# Adiabatic and Non-Adiabatic Electrochemical Electron Transfer in Terms of Green's Function Theory[1, 2]

## Wolfgang Schmickler

*Institute of Theoretical Chemistry, Ulm University D-89069 Ulm, Germany*
*e-mail: wolfgang.schmickler@uni-ulm.de*
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**Abstract**—We present a model Hamiltonian for electrochemical electron transfer, and use Green's functions as the starting point for three different approaches to the calculation of rate constants: first order perturbation theory, which is equivalent to the Levich and Dogonadze theory, the calculation of adiabatic free energy surfaces, and propagation in time. We discuss the similarities and differences between these methods.

## 1. INTRODUCTION

When I began to work on my Ph.D. thesis in 1972, my director, Wolf Vielstich, told me, that there was a new branch of theoretical electrochemistry based on quantum mechanics, and gave me a review article by Levich [1] on the theory of electrochemical electron transfer reactions to read, which later became known as the Levich and Dogonadze theory. He suggested that I should work in this area for my thesis, which I did with success. Later my interest shifted to other topics, and when I actually went to the famous Frumkin Institute in Moscow in 1979, I was working on adsorption and double layer problems, Levich had already left, and Dogonadze was busy setting up a scientific institute in Tbilisi in his native Georgia. I started a very fruitful cooperation with a few of the younger members of the Moscow group, in particular with Kornyshev and later with Kuznetsov, who had become the chief exponent of the Soviet theory of electron transfer; his book [2] has become the standard work on this topic.

During the course of the years I returned to problems of electron transfer several times, shifting from outer-sphere to bond-breaking electron transfer and later to electrocatalysis. Since so much of my work was inspired by reading the first review on the Levich and Dogonadze theory, I am happy to contribute to this special issue in honor of Levich. Writing a review on a subfield of electron transfer was out of the question;

rather, I decided to link three different approaches to outer sphere electron transfer, which can be derived from the same model Hamiltonian via Green's function theory: (1) the original Levich and Dogonadze theory based on first order perturbation; (2) calculation of potential energy surfaces from an exact solution of the Green's function; (3) time propagation of the initial state based on an exact solution. Each of these approaches has its own merits, and I hope that a comparison within the same framework will be useful especially for younger colleagues.

By necessity this work contains many equations. In order to avoid clustering them with constants I use atomic units throughout. However, at times I have written out Planck's constant $\hbar$ explicitly, so that the units of certain quantities can be verified.

## 2. THE MODEL HAMILTONIAN

Our model Hamiltonian, which we had first presented in [3], can be considered as a second-quantized version of the Levich and Dogonadze theory [1]. The advantage of this formalism is that it lends itself easily to the application of Green's function techniques. So we consider a reactant with a valence orbital labeled $a$, which can exchange an electron with a metal, whose electronic states are labeled by a continuous index $k$. We denote by $\varepsilon_k$ the electronic energy of the metals states, by $n_k$ their number operator, and by $c_k^+$ and $c_k$ the creation and annihilation operators. The corresponding quantities for the state $a$ are $\varepsilon_a$, $n_a$, $c_a^+$ and $c_a$. We consider the transfer of one electron in the outer sphere mode, so we can disregard spin. In this case the

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[1] This paper is the author's contribution to the special issue of Russian Journal of Electrochemistry dedicated to the 100th anniversary of the birth of the outstanding Soviet electrochemist Veniamin G. Levich.

[2] The article is published in the original.

electronic part of the Hamiltonian is a spinless version of the Anderson−Newns [4, 5] model:

$$H_{\text{el}} = \varepsilon_a n_a + \sum_k \varepsilon_k n_k + \sum_k \left[ V_k c_k^+ c_a + V_k^* c_a^+ c_k \right]. \quad (1)$$

