\infty}^{\infty} \frac{[f_L(\varepsilon) - f_R(\varepsilon)][\Delta_L(\varepsilon - \varepsilon_2(q_k)) + \Delta_R(\varepsilon - \varepsilon_1(q_k))]}{Z^2(\varepsilon)} d\varepsilon. \quad (48)$$

Thus, there is no function $E(q_k)$ which produces the occupation numbers $\langle n_1\rangle(q_k)$ and $\langle n_2\rangle(q_k)$ with the aid of equations $\langle n_1\rangle(q_k) = \partial E(q_k)/\partial\varepsilon_1(q_k)$ and $\langle n_2\rangle(q_k) = \partial E(q_k)/\partial\varepsilon_2(q_k)$ in the non-equilibrium case. The reason is as follows. When $\Delta_L = \Delta_R = 0$ (i.e., for the two-site system) we have two AFES $U_{ad,I}(q_k)$ and $U_{ad,II}(q_k)$. Only the lowest AFES is used for the calculations of the rate constant of the adiabatic electrochemical electron transfer reaction [33]. When Δ_L and Δ_R are non-zero, two adiabatic states of the two-site system are mixed which results in the absence of the AFES in the non-equilibrium case. At equilibrium, $f_L(\varepsilon) = f_R(\varepsilon)$, so the rhs of equation (48) equals zero.

If V_{12} tends to zero, the rhs of equation (48) also tends to zero. Then two AFES U_1 and U_2 can be defined as was done in section 3 whereas equation (24) can be obtained with the use of equations (44) and (45) in the limit $V_{12} \rightarrow 0$. In the opposite limit when V_{12} is large, the rhs of equation (48) tends to zero again. This case corresponding to the adiabatic electron transitions between the levels 1 and 2 with the rate constant determined by AFES $U_{ad,I}(q_k)$ (equation (B.8)) was considered approximately in [24].

When V_{12} takes arbitrary values, a particular case $\gamma_{2k} = C\gamma_{1k}$ (where C is a constant) is of interest because in this case the single effective phonon coordinate $q \sim \sum \gamma_{ik}q_k$ can be introduced. Then $\varepsilon_i(q) = \varepsilon_i^0 - \gamma_{i0}q$ where the new coupling constants γ_{10} and γ_{20} are related by the equation $\gamma_{20} = C\gamma_{10}$, and AFES

$$U_{ad}(q_k) = \frac{\hbar\omega}{2}q^2 - \gamma_{10} \int_0^q \langle n_1\rangle(q')dq' - \gamma_{20} \int_0^q \langle n_2\rangle(q')dq' \quad (49)$$

exists which produces the effective force F_k . However, in this particular case the derivatives $\partial\langle n_1\rangle(q_k)/\partial\varepsilon_2(q_k)$ and $\partial\langle n_2\rangle(q_k)/\partial\varepsilon_1(q_k)$ are still not equal so the equations $\langle n_i\rangle(q_k) = \partial U_{ad}(q_k)/\partial\varepsilon_i$ are not yet fulfilled in the non-equilibrium case.

When the Coulomb interaction U_{12} is large, we consider the case $V_{12} > 0.5E_{12}$ and, as in the previous section, take into account only the lowest state E_1^0 . Then the method of [31] of the calculation of the tunnel current in the totally adiabatic regime for the one-level bridge molecule can be used with the substitution of E_1^0 for ε_a^0 in the corresponding equations of [31].

6. Discussion

The results presented in the foregoing sections allow obtaining two major types of the current/voltage dependences, namely

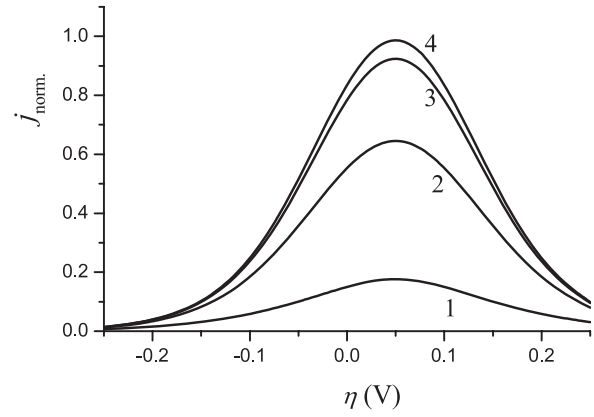


Figure 3. Dependence of the tunnel current on the overpotential according to equations (1)–(3). The current is normalized to the value at the maximum of the curve (4). Curve (4) is calculated with the use of approximate equation (21). $eV/k_B T = 4$, $z_1/L = 0.25$, $L_D/L = 0.3$, $E_r/k_B T = 20$. $k_L/k_0 = k_R/k_0 = 0.001$ (1); 0.1 (2); 1 (3).

the dependence of the current on the overpotential at fixed bias voltage and the dependence of the current on the bias voltage at fixed overpotential. At small bias voltage practically all limiting mechanisms considered above result in a current/overpotential characteristic with a maximum in the vicinity of the equilibrium potential (it is shifted from the equilibrium potential by $(\gamma - 0.5)eV/\xi$). The main difference is in the absolute values of the current and in the width of the maximum which depends on $k_B T$ and ξ for weak interaction with the electrodes and also on the width of the electron energy levels of the redox groups for the case of strong interaction with the electrodes. Room temperature is considered in what follows ($k_B T = 0.025$ eV).

Figures 3, 4(a) and (b) show the dependence of the current on the overpotential for the totally non-adiabatic case. The shape of the current/overpotential curve depends on the rate constants of the electron exchange with the electrodes. The higher the rate constants, the closer the curve is to the limiting curve corresponding to the equilibrium at the electrodes (see curves (3) and (4) of figure 3). Figure 4(a) shows the $j(\eta)$ dependence calculated according to approximate equation (21) which corresponds to the limiting case of equilibrium at electrodes. The position of the maximum of the current is independent of the position of the redox groups within the tunneling gap as it should be for the symmetric contact in this limit. The value of the current at the point of maximum depends on their position via the corresponding dependence of the values of $\gamma(z_1)$ and $\gamma(z_2)$ (figure 4(a)). The width of the maximum strongly depends on the electrolyte concentration and increases with the decrease of the latter (figure 4(b)). The dependence of the current on the bias voltage for this mechanism demonstrates a monotonic increase of the current in the interval of absolute values of the bias voltage not exceeding the reorganization energy for the electron transfer between the redox groups (figure 5). The $j(V)$ curve has no tendency to saturation.

