Simple Formula for Asymmetric Marcus-Hush Kinetics

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Abstract

The Marcus-Hush theory of electron transfer has seen increasing use as predictive alternative to the phenomenological Butler-Volmer (BV) equation for Faradaic reactions kinetics. Here, we analyze and simplify the asymmetric Marcus-Hush (AMH) model, first proposed by Marcus and recently used by Compton's group to fit experimental data that exhibit two different reorganization energies, depending on the sign of the overpotential. The AMH model has a single reorganization energy and an asymmetry parameter to account for different inner sphere force constants, but its practical use is hindered by the need to numerically evaluate the improper integral over electronic Fermi distribution. Moreover, the domain of integration must be arbitrarily truncated to avoid divergence, due to some ambiguities in the derivation, which also limit the validity of the AMH model to weakly curved Tafel plots. Nevertheless, by defining a region over which the formula applies, we derive a simple formula to replace the Fermi integral by exploiting similarities with our recent approximation of the symmetric limit of the Marcus-Hush-Chidsey (MHC) model. These results enable the AMH model to approach the same ease of use as both the MHC and BV models and highlight the need to develop a more comprehensive theory of asymmetric charge transfer.

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I. INTRODUCTION

The microscopic electron transfer theory [13], pioneered by Marcus [19, 20] and Hush [11, 12], has achieved great success in predicting reaction rates for both homogeneous bulk reactions and heterogeneous electrode reactions [21] that exhibit curved Tafel plots, which cannot be described by the phenomenological Butler-Volmer (BV) equation [2]. The fundamental assumption of Marcus-Hush (MH) theory is a quadratic dependence of the (excess) free energy of the reactant and product along a configurational reaction coordinate mainly associated with solvent reorganization, where electron transfer occurs iso-energetically at a transition state defined by the intersection of these parabolae. The forward and backward rates vary with overpotential, as the parabolae are shifted vertically (in energy) relative to each other.

For Faradaic reactions at electrodes the theory must further be augmented by integrating over all electron energy levels according to the Fermi distribution, which leads to so-called Marcus-Hush-Chidsey (MHC) kinetics [5, 17]. Chidsey first applied the MHC model to liquid-solid charge transfer mediated by self-assembled monolayers [5]. Recently, the MHC model has also been shown to predict solid-solid charge transfer in Li-ion batteries [1], thus opening the possibility of improving BV-based engineering models [23]. The expression for MHC kinetics involves an improper integral over the electron Fermi distribution that requires numerical evaluation, which has led to the development of a number of approximations to facilitate its implementation [4, 22, 24, 28], including both very accurate [4] and very simple [28] analytical approaches.

All these studies have examined the "symmetric" MHC model [8] in which the reactant and product free-energy parabolae have equal curvatures, controlled by a single outer-sphere reorganization energy, but "asymmetric" kinetics have been observed in many recent experiments [6, 9, 10, 14, 16, 25, 27], in which the MHC theory requires different reorganization energies to fit the curved Tafel plot of the high-rate cathodic and anodic reactions separately. Drawing from early work of Marcus [18], Compton and co-workers implemented and popularized the asymmetric Marcus-Hush (AMH) model, which has a single reorganization energy but introduces an asymmetry parameter to describe different inner-sphere force constants [7, 14, 15]. The BV, MHC, and AMH models are compared in Fig. 1 in a Tafel plot for moderately large over potentials.

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Unlike the symmetric MHC model, there are some ambiguities in the original derivation of the AMH model [18], related to the fact that two non-tangent parabolae of different curvatures have either two or zero intersections, rather than one in the symmetric case. Additional assumptions are thus required to calculate the reduction and oxidation rates. In the case of the AMH model, this leads to restrictions on the allowable overpotentials and truncation of the range of electron energy levels [15], in order to avoid the divergence of the improper integral over the Fermi distribution.