The first two terms denote the reactant and the metal, the last term effects electron exchange between the metal and the reactant with amplitudes $V_k$. Electron transfer is coupled to the reorganization of the solvent, and usually also to a few inner sphere vibration modes of the reactant. Just like in Marcus [6] (and polaron) theory, these modes are divided into a fast part, which is supposed to follow the electron transfer instantly, and a slow part. The former just renormalizes the electronic energy [2, 7], and will not be discussed further. The latter is modeled as a phonon bath, whose modes we label by $\nu$:

$$H_{\text{sol}} = \frac{1}{2} \sum_\nu \hbar \omega_\nu \left( q_\nu^2 + p_\nu^2 \right), \quad (2)$$

where $q_\nu$ and $p_\nu$ are dimensionless coordinates and momenta, and $\omega_\nu$ the frequencies. These modes interact linearly with coupling constants $g_\nu$ with the charge on the reactant. We consider the case in which the charge on the reactant vanishes when the orbital $a$ is empty. Then the interaction term is:

$$H_{\text{int}} = n_a \sum_\nu \hbar \omega_\nu g_\nu q_\nu. \quad (3)$$

Here we consider only classical modes, so that their coordinates can be considered as external parameters for the electronic system. For the sake of brevity, we shall refer to them as solvent modes. Towards the end we shall briefly comment on the effect of quantum modes.

Our model Hamiltonian $H$ is the sum of these three terms. For the application of Green's function theory it is convenient to split it into two terms: A transfer term $H_T$, which consists of the last two terms in Eq. (1), and the rest:

$$H = H_0 + H_T, \quad H_T = \left[ V_k c_k^+ c_a + V_k^* c_a^+ c_k \right]. \quad (4)$$

The corresponding retarded Green's [8, 9] functions are:

$$G^+(z) = \frac{1}{z - H + i\varepsilon}, \quad G_0^+(z) = \frac{1}{z - H_0 + i\varepsilon}, \quad (5)$$

where $\varepsilon$ is an infinitesimal quantity. They are related through the Dyson equation:

$$G^+(z) = G_0^+ + G^+(z) H_T G_0^+(z). \quad (6)$$

We limit ourselves to the case in which all relevant solvent modes are classical. In this case it is convenient to collect the terms in $n_a$ and write:

$$\left( \varepsilon_a + \sum_\nu \hbar \omega_\nu g_\nu q_\nu \right) n_a = \varepsilon_a' n_a. \quad (7)$$

## 3. FIRST ORDER PERTURBATION THEORY

The Dyson equation (6) can be used to obtain a systematic perturbation series in the transfer Hamiltonian $H_T$. To first order this gives:

$$G^+(z) = G_0^+ + G_0^+(z) H_T G_0^+(z). \quad (8)$$

In the Levich and Dogonadze version of electron transfer theory one considers electron transfer from $a$ to the manifold of metal states $k$, and the reverse. The corresponding amplitude is:

$$\left\langle a \left| G^+(z) \right| k \right\rangle = \frac{1}{z - \varepsilon_a' + i\delta} V_k^* \frac{1}{z - \varepsilon_k + i\delta}. \quad (9)$$

To obtain the time-development we use the relation between the Green's function and the propagator via the Fourier transform

$$F(G^+)(t) = \int_{-\infty}^{\infty} e^{-i\omega t} G^+(\omega) d\omega = -2\pi i e^{-iHt} \theta(t), \quad (10)$$

where $\theta(t)$ in the Heaviside step function. If we disregard the trivial factor $-2\pi i$, this is just the propagator in the forward direction. By taking the Fourier transform of Eq. (9) we obtain for the transition amplitude from the time zero to the time $t > 0$:

$$\left\langle a \left| e^{-iHt} \right| k \right\rangle = V_k^* \frac{e^{-i\varepsilon_a' t}}{\varepsilon_a' - \varepsilon_k} \left[ 1 - e^{i(\varepsilon_a' - \varepsilon_k t)t)} \right] \quad (11)$$

and the corresponding transition probability is given by:

$$W_{a \to k} = \left| \left\langle a \left| e^{-iHt} \right| k \right\rangle \right|^2. \quad (12)$$

Now follows the textbook derivation of Fermi's golden rule. The transition rate from $a$ to $k$ per time is:

$$r_{a \to k} = \frac{W_{a \to k}}{t} = \frac{|V_k|^2}{(\varepsilon_a' - \varepsilon_k)^2 t} \left[ 2 - 2\cos(\varepsilon_a' - \varepsilon_k)t \right]. \quad (13)$$

