



A Theory of Electron Transfer in Bridged and Supramolecular Systems

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Abstract. Expressions are derived for the tunnel electric current between two metals produced by the adiabatic transitions of the electrons through a bridge electron level. A new possible physical phenomenon is discussed, viz. electronically driven oscillations of the electron bridge level between two molecular wires.

Key words: bridged electrochemical contact, bridged molecular wires, electronically driven oscillations, inverted region, adiabatic electron transfer, overpotential and bias voltage.

1. Introduction

Electron transfer in organized molecular systems represents a broad, rapidly developing field of chemical kinetics. The systems under investigation involve thin molecular films on metal electrodes and at other interfaces, biological macromolecules, tunnel contacts, and a broad class of supramolecular systems. Unlike the electron transfer processes in simple homogeneous and electrochemical reactions, the systems under discussion often demand a modification and extension of the theory in order to take into account some new, specific features of the reacting species. In the former a direct overlap of the electron clouds of the donor and acceptor is usually possible and the intramolecular reorganization is rather small so that a harmonic approximation is applicable for its description [1–4]. The electron transfer in the latter systems occurs often over a long distance through intermediate chemical groups separating donor and acceptor sites. This is the case in long-distance electron transfer in biological macromolecules, electrochemical electron transfer through thin films, electron transfer in molecular wires and other supramolecular ensembles, in tunnel bridged contacts, etc. A direct overlap of the electron clouds of the donor and acceptor is then much weaker than overlap with

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the molecular orbitals of the bridge groups. The theory of the processes of this type is also quite well developed (see, e.g., [5]). It involves the consideration of transitions through several electron states.

Another specific feature of the systems under consideration consists of the fact that intramolecular reorganization accompanying the electron transfer is sometimes not small. Examples of chemically and electrochemically controllable rotaxanes and catenanes exist [6] where the electron transfer leads to a large rotational or translational intramolecular reorganization. The molecular potentials describing this reorganization are highly anharmonic. This significantly modifies the expressions for the rate constants [7]. Interesting new effects are expected for the processes in tunnel bridged contacts. Some aspects of the theory of the latter are discussed in the present paper.

2. Summary of Main Points of Traditional Electron Transfer Theory

The mechanism of electron transfer in a molecular environment depends on the strength of electron interaction with the surroundings. Usually it is large and strongly affects the positions of the electron energies in the donor and acceptor, ϵ_I and ϵ_f . In the simple Marcus approach the transition probability is determined by the probability of the fluctuation of the solvent polarization to the transitional configuration q_s corresponding to matching of the electron energies ϵ_I and ϵ_f : $\epsilon_I(q_s) = \epsilon_f(q_s)$. In the classical limit this configuration corresponds to the saddle point on the crossing of the free energy surfaces of the initial and final states, U_i and U_f .

The activation free energy F_a is a quadratic function of the free energy of the transition ΔF [1]

$$F_a = (E_s + \Delta F)^2/4E_s, \quad (1)$$

where E_s is the reorganization energy of the nuclear reactive modes.

An important quantity characterizing the dependence of the activation free energy on the free energy of the transition (free energy relationship) is the so-called symmetry factor

$$\alpha = dF_a/d\Delta F = (1/2)(1 + \Delta F/E_s). \quad (2)$$

According to quantum mechanical theory the transition probability is also determined by the electron transmission coefficient κ [3, 4]. If $\kappa \ll 1$, the reaction is called non-adiabatic. If $\kappa = 1$ the reaction is adiabatic.

Equation (1) shows that the activation free energy decreases with the increase of $-\Delta F$ vanishing at $-\Delta F = E_s$ (activationless region with $\alpha = 0$; the backward transition is then barrierless with $\alpha = 1$). As $-\Delta F$ increases further the activation free energy also increases. This is the so-called *inverted region*. For electrochemical reactions on metals the inverted region cannot be observed due to a broad

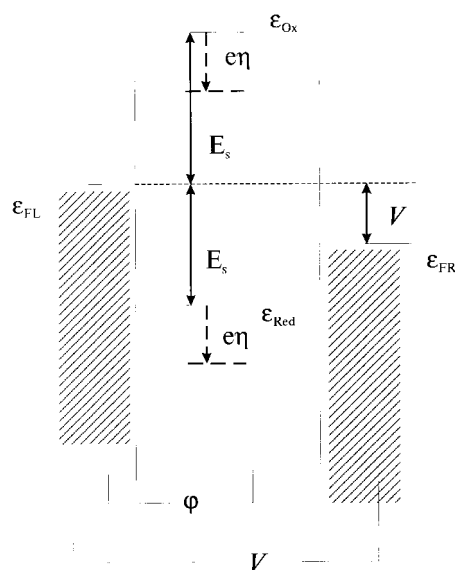


Figure 1. A scheme of electron transfer through a bridged tunnel electrochemical contact.

continuous electron energy spectrum providing the activationless conditions at any large values of $-\Delta F (> E_s)$. Attempts to observe the inverted region were made using a bridged STM configuration with a very small bias voltage V between the electrode and STM tip (see e.g., [8]). Only a narrow energy interval ('energy tip') is allowed for the electron transitions from the left metal to the right one (Figure 1). We shall analyze this problem in detail below.

