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Does the electron spin affect the rates of electron tunneling in electrochemical systems?

Alexander M. Kuznetsov *, Igor G. Medvedev

The A.N. Frumkin Institute of Physical Chemistry and Electrochemistry of Russian Academy of Sciences, Leninskii Prospect 31, 119991 Moscow, Russia

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Abstract

An effect of spin degeneracy of electron energy levels in the metal electrode on the observable characteristics of electrochemical systems in the absence of magnetic field is discussed. Single-electrode outer-sphere electron transfer reactions are considered as well as redox-mediated electron tunneling in electrochemical contacts. Particular attention is paid to the difference between the spin-less model and the limit of infinitely large Coulomb repulsion of the electrons occupying the same valence orbital in the redox group. Adiabatic and non-adiabatic regimes of the transitions are studied and the expressions for the tunnel current are obtained.

Keywords: Spin degeneracy; Electron transfer reactions; Electron tunneling; Sequential mechanism; Adiabatic transitions; Strong coupling with phonons

1. Introduction

Quantum mechanical treatment of electrochemical electron transfer processes has begun in late 1950s of the last century [1,2]. Non-adiabatic electron transfer reactions were considered first and the Fermi golden rule was used for the calculation of the transition probabilities. Most of works used spin-less model where the degeneracy of the electron energy levels in the metal due to the electron spin was ignored. A similar approximation was used in later works on adiabatic electrochemical electron transfer reactions [3–8] and in the works on electron tunneling in electrochemical contacts [9–18]. This model at first sight seems to be reasonable for single-electron outer-sphere electron transfer reactions in the absence of magnetic field when only one electron occupies the valence orbital of the redox group. An assumption on infinitely large Coulomb repulsion between the electrons located on the valence orbital of the redox group is invoked for the justification of this model. However, a proof of the equivalence of the spin-less model and the infinite Coulomb repulsion case is absent. As will be shown in the present article, this equivalence, strictly speaking, does not exist. In addition, a more detail analysis of the problem of electron spin in electrochemical kinetics is dictated by the recent experimental studies of redox-mediated electron tunneling in STM configuration [19–21] and theoretical results on Anderson model beyond spin-less approximation [22–24].

2. Electron spin in the theory of single-electrode electrochemical reactions

We start from *non-adiabatic electron transfer reactions* on a metallic electrode. The calculation of the probability (per unit time) of the transition of one electron from the metal to the reactant should take into account the fact that the electron transfer may take place from different electron energy levels in the metal. Every energy level in the metal (denoted as L) may be occupied by two electrons having opposite spin directions. The probability of occupation is determined by the Fermi distribution function $f_L(\varepsilon)$. As

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* Corresponding author. Tel.: +7 495 955 46 78.
E-mail address: theor@elchem.ac.ru (A.M. Kuznetsov).

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for the reacting species the occupation of a one-electron energy level depends on the value of the repulsion energy U between two electrons having opposite spin directions. Depending on the properties of the reactants the reaction may have one- or two-electron character. One-electron reaction with the electron transfer to a vacant energy level in the reactant formally corresponds to a very large value of the repulsion energy $U(U \to \infty)$. Two-electron reactions correspond to small values of U. However, unlike the processes in vacuum or in non-polar matrices the two-electron reactions in polar solvents proceed usually in two sequential steps. This is due to a strong interaction with solvent polarization (phonons). The solvent reorganization energy for the simultaneous transition of two electrons is four times the reorganization energy for the transition of one electron E_{rL}. Therefore, the sequential one-electron transitions are more probable here than the simultaneous transition of two electrons. Thus only one electron is transferred in each step.

One-electron reactions or the first step of two-electron reactions will be considered below. Only one electron occupies then the energy level in the reactant (denoted as B). This results in the difference in the transition probabilities for the forward k_{LB} and backward k_{BL} reactions:

$$k_{\mathrm{LB}} = 2k_{\mathrm{L}}^{0} \int \frac{\mathrm{d}\varepsilon}{k_{\mathrm{B}}T} f_{\mathrm{L}}(\varepsilon) \times \exp\left\{-[E_{\mathrm{rL}} - \Delta F_{\mathrm{BL}} - (\varepsilon - \varepsilon_{\mathrm{FL}})]^2/4E_{\mathrm{rL}}k_{\mathrm{B}}T\right\} \tag{1}$$

$$k_{\mathrm{BL}} = k_{\mathrm{L}}^{0} \int \frac{\mathrm{d}\varepsilon}{k_{\mathrm{B}}T} [1 - f_{\mathrm{L}}(\varepsilon)] \times \exp\left\{-[E_{\mathrm{rL}} + \Delta F_{\mathrm{BL}} + (\varepsilon - \varepsilon_{\mathrm{FL}})]^2/4E_{\mathrm{rL}}k_{\mathrm{B}}T\right\} \tag{2}$$

where the factor 2 in Eq. (1) takes into account that either of two electrons with opposite spin projections occupying a given energy level ε in the metal L may be transferred to the reactant B. However, this factor is absent in Eq. (2) since only one electron can be transferred from the singly occupied molecular orbital of the reactant B back to the metal. In Eqs. (1) and (2) ΔF_{BL} is the free energy of transition from the Fermi level of the metal $\varepsilon_{\mathrm{FL}}$ to the energy level in the reactant ε_{B}

$$\Delta F_{\mathrm{BL}} = \varepsilon_{\mathrm{FL}} - \varepsilon_{\mathrm{B}} - \Delta F_{\mathrm{solv.}} - e\varphi_{\mathrm{L}} + e\psi \tag{3}$$