Taking the limit $t \to \infty$ we obtain:

$$r_{a \to k} = |V_k|^2 \delta(\varepsilon_a' - \varepsilon_k), \quad (14)$$

where a well-known relation for the $\delta$-function has been used [10]. The rest is elementary, but it may be useful to give a few details. Next we perform the thermal average over the solvent coordinates $q_\nu$. For this purpose it is useful to take the Fourier transform of the $\delta$-function:

$$\delta\left( \varepsilon_a' - \varepsilon_k \right) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\left( \varepsilon_a' - \varepsilon_k \right)t} dt$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp\left[ it \left( \varepsilon_a - \varepsilon_k + \sum_\nu \hbar \omega_\nu g_\nu q_\nu \right) \right] dt. \quad (15)$$

For the thermal average we need the partition function of the oscillator bath in the initial state. For each oscillator we have:

$$Z_v = \sqrt{\frac{2\pi kT}{\hbar\omega_v}}. \tag{16}$$

The total partition function is the product over $v$. For didactical purposes we show how the average over one mode is performed. We need:

$$\frac{1}{Z_v}\int_{-\infty}^{\infty} dq_v \exp\left[-\beta\hbar\omega_v q_v^2 + \hbar\omega_v g_v q_v t\right] \tag{17}$$
$$= \exp-\lambda_v kTt^2,$$

where $\beta = 1/kT$, and $\lambda_v = \hbar\omega_v g_v^2/2$ is the contribution of one mode to the energy of reorganisation of the solvent. For the thermally averaged rate we then obtain:

$$\bar{r}_{a\to k} = |V_k|^2 \int_{-\infty}^{\infty} \exp\left[i(\varepsilon_a - \varepsilon_k)t - \lambda kTt^2\right] \tag{18}$$
$$= |V_k|^2 \sqrt{\frac{1}{4\pi\lambda kT}} \exp-\frac{(\varepsilon_a - \varepsilon_k)^2}{4\lambda kT},$$

where $\lambda = \sum_v \lambda_v$ is the total energy of reorganisation.

So far we have not specified any reference energies. For the metal it is convenient to take the Fermi level as zero, so all $\varepsilon_k$ are referred to this level. We next look at the energy of the reactant plus the solvent, when the former is far from the electrode, so that $H_T$ does not contribute to the energy. When $a$ is occupied, a simple calculation gives that the solvent is in equilibrium when $q_v = -g_v$ for all modes. This gives an energy of $\varepsilon_a - \lambda$ for this subsystem. When $a$ is empty, the equilibrium condition is $q_v = 0$, and the energy vanishes. At equilibrium there must be no gain in energy when the electron is transferred to the Fermi level, therefore $\varepsilon_a = -\lambda$ at equilibrium, and in general we may write: $n_a = -\lambda + e_0\eta$, where $\eta$ is the overpotential. Hence:

$$\bar{r}_{a\to k} = |V_k|^2 \sqrt{\frac{1}{4\pi\lambda kT}} \exp-\frac{(\lambda + e_0\eta - \varepsilon_k)^2}{4\lambda kT}. \tag{19}$$

Electron transfer can only occur to empty levels. To get the total rate we multiply the r.h.s. by $[1 - f(\varepsilon_k)]$, where $f$ is the Fermi–Dirac distribution, and integrate over all $\varepsilon_k$:

$$r = \sqrt{\frac{1}{4\pi\lambda kT}}\int_{-\infty}^{\infty} dk |V_k|^2 [1 - f(\varepsilon_k)]$$
$$\times \exp-\frac{(\lambda + e_0\eta - \varepsilon_k)^2}{4\lambda kT}. \tag{20}$$

Usually the overpotential is smaller than $\lambda$, and inspection shows that in this case only states near the Fermi level participate in the reaction. In this case we may take the coupling as constant: $V_k = V$, and replace the integral over $k$ by an integral over $\rho(\varepsilon)d\varepsilon$, where $\rho(\varepsilon)$ is the electronic density of states of the metal. This finally results in:

$$r = \sqrt{\frac{1}{4\pi\lambda kT}}|V|^2 \int_{-\infty}^{\infty} d\varepsilon\rho(\varepsilon)[1 - f(\varepsilon_k)]$$
$$\times \exp-\frac{(\lambda + e_0\eta - \varepsilon)^2}{4\lambda kT}. \tag{21}$$