Despite these and other difficulties in developing theories of asymmetric inner-sphere charge transfer [13], we focus here on describing the mathematical properties of the AMH model and deriving a simple formula to approximate the Fermi integral. Unlike the symmetric MHC model, we are not aware of any simplifying expressions or algorithms for the AMH model, so this result should facilitate experimental comparisons and engineering applications.
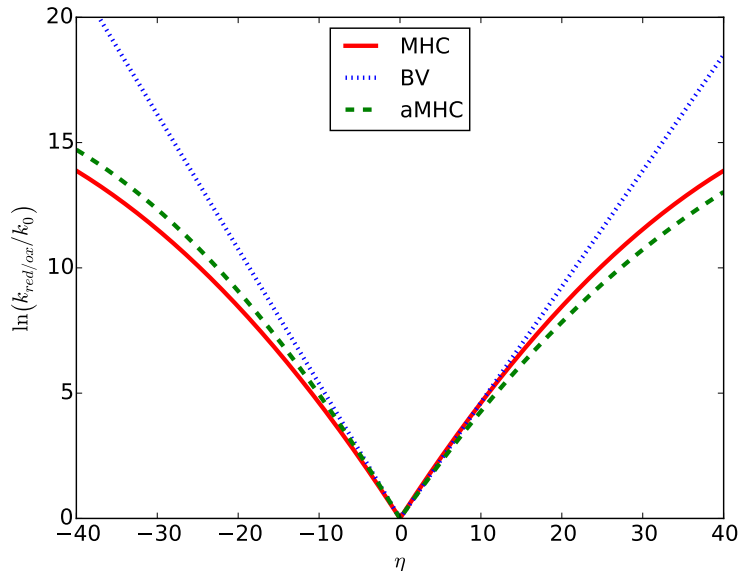

FIG. 1. Comparison of Butler-Volmer (BV), symmetric Marcus-Hush-Chidsey (MHC), and asymmetric-Marcus-Hush (AMH) kinetics as a function of applied overpotential. Note that at small overpotentials, the AMH rates are well captured by BV with $\alpha \neq \frac{1}{2}$. However, for large overpotentials, BV significantly over-predicts the rate.

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II. THEORY

A. Marcus-Hush-Chidsey kinetics

The symmetric Marcus-Hush-Chidsey (MHC) model for electrode kinetics assumes equal force constants for reactants and products, and results in the following expression for the reduction and oxidation rate constants [5, 17]:

$$
k_{red/ox,s}(\lambda, \eta) = A \int_{-\infty}^{+\infty} \exp\left(-\Delta G_{red/ox,s}(x)\right) \frac{1}{1 + \exp(\mp x)} dx,
$$
$$
\Delta G_{red/ox,s}(x) = \frac{\lambda}{4}\left(1 \pm \frac{x + \eta}{\lambda}\right)^2,
$$
(1)

where A is a pre-exponential constant factor, λ is the dimensionless reorganization energy, η is the dimensionless overpotential, x is the dimensionless integration variable, and $\Delta G_{red/ox,s}$ is the activation energy. When two signs are present, the top refers to reduction and the bottom to oxidation. Especially for concentrated solutions and solids [1, 3], it is important to note that this overpotential is defined as the departure of the electrode potential (interfacial voltage difference between electrons and ions) from the *formal* potential (including logarithmic concentration terms), often used in chemistry for studies of electrode kinetics, rather than from the *equilibrium* potential (given by the Nernst equation), which is the standard definition used in chemical engineering [3, 23].

B. Asymmetric Marcus-Hush kinetics

The AMH model for electron-transfer kinetics takes into account unequal inner-sphere reorganization energies by introducing an asymmetry parameter, γ, which describes the difference between inner-shell force constants of oxidized and reduced species a Faradaic reaction. The AMH model is defined as follows:

$$
k_{red/ox,a}(\lambda, \eta, \gamma) = A \int_{-\infty}^{+\infty} \exp\left(-\Delta G_{red/ox,a}(x)\right) \frac{1}{1 + \exp(\mp x)} dx,
$$
$$
\Delta G_{red/ox,a}(x) = \frac{\lambda}{4}\left(1 \pm \frac{x + \eta}{\lambda}\right)^2 + \gamma\left(\frac{\eta + x}{4}\right)\left[1 - \left(\frac{\eta + x}{\lambda}\right)^2\right] + \gamma^2 \frac{\lambda}{16},
$$
(2)

Note that when $\gamma = 0$, this asymmetric formula reduces to the symmetric MHC model. Importantly, Eq. 2 is restricted in applicability based on the truncation of the approximating

series by which it was derived [15]. Although the restrictions in relevant parameter ranges vary system to system, conservative estimates require $|\gamma| < 0.35$, $\lambda \gg 1$, and $|\eta| \lesssim 10$ [14]. Nevertheless, $\lambda \gg 1$ is typical for a variety of asymmetric reactions [15].

