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Short Communication

On the evaluation of the Marcus–Hush–Chidsey integral

Agostino Migliore*, Abraham Nitzan

School of Chemistry, Tel Aviv University, Tel Aviv 69978, Israel

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ABSTRACT

The electrochemical rate constant obtained from the Marcus–Hush theory of heterogeneous electron transfer is given as a relatively complex integral. Recently, two apparently different expressions of this rate constant in the form of a series of analytical functions appeared in the literature. We demonstrate here the equivalence of these expressions and discuss their different approximations, resulting from the two distinct analytical derivations, which have implications in the practical calculation of electron transfer rate constants at electrode surfaces.

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The Marcus–Hush theoretical model of heterogeneous electron transfer [1–3], usefully implemented in the context of electrode reactions [4,5], has been increasingly employed in recent years [6] as an alternative to Butler–Volmer equations. Considering a metal electrode in contact with a redox molecule, and assuming that the electronic coupling between metal and molecule and the density of states in the metal are independent of the energy, one arrives at an expression of the interfacial electron transfer rate constant as an integral of the Fermi–Dirac distribution of the electrons and the Marcus free energy factor, where a potential-dependent activation energy appears. For a single electron transition it can be written as

$$R_{\text{ox/red}} = \frac{\gamma}{2\sqrt{\pi\lambda k_B T}} \int_{-\infty}^{\infty} dx \frac{1}{\exp\left(\frac{x}{k_B T}\right) + 1} \exp\left[-\frac{(x - \lambda \pm e\Delta E)^2}{4\lambda k_B T}\right]. \quad (1)$$

In Eq. (1), γ is the coupling strength to the electrode, which depends on the electronic coupling and the density of electronic states in the metal. e , k_B , and T are the electron charge, Boltzmann constant, and temperature, respectively. λ is the reorganization energy and ΔE is the overpotential. The \pm signs refer to the oxidative and reductive transition rate constants. Evaluation of the integral (1) is facilitated by expressing it as a series. This has been first elegantly done in Ref. [7], exploiting the expansion

$$\text{sech}(x) = 2 \sum_{j=0}^{\infty} (-1)^j \exp[-(2j+1)x], \quad (2)$$

which leads to the expression

$$R_{\text{ox/red}}(\Delta E) = \frac{\gamma}{2} \exp\left[-\frac{(\pm e\Delta E - \lambda)^2}{4\lambda k_B T}\right] S(\lambda, \Delta E), \quad (3)$$

where

$$S = \sum_{j=0}^{\infty} (-1)^j w_j, \quad (4a)$$

with

$$w_j = \exp(\vartheta_+^2) \text{erfc}(\vartheta_+) + \exp(\vartheta_-^2) \text{erfc}(\vartheta_-), \quad \vartheta_{\pm} = \frac{(2j+1)\lambda \pm e\Delta E}{2\sqrt{\lambda k_B T}}. \quad (4b)$$

Moreover, useful approximations to S in different ranges of the overpotential are provided [7].

In Ref. [7], it is noticed that the expansion (2) “fails at $x = 0$, but this causes no problems in practice.” An alternative procedure, recently offered by us [8], does not use this expansion. Considering that the transition rate constants are most sensitive to the overpotential at $e|\Delta E| = \lambda$ and that, at such ΔE , the integrand in Eq. (1) has a maximum for $x = 0$, an optimal series solution of the integral can be obtained by an expansion of the Fermi function describing the electron distribution on the metal levels

$$f(\varepsilon) = \frac{1}{\exp\left(\frac{\varepsilon - \mu}{k_B T}\right) + 1}, \quad (5)$$

(where ε is the metal level energy and μ is the overpotential-dependent Fermi level of the electrode) that is rapidly convergent and particularly effective at and near $x = 0$. Thus we used [8]

* Corresponding author. Tel.: +972 3 6407634; fax: +972 3 6409293.

E-mail addresses: migliore@post.tau.ac.il (A. Migliore), nitzan@post.tau.ac.il (A. Nitzan).

$$\frac{1}{\exp(x) + 1} = \frac{\exp(-x)}{1 + \exp(-x)} = \frac{1}{2} \frac{\exp(-x)}{1 - [1 - \exp(-x)]/2}$$

$$= \frac{1}{2} \exp(-x) \sum_{n=0}^{\infty} \frac{1}{2^n} [1 - \exp(-x)]^n, \quad (6)$$

and exploited the binomial theorem, obtaining an expression of $R_{ox/}$ red as in Eq. (3) but with the series S replaced by

$$T = \frac{1}{2} \sum_{n=0}^{\infty} \frac{1}{2^n} \sum_{j=0}^n (-1)^j \binom{n}{j} w_j. \quad (7)$$