This equation has a nice interpretation in the theory of Gerischer: He interprets:

$$\sqrt{\frac{1}{4\pi\lambda kT}}\exp-\frac{(\lambda + e_0\eta - \varepsilon)^2}{4\lambda kT} \tag{22}$$

as the density of occupied states of the solution, and

$$\rho(\varepsilon)[1 - f(\varepsilon_k)] \tag{23}$$

as the density of empty states on the metal, so that the rate is proportional to the product of these two densities. For more details, we refer to the original publication [10], and to the textbook [11].

## 4. ADIABATIC POTENTIAL ENERGY SURFACES

Instead of using perturbation theory we can solve for the matrix elements of the Green's function exactly. We are interested in the properties of the reactant; we start from Dyson's equation (6):

$$\langle a|G^+|a\rangle = \langle a|G_0^+|a\rangle + \langle a|G^+ H_T G_0^+|a\rangle$$
$$= \frac{1}{z - \varepsilon_a' + i\delta}\left[1 + \sum_k V_k^* \langle a|G^+|k\rangle\right]. \tag{24}$$

Similar we obtain:

$$\langle a|G^+|k\rangle = \frac{1}{z - \varepsilon_k + i\delta}\langle a|G^+ H_T|k\rangle$$
$$= \frac{V_k}{z - \varepsilon_k + i\delta}\langle a|G^+|a\rangle. \tag{25}$$

We combine the two equations:

$$(z - \varepsilon_a' + i\delta)\langle a|G^+|a\rangle$$
$$= 1 + \langle a|G^+|a\rangle \sum_k \frac{|V_k|^2}{z - \varepsilon : k + i\delta}. \tag{26}$$

We use the relation [12]

$$\frac{1}{z - \varepsilon_k + i\delta} = P\frac{1}{z - \varepsilon_k} - i\pi\delta(z - \varepsilon_k), \tag{27}$$

where $P$ denotes the principal part. We define the two so-called chemisorption functions:

$$\Lambda(z) = P\sum_k \frac{|V_k|^2}{z - \varepsilon_k} \quad \Delta(z) = \pi\sum_k |V_k|^2 \delta(z - \varepsilon_k), \quad (28)$$

which obey the equation:

$$\Lambda(z) = \frac{1}{\pi} P \int \frac{\Delta(x)}{z - x} dx. \quad (29)$$

With these definitions, we can write the matrix element in the compact form:

$$\langle a | G^+ | a \rangle = \frac{1}{z - \left[\varepsilon_a' + \Lambda(z)\right] + i\Delta(z)}. \quad (30)$$

The two chemisorption functions have different effects on the energy $\varepsilon_a'$: $\Lambda$ shifts this energy, and $\Delta$ adds an imaginary part, so that the state $a$ attains a finite lifetime. We shall return to these points below. Note that this Green's function contains solvent terms in $\varepsilon_a'$. In its general form, Eq. (30) plays an important role in the Santos and Schmickler theory of electrocatalysis [13, 14]. Without the solvent, but with consideration of spin, it forms the basis of the Newns theory of adsorption [5].

We are considering outer sphere electron transfer, where the interaction with the metal is much weaker than in adsorption, and the detailed electronic structure of the metal plays no role. In this case the *wide-band approximation* is useful, in which the coupling elements $V_k = V = \text{constant}$ are taken as constant. In this case, $\Delta$ is constant and $\Lambda$ vanishes for reasons of symmetry. We had made the same assumption in the derivation of Eq. (21), and we shall use it in the rest of this article.

From the Green's function we can obtain the density of states (DOS) of $a$ [8]:

$$\rho_a(\varepsilon) = -\frac{1}{\pi}\Im\langle a | G^+ | a \rangle$$
$$= \frac{1}{\pi}\frac{\Delta}{(\varepsilon - \varepsilon_a - \sum_\nu \hbar\omega_\nu g_\nu q_\nu)^2 + \Delta^2}, \quad (31)$$

where $\Im$ denotes the imaginary part. Here and in the rest of this work we shall denote real energies by $\varepsilon$, and use the general term $z$ when we need the extension into the complex plane. The DOS of $a$ has the simple form of a Lorentzian of width $\Delta$. The center of this distribution depends on the solvent coordinates, and thus on the fluctuations of the solvent.