3. Electron Transitions in Bridged Tunnel Contacts

The modern theory underlying the elementary act of charge transfer predicts interesting new phenomena for the processes of electron transfer in bridged electrochemical contacts and in bridged supramolecular systems [9]. Situations of this type are feasible for example in STM studies of adsorbed molecules or in electron tunnelling between molecular wires. We start the discussion from the bridged STM configuration, restricting ourselves to *adiabatic electron transfer*.

3.1. BRIDGED ELECTROCHEMICAL CONTACT

It is assumed that an electron energy level of a bridge molecule between two metal electrodes is coupled to environmental or local vibrational modes [9] (Figure 1). The adiabatic character of the electron transfer may be described as multiple electron transitions between the electron level of the bridge and various electron levels of metals [9]. Two different potential jumps can be controlled in principle: the

potential between the left electrode φ and the bulk of the solution and the bias potential between two electrodes V (Figure 1).

3.1.1. Normal Region

In the normal region the equilibrium positions of the vacant and occupied bridge electron level are far above and far below the Fermi level of the left metal, respectively (Figure 1). The first step of the physical mechanism of the transition is similar to that for the ordinary electrochemical or bulk electron transfer reactions. Due to the fluctuations of vibrational reactive modes the bridge level lowers and matches the occupied energy levels of the left metal below its Fermi level ϵ_{FL} and the electron transition from the latter to the former may occur. However, unlike ordinary electrochemical reactions, in the bridged system in the process of further lowering of the (now occupied) bridge level, an electron transfer to the unoccupied energy levels of the right metal (located between the Fermi levels of the left and right metals) may occur and this process continues repeatedly unless the bridge level reaches its equilibrium position where it is occupied (Figure 1). Thus, in the process of the motion of the system along the reaction coordinate in the forward direction, many electron transitions take place from the left metal to the right one [9].

If the reduced form is immediately removed from the interface region, the dependence of the electric current here combines the features of the Tafel-like electrochemical current and tunnel current

$$i = en_{\text{Ox}}k_{\text{Ox}}C_{\text{Ox}} = A[V + (E_s - e\eta - V)\theta(V - E_s)]e^{\alpha e\eta/k_B T}, \quad (3)$$

where α is the symmetry factor, k_{Ox} is the rate constant of the conversion of the oxidized form into the reduced one as a result of a single passage along the reaction coordinate in the forward direction, η is the overpotential, n_{Ox} determines the number of the electrons passed from the left metal to the right one after one-fold passage along the reaction coordinate, A is a constant and $\theta(x)$ is a step-wise function. Equation (3) shows that the current depends on both η and bias potential V .

3.1.2. Activationless Region

When due to the variation of the overpotential η the position of the vacant bridge level lies within the interval between ϵ_{FL} and ϵ_{FR} , the process is *activationless* and the dependence of the current on η and V has the form

$$i = B([V - (e\eta - E_s)] + \{2E_s - [V - (e\eta - E_s)]\}\theta(V - (e\eta + E_s))). \quad (4)$$

At constant bias the electric current decreases with increasing η . This is due to the decrease of the energy interval passed by the bridge level and is *not related to*

the inverted region. When the bridge level falls in the region below the Fermi level of the right metal, the tunnel current vanishes.

If at a constant overpotential the bias voltage increases up to the value $V = E_s + e\eta$ the process becomes barrierless. Thus it is possible in principle to observe the barrierless process for a simple redox reaction.

3.1.3. Redox System in the Adsorbed Layer

It was assumed above that the occupied bridge levels do not participate in the electron transfer to the right metal, i.e., the reduced species are quickly removed from the gap between two metals. However, if the reduced form remains in the gap, as for example in the case of the redox pairs in a film attached to the electrode, the occupied bridge levels may also in principle participate in the tunnel current.