Inverting the two sums in Eq. (7) and using the ordinary generating function of the binomial coefficients (for a given j) [9]

$$\sum_{n=0}^{\infty} \binom{n}{j} y^n = \frac{y^j}{(1-y)^{j+1}}, \quad (8)$$

with $y = 1/2$, we get

$$T = \frac{1}{2} \sum_{j=0}^{\infty} (-1)^j \sum_{n=j}^{\infty} \frac{1}{2^n} \binom{n}{j} w_j = \frac{1}{2} \sum_{j=0}^{\infty} (-1)^j 2 w_j = \sum_{j=0}^{\infty} (-1)^j w_j = S, \quad (9)$$

which establishes the identity of the two series expressions of the integral (1). However, any application of this formula requires its truncation to a finite number of terms. Hence, the quantities of interest are the partial sums of suitable order N :

$$S_N \equiv \sum_{j=0}^N (-1)^j w_j, \quad (10)$$

and

$$T_N \equiv \frac{1}{2} \sum_{n=0}^N \frac{1}{2^n} \sum_{j=0}^n (-1)^j \binom{n}{j} w_j = \sum_{j=0}^N (-1)^j c_j(N) w_j, \quad (11a)$$

where the coefficients

$$c_j(N) \equiv \sum_{n=j}^N \frac{1}{2^{n+1}} \binom{n}{j}, \quad (11b)$$

tend to unity for $N \rightarrow \infty$. The two partial sums S_N [7] and T_N [8] involve the same set of functions w_j but with different coefficients. Such difference results from the different expansions used in the two approaches and brings about different convergence proprieties of the two solutions. As shown in Fig. 1, T_N tends smoothly to the exact value T for very small N values, while S_N shows a damped oscillation toward the same exact value, $S = T$. T_N , compared to S_N , offers a much more efficient route to the calculation of the rate constants over a wide overpotential range, all the more that most computational time is spent in evaluating the common set of functions w_j .

The continuous oscillation in the value of S_N at each term addition is a consequence of the failure of expansion (2) at $x = 0$. Because of the indeterminate character of the series for $x = 0$, its

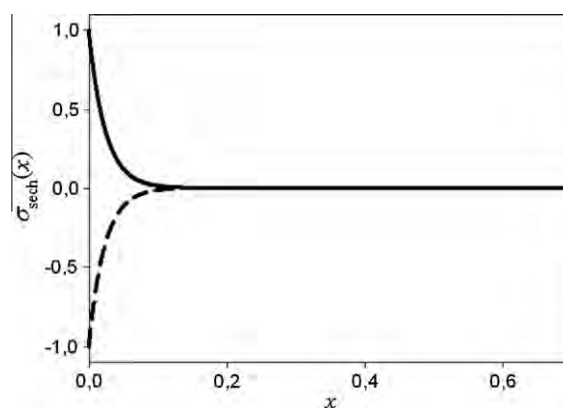


Fig. 2. Relative error σ_{sech} made by truncating the series expansion of the hyperbolic secant in Eq. (2) to 20 (solid line) and 21 (dashed line) terms.

truncation at the N th term has a relative error of ± 1 , with sign dependent on the parity of N and magnitude independent of the value of N (see Fig. 2). As $N \rightarrow \infty$, the x range where the error is considerable reduces to the zero measure interval $x = 0$, so that the series of integrated terms in Eq. (4) yields the exact result.

On the other hand, for $\Delta E \gg \lambda/e$, S_N is very close to S for each N . The behavior of T_N is similar to that at smaller ΔE values, with a smooth and quick convergence to T (see Fig. 3). $T_N - T$ finally becomes smaller than $S_N - S$ (right panel in Fig. 3). Notice that N values less than 10 ensure a relative difference between T_N and T smaller than 0.1% over all the explored ΔE range.

Let us compare the applications of the rate constant expressions using S_N and T_N to the description of a typical linear sweep voltammogram. Indeed, the expressions of the interfacial rate constants in Eq. (1) have been widely used not only in the study of electrochemical redox reactions [4,5], but also in the context of redox molecular junctions [10,11]. Therefore, we will formulate our discussion on a “per molecule” basis, which, on the one hand, provides an immediate link to the literature on diffusionless electrochemical systems [12,13] and, on the other hand, can be directly exploited in the study of sequential charge transport through redox molecular junctions [8,10,11]. The molecule adsorbed at the electrode surface is modeled as a two-state (A and B) system. Either A or B can represent the oxidized or reduced adsorbate, consistently with the sign convention for ΔE . On a per-molecule basis, the surface concentration of the electroactive species in a given redox state is replaced by the occupation probability P of the molecular redox site. In terms of P and of the rate constants $R_{A \rightarrow B}$ and $R_{B \rightarrow A}$ for the A -to- B and B -to- A transitions, respectively, the current at the electrode is proportional to the quantity [12,13]

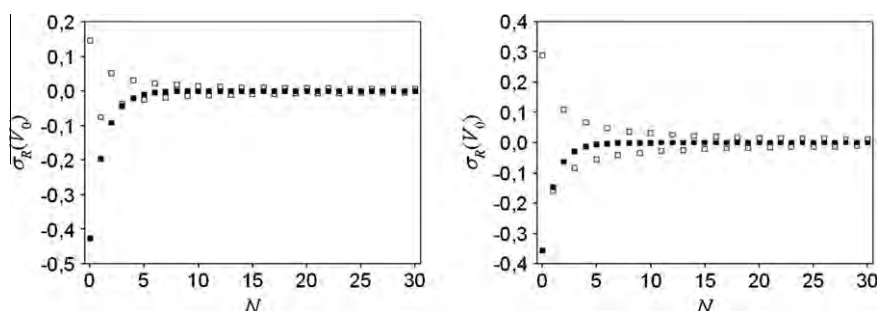


Fig. 1. Relative errors $\sigma_R = (S_N - S)/S$ (empty squares) and $(T_N - T)/T$ (full squares) in the rate constant, plotted against N , at a fixed overpotential ΔE_0 of (left) 0.1 V and (right) 0.6 V. The model parameters are $T = 298$ K, $\lambda = 0.7$ eV.