From the DOS we can obtain the occupation $\langle n_a \rangle$ of the orbital. To a good approximation we can replace the Fermi–Dirac function by a step function, and integrate the DOS to the Fermi level $E_F = 0$:

$$\langle n_a \rangle = \int_{-\infty}^{\infty} \rho_a(\varepsilon)d\varepsilon = \frac{1}{\pi}\arctan\frac{\varepsilon_a + \sum_\nu \hbar\omega_\nu g_\nu q_\nu}{\Delta}. \quad (32)$$

The electronic energy is obtained from the integral:

$$E_{el} = \int_{-\infty}^{0} \varepsilon\rho_a(\varepsilon)d\varepsilon = \varepsilon_a'\langle n_a \rangle + \frac{\Delta}{\pi}\int_{-\infty}^{\varepsilon'} \frac{\omega}{\omega^2 + \Delta^2}d\omega, \quad (33)$$

where we have made the substitution $\omega = \varepsilon - \varepsilon_a'$. The integrand has the indeterminate integral $\ln(\omega^2 + \Delta^2)/2$. So the determinate integral diverges, which is a consequence of the wide band approximation. However, the difference between two states with different solvent configurations is finite. We choose the reference state as $q_\nu = 0$, so that we obtain:

$$E_{el} = \varepsilon_a'\langle n_a \rangle + \frac{\Delta}{2\pi}\ln\frac{(\varepsilon_a + \sum_\nu \hbar\omega_\nu g_\nu q_\nu)^2 + \Delta^2}{\varepsilon_a^2 + \Delta^2}. \quad (34)$$

The two terms have a simple interpretation: the first is the electronic energy multiplied by the occupation probability, and the second term is the correction due to the finite width $\Delta$, which lowers the energy, and which vanishes for $\Delta = 0$.

Equation (34) gives the potential energy as a function of the solvent coordinates $q_\nu$, which, since they are considered as classical, act as external parameters. The stationary points of the surface are of special interest; they are given by:

$$\left\langle \frac{\partial H}{\partial q_\nu} \right\rangle = 0, \quad (35)$$

which gives the simple relations for the solvent coordinates:

$$q_\nu = -<n_a> g_\nu \quad (36)$$

This leads to a self-consistent equation for $\langle n_a \rangle$, which is examined in [3, 15]. We consider adiabatic outer-sphere electron transfer, where the interaction is sufficiently strong to ensure adiabaticity, but the absence of adsorption ensures that $\Delta \ll \lambda$. Under this condition there are always three stationary points at equilibrium conditions: two minima corresponding to the initial and the final states, separated by a saddle point. From Eq. (36) it can be seen that they lie on a straight line. This makes it possible to define a single reaction coordinate $q$ on this line. This can be normalized such that for $q = 0$ the solvent is in equilibrium with the reduced state, and for $q = -1$ with the oxidized state. Details of the normalization can be found in [12].
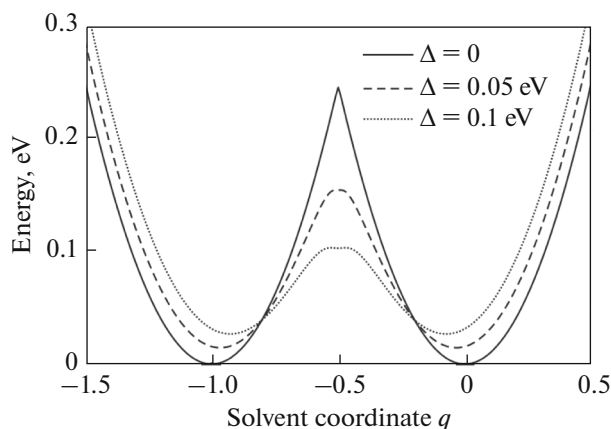
**Fig. 1.** Adiabatic potential energy curves for various values of $\Delta$ in the equilibrium configuration. The energy of reorganization was taken as $\lambda = 1$ eV.