Normal region. Let us consider a simple redox system with the equilibrium redox potential φ_0 with respect to the left metal. Due to electron transitions, an interconversion of the reduced and oxidized forms takes place, their total concentration C remaining unchanged. We define the overpotential here in such a way that at high negative overpotential η all the species are oxidized and $C_{\text{Ox}} = C$ whereas $C_{\text{Red}} = 0$. If some overpotential is applied at $t = 0$, in the potentiostatic regime the time dependence of the concentrations of the oxidized and reduced forms have the form

$$\begin{aligned} C_{\text{Ox}} &= C \frac{(k_{\text{Ox}}/k_{\text{Red}})e^{-(k_{\text{Ox}}+k_{\text{Red}})t} + 1}{1 + k_{\text{Ox}}/k_{\text{Red}}}; \\ C_{\text{Red}} &= C \frac{(k_{\text{Ox}}/k_{\text{Red}})[1 - e^{-(k_{\text{Ox}}+k_{\text{Red}})t}]}{1 + k_{\text{Ox}}/k_{\text{Red}}}, \end{aligned} \quad (5)$$

where k_{Ox} and k_{Red} are the corresponding rate constants for the reduction and oxidation processes.

Unlike the ordinary electrochemical process where the electric current is equal to $i = en_{\text{Ox}}k_{\text{Ox}}C_{\text{Ox}}$ and exponentially decreases in time, the tunnel electric current between two metals is produced by both forms

$$\begin{aligned} i_{\text{tunn}} &= i_{\text{Ox}} + i_{\text{Red}} = e(n_{\text{Ox}}k_{\text{Ox}}C_{\text{Ox}} + n_{\text{Red}}k_{\text{Red}}C_{\text{Red}}) \\ &= \frac{eCk_{\text{Ox}}}{1 + k_{\text{Ox}}/k_{\text{Red}}} [n_{\text{Ox}} + n_{\text{Red}} - (n_{\text{Red}} - n_{\text{Ox}}k_{\text{Ox}}/k_{\text{Red}})e^{-(k_{\text{Ox}}+k_{\text{Red}})t}]. \end{aligned} \quad (6)$$

Thus at $t \rightarrow \infty$ the tunnel current reaches a finite value

$$i_{\text{tunn}}(\infty) = eC(n_{\text{Ox}} + n_{\text{Red}})k_{\text{Ox}}k_{\text{Red}}/(k_{\text{Ox}} + k_{\text{Red}}). \quad (7)$$

Note that, although Equation (7) formally looks as if we are dealing with a stepwise process, in fact we have two separate processes which are coupled only by the condition of conservation of the number of the redox species in the gap.

In the normal region $n_{\text{Ox}} = n_{\text{Red}} = V/\Delta\epsilon$ where $\Delta\epsilon \sim 2/\kappa\rho$ is the electron energy interval in which the transition of one electron takes place [9]. (Here κ and ρ are the electron transmission coefficient for the transition from a particular energy level and the density of electron states in the metal.) Therefore

$$i_{\text{tunn}}(\infty) = 2eC(V/\Delta\epsilon)k_{\text{Ox}}k_{\text{Red}}/(k_{\text{Ox}} + k_{\text{Red}}). \quad (8)$$

In the simple harmonic approximation for the vibrational modes the expressions for the rate constants have the form

$$\begin{aligned} k_{\text{Ox}} &= \frac{\omega_{\text{eff}}}{2\pi} \exp \left\{ -\frac{(E_s - e\eta)^2}{4E_s k_B T} \right\}; \\ k_{\text{Red}} &= \frac{\omega_{\text{eff}}}{2\pi} \exp \left\{ -\frac{(E_s - V + e\eta)^2}{4E_s k_B T} \right\}. \end{aligned} \quad (9)$$

Then for the tunnel current we obtain

$$i_{\text{tunn}}(\infty) = 2eC(V/\Delta\epsilon) \frac{\omega_{\text{eff}}}{2} \frac{1}{e \frac{(E_s - e\eta)^2}{4E_s k_B T} + e \frac{(E_s - V + e\eta)^2}{4E_s k_B T}}. \quad (10)$$

Thus we see that at fixed bias voltage the tunnel current as a function of the overpotential has a *maximum* (Figure 2). The position of the maximum point and the value of the maximum current depend on the bias voltage (Figure 2)

$$e\eta_{\text{max}} = V/2; \quad i_{\text{tunn}}^{\text{max}}(\infty) = eC(V/\Delta\epsilon) \frac{\omega_{\text{eff}}}{2\pi} \exp \left\{ -\frac{(E_s - V/2)^2}{4E_s k_B T} \right\}. \quad (11)$$

Note that the decrease of the current after the maximum point occurs in the *normal region*. Therefore one should be careful with the interpretation of the i/φ dependencies. The decrease of the current itself is not the evidence of the onset of the inverted region. In the system under consideration it is due to the fact that the major contribution to the current is now provided by the reduced form, the concentration of which dominates in this overpotential region [10].

