Exactly Solvable Quantum Model for Electrochemical Electron-Transfer Reactions

Jörg-Heinrich Mohr and Wolfgang Schmickler
Abteilung Elektrochemie, Universität Ulm, D-89069 Ulm, Germany

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We consider electron exchange between a metal electrode and a solvated reactant coupled to a harmonic oscillator bath. In the wide-band approximation the time development of the occupation probability for the reactant orbital can be calculated explicitly. From the behavior at long times we derive an expression for the reaction rate that is valid for all strengths of the electronic interaction between the metal and the reactant. The rate constant is related to the scattering matrix for electron exchange between a metal substrate and a scanning tunneling microscope via an electroactive adsorbate.

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Electron transfer plays a fundamental role in many physical and chemical phenomena. It is of particular importance in electrochemistry, where it constitutes one of two possible mechanisms for charge transfer through the interface, the other mechanism being ion transfer. Electrochemical electron transfer is always coupled to solvent modes, which can be modeled as a harmonic oscillator bath, and often also to localized quantum modes. It has therefore many similarities to polaron theory and to electron tunneling through quantum dots [1] or through electronic states in the gap of a scanning tunneling microscope [2].

The theories of electrochemical electron-transfer reactions can be classified into two groups: On the one hand, there are classical and semiclassical theories derived from the models of Hush [3] and Marcus [4]; these are based on transition-state theory or its modern extensions, and pertain mainly to the adiabatic limit, in which the interaction between the electrode and the reactant is strong. On the other hand, there are quantum theories based on the work of Levich and Dogonadze [5], which rely on perturbation theory and therefore presume a weak interaction and hence nonadiabatic transfer. Both classes of theories are well reviewed in the recent monograph by Kuznetsov [6].

Thus the two limiting cases, classical theory with strong electronic interaction and quantum theory with weak electronic interaction, are well covered in the literature, but a general quantum theory valid for all strengths of the electronic interaction has been missing. In this work we fill this gap and solve an extension of the original Levich and Dogonadze theory exactly.

We consider electron exchange between a metal electrode and a reactant solvated in an electrolyte solution. We restrict ourselves to outer-sphere electron transfer, in which no chemical bonds are formed or broken; practically all theories are limited to that case. The electron transfer is coupled to a phonon bath, which represents the solvent and any local vibrational modes that interact with the electron. The solvent modes are mostly classical, but modes localized close to the reactant may have to be treated by quantum mechanics [7]. The vibrational modes are usually quantum mechanical; i.e., their frequencies obey the relation $k_BT \leq \hbar\omega$. As our starting point we use a Hamiltonian which one of us had proposed as a second-quantized form of the Levich-Dogonadze model [8]. It consists of an electronic part, which takes the form

$$H_e = \varepsilon_a n_a + \sum_k \varepsilon_k n_k + \sum_k [V_k c_k^+ c_a + V_k^* c_a^+ c_k]. \quad (1)$$

Here, n denotes a number operator, c^+ a creation and c an annihilation operator, and ε an energy. The first term with the label a describes the reactant, the second term the metal electrons, which are labeled by their quasimomentum k, and the last term accounts for electron exchange between the reactant and the metal; V_k is the corresponding matrix element. This part of the Hamiltonian is similar to that of the Anderson-Newns model [9], but without spin. The neglect of spin is common in electron-transfer theory, and is justified by the comparatively weak electronic interaction.

Both the solvent and the local vibrations are modeled as harmonic oscillators, which are coupled linearly to the reactant; the corresponding Hamiltonian is written in the form

$$H_{\text{osc}} = \frac{1}{2} \sum_\nu \hbar\omega_\nu [p_\nu^2 + (q_\nu - n_a g_\nu)^2], \quad (2)$$

where ν labels the oscillator modes, which have frequencies ω_ν, momenta p_ν, and coordinates q_ν; g_ν denotes the coupling constants. For classical solvent modes other models such as the dipolar interaction model [10] can also be used without affecting our results as long as the coupling is linear. Our model Hamiltonian is the sum of H_{e} and H_{osc}.

