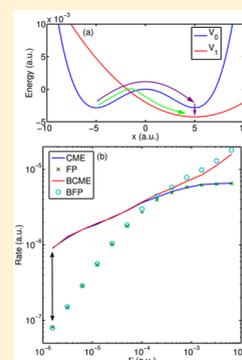


Dynamics of Barrier Crossings for the Generalized Anderson–Holstein Model: Beyond Electronic Friction and Conventional Surface Hopping

Wenjun Ouyang, Wenjie Dou, Amber Jain, and Joseph E. Subotnik*

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States

ABSTRACT: We investigate barrier crossings within the context of the Anderson–Holstein model, as relevant to coupled nuclear–electronic dynamics near a metal surface. Beyond standard electronic friction or conventional surface-hopping dynamics, we show that a broadened classical master equation can recover both the correct nonadiabatic and the correct adiabatic dynamics for a general escape problem (even with possibly multiple escape channels). In the case of a large barrier with only a single escape channel, we also find a surprising conclusion: electronic friction can recover Marcus’s nonadiabatic theory of electron transfer in the limit of small molecule–metal couplings. The latter conclusion establishes a hidden connection between Marcus’s nonadiabatic theory and Kramer’s adiabatic theory of rate constants.



1. INTRODUCTION

The Anderson–Holstein (AH) model is the most basic model describing electron transfer (ET) at a metal surface: it captures the necessary electronic coupling (i.e., electronic tunneling), nuclear–electronic coupling (which leads to nuclear motion), and electronic relaxation (which leads to broadening). In short, the model can be considered the generalization of the simple spin-boson model,¹ but now with a manifold of donor and acceptor states.²

While the usual AH model requires diabatic potential energy surfaces (PESs), a generalized AH model can be written as follows:³

$$H = H_s + H_b + H_c \quad (1a)$$

$$H_s = E(x)d^\dagger d + V_0(x) + \frac{p^2}{2m} \quad (1b)$$

$$H_b = \sum_k (\epsilon_k - \mu)c_k^\dagger c_k \quad (1c)$$

$$H_c = \sum_k W_k(c_k^\dagger d + d^\dagger c_k) \quad (1d)$$

$E(x)$ represents the change in the nuclear PES that occurs when the electronic impurity level (d^\dagger , d) becomes occupied, and μ is the Fermi level of the bath. If $V_0(x)$ is the diabatic PES for the unoccupied state, we define the diabatic PES for the occupied state to be

$$V_1(x) \equiv V_0(x) + E(x) \quad (2)$$

The key parameters for the AH model are the molecule–metal coupling ($\Gamma(\epsilon) \equiv 2\pi \sum_k |W_k|^2 \delta(\epsilon_k - \epsilon)$), the nuclear motion ($\omega \equiv \sqrt{V_0''(x_{\text{eq}})/m}$), the temperature of the metal (T), and the

nuclear–electronic coupling ($E(x)$). Note that, in the wide band approximation, $\Gamma(\epsilon)$ is independent of energy, $\Gamma(\epsilon) = \Gamma$.

In this report, we will work exclusively in the high temperature limit ($\omega \ll k_b T$) whereby the nuclear degree of freedom can be calculated classically. Whereas there are many studies in the literature regarding the activated nonadiabatic ET rate between two level systems in solution,^{4–8} there is a far smaller set of works in the literature studying barrier crossings in the presence of a manifold of electronic states at high temperatures (without tunneling) using mixed quantum-classical dynamics. A few research groups have investigated this problem in the electrochemistry community. Mohr et al.^{9,10} have investigated short time dynamics (ignoring some feedback of the solvent) to estimate rates. Mishra and Waldeck^{11,12} have hypothesized two different approaches for treating the continuum of states: one (a “density of states” model) averages Fermi Golden Rule rates over a degree of freedom that implicitly represents a solvent parameter; the other (a “potential energy curve” model) treats the nuclei explicitly and uses a variation of Landau–Zener transition state theory. These authors have not directly investigated the nonadiabatic dynamic trajectories.