Activationless and 'inverted' regions. If, after the application of the stepwise overpotential, the unoccupied bridge level falls into the interval between the Fermi levels of the left and right metals, the conversion of the oxidized form into the reduced one occurs in an activationless manner. Therefore the tunnel current at the initial time moment is independent of the overpotential and decreases in time, reaching its steady-state value.

Since $k_{\text{Ox}} \gg k_{\text{Red}}$ in this region, the steady-state current is approximately equal to

$$i_{\text{tunn}}^{\text{a.l.}}(\infty) \approx eC(n_{\text{Ox}} + n_{\text{Red}})k_{\text{Red}} = eC(n_{\text{Ox}} + n_{\text{Red}}) \frac{\omega_{\text{eff}}}{2\pi} e^{-\frac{(E_s - V + e\eta)^2}{4E_s k_B T}}, \quad (12)$$

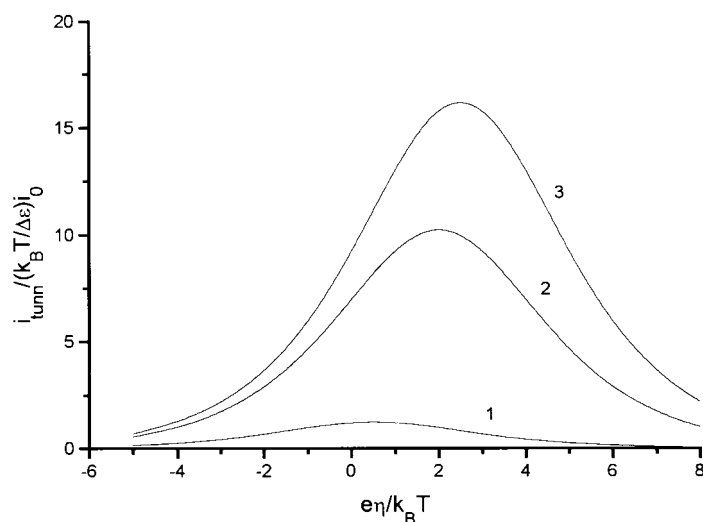


Figure 2. Dependence of the tunnel current on the overpotential calculated according to Equation (10). For all curves the reorganization energy $E_s = 1$ eV, $i_0 = 2eC(\omega_{\text{eff}}/2\pi) \exp[-E_s/4k_B T]$. 1: $V = 0.025$ eV; 2: $V = 0.1$ eV; 3: $V = 0.125$ eV.

where $n_{\text{Ox}} = n_{\text{Red}} = (V + E_s - e\eta)/\Delta\epsilon$ and since it is assumed that $E_s > V$, the steady-state tunnel current *decreases* with *increasing* overpotential in this region.

It should be emphasized that the steady-state tunnel current is provided here by the *barrierless* process of the temporal (i.e., dynamic) conversion of the reduced form to the oxidized one and immediate *activationless* backward transition.

When the value of the overpotential is high enough so that the unoccupied bridge level lies in the region below the Fermi level of the right metal, the tunnel current at $t = 0$ is equal to zero since the corresponding energy levels in both metals are occupied as well as the bridge level which relaxes to the equilibrium position. However, after this relaxation is complete, a small steady-state tunnel current will exist due to electron transitions from the reduced form into the right metal. This process proceeds in the ‘*inverted*’ region, but unlike the inverted region which is located behind the *activationless* region (this inverted region is usually discussed in the literature on the electron transfer reactions), the ‘*inverted region*’ under discussion is located behind the *barrierless* region. The expression for tunnel current is similar to Equation (12).

3.2. ELECTRON TUNNELING BETWEEN BRIDGED MOLECULAR WIRES

Interesting features are feasible in the process of the bridge-assisted adiabatic electron transfer between two atomic chains (‘molecular wires’) (Figure 3) [9]. It is assumed below that the energy levels of the terminal atoms of the molecular wires are different (e.g., due to some bias voltage) and the positions of the unoccupied and occupied bridge electron energy levels are above the upper and below the lower