For the remainder of the analysis, we will focus only on the oxidation rate constant and free energy, as the results are easily repeated for reduction. For ease of notation, we refer to the oxidation rate constant and free energy barrier as simply k_a and ΔG_a.

C. Clarification of the AMH model

This AMH formula has already demonstrated good agreement with experimental data in numerous studies [9, 15, 26] and is becoming increasingly important in understanding electrochemical systems, whenever symmetric MHC kinetics fails. Mathematically, however, the model is not well posed. In particular, the improper integral in Eq. 2 does not converge. Therefore, we must modify the original formula, in agreement with observations made by Compton *et al.* [14]. This change does not affect the results of previous studies and may enable better understanding of this asymmetric kinetic theory.

As has been previously noted, the integrand in Eq. 2 is a function with a peak similar to a Gaussian for small x, and numerical evaluation of the integral must be done within some finite x range, typically ± 50 [7]. This integration limit is not solely for computational speed; we will show that the integrand diverges as x goes to either positive or negative infinity unless γ is exactly zero (the symmetric MHC case).

The cause of the divergence of the integrand is that the nondimensional Gibbs free energy barrier, $\Delta G_a(x)$, is a cubic function of x when γ is non-zero. Depending on the sign of γ, $\Delta G_a(x)$ must tend to negative infinity at either $x = \infty$ or $x = -\infty$ with a speed of $\mathcal{O}\left(|x|^3\right)$. The second part of the integrand, $(1 + \exp(x))^{-1}$, which is related to the Fermi distribution, decays no faster than $\mathcal{O}\left(\exp(-|x|)\right)$. Thus, the integrand diverges at a rate of $\mathcal{O}\left(\exp(x^3)\right)$, and the integral in Eq. 2 must diverge for any $\gamma \neq 0$. A numerical demonstration is provided in Fig. 2. For x within ± 50, the integrand is nearly a Gaussian function with a peak close to zero. However, when $x > 300$, it grows quickly and dominates the peak around zero.

In order to avoid the divergence in Eq. 2, instead of integrating over the entire real axis, we have to restrict the integral within a certain domain $\mathcal{D}$, such that the integrand has a peak within this domain, but takes small enough values on both boundaries. Thus, we
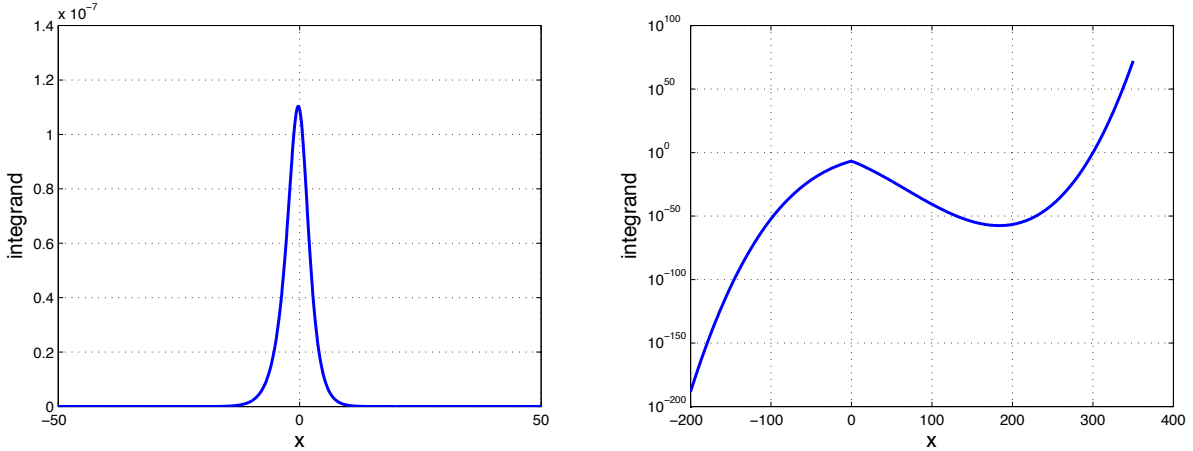
FIG. 2. Numerical evaluation of the integrand in Eq. 2 with $\lambda = 60$, $\gamma = 0.3$ and $\eta = 0$. We see on the right that for $x \gg 50$, the integrand is dominated by the growing cubic term, which results from series truncation in the derivation of Eq. 2.