Consequently we can plot one-dimensional potential energy curves for the electron transfer, in the same way as is familiar from Marcus [6] and Hush [16] theory. An example is shown in Fig. 1 for the case where the reaction is at equilibrium. Similar to Marcus theory, the interaction energy $\Delta$ lowers the energy of the saddle point. In addition, high values of $\Delta$ affect the energies of the initial and the final state. Such potential energy curves can be combined with Kramers' theory [17] to calculate rate constants.

This theory holds equally well for electron exchange with a semiconductor. In this case, simple approximations like the wide band approximation hold only for energies inside the conduction and the valence band. A good introduction to this problem is contained in the recent article by Nazmutdinov et al. [18].

## 5. PROPAGATION IN TIME

In the wide band approximation, the electronic energy $\varepsilon_a$ acquires an imaginary part $i\Delta$. In order to obtain the time development, we can use the results of perturbation theory by replacing $\varepsilon_a \to \varepsilon_a - i\Delta$ in order to obtain the exact result. For example, from

$$\langle a|G^+|a\rangle = \frac{1}{z - \varepsilon_a' + i\Delta} \qquad (37)$$

we obtain by Fourier transformation:

$$\langle a|e^{-iHt}|a\rangle = e^{-\Delta t - i\varepsilon_a' t} \qquad (38)$$

so that an initially prepared state decays exponentially with a decay time $\hbar/2\Delta$, where we have explicitly put in $\hbar$ to clarify the units. This confirms our interpretation of $\Delta$ as a life-time broadening.

In the same way we obtain from Eq. (13) for the transition probability from a state $k$ to $a$:

$$W_{a\to k} = \left|\langle a|e^{-iHt}|k\rangle\right|^2$$
$$= \frac{|V_k|^2}{(\varepsilon_a' - \varepsilon_k)^2 + \Delta^2}\left[1 + e^{-2\Delta t} - 2e^{-\Delta t}\cos(\varepsilon_a' - \varepsilon_k)t\right]. \qquad (39)$$

Note that this is not the rate, but the probability to find a state $k$ prepared at $t = 0$ in state $a$ at a later time $t$. At large times it tends to a finite value, so that, in contrast to the results of perturbation theory, the rate $W_{a\to k}/t$ tends to zero. In order to interpret the result, we sum the limiting value over all occupied states $k$:

$$\sum_k f(\varepsilon_k)\frac{|V_k|^2}{\left(\varepsilon_a' - \varepsilon_k\right)^2 + \Delta^2}$$
$$= \int d\varepsilon f(\varepsilon)\frac{|V_k|^2}{\left(\varepsilon_a' - \varepsilon_k\right)^2 + \Delta^2}\delta(\varepsilon - \varepsilon_k) = \int f(\varepsilon)\rho_a(\varepsilon)d\varepsilon. \qquad (40)$$

This shows, that at long times electronic equilibrium has been achieved.

Equations (39) and (40) depend on the solvent coordinates through $\varepsilon'$, so we next have to perform the thermal average. The calculations are not difficult but cumbersome, so we only note that it is useful to replace the Lorentzian by its Fourier transform; we integrate over $\varepsilon_k$ so that we obtain the total occupation probability as a function of time [19]:

$$\langle n_a(t)\rangle = \frac{1}{\pi}\int d\varepsilon f(\varepsilon, T)\times\Re\left\{\int_0^t d\tau\exp[-i(\varepsilon_a - \varepsilon + \lambda)\tau]\right.$$
$$\left.\times \left(e^{-\Delta\tau} - e^{-2\Delta t + \Delta\tau}\right)e^{-kT\lambda\tau^2}\right\}, \qquad (41)$$

where $\Re$ denotes the real part. Admittedly, this result does not look very pretty; it even oscillates at short times. However, at long times it can be shown to obey a relaxation equation of the form:

$$\frac{d}{dt}\langle n_a(t)\rangle = -\frac{2\Delta}{\hbar}(\langle n_a(t)\rangle - \langle n_a(t \to \infty)\rangle), \qquad (42)$$

with the relaxation time $\tau_r = \hbar/2\Delta$. This can be verified by taking the long-time limit of Eq. (41) and substituting it into Eq. (42); again the calculations are straightforward, but cumbersome.