Here $\Delta F_{\mathrm{solv.}}$ is the difference of the solvation free energies of the reduced and oxidized forms, φ_{L} is the electrode potential with respect to the potential in the bulk of the solution (taken to be zero) and ψ is the potential at the site of the reactant.

The factor k_{L}^{0} is equal to [25]

$$k_{\mathrm{L}}^{0} = \frac{\omega}{2\pi} 2\kappa_{\mathrm{L}}\rho_{\mathrm{L}}k_{\mathrm{B}}T \exp(-\sigma) \tag{4}$$

where ω is the effective frequency of vibrational subsystem, ρ_{L} is the density of electron states in the metal with neglect of the spin degeneracy, κ_{L} is the electron transmission coefficient for single passage through the crossing of two diabatic free energy surfaces and the exponential represents the Franck–Condon factor for quantum degrees of freedom of the solvent and the reactant. The corresponding Franck–Condon factor for classical degrees of freedom is represented by the exponentials under the integral signs in Eqs. (1) and (2). General expressions for the transition probability for arbitrary frequency spectrum of vibrational subsystem can be found elsewhere (see e.g. Ref. [4]).

It follows from Eqs. (1) and (2) that the transition probabilities for forward and backward reactions are related to each other by the detailed balance principle relationship

$$k_{\mathrm{BL}} = k_{\mathrm{LB}} \exp\left(-\frac{\Delta F_{\mathrm{BL}}^{(2)}}{k_{\mathrm{B}}T}\right) \tag{5}$$

where $\Delta F_{\mathrm{BL}}^{(2)}$ is defined as follows:

$$\Delta F_{\mathrm{BL}}^{(2)} = \Delta F_{\mathrm{BL}} + k_{\mathrm{B}}T \ln 2 \tag{6}$$

Here the last term takes into account the degeneracy of the electron energy levels in the metal. This term results in a shift (of ca. 0.7 $k_{\mathrm{B}}T$) of the equilibrium potential φ_{L}^{0} as compared to that emerged from the spin-less model. The equilibrium potential is defined by the equation:

$$\Delta F_{\mathrm{BL}}^{(2)} + k_{\mathrm{B}}T \ln \frac{C_{\mathrm{Ox}}}{\mathrm{C}_{\ \mathrm{Red}}} = \Delta F_{\mathrm{BL}}^{(0)} + k_{\mathrm{B}}T \ln 2 + k_{\mathrm{B}}T \ln \frac{C_{\mathrm{Ox}}}{\mathrm{C}_{\mathrm{Red}}} = 0 \tag{7}$$

where C_{Ox} and C_{Red} are the concentrations of the oxidized and reduced forms of the reacting species and the superscript (0) means that the electric potential involved in the free energy is the equilibrium one.

In what follows we will consider the "cathodic" overpotential η

$$\eta = \varphi_{\mathrm{L}}^{0} - \varphi_{\mathrm{L}} \tag{8}$$

Then at small overpotentials (as compared to the reorganization energy) the transition probabilities are equal approximately to

$$\begin{aligned} k_{\mathrm{LB}} &\approx 2\pi k_{\mathrm{L}}^{0} \exp(-E_{\mathrm{rL}}/4k_{\mathrm{B}}T) \exp(\Delta F_{\mathrm{BL}}/2k_{\mathrm{B}}T) \\ k_{\mathrm{BL}} &\approx \pi k_{\mathrm{L}}^{0} \exp(-E_{\mathrm{rR}}/4k_{\mathrm{B}}T) \exp[(-\Delta F_{\mathrm{BL}})/2k_{\mathrm{B}}T] \end{aligned} \tag{9}$$

and the electric current (with the neglect of Frumkin correction) is described by the following equation:

$$i = i_0[\exp(e\eta/2k_{\mathrm{B}}T) - \exp(-e\eta/2k_{\mathrm{B}}T)] \tag{10}$$

where the exchange current i_0 is $\sqrt{2}$ times as large as the exchange current in the spin-less model [1,2,8]. The reason for the appearance of the factor 2 in Eq. (9) is the same as in Eq. (1).

The situation is different in the case of *adiabatic electrochemical reactions*. Due to strong electronic coupling of the reactant with the electrode multiple electron transitions take place during passage of the electron energy level of the reactant through a region near the Fermi level of the electrode [13,14,26]. The electron transmission coefficient in the expressions for the rate constants here is equal to one independent of the spin degeneracy and e.g. for k_{LB} we have