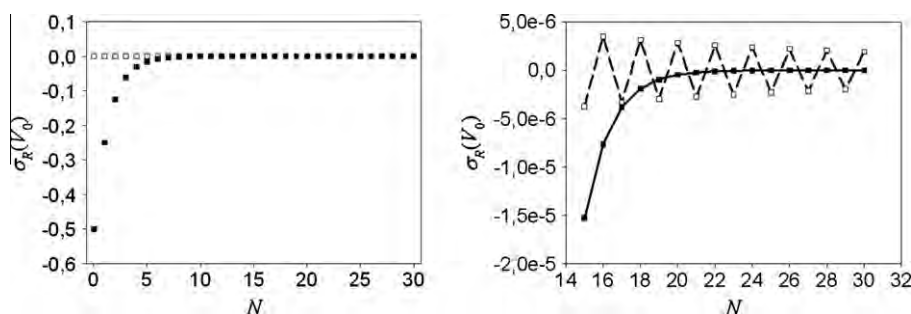


Fig. 3. Relative errors $\sigma_R = (S_N - S)/S$ (empty squares) and $(T_N - T)/T$ (full squares) in the electron transfer rate constant, plotted against N , at $\Delta E_0 = 1.4$ V. Smaller ranges of N and correspondingly of the ordinate are reported in the right panel.

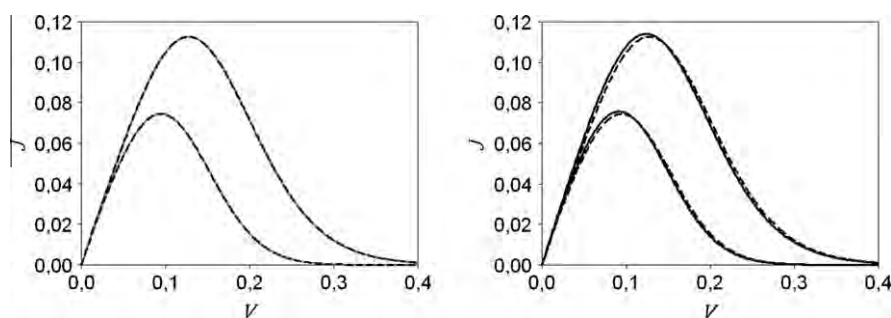


Fig. 4. J versus V , for a model system with $T = 298$ K, $\lambda = 0.15$ eV, and $m = 0.08$ (lower curves), 0.04 (upper curves). *Left:* $S = T$ as simulated by $N = 30$ (full gray lines) and T_N with $N = 6$ (dash). *Right:* dashed lines reported from the left panel and results using S_N with $N = 6$ (full lines). Visible differences are seen between the J - ΔE responses resulting from S_N and T_N .

$$J \equiv \frac{dP}{dt} = v \frac{dP}{dV} = (1 - P)R_{A \rightarrow B}(V) - PR_{B \rightarrow A}(V), \quad (12)$$

where $v = \Delta E/t$ is the sweep rate. The assumptions and conditions underlying the above equation as well as its suitable inclusion in a more complete mechanism that ensures charge balance through appropriate inter-phase transport are well known [14,15]. The peak position and the shape of the voltammogram resulting from Eq. (12) depend on the competition between the interfacial charge transfer rates and the scan rate, which can be quantified by the parameter $m = R_{A \rightarrow B}(0)k_B T / ev$ [12].

Eq. (12) has been implemented in a finite differences simulation, as described by Eq. (13) of Ref. [13], but inserting the expressions of the rate constants that result from Eq. (3) with S approximated either by S_N or by T_N . Results are shown in Fig. 4. Note that the employed small value of λ can be easily encountered also in the context of molecular junctions [16]. The use of T and T_N with $N = 6$ in the rate constants of Eq. (12) yields indistinguishable voltammograms in Fig. 4, while a visible departure from such curves results from S_N .

The value of the theoretical development in Ref. [7] is not affected by these results. Yet, Fig. 4 demonstrates that analytical conditions that may appear as mathematical ‘pedantry’ from the viewpoint of the description of a physical system, can lead to observable effects in the accuracy of such description. Moreover, the present analysis aims to shed light on the level of accuracy that needs to be kept truncating the series expression of the electron transfer rate constant as S_N [7] or T_N [8]. Ultimately, it may also

be worth reconsidering the valuable and useful reformulations and approximations of S in [7] in terms of the partial sums T_N .

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