Let us see how this helps in defining the rate constant. The electron transfer takes place in both directions, and in formal kinetics we can define rate constants $k_{red}$ and $k_{ox}$, so that:

$$\frac{d}{dt}\langle n_a(t)\rangle = k_{red}\left[1 - \langle n_a(t)\rangle\right] - k_{ox}\langle n_a(t)\rangle. \qquad (43)$$

This is a standard problem of chemical kinetics. The equilibrium value is:

$$\langle n_a(\infty) \rangle = \frac{k_{\text{red}}}{k_{\text{red}} + k_{\text{ox}}} \tag{44}$$

and the decay time towards equilibrium is:

$$\tau = \frac{1}{k_{\text{red}} + k_{\text{ox}}} \tag{45}$$

so that:

$$k_{\text{red}} = \langle n_a(\infty) \rangle / \tau_r \quad \text{and} \quad k_{\text{ox}} = [1 - \langle n_a(\infty) \rangle] / \tau_r. \tag{46}$$

Applying these relations to the case at hand, results in:

$$k_{\text{red}} = \int d\varepsilon f(\varepsilon,) w_{\text{red}}(\varepsilon), \tag{47}$$

where:

$$w_{\text{red}}(\varepsilon) = \frac{\Delta}{\hbar} (\pi \lambda k_B T)^{-1/2}$$
$$\times \Re \left[ w \left( \frac{1}{2} \sqrt{\frac{\beta}{\lambda}} (\varepsilon_a - \varepsilon + \lambda + i\Delta) \right) \right], \tag{48}$$

where $w(z) = e^{-z^2} \text{erfc}(-iz)$ is the complex error function [20]. The corresponding equation for the oxidation is:

$$k_{\text{ox}} = \int d\varepsilon [1 - f(\varepsilon)] w_{\text{ox}}(\varepsilon), \tag{49}$$

$$w_{\text{ox}}(\varepsilon) = \frac{\Delta}{\hbar} (\pi \lambda k_B T)^{-1/2}$$
$$\times \Re \left[ w \left( \frac{1}{2} \sqrt{\frac{\beta}{\lambda}} (\varepsilon_a - \varepsilon - \lambda + i\Delta) \right) \right]. \tag{50}$$

Note that these rates have the same form as in perturbation theory—see Eq. (21)—and the expressions (48) and (50) are the generalizations for the densities of states of Eq. (22) in the sense of Gerischer.

These equations are valid for all strengths of the interaction $\Delta$. In addition, they give the absolute values of the rate, which depends only on $\Delta$ and on the solvent reorganization energy $\lambda$. This makes it possible to investigate the rate and the effective activation energy, defined through: $E_{\text{act}} = -d \ln(k_{\text{red}}) / d(1/kT)$, as a function of the interaction energy $\Delta$. The results are shown in Fig. 2 for the equilibrium situation. For small values of $\Delta$ the rate is proportional to $\Delta$, and the activation energy is constant and equal to $\lambda/4$ like in Marcus theory. This is the range where first order perturbation theory holds. For stronger interactions the rate rises faster than linearly, and the activation energy starts to decrease—this is the same effect as in Fig. 1.

## 6. DISCUSSION

We have presented three different ways of investigating electrochemical electron transfer reactions in the outer sphere, which start from the same model Hamiltonian, and which use the Green's function formalism as the starting point. The physical model is the
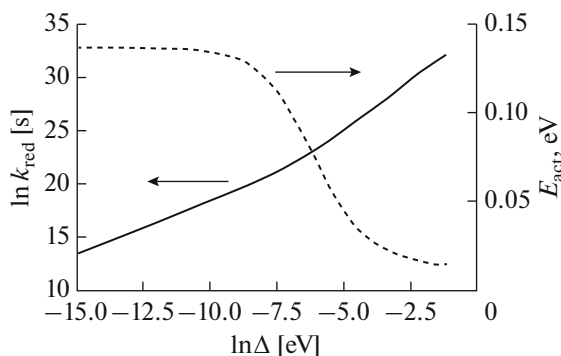


**Fig. 2.** Dependence of the reduction rate $k_{\text{red}}$ and the activation energy at equilibrium on the energy broadening $\Delta$ for a system that couples to classical modes only; $\lambda = 0.5$ eV. Full line: reaction rate; dotted line: activation energy.

same as in the original works of Marcus, Hush, Levich and Dogonadze: electron transfer is coupled to the reorganization of solvent modes.