For the second mechanism when the interaction between the groups is still weak but coupling with the metals is strong

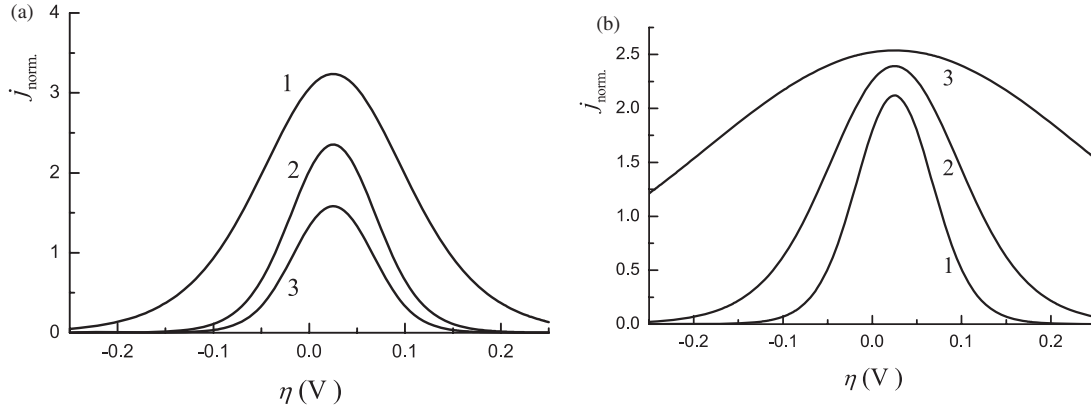


Figure 4. Dependence of the tunnel current $j_{\text{norm.}} = 2j/[ek_0 \exp(-E_{12}/4k_B T)]$ on the overpotential according to approximate equation (21). $eV/k_B T = 2$, $E_r/k_B T = 20$. (a) $L_D/L = 0.3$. $z_1/L = 0.1$ (1); 0.25 (2); 0.45 (3). (b) $z_1/L = 0.3$. $L_D/L = 0.3$ (1); 0.5 (2); 1 (3).

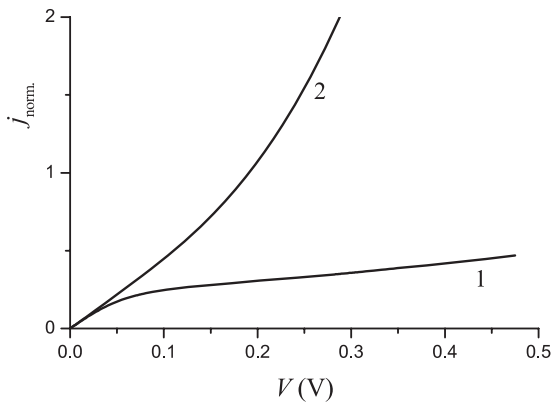


Figure 5. Dependence of the tunnel current on the bias voltage according to equations (1)–(3). $j_{\text{norm.}} = (j/k_0)10^7$. $\eta = 0$, $z_1/L = 0.15$, $E_r/k_B T = 20$, $k_L/k_0 = k_R/k_0 = 5$. $L_D/L = 0.1$ (1); 0.3 (2).

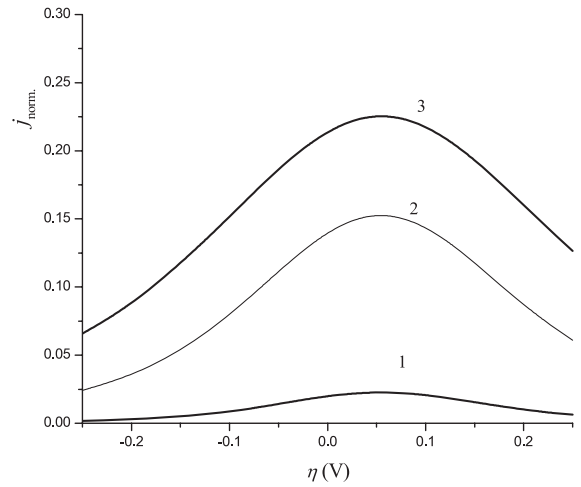


Figure 6. Dependence of the tunnel current on the overpotential at different values of the widths of the energy levels in the case of strong coupling with electrodes and weak coupling between the groups. $eV = 0.2E_r$, $z_1/L = 0.25$, $L_D/L = 0.3$, $E_r = 0.5$ eV. $\Delta = 0.1E_r$ (1); $\Delta = 0.3E_r$ (2); $\Delta = 0.5E_r$ (3). The current is normalized to $e2\pi V_{12}^2/\hbar E_r$.

the maximum of the $j(\eta)$ dependence is located in the same region as in figures 3 and 4. The width of the maximum depends significantly on Δ (figure 6). The larger Δ , the broader the maximum.

The dependences of the tunnel current on the bias voltage at $\eta = 0$ and different values of E_r , z_1 , L_D and Δ are shown in figures 7(a)–(c). Like for the totally non-adiabatic case, the dependence on the bias voltage is monotonically increasing at values of the bias voltage that are not large (figure 7(a)) and reaches a maximum value at $V = V_{\text{max}}$. Only for $E_r = 0.2$ eV and $L_D/L = 0.1$ does it have a tendency to saturation in the region $V \leq 0.5$ V (see figure 7(b)).