Now, in the molecular conduction community, there is an enormous literature on the study of the AH model with a focus on electron–phonon effects at low temperatures, for which vibrational degrees of freedom are kept quantum mechanical (without passing to the classical limit). For instance, a great deal of work with non-equilibrium Green’s functions has been published by Nitzan and Galperin and others predicting inelastic electron tunneling spectra (IETS) as occurs when

Received: May 23, 2016

vibrations scatter with tunneling electrons.^{13–16} In the context of heterogeneous electron transfer, Wang et al. partially diagonalized the AH model Hamiltonian to study an ultrafast electron transfer reaction at a dye–semiconductor interface.^{17–20} Very recently, Wang and co-workers have investigated the dynamics of barrier crossings through reduced density matrices^{21,22} in order to examine hysteresis at very low temperatures and quantify the effects of tunneling.^{23–26} We also note that refs 2 and 14 have connected the rates of electronic transport for the AH model to semiclassical Marcus rates of ET in solution.

In the present article, our focus is not low temperature physics (which is difficult because of vibrational quanta) but rather high temperature physics (which is more tractable). Our goal is to implement a host of relatively new, semiclassical techniques to directly calculate the rate of activated barrier crossings for the AH model at classical temperatures. We will explore barrier crossings over a range of parameter regimes, all the way from the nonadiabatic (small Γ) to the adiabatic (large Γ). We will focus on two dynamical approaches: surface hopping (SH)²⁷ and electronic friction (EF).^{28–30} (i) On the one hand, SH captures the correct physics when Γ is small and is consistent with Marcus's theory of outer sphere ET.²⁷ (ii) On the other hand, EF dynamics are appropriate when nuclear velocities are small, such that dynamics can be approximated along a single adiabatic PES—almost in a Born–Oppenheimer picture (with large Γ)—but with a new source of electronic friction.^{28–36} (iii) Beyond SH and EF dynamics, we will also benchmark a third approach, namely, a broadened classical master equation (BCME) approach, that we recently proposed as an extrapolation between the two limits.^{3,37,38} Below, we will show that BCME dynamics do in fact recover the correct rates of barrier crossings in the presence of a manifold of electronic states for all values of Γ ; thus, we will conclude that BCME trajectories can be used to guide our intuition for the appropriate dynamics.

2. THEORY

2.1. Dynamics. To begin our discussion, we review how to propagate the dynamics for the Hamiltonian in eq 1 using SH and EF dynamics.

2.1.1. Surface Hopping/Classical Master Equation. For SH dynamics, we assume we are in the limit of small Γ ($\Gamma \ll k_b T$) and, as always, classical nuclear motion ($\omega \ll k_b T$) so that electronic transitions between diabats are rare and there is a valid separation of vibrational and electronic time scales. SH dictates (as derived by Redfield's perturbation theory^{39,40}) that one propagate dynamics on the diabatic surfaces with hops between them. Let $P_0(x, p, t)$ ($P_1(x, p, t)$) be the probability density for the electronic impurity level to be unoccupied (occupied) at time t with the nucleus at position (x, p) in phase space. Mathematically, one must solve the following classical master equation (CME):²⁷

$$\begin{aligned} \frac{\partial P_0(x, p, t)}{\partial t} = & \frac{\partial V_0(x, p)}{\partial x} \frac{\partial P_0(x, p, t)}{\partial p} - \frac{p}{m} \frac{\partial P_0(x, p, t)}{\partial x} \\ & - \frac{\Gamma}{\hbar} f(E(x)) P_0(x, p, t) \\ & + \frac{\Gamma}{\hbar} (1 - f(E(x))) P_1(x, p, t) \end{aligned} \quad (3a)$$

$$\begin{aligned} \frac{\partial P_1(x, p, t)}{\partial t} = & \frac{\partial V_1(x, p)}{\partial x} \frac{\partial P_1(x, p, t)}{\partial p} - \frac{p}{m} \frac{\partial P_1(x, p, t)}{\partial x} \\ & + \frac{\Gamma}{\hbar} f(E(x)) P_0(x, p, t) \\ & - \frac{\Gamma}{\hbar} (1 - f(E(x))) P_1(x, p, t). \end{aligned} \quad (3b)$$