atomic chain energies, respectively (Figure 3). The electrons are supplied to the left molecular wire and removed from the right one. It is assumed that the bridge level is coupled to a vibrational mode. The physical mechanism of the transition may be seen as follows [9]. Due to a thermal fluctuation of the vibrational mode the unoccupied bridge energy level is lowered to match the occupied atomic level of the left molecular wire. An adiabatic electron transfer from the molecular wire to the bridge atom occurs at this point, leading to the transition of the system from the free energy surface of the initial state U_{un} to the free energy surface of the state corresponding to the occupied bridge level U_0 . After this transition the configuration of the vibrational mode becomes out of equilibrium, and the motion to a new equilibrium position will occur. Further lowering of the bridge level will occur during this motion. At the point when the unoccupied energy level of the right molecular wire is matched, the adiabatic electron transfer from the bridge level will occur, corresponding to the transition from the free energy surface U_0 to the free energy surface of the unoccupied bridge state U'_{un} . After the reverse of the motion at the turning point on this free energy surface the system will move in the opposite direction, leading to raising the bridge level (now empty). If the removal of the electron from the terminal atom of the right molecular wire, is sufficiently fast, no electron transfer will occur when the bridge level matches the energy level of the right molecular wire and the system will relax to its initial equilibrium position. However, if at the moment of crossing the electron energy level of the left molecular wire the latter becomes occupied due to the electron supply from the left end of this molecular wire, then electron transfer to the bridge atom will occur with transition to the free energy surface U'_0 . If the level of the terminal atom of the left molecular wire is quickly refilled, the occupied bridge level will move down without electron transitions, until it crosses the energy level of the right molecular wire and the process will repeat. Thus we have here *electronically driven oscillations*. These oscillations cause the unidirectional electron flow and are maintained by this flow. This phenomenon can be used for the elements of molecular electronics. In particular, the oscillations can be stopped if the electron is not removed from the terminal atom of the right molecular wire. The electron will be caught on the bridge level located below the right energy level. This state will remain unchanged during quite a long time at sufficiently low temperature, even if the electron is removed from the right terminal atom. If the vibrations of the local mode above the threshold level, corresponding to the energy gap between these two levels, are excited the oscillations will be triggered. On the other hand, if the electrons are not supplied to the left terminal atom, oscillations will be stopped again, but with the empty bridge level. They may also be triggered by an external electromagnetic field.

The processes of electron transfer may also be monitored by an electric field changing the position of the bridge energy levels relative to those of the molecular wires.

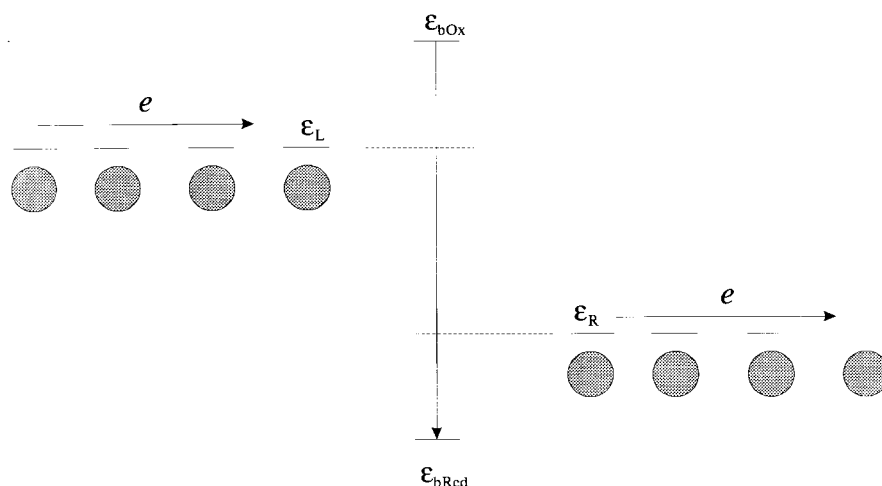


Figure 3. A scheme of electron transfer through a bridge between two molecular wires.

4. Concluding Remarks

The main results of the paper are briefly summarized below.

1. Expressions have been derived for the tunnel electric current between two metals produced by the adiabatic transitions of the electrons through a bridge electron level. It has been shown that the dependence of the current on the overpotential may reveal a maximum in the *normal region* the position and height of which depend on the bias voltage. A possibility of observing the *new abnormal region located behind the barrierless region* is discussed.

2. A new possible physical phenomenon is discussed. This is electronically driven oscillations of the electron bridge level between two molecular wires. This may be used in the elements of the molecular electronics as a memory, switching or sensor device.

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10. It was assumed throughout the paper that the bias potential does not act on the bridge level whereas the whole overpotential does. If, however, some portions of overpotential $\xi\eta$ and bias potential γV act on the bridge level, η in Equations (9)–(11) must be replaced by $\xi\eta + \gamma V$.