The results presented in figures 7(a) and (b) can be rationalized using the following simple approach. In a certain approximation (e.g., the neglect of Δ) the densities of the electronic states $\rho_{M_i}(\varepsilon)$ (see equation (23)) averaged over the free energy surfaces $U_i(q_k)$ (equations (24) and (27)) coincide with the electronic densities of the reduced and oxidized forms of the redox groups 1 and 2, respectively, i.e., $\rho_1(\varepsilon) \approx \exp\{-[\varepsilon + E_r + e\gamma(z_1)V]^2/(4E_r k_B T)\}/(4E_r k_B T)^{1/2}$ and $\rho_2(\varepsilon) \approx \exp\{-[\varepsilon - E_r + e\gamma(z_2)V]^2/(4E_r k_B T)\}/(4E_r k_B T)^{1/2}$. Then, as in [21], the current is proportional to $\int_{-eV}^0 \rho(\varepsilon) d\varepsilon$

where $\rho(\varepsilon) = \rho_1(\varepsilon)\rho_2(\varepsilon)$. However, in contrast to the case for [21], it is important that $\rho(\varepsilon)$ depends on V :

$$\rho(\varepsilon) = \frac{1}{4\pi E_r k_B T} \exp\left[-\frac{(E_r - eD\gamma V/2)^2}{2E_r k_B T}\right] \times \exp\left[-\frac{(\varepsilon + eS\gamma V/2)^2}{2E_r k_B T}\right] \quad (50)$$

where $D\gamma = \gamma(z_2) - \gamma(z_1)$ and $S\gamma = \gamma(z_2) + \gamma(z_1)$. The product of the first factor and the first exponential function in the rhs of equation (50) equals the maximum value ρ_{max} of $\rho(\varepsilon)$ which depends essentially on $D\gamma$ and V . The second exponential function in the rhs of equation (50) shows that the position of the maximum shifts with the change of the bias voltage. The magnitude of this shift is proportional to $S\gamma$. Since $\gamma(z_2) > \gamma(z_1)$, the valence level ε_2^0 approaches the level ε_1^0 with the increase of the bias voltage in the region $V < V_{\text{max}}$. Therefore, the tunnel current also increases due to the increase of the overlap of the densities of states $\rho_1(\varepsilon)$ and $\rho_2(\varepsilon)$. Then,

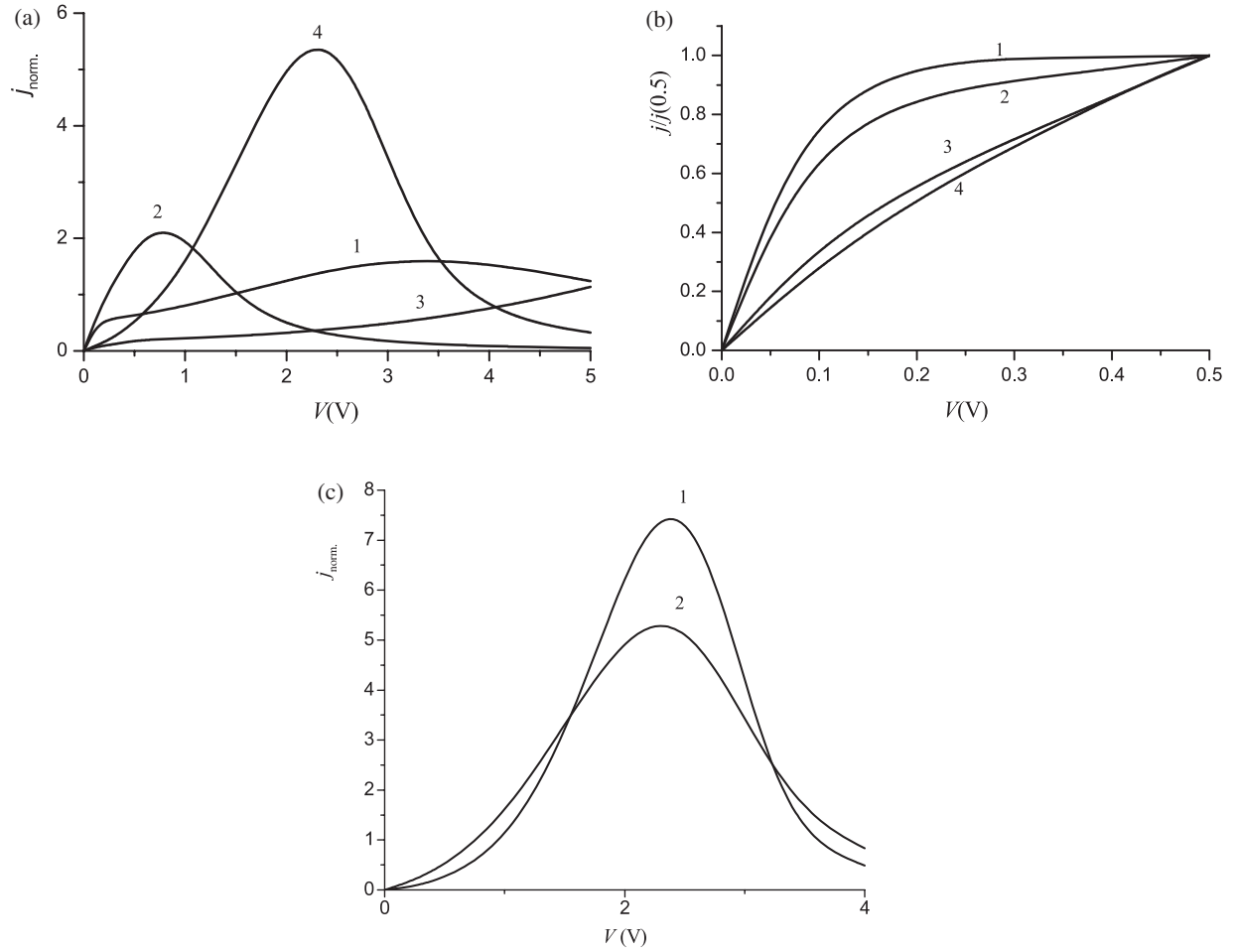


Figure 7. Dependence of the tunnel current on the bias voltage at $\eta = 0$ and different values of physical parameters in the case of strong coupling with electrodes and weak coupling between the groups. The current is normalized to $e2\pi V_{12}^2/\hbar E_r$. (a) $z_1/L = 0.25$, $\Delta = 0.1$ eV. 1. $L_D/L = 0.1$, $E_r = 0.2$ eV; 2. $L_D/L = 0.3$, $E_r = 0.2$ eV; 3. $L_D/L = 0.1$, $E_r = 0.5$ eV; 4. $L_D/L = 0.3$, $E_r = 0.5$ eV. (b) $\Delta = 0.1$ eV, $E_r = 0.2$ eV. 1. $L_D/L = 0.1$, $z_1/L = 0.375$; 2. $L_D/L = 0.1$, $z_1/L = 0.25$; 3. $L_D/L = 0.3$, $z_1/L = 0.375$; 4. $L_D/L = 0.3$, $z_1/L = 0.25$. (c) $z_1/L = 0.25$, $L_D/L = 0.3$, $E_r = 0.5$ eV. 1. $\Delta = 0.1E_r$; 2. $\Delta = 0.2E_r$.