We introduce the *energy of reorganization* of the mode ν through

$$\lambda_\nu = \frac{1}{2} \hbar\omega_\nu g_\nu^2, \quad (3)$$

and the resonance width

$$\Delta(\varepsilon) = \pi \sum_k |V_k|^2 \delta(\varepsilon - \varepsilon_k). \quad (4)$$

We use the so-called *wide-band approximation* and assume that Δ is independent of the electronic energy ε over the range of energies that contribute to the electron-transfer reaction. In most situations electron transfer is limited to a region with a width of a few $k_B T$ near the Fermi level [11], so this is not a restrictive condition. The time development of the system can then be derived by solving the equations of motion or by calculating the Green's function directly. The mathematical techniques involved in the former approach are an extension of those used by Brako and Newns [12] (for the electronic part) and those in Refs. [1,2] (for the phonon bath). As an example we give the expression for the annihilation operator c_a in the Heisenberg picture. We consider a system prepared at the time $t = 0$ and denote by $\langle n_{a0}\rangle$ the occupation probability of the redox orbital at that time; we obtain

$$\begin{aligned} c_a(t) = {} & \exp\left\{-\frac{i}{\hbar}[\varepsilon_a + \lambda(1 - 2\langle n_{a0}\rangle) - i\Delta]t\right\}\exp\left[-i\sum_\nu g_\nu \hat{p}_\nu(t)\right]\exp\left[i\sum_\nu g_\nu \hat{p}_{\nu 0}\right]c_{a0} \\ & - \frac{i}{\hbar}\sum_k \int_0^t \left\{V_k e^{-(i/\hbar)\varepsilon_k \tau}\exp\left\{-\frac{i}{\hbar}[\varepsilon_a + \lambda(1 - 2\langle n_{a0}\rangle) - i\Delta](t - \tau)\right\}\right. \\ & \left.\times \exp\left[-i\sum_\nu g_\nu \hat{p}_\nu(t)\right]\exp\left[i\sum_\nu g_\nu \hat{p}_\nu(\tau)\right]c_{k0}\right\}d\tau\,. \end{aligned} \tag{5}$$

$\hat{p}_\nu(t)$ is the momentum of the free harmonic oscillator with frequency ω_ν, and $\lambda = \sum_\nu \lambda_\nu$ is the total energy of reorganization; initial values are indicated by a subscript 0.

In order to calculate the rate constant we consider a system prepared in the oxidized state at $t = 0$, i.e., $\langle n_{a0}\rangle = 0$, and assume that the phonon bath is in thermal equilibrium with that electronic state at $t = 0$. We obtain for the thermal expectation value of the number operator n_a

$$\begin{aligned} \langle\langle n_a(t)\rangle\rangle = {} & \frac{1}{\pi\hbar}\int d\varepsilon\, f(\varepsilon, T) \\ & \times \mathrm{Re}\left\{\int_0^t d\tau \exp\left[-\frac{i}{\hbar}(\varepsilon_a - \varepsilon + \lambda)\tau\right]\right. \\ & \left.\times (e^{-(\Delta/\hbar)\tau} - e^{-(2\Delta/\hbar)t + (\Delta/\hbar)\tau})K(\tau)\right\}, \end{aligned} \tag{6}$$

where $f(\varepsilon, T)$ is the Fermi-Dirac distribution, and the thermal correlation function $K(\tau)$ factorizes into a product of terms for each mode:

$$\begin{aligned} K_\nu(\tau) = \prod_\nu \exp\left\{-\frac{\lambda_\nu}{\hbar\omega_\nu}\left[\coth\left(\frac{1}{2}\beta\hbar\omega_\nu\right)(1 - \cos\omega_\nu\tau)\right.\right. \\ \left.\left. - i\sin\omega_\nu\tau\right]\right\}. \end{aligned} \tag{7}$$

For classical modes the product can be calculated explicitly, and the correlation function takes the simple form

$$K_{\mathrm{cl}}(\tau) = \exp\left[-\frac{\lambda_{\mathrm{cl}}}{\beta}\frac{\tau^2}{\hbar^2}\right], \tag{8}$$

where λ_{cl} is the total reorganization energy of all classical modes, and $\beta = 1/k_B T$. Both forms of the correlation function are familiar from the statistical mechanics of harmonic oscillators [13].

