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ORIGINAL PAPER

Analytical evaluation of the Marcus–Hush–Chidsey function using binomial expansion theorem and Error functions

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Abstract A simple and straightforward analytical method is presented for calculating the Marcus–Hush–Chidsey function. We present here an alternative derivation method which leads to a simpler series analytical formula, based on the use of the binomial expansion theorem. The convergence of the series is tested by calculating concrete cases for arbitrary values of parameters. Comparison with available analytical results validates the accuracy and efficiency of this method.

Keywords Electron transfer · Rate constant · Electrode kinetics · Binomial coefficients

1 Introduction

It is well known that, the Marcus theory has played a central role in various fields of chemistry and biology including photosynthesis, corrosion, some types of chemiluminescence, charge separation in solar cells and heterogeneous electron transfer [1–15]. Also, this theory applies to the outer sphere electron transfer and the potential-dependence of electrochemical rate constants [16–19]. A great many important aspects of biology and biochemistry involve electron transfer reactions. Most significantly, all of respiration (the way we get energy from food and oxygen) and photosynthesis (they way plants make the food and oxygen we consume) rely entirely on electron transfer reactions between cofactors in proteins [19,20]. The Marcus theory of electron transfer has been developed for inner-sphere electron transfer by Hush and Marcus [20,21]. Note that the Marcus–Hush–Chidsey (MHC) theory is semiclassical in nature.

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Jorttner and Kuznetsov extended the theory by using quantum mechanical treatments [22–25]. The MHC theory, given in paper [15], has been focused on fundamental general aspects and results of specific systems. In recent years, an interesting series of articles has been published to attempt analytical calculations of the MHC function and its applications [5–17]. In spite of these developments, in analytical evaluation of the MHC function, it remains a computational problem. Here we present a more general analytical approach to the calculation of the MHC function which is valid for arbitrary values of the integral parameters. As seen, the progress and practical applications of the heterogeneous electron transfer are dependent on accurate evaluation of this function. The analytical expression is obtained in terms of binomial coefficients and Error functions. Calculation results show that there is a good level of congruence between the present method and direct numerical integration approaches. This method improves significantly the accuracy of the MHC function and is fast enough for its implementation in interpolating algorithms.

2 General definition and unified analytical relation for Marcus–Hush–Chidsey function

The MHC function for single electron transition is defined as [16]:

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

where γ the coupling strength to the electrode, λ the reorganization energy and ΔE the overpotential, e, k_B, T are the electron charge, Boltzmann constant and temperature, respectively. The $\pm$ signs refer to the oxidative and reductive transition rate constants. In order to establish expressions for the MHC functions we shall first consider the well known binomial expansion theorems as follows [26–29]:

$$(x \pm y)^n = \lim_{N\to\infty} \sum_{m=0}^{N} (\pm 1)^m F_m(n) x^{n-m} y^m, \tag{2}$$

Here N is the upper limit of summations and $F_m(n)$ are binomial coefficients defined by

$$F_m(n) = \begin{cases} \dfrac{n(n-1)\dots(n-m+1)}{m!} & \text{for integer } n \\ \dfrac{(-1)^m \Gamma(m-n)}{m!\Gamma(-n)} & \text{for noninteger } n \end{cases} \tag{3}$$

Finally, we substitute Eq. (2) in the integral representation Eq. (1). This procedure yields the required series expansion for MHC function in terms of binomial coefficients:

$$R_{ox/red}(\Delta E, T, \lambda, \gamma) = \frac{\gamma \exp\left[-\frac{(\lambda \mp e\Delta E)^2}{4\lambda k_B T}\right]}{2\sqrt{\pi \lambda k_B T}} \lim_{N' \to \infty} \sum_{i=0}^{N'} F_i(-1) \left[G\left(\lambda k_B T, \frac{i}{k_B T} + \frac{\lambda \mp e\Delta E}{2\lambda k_B T}\right) + G\left(\lambda k_B T, \frac{i+1}{k_B T} - \frac{\lambda \mp e\Delta E}{2\lambda k_B T}\right)\right] \quad (4)$$

where the indices N is the upper limits of summation. In Eq. (4), function $G(\beta, \gamma)$ is defined as [26]

$$G(\beta, \gamma) = \int_0^\infty \exp\left(-\frac{x^2}{4\beta} - \gamma x\right) dx \quad (5a)$$

$$= \sqrt{\pi\beta} e^{\beta\gamma^2} [1 - Erf(\gamma\sqrt{\beta})] \quad (5b)$$

where $Erf(x)$ is the well known Error function [26]

$$Erf(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt \quad (6)$$

These analytical formulas offer the advantage of direct and precise calculation of the MHC functions and of an easy parametrical investigation for evaluating the effects of various parameters, without the use of numerical methods.