rewrite the AMH formula as,

$$k_a(\lambda, \eta, \gamma) = A \int_{\mathcal{D}} \exp\left(-\Delta G_a(x)\right) \frac{1}{1 + \exp(x)} dx,$$

$$\Delta G_a(x) = \frac{(x - \lambda + \eta)^2}{4\lambda} + \gamma \left(\frac{\eta + x}{4}\right) \left[1 - \left(\frac{\eta + x}{\lambda}\right)^2\right] + \gamma^2 \frac{\lambda}{16}, \quad (3)$$

Unfortunately, the domain $\mathcal{D}$ has to be specified case by case according to the parameter choices. In general, $\mathcal{D} = \{x \in \mathbb{R} | -50 \leq x \leq 50\}$ is a very good choice as suggested by Compton's group [14], but a check of the validity of this integral region needs to be done for any new parameter choices.

In addition, for small values of the nondimensional reorganization energy, λ, the peak domain $\mathcal{D}$ is not well separated from the "blow up region". A typical example is shown in Fig. 3. In this case, the integral domain $\mathcal{D}$ cannot be clearly defined, and the AMH model in Eq. 3 is out of its valid range. In the remainder of the paper, we will always restrict our discussions to the cases in which the integral domain $\mathcal{D}$ can be consistently defined.

D.   Derivation of the AMH formula

Based on this discussion, it is clear that the AMH model is incomplete and could be modified in various ways to more accurately capture inner-sphere effects on electron transfer
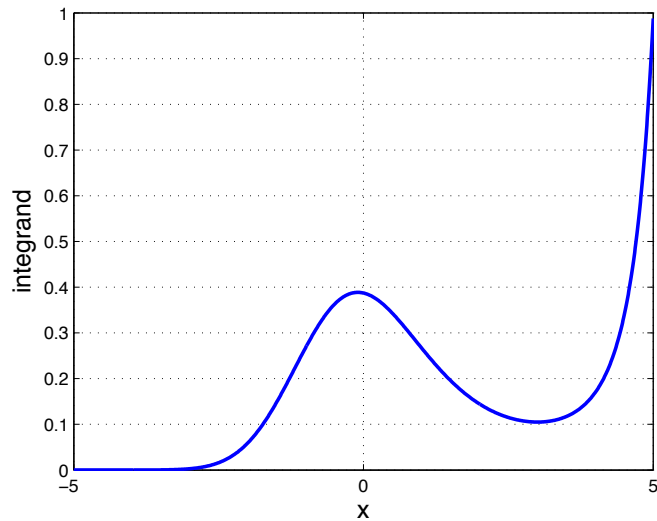
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FIG. 3. Numerical evaluation of the integrand in Eq. 3 with parameters $\lambda = 1$, $\gamma = 0.3$ and $\eta = 0$.

kinetics. It is beyond the scope of this paper to examine the theoretical basis for the AMH model or propose any alternatives, but we briefly draw attention to a key step in the original derivation that we are not able to reproduce. In his classic 1965 paper [18], Marcus considered the possibility of free-energy parabolae with different curvatures (force constants) for the reduced and oxidized states and proposed the first asymmetric theory in Appendix IV. With the aid of numerical estimates, he concluded that, for cases of relatively small driving forces, the asymmetric factors in his equation (A13) can be neglected, while for relatively large driving forces, equation (A13) should be replaced by his equation (A14a). In this step, both the $\lambda_i^2 \langle \ell_s \rangle^2 / 16\lambda$ term and the kT term from equation (A13) were neglected, but a cubic term $\lambda_i \langle \ell_s \rangle (\Delta F_R^{o\prime}/\lambda)^3/4$ was added, which we are not able to derive systematically from equation (A13). As noted above, this cubic term is responsible for the divergence of the Fermi integral over all election energy levels and causes the need to arbitrarily truncate the domain of integration.

The AMH model corresponds to the electrochemical variant of Marcus' equation (A14a) plus the $\lambda_i^2 \langle \ell_s \rangle^2 / 16\lambda$ term. The resulting expression has been successfully used to fit experimental data with asymmetric curved Tafel plots [7, 14, 15], despite the ambiguities in both its derivation and implementation. As such, we proceed to approximate the AMH model so as to eliminate cumbersome Fermi integral.