At short times the occupation probability $\langle\langle n_a(t)\rangle\rangle$ oscillates, but at long times, for $t \gg \frac{2\hbar}{\Delta}$ or $t \gg \hbar\sqrt{\frac{\beta}{\lambda_{\mathrm{cl}}}}$, it decays exponentially and obeys a relaxation equation of the form

$$\frac{d}{dt}\langle\langle n_a(t)\rangle\rangle = -\frac{2\Delta}{\hbar}[\langle\langle n_a(t)\rangle\rangle - \langle\langle n_a(t \to \infty)\rangle\rangle], \tag{9}$$

with a relaxation time of $\tau_r = \hbar/2\Delta$. This can be verified by substituting Eqs. (6) and (7) into Eq. (8) and taking the limit of long times. The reaction rates k_{red} for the reduction and k_{ox} for the oxidation are then obtained from

$$k_{\mathrm{red}} = \langle\langle n_a(\infty)\rangle\rangle/\tau_r \quad \text{and} \quad k_{\mathrm{ox}} = [1 - \langle\langle n_a(\infty)\rangle\rangle]/\tau_r\,. \tag{10}$$

These rate constants can be written in the transparent form

$$\begin{aligned} k_{\mathrm{red}} &= \int d\varepsilon\, f(\varepsilon, T) w_{\mathrm{red}}(\varepsilon)\,, \\ k_{\mathrm{ox}} &= \int d\varepsilon\,[1 - f(\varepsilon, T)] w_{\mathrm{ox}}(\varepsilon)\,, \end{aligned} \tag{11}$$

where $w_{\mathrm{red}}(\varepsilon)$ is the rate of electron transfer from an occupied level with energy ε on the metal to the reactant, and w_{ox} is the rate of electron transfer from the reactant to an empty level on the metal. The former rate is proportional to the so-called *density of oxidized states* introduced by Gerischer [14], and the latter to the *density of reduced states*. These energy-resolved rates are given by

$$\begin{aligned} w_{\mathrm{red}}(\varepsilon) = {} & \frac{\Delta}{\pi\hbar^2}\int_{-\infty}^{\infty} d\tau \exp\left[-\frac{i}{\hbar}(\varepsilon_a - \varepsilon + \lambda)\tau\right] \\ & \times e^{-(\Delta/\hbar)|\tau|}K(\tau)\,, \end{aligned} \tag{12}$$

$$\begin{aligned} w_{\mathrm{ox}}(\varepsilon) = {} & \frac{\Delta}{\pi\hbar^2}\int_{-\infty}^{\infty} d\tau \exp\left[-\frac{i}{\hbar}(\varepsilon_a - \varepsilon - \lambda)\tau\right] \\ & \times e^{-(\Delta/\hbar)|\tau|}K(\tau)\,. \end{aligned} \tag{13}$$

They obey the relations

$$\int_{-\infty}^{\infty} w_{\mathrm{red}}(\varepsilon)\, d\varepsilon = \frac{\Delta}{\hbar}\,, \tag{14}$$

$$\lim_{\Delta \to \infty} w_{\mathrm{red}}(\varepsilon) = \frac{2}{\pi\hbar}\,, \tag{15}$$

with corresponding relations for w_{ox}. In addition, detailed balancing holds.

The combination of Eqs. (11), (12), and (13) is our general expression for the rate constants. For small values of the width Δ we may replace the term $\exp(-\Delta|\tau|/\hbar)$ in Eqs. (12) and (13) by unity, and we obtain the rate expressions familiar from the Levich-Dogonadze theory [6].