3 Numerical results and discussion

In this paper, an alternative analytical calculation scheme is proposed for the MHC function. In numerical computation of the MHC function in Eq. (1) with the datas reported in Tables 1, 2 and 3, the calculations were performed using the scientific software Mathematica 7.0 with the values of constants $k_B = 8.6173324.10^{-5} eV K^{-1}$ *and* $\gamma = 1$. The desktop computer with typical configuration, Pentium, Intel (R), 2.20 GHz, 3.0 GB RAM, was utilized. To verify the representations that we obtained for various cases, including the exact representation, we compared the results of the new formulations with the results of a direct Mathematica numerical integration technique. It is clear from Tables 1 and 2, the comparison results between numerical integration and the analytical method proposed in this paper are congruent with all sets of parameters. As can be seen from the calculation results, the analytical formula is very convenient in practical applications. The discrepancy of the some computation results between the numerical and the obtained formula arises from insufficiencies in the numerical methods used for these values of parameters. Table 3 lists partial summations corresponding to progressively increasing upper summation limits of Eq. (4) for this expression. As can be seen in Table 3, the computation results demonstrate the improvements in convergence rates. The author believes that the formula obtained in this paper is natural and it will be useful in practical applications of the Marcus theory.

Table 1 The comparative values of oxidative Marcus–Hush–Chidsey function for $N' = 30$

$e\Delta E$ (eV)	λ (eV)	T(K)	Eq. (4)	Mathematica numerical integration results
0.6	0.5	298	0.72380975102283	0.72564171035595
0.6	0.6	298	0.5	0.49999999999999
0.1	0.6	298	0.00383667573353	0.00297656139004
0.1	0.6	280	0.00287712193672	0.00223434298636
0.2	0.3	275	0.21795089233552	0.21473600812888
0.5	0.7	273	0.16738904171902	0.14162356353222
0.8	0.9	310	0.36976004664749	0.32800731650488
1.6	1.2	320	0.92500255224328	0.93653943633088
2.1	1.6	260	0.96907249397581	0.96756653770802
3.2	2.6	240	0.96634554917206	0.96544866158158
5.3	3.2	340	0.99999938135975	0.99999925414760
7.5	5.3	360	0.99993759288508	0.99993271246412

Table 2 The comparative values of reductive Marcus–Hush–Chidsey function for $N' = 30$

$e\Delta E$(eV)	λ(eV)	T(K)	Eq. (4)	Mathematica numerical integration results
0.6	0.5	298	5.157259853836677E−11	5.170312856131819E−11
0.6	0.6	298	3.562579701744072E−11	3.562579701744072E−11
0.1	0.6	298	7.811855345095961E−5	6.060576556314478E−5
0.1	0.6	280	4.560760931771201E−5	3.541769224379977E−5
0.2	0.3	275	4.710478859628959E−5	4.640996950519649E−5
0.5	0.7	273	9.848342023310416E−11	8.332428920685407E−11
0.8	0.9	310	3.647871183276227E−14	3.235959235267481E−14
1.6	1.2	320	5.851261170856247E−26	5.924239695867584E−26
2.1	1.6	260	1.907442550768151E−41	1.9044783503779525E−41
3.2	2.6	240	6.138796780075929E−68	6.133099221208672E−68

Table 3 Convergence of derived expression Eq. (4) for $R_{\frac{ox}{red}}(\Delta E, T, \lambda, \gamma)$ as a function of summation limits N'

N'	$\lambda = 0.2\,eV; e\Delta E = 0.4\,eV; T = 275K$	$\lambda = 8.5\,eV; e\Delta E = 5.7\,eV; T = 298K$
4	0.9753595166354784	0.000011286741622096308
6	0.9753595166354784	0.000011286741622096308
8	0.9753595166354784	0.000011286741622096308
10	0.9753595166354784	0.000011286741622096308

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