for $V > V_{\text{max}}$, the current decreases, which is evidence of an inverted region for the electron transfer between the redox groups (figure 7(a)). Unlike the situation for the bulk of the solution, here the inverted region appears due to the decreasing overlap of the electron densities of states of two groups. The behavior of the current described above is mainly related to the dependence of ρ_{max} on V . Using this dependence, a value of V_{max} can be estimated as $2E_r/D\gamma$. The smaller L_D/L , the smaller $D\gamma$ (e.g., for $z_1/L = 0.25$ one obtains that $D\gamma = 0.08$ for $L_D/L = 0.1$ and $D\gamma = 0.3$ for $L_D/L = 0.3$).

The tunnel current is proportional to ρ_{max} and the sum of two error functions $2 \int_0^u \exp(-x^2) dx/\pi^{1/2} + 2 \int_0^v \exp(-x^2) dx/\pi^{1/2}$ where

$$\begin{aligned} u &= eV(1 - S\gamma/2)/(2E_r k_B T)^{1/2}, \\ v &= (eVS\gamma/2)/(2E_r k_B T)^{1/2}. \end{aligned} \quad (51)$$

When $u > 1$, the first term of the sum is almost independent of V and equal approximately to 1 so that the sum at small values of L_D/L (strong screening, small $S\gamma$) shows a tendency to saturation increasing very slowly from 1 to 2 with

the increase of V due to the V dependence of the second term. Finally, for $v > 1$, the sum equals approximately 2. Since at large L_D/L (the weak screening) the parameter $S\gamma \approx 1$, it follows from equation (51) that $u \approx v$. Therefore, the sum increases first from 0 to 2 with the increase of V and then takes an almost constant value at $u = v > 1$. Thus, the dependences of the current on the bias voltage shown in figures 7(a) and (b) are ruled by the parameters $2k_B T/D\gamma$, u and v . The critical values of the latter parameters are $u = v = 1$. For example, we have $2k_B T/(eD\gamma) \approx 0.6$ V, $V \approx 0.10$ V at $u = 1$ and $V \approx 2.4$ V at $v = 1$ for $E_r = 0.2$ eV, $L_D/L = 0.1$. Therefore, for $V > 0.1$ V, the current shows a tendency to saturation and takes an almost constant value until $V < 0.6$ V (see curves (1) and (2) in figure 7(b)). As a result, curves (1) and (2) in figure 7(b) have almost sigmoidal form and can imitate the experimental result of [22]. Then, for $V > 0.6$ V, the current begins to increase due to the increase of ρ_{max} (see curve (1) in figure 7(a)). For $E_r = 0.2$ eV and $L_D/L = 0.3$, one obtains that $2k_B T/(eD\gamma) \approx 0.2$ V, $V \approx 0.13$ V at $u = 1$ and $V \approx 0.4$ V at $v = 1$ so that the current increases monotonically with the increase of V and has no tendency to saturation even

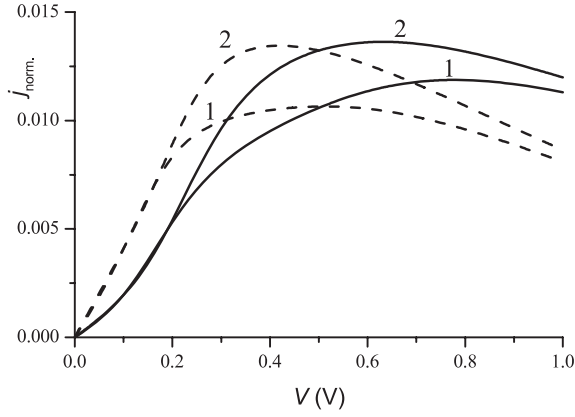


Figure 8. Dependence of the tunnel current on the bias voltage at different values of the overpotential and reorganization free energy in the case of totally adiabatic electron transitions in the spinless model. $\Delta = 0.05$ eV, $V_{12} = 0.1$ eV, $z_1/L = 0.25$, $L_D/L = 0.3$, $\hbar\omega = 0.02$ eV. $E_r = 0.5$ eV (solid lines); $E_r = 0.2$ eV (dashed lines). $\eta = 0$ (1); $\eta = 0.1$ V (2). The current is normalized to $2eV_{12}^2\Delta^2/\pi\hbar(\hbar\omega)^3$.

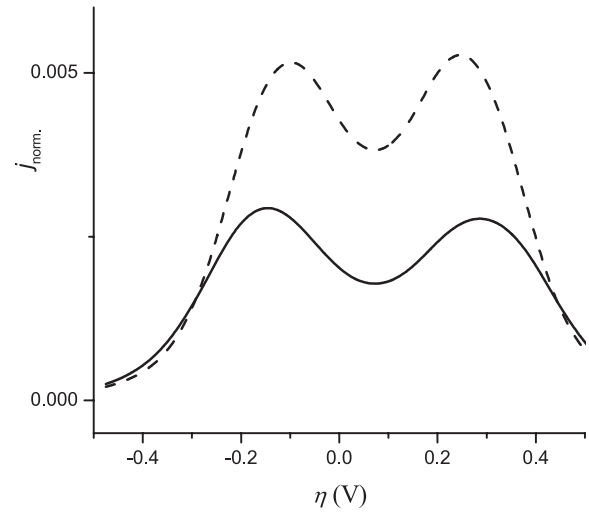


Figure 9. Dependence of the tunnel current on the overpotential at different values of the reorganization free energy in the case of totally adiabatic electron transitions in the spinless model. $\Delta = 0.05$ eV, $V_{12} = 0.1$ eV, $V = 0.1$ V, $z_1/L = 0.25$, $L_D/L = 0.3$, $\hbar\omega = 0.02$ eV. $E_r = 0.5$ eV (solid line); $E_r = 0.2$ eV (dashed line). The current is normalized to $2eV_{12}^2\Delta^2/\pi\hbar(\hbar\omega)^3$.

in the region $V < 0.5$ V (see curves (2) and (4) in figure 7(a) and curves (3) and (4) in figure 7(b)).