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III.   RESULTS

A.   Approximation of the AMH integral

In this section, we present a closed-form analytical approximation for the domain-restricted AMH formula, Eq. 3, based on some empirical observations of the integrand. A mathematical reasoning on the validity of such an approximation is also discussed. Because Eq. 3 already relies on an empirical restriction of parameter values, the focus of this work is on providing a useful approximation formula for the applicable parameter ranges rather than formally deriving a uniformly valid approximation.

Compared to the symmetric MHC theory, the asymmetric formula only differs by the cubic term in ΔG_a. Since the integral domain $\mathcal{D}$ normally consists of only a small range of x, we may make some observations of the quadratic term and the cubic term within this range.
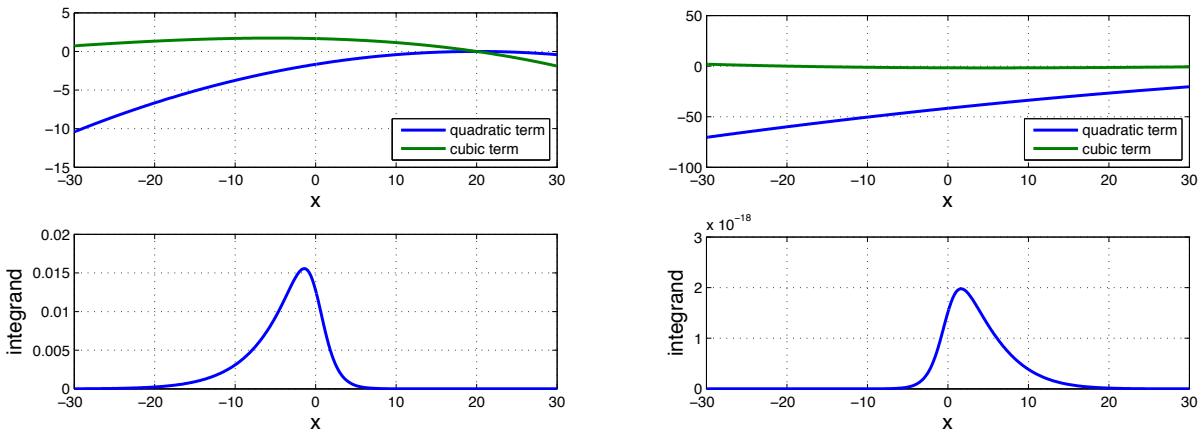

FIG. 4. Comparisons of the quadratic term and the cubic term in Eq. 3 within the integral domain $\mathcal{D}$ with parameters $\lambda = 60$, $\gamma = 0.3$. The nondimensional overpotential η is chosen to be 40 (left) and -40 (right).

Typically, the cubic term varies considerably less than the quadratic term within the peak region of the integrand. Two examples are shown in Fig. 4. Therefore, one possible choice for approximating Eq. 3 is to treat the cubic term as independent of x over the integral domain $\mathcal{D}$. This is mathematically equivalent to taking only the first term of the Maclaurin

series of the cubic term, and neglecting all higher order terms. Then we get,

$$\Delta G_a(x) = \frac{(x - \lambda + \eta)^2}{4\lambda} + \gamma \left(\frac{\eta + x}{4}\right) \left[1 - \left(\frac{\eta + x}{\lambda}\right)^2\right] + \gamma^2 \frac{\lambda}{16}$$

$$\approx \Delta G_s(x) + \gamma \left(\frac{\eta}{4}\right) \left[1 - \left(\frac{\eta}{\lambda}\right)^2\right] + \gamma^2 \frac{\lambda}{16},$$

(4)

where ΔG_s is the corresponding free energy function of the symmetric MHC theory in Eq. 1. Since the cubic term is independent of x, it can be moved out of the integral. Then we obtain the approximated reaction rate,

$$k_a(\lambda, \eta, \gamma) \approx A \exp\left\{-\gamma \left(\frac{\eta}{4}\right) \left[1 - \left(\frac{\eta}{\lambda}\right)^2\right] - \gamma^2 \frac{\lambda}{16}\right\} \int_{\mathcal{D}} \exp\left(-\Delta G_s(x)\right) \frac{1}{1 + \exp(x)} dx$$

$$= \exp\left\{-\gamma \left(\frac{\eta}{4}\right) \left[1 - \left(\frac{\eta}{\lambda}\right)^2\right] - \gamma^2 \frac{\lambda}{16}\right\} k_s(\lambda, \eta),$$