In the first formalism the electronic interaction between the reactant and the metal is considered to be weak, and the rate is calculated by first order perturbation theory. This is the approach of the Levich and Dogonadze theory. We have derived the corresponding equations from Green's function theory, but any other derivation leads to the same results. The transition probability is proportional to time, and defining the rate is not problematic. It takes the form of an integral over the electronic energy of the transferring electron. The integrand can be considered as a thermal density of states as suggested by Gerischer, or as an energy resolved rate. Electron transfer is a rare event, so that solvent dynamics play no role. This theory should hold, whenever the electronic interaction is weak; an important application is electron transfer on film-covered metals.

The second approach has been developed by myself; using ideas of Anderson–Newns theory, the Green's functions can be calculated exactly. This allows us to obtain the adiabatic potential energy of the system as a function of the solvent coordinates. These involve electron exchange with all levels on the metal, but they do not appear as individual contributions. The results are particularly simple in the wide-band approximation, where the interaction is taken as constant and the details of the electronic structure of the metal are ignored. For outer sphere electron transfer this is a reasonable approximation. For weak and medium strong interactions, $\Delta \ll \lambda$, the potential energy curves are the same as in Marcus theory; stronger interactions lower the activation barrier. The calculated potential energy curves can be combined with Kramers' theory to obtain reaction rates. The approach is limited to adiabatic electron transfer. It can be extended to electrocatalytic reactions by incorporating results from quantum-chemical calculations. This line of theory has been developed in my group during the last couple of years [13, 14].

By taking the Fourier transform of the exact Green's function, the corresponding time development of the electronic states can be derived. In the wide-band approximation, the transformation can be calculated analytically. The results are formally similar to those of first-order perturbation theory, but valid for any interaction strength. The transition probability oscillates at short times, but at long times it obeys a simple relaxation equation, which makes it possible to define and extract the rate constants. Here, like in perturbation theory, the total rate is the integral over electron exchange with individual metal states. The results are valid for all interaction strengths. Solvent dynamics are not included; however, they can be considered by combining the equations of motion with stochastic molecular dynamics [21].

Finally, a comment on the reorganization of quantum vibrations, which we have not considered. They can and have been included both in the perturbation and in the time propagation approaches, so they pose no principal problem. So far, they have not been considered in the calculation of adiabatic potential energy surfaces. This would involve the calculation of individual surfaces for each vibrational transition, with the appropriate thermal averaging. So far, to the best of our knowledge, this has not been done.

## 7. CONCLUDING REMARKS

As stated in the introduction, this is by no means a review of electrochemical electron transfer theory. Our aim has been to start from a model Hamiltonian in second quantized form, calculate the corresponding Green's function, and compare three different approaches for the calculation of the rate of electron transfer. Each of them has its own merits and range of applicability. We hope that this unifying approach to three different methods has shed some light on electron transfer theory.

Obviously, this is not the place to discuss experimental results, but a brief comment is in order. First order perturbation theory by definition holds when the interaction is weak. It is therefore the theory of choice for electron transfer on electrodes covered by a thin insulating film. The second approach has been used to explain, why outer sphere electron transfer on metal electrodes is independent of the nature of the metal [22], and also forms the basis of our theory electrocatalysis [14]. A big advantage of the equations-of-motion approach is the fact, that it is valid for all interaction strengths, and that quantum vibrations can be incorporated directly.

On a personal note, writing all these equation made me feel somewhat nostalgic. Nowadays papers in theoretical electrochemistry are usually based on density functional theory (DFT), which most scientists use as a boxed program. While I admit, that DFT is very useful—we use it ourselves extensively in my group − its results cannot compete with the beauty and the rigor of a mathematical derivation.

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