It should be noted that in the model of [21] the dependence of the energies of the valence levels on the bias voltage is ignored ($\gamma(z_2) = \gamma(z_1) = D\gamma = S\gamma = 0$), so the dependence of the tunnel current on the bias voltage is characterized only by the single parameter $u = eV/(2E_r k_B T)^{1/2}$. Therefore, the current takes an almost constant value when $u > 1$ as was obtained in [21]. On the other hand, the dependence of the energies of the valence levels on the bias voltage was taken into account in [26] but the effect of the Debye screening on this dependence was ignored. As a result, a tendency to saturation of the current in the region $V < 0.5$ V was not obtained.

Figure 7(c) shows that for the bias voltage values on the left and on the right (inverted region) of the maximum the current is larger for larger Δ due to a stronger overlap of the electron densities of states of the redox groups. In the region of the maximum, in contrast, the current is larger for smaller Δ due to a better overlap of electron densities of states with the energy window between the Fermi levels of the leads.

For the totally adiabatic case we start from the spinless model which may be envisaged if the Coulomb repulsion between two electrons located in the same group is very large whereas it is negligibly small for the electrons located on the valence orbitals of different groups. As was discussed in section 5 the case of interaction of both redox groups with the same single vibrational mode q is considered since only in this case can AFES be constructed. This may correspond to the situation where a local oscillator is located symmetrically with respect to both groups. We discuss below the most interesting case when $\gamma_{10} = -\gamma_{20} = -\gamma_0$ (when $\gamma_{10} = \gamma_{20}$, both electron energy levels shift in the same direction with the motion along the vibrational mode), so $\varepsilon_1(q) = \gamma_0 q - e\xi\eta - e\gamma(z_1)V$ and $\varepsilon_2(q) = -\gamma_0 q - e\xi\eta - e\gamma(z_2)V$. The equilibrium potential corresponds here to the situation where the depths of the potential wells of AFES are the same at $\eta = V = 0$. The values of the coordinate q at the stationary points

(maximum and minima of AFES) are equal approximately to $\langle n_2 - n_1 \rangle$, so in the neighborhood of one minimum one of the energy levels is oxidized whereas the other one is reduced and vice versa for the second minimum. At the transition point, $q = 0$. Near the top of the AFES both energy levels of the redox groups lie approximately within the energy window between the Fermi levels of the electrodes. The reorganization energy for the electron transition between the redox groups is defined in a usual way as $E_r = \hbar\omega(\Delta q_0)^2/2 = 2\gamma_0^2/\hbar\omega$. Only the symmetric case $\Delta_L = \Delta_R = \Delta$ is considered. The tunnel current is calculated as the thermal Boltzmann average of the partial tunnel current (equation (44)) with AFES given by equation (49). The Fermi distribution functions in equations (42)–(44) were replaced by the stepwise functions.

Figure 8 shows the dependence of the current on the bias voltage for different values of the reorganization free energy and overpotential. Like for other limiting cases discussed above there is no tendency to saturation. The smaller η , E_r , Δ and V_{12} , the earlier the inverted region starts. The physical meaning of this result is similar to that considered above for partially adiabatic limit.

The system under consideration demonstrates an interesting new effect shown in figure 9. Unlike single-level bridged contacts the current/overpotential dependence has two distinctive maxima (when $V_{12} > \Delta$) at the points shifted from the equilibrium potential in the negative and positive directions. The positions of the maxima can be estimated as $V/2 \pm (2/e\xi)\sqrt{V_{12}^2 - \Delta^2 - (eV/2)^2}$. The position of the minimum between these maxima equals approximately $V/2$. It should be noted that a weakly pronounced strongly overlapping double-peak structure of the current/overpotential dependence obtained in [26] appears only in the case when the reorganization energies E_L and E_R are not equal to each other and has a different physical nature from the effect discussed above.

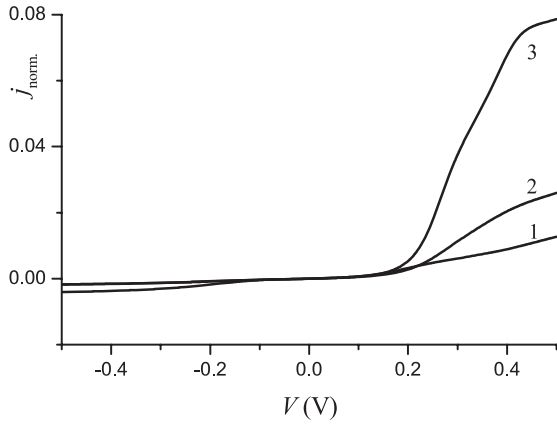


Figure 10. Dependence of the tunnel current on the bias voltage at different values of Δ and V_{12} in the case of totally adiabatic electron transitions in the spinless model. $\eta = 0.5$ V, $z_1/L = 0.25$, $L_D/L = 0.3$, $\hbar\omega = 0.02$ eV, $E_r = 0.5$ eV. 1: $\Delta = 0.05$ eV; $V_{12} = 0.1$ eV; 2: $\Delta = 0.05$ eV; $V_{12} = 0.05$ eV; 3: $\Delta = 0.025$ eV; $V_{12} = 0.05$ eV. The current is normalized to $2eV_{12}^2\Delta^2/\pi\hbar(\hbar\omega)^3$.

This effect is peculiar for a two-redox-group system because maxima appear when the bonding or antibonding levels enter the energy window. It disappears when $V_{12} < \Delta$ and the role of the hybridization of electron orbitals of two groups is less pronounced, so the system behaves similarly to a single-level system.

Figure 10 demonstrates a rectification effect which appears at non-zero overpotential. The rectification ratio increases with decrease of Δ and V_{12} . A similar result was obtained in [26]. However, as was discussed above, we take into account both reduced and oxidized states of the redox groups, whereas only the reduced state of group 1 and oxidized state of group 2 were considered in [26].