(5)

where $k_s(\lambda, \eta)$ is the corresponding reaction rate of the symmetric MHC kinetics, which can be approximated a number of ways as discussed above. For simplicity, we apply our previous approximation for the symmetric MHC kinetics formula here and finally obtain a closed form approximation for the AMH theory [28],

$$k_{red/ox,a}(\lambda, \eta, \gamma) \approx A \exp\left\{-\gamma \left(\frac{\eta}{4}\right) \left[1 - \left(\frac{\eta}{\lambda}\right)^2\right] - \gamma^2 \frac{\lambda}{16}\right\} \frac{\sqrt{\pi\lambda}}{1 + \exp(\pm\eta)} \operatorname{erfc}\left(\frac{\lambda - \sqrt{1 + \sqrt{\lambda} + \eta^2}}{2\sqrt{\lambda}}\right).$$

(6)

where the double sign corresponds to reduction (above) and oxidation (below). The reduction and oxidation formulas differ only in the substitution of the reduction/oxidation symmetric rate constant for k_s.

The approximation formula in Eq. 6 works well when $|\gamma| < 0.35$, in agreement with the valid region suggested by Compton and coworkers [14]. In addition, this requires $\lambda \gg 1$ because of the integral domain validation requirement. However, $\lambda \gg 1$ is typical for an asymmetric reaction [15]. It is critical that the absolute value of the nondimensional overpotential η should not exceed the value of nondimensional reorganization energy λ, $|\eta| < \lambda$, as also previously noted [14].

Finally, we consider the choice of the approximation for k_s. We note that the approximation for symmetric MHC kinetics as used in Eq. 6 is less accurate for large λ and $\eta \approx 0$ [28]. However, over the entire relevant parameter space, small errors in η ($\lesssim 15$ mV) correspond to the same magnitude of error as introduced by using the chosen uniformly valid approximation. Thus, it is unlikely that practical applications will require more accuracy for the

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symmetric part. Nevertheless, more accurate computational methods to evaluate k_s can be implemented instead [4].

B. Numerical Study

In Fig. 5, we compare our approximate formula Eq. 6 to the numerical integration of the original AMH formula in Eq. 3 with different choices of γ and η, under the same conditions considered in recent experiments [6, 9, 10, 14, 16, 25, 27] in which the curvature of the Tafel plot is relatively weak, corresponding to large reorganization energy $\lambda \gg 1$. For the case $\lambda = 60$ (roughly 1.5 eV at room temperature), even though the reaction rate varies by about 20 orders of magnitude over this parameter range, the approximations show good agreement with the numerical results. The asymmetry caused by nonzero values of γ is also accurately captured.
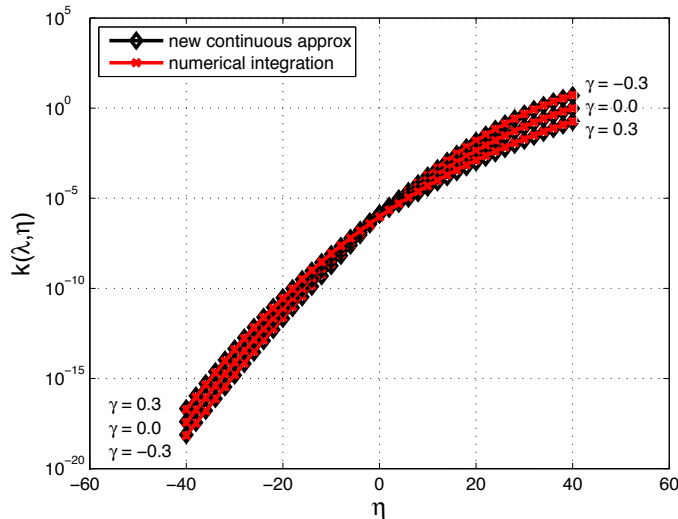

FIG. 5. Comparisons of asymmetric reaction rates obtained by numerically evaluating Eq. 3 with the simple closed-form approximation, Eq. 6 for a typical reorganization energy, $\lambda = 60$ (roughly 1.5 eV at room temperature), inferred from recent from recent experiments [14].