If only classical modes are coupled to the electron transfer, the remaining integral in Eqs. (12) and (13) can be calculated explicitly,

$$w_{\mathrm{red}}(\varepsilon) = \frac{\Delta}{\hbar}(\pi\lambda k_B T)^{-1/2} \times \mathrm{Re}\left[w\left(\frac{1}{2}\sqrt{\frac{\beta}{\lambda}}(\varepsilon_a - \varepsilon + \lambda + i\Delta)\right)\right], \tag{16}$$

where $w(z) = e^{-z^2}\mathrm{erfc}(-iz)$ is the complex error function [15]. The rate w_{ox} is obtained by changing the sign of λ in the argument of the error function; this is a consequence of the detailed balancing condition. Figure 1 shows the corresponding reduction rate at equilibrium, when ε_a equals the Fermi level of the metal, as a function of the energy width Δ. For small interactions this dependence is linear; this is the range in which perturbation theory is valid. If we neglect the width Δ in the last term Eq. (16) simplifies to

$$w_{\mathrm{red}}(\varepsilon) = \frac{\Delta}{\hbar}(\pi\lambda k_B T)^{-1/2} \exp - \frac{(\varepsilon_a - \varepsilon + \lambda)^2}{4\lambda kT}. \tag{17}$$

The exponential term is familiar from the theories of Hush [3] and Marcus [4], and determines the classical activation energy. In the adiabatic theory [8] the classical activation energy decreases with increasing electronic interaction Δ. A similar effect is observed in our model: the effective activation energy, defined through $E_{\mathrm{act}} = -d\ln(k_{\mathrm{red}}^{\mathrm{cl}})/d(1/kT)$, where $k_{\mathrm{red}}^{\mathrm{cl}}$ is the classical rate constant obtained from Eqs. (11) and (16), also decreases with increasing Δ (see Fig. 1).

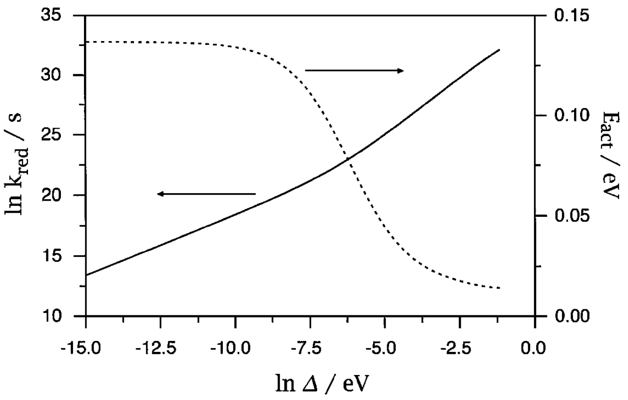

FIG. 1. Dependence of the reduction rate k_{red} and the activation energy at equilibrium on the energy broadening Δ for a system that couples to classical modes only; $\lambda_{\mathrm{cl}} = 0.5$ eV.

In many cases the electron transfer is coupled to a classical solvent bath and a few quantum modes. A comparatively simple formula is obtained if one quantum mode only is reorganized; in this case the energy-resolved rate can be written in the form

$$w_{\mathrm{red}}(\varepsilon) = \frac{\Delta}{\hbar}\sqrt{\frac{\beta}{4\pi\lambda_{\mathrm{cl}}}} \exp\left(-\frac{\lambda_1}{\hbar\omega_1}\coth x_1\right)\sum_{n=-\infty}^{\infty} I_n\left(\frac{\lambda_1}{\hbar\omega_1}\mathrm{csch} x_1\right)e^{-nx_1} \times \mathrm{Re}\left[w\left(\frac{1}{2}\sqrt{\frac{\beta}{\lambda_{\mathrm{cl}}}}(\varepsilon_a - \varepsilon - n\hbar\omega_1 + \lambda + i\Delta)\right)\right], \tag{18}$$

where the index 1 labels the quantum mode, and I_n is a modified Bessel function of the first kind. Figure 2 shows a few illustrative cases: If the reactant is fully solvated the two energies of reorganization λ_{cl} and λ_1 are typically of the same order of magnitude. In this case $w_{\mathrm{red}}(\varepsilon)$ is broad and featureless (full line); it resembles the Gaussian form familiar from Marcus theory, but the decay at high energies, which corresponds to the Marcus inverted region, is not so fast. If the reactant is embedded in a film its interaction with the solvent is weak, and the energy-resolved rate may exhibit quantum oscillations (dotted line); these are smeared out if the energy width is of the same order of magnitude as the quantum $h\nu$ (dashed line).