The limit of weak Coulomb repulsion U_{12} between the electrons considered above may be the case when the valence orbitals are rather diffuse, so this does not contradict with large values of hybridization parameter V_{12} . Another limit is considered below where both the Coulomb repulsion U_{12} and the hybridization parameter are large. This can take place when the valence orbitals are rather localized but their overlap is strong. Figure 11 shows the dependence of the tunnel current on the bias voltage at $\eta = 0$ for different values of L_d/L . Solid lines are calculated for the case of strong interaction between the redox groups and weak interaction of the groups with the electrodes in the limit of a large value of U_{12} , using equation (39). The dashed line corresponds to the totally adiabatic case and is calculated also in the limit of a large value of U_{12} using the method of [31] as was discussed at the end of section 5.

The behavior of the current given by equation (39) is also ruled by the parameters u and v (see equation (51)). Since equation (39) corresponds to the electron tunneling through a single (bonding) state of the redox groups, the parameter $2k_B T/D\gamma$ has no effect on the current in this case. However, a new parameter $V_{12}/D\gamma$ appears because the tunnel current depends essentially on the parameter $A = [(eVD\gamma)^2 + 4V_{12}^2]^{1/2}$ for large values of V . When $eV < V_{12}/D\gamma$, the

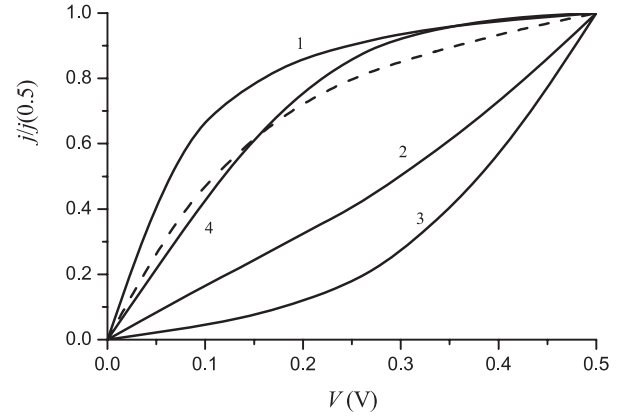


Figure 11. Dependence of the tunnel current on the bias voltage at different L_d and E_r in the limit of large values of U_{12} in the case of strong interaction between the redox groups and weak interaction of the groups with the electrodes (equation (39)) (solid lines) and for the totally adiabatic transitions (dashed line). $\eta = 0$, $z_1/L = 0.375$, $V_{12} = 0.3$ eV. 1. $L_d/L = 0.1$, $E_r = 0.5$ eV; 2. $L_d/L = 0.3$, $E_r = 0.5$ eV; 3. $L_d/L = 0.5$, $E_r = 0.5$ eV; 4. $L_d/L = 2$, $E_r = 0.05$ eV. For the dashed curve $L_d/L = 0.1$, $\Delta_L = 0.5\Delta \cos^2 \theta$, $\Delta_R = 0.5\Delta \sin^2 \theta$, $\Delta = 0.1$ eV. The current is normalized to $j(0.5)$.

current increases with increase of V and, as in the case of the one-level bridge molecule, tends to a constant value $4j_{\max}/3$ for $v > 1$. However, the rate of approach of the tunnel current to this constant value is determined by the dependence of $\Delta F_{\text{IL}}^{(2)}$ on V . It follows from the physical meaning of $\Delta F_{\text{IL}}^{(2)}$ that for large electrolyte concentrations (small L_D/L , strong screening) $\Delta F_{\text{IL}}^{(2)}$ is almost independent of V , which results in a very slow increase of the tunnel current with increase of V (see curve (1) in figure 11 which is similar to curves (1) and (2) in figure 8(b)). Indeed, the sum $S\gamma = \gamma(z_1) + \gamma(z_2)$ as well as the difference $D\gamma = \gamma(z_1) - \gamma(z_2)$, which enter the rhs of equation (35), behave as $\exp[-L/(2L_D)]$ at small L_D/L , i.e., are exponentially small. Therefore, curve (1) has almost sigmoidal form in the region $V < 0.5$ V and can also imitate the experimental result of [22] ($V = 0.16$ V at $u = 1$ and $V = 12.7$ V at $v = 1$ for $E_r = 0.5$ eV, $L_D/L = 0.1$ and $z_1/L = 0.375$). In the totally adiabatic case the tunnel current increases faster at the same value of L_D/L as compared with curve 1 due to a faster decrease of the activation barrier of the redox reaction with increase of V in the small bias voltage region at values of the width Δ of the antibonding level inherent to the adiabatic reactions [31]. When L_D/L increases, $S\gamma$ and $D\gamma$ increase too and tend to 1 and δ/L , respectively, so the tunnel current for $E_r = 0.5$ eV, $L_D/L = 0.3$ and $L_D/L = 0.5$ increases monotonically and has no tendency to saturation (see curves (2) and (3) in figure 11).

Since the tunnel current is independent of the parameter $2k_B T/D\gamma$ in the case under consideration, the current–bias voltage dependence of sigmoidal form can also be obtained in the weak screening limit for small values of E_r . As was discussed above, we have $u \approx v$ for large values of L_D/L , so the regions of V where $u > 1$ and $v > 1$ coincide. One obtains that $V \approx 0.1$ V at $u = v = 1$, $E_r = 0.05$ eV and $L_D/L = 2$. As a result, the tunnel current takes almost constant values in

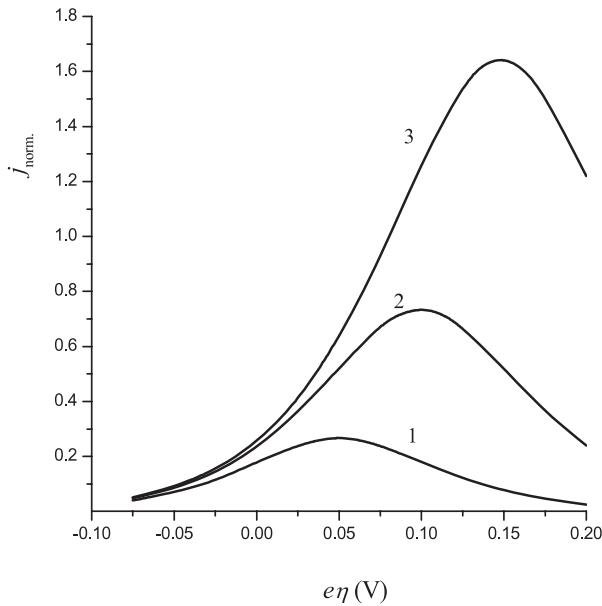


Figure 12. Dependence of the tunnel current $j_{\text{norm.}} = j/(2^{1/2}j_{\text{max}}) \times 10^2$ on the overpotential at different values of the bias voltage in the limit of large values of U_{12} in the case of strong interaction between the redox groups and weak interaction of the groups with the electrodes (equation (39)). $z_1/L = 0.375$, $L_d/L = 0.1$, $V_{12} = 0.3$ eV, $E_r = 0.5$ eV. $V = 0.1$ V (1), $V = 0.2$ V (2), $V = 0.3$ V (3).

the interval $0.3 \text{ V} < V < 1 \text{ V}$ in this case (see curve (4) in figure 11).