As expected from our analysis above, the numerical results show that the approximation loses significant accuracy only when $|\eta|$ gets larger than λ. A numerical demonstration in Fig. 6 shows that when $|\eta| > \lambda \gg 1$, the approximation can be several orders off from the true value. Therefore, the application of approximate formula in Eq. 3 should be limited

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to the range $|\eta| < \lambda$. Nevertheless, the original AMH formula is generally only accurate for $|\eta| < \lambda$ [14], so this restriction does not further limit the use of the the approximation. This only highlights the need to develop a more comprehensive model of asymmetric charge transfer for a broader range overpotentials and reorganization energies.
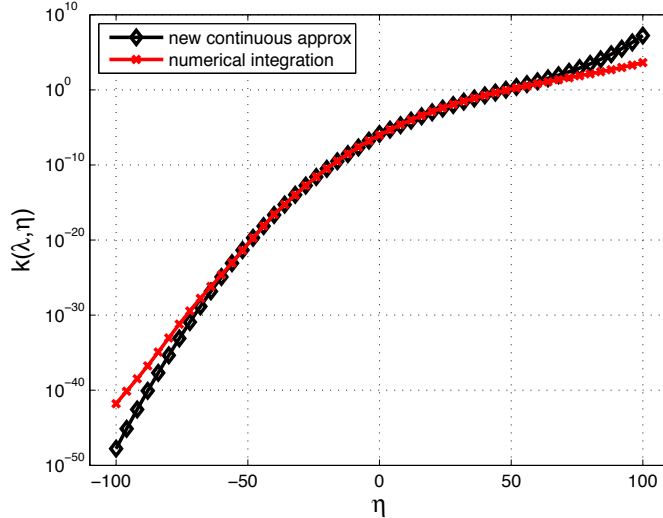

FIG. 6. Comparisons of asymmetric reaction rates by numerically evaluating Eq. 3 and a direct calculation of approximation in Eq. 6. As in Fig. 5, $\lambda = 60$. The approximation values differ significantly from the true values when $|\eta| > \lambda$.

IV. CONCLUSION

We have derived a simple closed-form approximation for AMH kinetics, Eq. 6, which eliminates the need to evaluate the divergent Fermi integral in Eq. 2. The new approximation relies on the observation that the integrand in the original expression can be approximated as having a nearly-constant factor over relevant parameter regions and associated integration limits, so that the remaining improper integral can be approximated by our previously derived simple formula for MHC kinetics [28]. As previously noted [14], for small over-potentials, $|\eta| \lesssim 1$, the AMH model is similar to the asymmetric Butler-Volmer equation with $\alpha \neq \frac{1}{2}$, which provides an alternative to the formula presented here. At larger over potentials, the BV equation neglects all curvature in the Tafel plot, which becomes significant

even at moderate overpotentials (Fig. 1) and corresponds to orders of magnitude differences in the predicted reaction rates.

Our mathematical study also clarifies the range of validity of the AMH model itself. The original model and our simple approximation are both only valid for large reorganization energies $\lambda \gg 1$ (scaled to $k_B T$) and moderate overpotentials, $|\eta| \ll \lambda$. With these parameter constraints, the curvature of the Tafel plot is relatively small (on a logarithmic scale), although significant differences with BV kinetics by orders of magnitude at large over potentials are still captured by the model. This regime is consistent with the observed rates for a variety of liquid-solid Faradaic reactions recently fitted to the AMH model [6, 9, 10, 14, 16, 25, 27], and in such cases, the present approximation would be a useful mathematical simplification for data fitting or engineering models.

On the other hand, the AMH model cannot be applied to other reactions with smaller reorganization energies ($\lambda < 10$) and more strongly curved Tafel plots approaching a constant limiting rate, which have been observed experimentally for both liquid-solid [5] and solid-solid [1] interfaces. These studies have not detected any significant asymmetry in the over-potential dependence, but in principle some Faradaic reactions with low reorganization energies will have significant asymmetry from inner sphere force-constant variations that cannot not be captured by the original AMH model. Therefore, there remains a need to develop more comprehensive, but still simple, models of asymmetric charge transfer at electrodes.

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