It has recently been demonstrated that a reactant adsorbed on the electrode surface may be observed by a scanning tunneling microscope [16]. In this case the transferring electron is scattered by the reactant, and the process can be described by a scattering matrix $T(\varepsilon, \varepsilon')$, where ε is the energy of the incoming electron, and ε' that of the outgoing electron. An explicit formula for the scattering matrix has been derived in [2] using results obtained for quantum dots [1]. If the electronic width Γ caused by the interaction with the tip is much smaller than the width Δ acquired through the interaction with the metal—this would be the typical case—the energy resolved rates derived here are related to the scattering matrix by

$$w_{\mathrm{red}}(\varepsilon) = \Gamma\int T(\varepsilon, \varepsilon')\,d\varepsilon'. \tag{19}$$

If only classical modes are coupled to the electronic transition, the electron is always scattered elastically. In this case the scattering matrix contains a factor $\delta(\varepsilon - \varepsilon')$, and is directly proportional to the energy-resolved rate $w_{\mathrm{red}}(\varepsilon)$.

The rate constants that we have derived in this work are for an ensemble of identical reactants with a given value for the energy width Δ. In an experiment one measures the average rate of an ensemble of particles distributed in the vicinity of the electrode, which have different interactions with the electrode and hence different widths Δ.

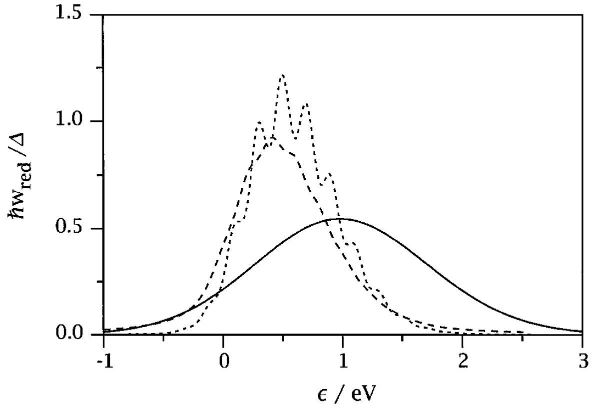

FIG. 2. Normalized energy-resolved rates $\hbar w_{\mathrm{red}}/\Delta$. Full line: $\lambda_{\mathrm{cl}} = 0.5$ eV, $\lambda_1 = 0.5$ eV, $h\nu_1 = 0.2$ eV, $\Delta = 0.01$ eV; dotted line: $\lambda_{\mathrm{cl}} = 0.1$ eV, $\lambda_1 = 0.5$ eV, $h\nu_1 = 0.2$ eV, $\Delta = 0.01$ eV; dashed line: $\lambda_{\mathrm{cl}} = 0.1$ eV, $\lambda_1 = 0.5$ eV, $h\nu_1 = 0.1$ eV, $\Delta = 0.1$ eV.

The work presented above is the first quantum theory of electrochemical electron transfer reactions valid for arbitrary strengths of the electronic interaction. It is interesting to compare our results with those obtained for electron transfer between two solvated reactants [17]. The wide-band approximation that we have used here can be applied only if one of the reactants has a continuum of electronic levels, therefore it is not applicable to the reaction between two molecules. Nevertheless, our equations for the energy-resolved rates do show a certain similarity with approximate expressions obtained for the two-level problem. This is not surprising, since both rates are influenced by the same effects: a thermal broadening of the levels caused by the classical bath, discrete vibrational levels, and an electronic interaction responsible for the electron transfer.

Since we have represented the solvent as a bath of undamped oscillators, our model does not account for solvent friction. Therefore it will not reduce to the Grothe-Hynes [18] theory in the classical limit. As has been pointed out by Morgan and Wolynes [19], solvent dynamics is likely to become the rate-determining step for very strong electronic coupling. Obviously, our model will not apply in that case.

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