When the bias voltage is larger than $V_{12}/(eD\gamma)$ ($V_{12}/(eD\gamma) = 14, 1.8$ and 1.2 V for $V_{12} = 0.3$ eV and $L_D/L = 0.1, 0.3$ and 0.5 , respectively), the tunnel current tends to $j_{\text{lim}}(V) = 8j_{\text{max}}V_{12}^2/[A^2(\cos^2\theta + 1)]$ and, in contrast to the case for the one-level bridge molecule, goes to zero if V tends to infinity.

The current–bias voltage dependences presented in figure 11 were obtained at $\eta = 0$. The dependences of the tunnel current on the overvoltage calculated with the use of equation (39) are presented in figure 12. Since η_{max} has the order of $V/2$ and, therefore, strongly affects $\Delta F_{\text{IL}}^{(2)}$ (see equation (35)), values of $j(\eta_{\text{max}})$ increase quickly with increase of V even for $L_D/L = 0.1$ as shown in figure 12.

7. Concluding remarks

In the present paper we have considered in detail the electron tunneling through a symmetric electrochemical contact involving two redox groups in the tunnel gap. Various limiting cases are studied. The treatment is more rigorous and complete as compared to other works [21, 24–26]. The expressions (21), (24), (27), (39), (42)–(43) and (49) for the tunnel current and AFES are obtained for different limiting cases. The results of calculations of the tunnel current for totally non-adiabatic, partially adiabatic and totally adiabatic limits are presented.

The following conclusions can be drawn from these results:

- (1) The system under discussion manifests negative differential resistance and rectification. In contrast to the findings of [1], the rectification is due not to the intrinsically asymmetric location of the energy levels of the redox groups but due to the non-zero overpotential in purely symmetric contact, which is peculiar to the electrochemical contacts.
- (2) The dependence of the current on the bias voltage in most cases reaches a maximum in the neighborhood of the reorganization energy. At the same time, in the partially adiabatic limits considered in sections 3 and 4, a tendency to saturation of the current–bias voltage dependence was obtained at small values of the bias voltage and L_D/L (see figures 7(b) and 11). In both limits, the current monotonically increases with the bias voltage at small V . However, if the screening of the electric potential in the tunnel gap is strong, this increase is very slow, resembling the sigmoidal curve observed in [22] at least in the experimental range of the bias voltage variation. It should be noted that the polarization of the parts of the long chain molecule adjacent to the electrodes can also give a contribution to the screening, reducing thereby the effective ratio L_D/L . It should also be noted that the sigmoidal curves of $j(V)$ were obtained for quite different limiting cases: strong interaction of the redox groups with the electrodes and weak interaction between the redox groups at $U_{12} \approx 0$ (section 3) and strong interaction between the redox groups and weak interaction of the groups with electrodes at large U_{12} (section 4). These cases can be distinguished experimentally when the region $V > 0.5$ V is investigated. Namely, the current starts to increase rapidly with the increase of V above 0.5 V in the first case and proceeds to increase slowly in the second one. The tendency to saturation of the $j(V)$ curve was also obtained in the case of weak screening of the potential in the tunnel gap for small values of E_r (see curve (4) in figure 7(b)).
- (3) For most limiting cases considered, the dependence of the current on the overpotential has a maximum in the neighborhood of the equilibrium potential similar to that for the one-level system. However a new effect was found when U_{12} is negligibly small in the limit of the totally adiabatic regime. The current/overpotential dependence exhibits then two maxima. Each maximum corresponds to resonance tunneling through bonding or antibonding orbitals, depending on the value of the overpotential. Therefore the separation of the positions of the maxima depends on V_{12} .

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Appendix A

The quantities a , b and d in equation (16) and the rate constants are determined by the following relationships:

$$a = k_{12}k_{L1}(1 - u)(1 + 1/v), \quad (\text{A.1})$$

$$b = k_{L1}k_{12}(2u + u/v - 1) + k_{L1}k_{2R}(1 + w)(1 + 1/v) + k_{12}k_{2R}(1 + uw), \quad (\text{A.2})$$

$$d = k_{L1}[k_{12}u + k_{2R}(1 + w)] + k_{12}k_{2R}uw, \quad (\text{A.3})$$

where

$$u = \exp\left\{\frac{e(\xi_1 - \xi_2)\eta + e[\gamma(z_1) - \gamma(z_2)]V}{k_B T}\right\}, \quad (\text{A.4})$$

$$v = \exp\left\{\frac{e\xi_1\eta + e\gamma(z_1)V}{k_B T}\right\}, \quad (\text{A.5})$$

$$w = \exp\left\{\frac{e\xi_2\eta - e[1 - \gamma(z_2)]V}{k_B T}\right\}, \quad (\text{A.6})$$

$$k_{12} = k_0 \exp\left\{-\frac{\{E_{12} + e[\gamma(z_1) - \gamma(z_2)]V\}^2}{4E_{12}k_B T}\right\}, \quad (\text{A.7})$$

$$k_{L1} = 2k_L \int \frac{d\varepsilon}{2k_B T} f_L(\varepsilon) \times \exp\left\{-\frac{[E_L + \Delta F_{L1} - (\varepsilon - \varepsilon_{FL})]^2}{4E_L k_B T}\right\} \quad (\text{A.8})$$

$$k_{2R} = k_R \int \frac{d\varepsilon}{2k_B T} [1 - f_R(\varepsilon)] \times \exp\left\{-\frac{[E_R + \Delta F_{2R} + (\varepsilon - \varepsilon_{FR})]^2}{4E_R k_B T}\right\}. \quad (\text{A.9})$$

Here E_L and E_R are the medium reorganization energies for the electron transitions at the electrodes ($E_L = E_R = E$ for symmetric contacts), k_L and k_R are the pre-exponential factors. The factor 2 in the rhs of equation (A.8) takes into account the spin degeneracy of the electronic states of the electrode.

The rate constants for forward and backward transitions are related by detailed balance relationships as follows:

$$k_{21} = k_{12}u; \quad k_{1L} = k_{L1}/v; \quad k_{R2} = k_{2R}w. \quad (\text{A.10})$$

Equations (A.8) and (A.9) can be rewritten in the form

$$k_{L1} = 2k_L \exp\{-[E_L + \Delta F_{L1}]^2/4E_L k_B T\} I_L, \quad (\text{A.11})$$

$$k_{2R} = k_R \exp\{-[E_R + \Delta F_{2R}]^2/4E_R k_B T\} I_R \quad (\text{A.12})$$

where

$$I_L = \int \frac{dx \exp[x(1 + \Delta F_{L1}/E_L - k_B T x/E_L)]}{1 + \exp(2x)}, \quad (\text{A.13})$$

$$I_R = \int \frac{dx \exp[x(1 + \Delta F_{2R}/E_R - k_B T x/E_R)]}{1 + \exp(2x)}. \quad (\text{A.14})$$

If $|\Delta F_{L1}| \gg E_L$ and $|\Delta F_{2R}| \gg E_R$, then

$$I_L \approx \left(\frac{\pi E_L}{k_B T}\right)^{1/2} \exp\{[E_L + \Delta F_{L1}]^2/4E_L k_B T\}, \quad (\text{A.15})$$

$$I_R \approx \left(\frac{\pi E_R}{k_B T}\right)^{1/2} \exp\{[E_R + \Delta F_{2R}]^2/4E_R k_B T\}. \quad (\text{A.16})$$

Appendix B

The term H_{int} in equation (29) has the form

$$H_{\text{int}}(n_i, q_k) = -\sum_k (\gamma_{1k} q_k n_1 + \gamma_{2k} q_k n_2) \quad (\text{B.1})$$

where the γ_{ik} are the coupling constants. Since the operator of the total number of electrons $N = n_1 + n_2$ commutes with the total Hamiltonian of equation (29) we have $N|\psi\rangle = 1|\psi\rangle$ for arbitrary one-electron state $|\psi\rangle$ and therefore one can transform the Hamiltonian as follows:

$$H = H_{12} - n_1 \left[\sum_k \gamma_k (q_k - q_{2k}) + E_{\text{mix}} - 2E_R \right] + H_{\text{ph}}(p_k, q_k - q_{2k}) - E_R \quad (\text{B.2})$$

where $\gamma_k = \gamma_{1k} - \gamma_{2k}$, $q_{2k} = \gamma_{2k}/\hbar\omega_k$,

$$E_L = \frac{1}{2} \sum_k \frac{\gamma_{1k}^2}{\hbar\omega_k}, \quad E_R = \frac{1}{2} \sum_k \frac{\gamma_{2k}^2}{\hbar\omega_k}, \quad (\text{B.3})$$

$$E_{\text{mix}} = \sum_k \frac{\gamma_{1k}\gamma_{2k}}{\hbar\omega_k}$$

and $E_L = E_R$ for the symmetric contact.

Within the BOA the adiabatic free energy surface (AFES) $U_{\text{ad},I}(q_k)$ is given by the expression

$$U_{\text{ad},I}(q_k) = \frac{1}{2} \sum_k \hbar\omega_k (q_k - q_{2k})^2 + E_I(q_k). \quad (\text{B.4})$$

Here $E_I(q_k)$ is the energy of the electronic subsystem. It is the eigenvalue of the Hamiltonian presented by the first two terms in the rhs of equation (B.2). The energy $E_I(q_k)$ can be calculated with the use of equation (31) with the substitution of $\varepsilon_1(q_k)$ for ε_1^0 where

$$\varepsilon_1(q_k) = \varepsilon_1^0 - \sum_k \gamma_k (q_k - q_{2k}) + 2E_R - E_{\text{mix}}. \quad (\text{B.5})$$

As in [33], a single effective coordinate q can be introduced:

$$q = \sum_k \gamma_k (q_k - q_{2k}) / (2E_{12}) \quad (\text{B.6})$$

where

$$E_{12} = \frac{1}{2} \sum_k \frac{(\gamma_{1k} - \gamma_{2k})^2}{\hbar\omega_k} = E_L + E_R - E_{\text{mix}}. \quad (\text{B.7})$$

The AFES then takes the form

$$U_{\text{ad},I}(q) = E_{12}q^2 + E_I(q) \quad (\text{B.8})$$

where

$$E_I(q) = \left\{ \varepsilon_1(q) + \varepsilon_2^0 - [(\varepsilon_1(q) - \varepsilon_2^0)^2 + 4V_{12}^2]^{1/2} \right\} / 2 \quad (\text{B.9})$$

and

$$\varepsilon_1(q) = \varepsilon_1^0 - 2E_{12}q + 2E_R - E_{\text{mix}}. \quad (\text{B.10})$$

It is known [30] that the AFES of equation (B.8) has a single potential well if $V_{12} > 0.5E_{12}$ (the adsorption regime). Let us assume that $E_L = E_R = E_{\text{mix}}$ when γ_{1k} and γ_{2k} have arbitrary values (in particular when $\gamma_{2k} \neq C\gamma_{1k}$). Then, since $\varepsilon_1^0 - \varepsilon_2^0 = e|[\gamma(z_1) - \gamma(z_2)]V| \ll E_{12}$, AFES $U_{\text{ad},l}(q)$ is an even function of $q - 1/2$, and, therefore, the coordinate q_s of the minimum of the potential well in the adsorption regime equals approximately 0.5. It can be shown that $q_s = \langle n_1 \rangle$. Thus, for the adsorption state of the bridge molecule we have $\langle n_1 \rangle \approx \langle n_2 \rangle \approx 1/2$.

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