Here $f(\epsilon) \equiv 1/(1 + e^{\beta(\epsilon - \mu)})$ is the Fermi function with $\beta \equiv 1/(k_b T)$. Note that the SH dynamics in eq 3 are appropriate for open electronic systems (where energy can flow to or from the bath when the system hops between states). These dynamics are distinct from the more conventional, energy-conserving dynamics proposed by Tully⁴¹ that are appropriate in a closed system.

2.1.2. Electronic Friction. As an alternative to SH dynamics, EF dynamics are relevant for “slow” nuclear velocities (where the meaning of slow will be discussed below). For EF, one propagates nuclei along an “adiabatic” potential of mean force (PMF) subject to Langevin dynamics. One can define two different PMFs, one PMF with the correct broadening (BPMF) prescribed by non-equilibrium Green's functions^{3,29,30}

$$U^{(b)}(x) = V_0(x) + \int_{x_0}^x dx' n(E(x')) \frac{\partial E(x')}{\partial x'} \quad (4)$$

$$n(E) \equiv \int_{-\infty}^{\infty} \frac{d\epsilon}{2\pi} \frac{\Gamma}{(\epsilon - E)^2 + \Gamma^2/4} f(E) \quad (5)$$

and one approximate PMF without broadening

$$U(x) = V_0(x) - \frac{1}{\beta} \log(1 + e^{-\beta E(x)}) \quad (6)$$

Here, x_0 is an arbitrary constant. See Figure 1a for a plot of these potentials. At high temperature, broadening is not important and $U(x) = U^{(b)}(x)$.

For the Langevin dynamics, the correct form of electronic friction (with broadening) is^{3,29,30,34–36}

$$\gamma_e^{(b)} = \frac{\hbar\beta}{\Gamma} D(E(x)) \left(\frac{dE(x)}{dx} \right)^2 \quad (7)$$

$$D(E) \equiv \Gamma \int_{-\infty}^{\infty} \frac{d\epsilon}{\pi} \left(\frac{\Gamma/2}{(\epsilon - E)^2 + \Gamma^2/4} \right)^2 f(E)(1 - f(E)) \quad (8)$$

and an approximate form (without broadening) is

$$\gamma_e = \frac{\hbar\beta}{\Gamma} f(E(x))(1 - f(E(x))) \left(\frac{dE(x)}{dx} \right)^2 \quad (9)$$

Henceforward, we will refer to Langevin dynamics with eqs 4 and 7 as broadened Fokker–Planck (BFP) dynamics and Langevin dynamics with eqs 6 and 9 as (unbroadened) Fokker–Planck dynamics (FP) dynamics. We emphasize that, in order to derive the notion of electronic friction, one must necessarily throw out several terms in any derivation and take the limit of “slow”-moving nuclei.⁴² Previously, we have argued that, in the context of parabolic diabatic surfaces (with frequency ω), electronic friction should be relevant only when $\Gamma > \omega$;³⁰ as shown below, this condition should be sufficient for the validity of electronic friction, but not always necessary if there is a source of external, non-electronic nuclear friction ($\gamma_n \neq 0$).

2.1.3. Broadened Classical Master Equation. Lastly, we have recently proposed a third option for running dynamics for the Hamiltonian in eq 1. For these dynamics, denoted broadened classical master equation, we run SH along broadened diabatic PESs, defined as ($i = 0, 1$):³⁷

$$V_i^{(b)}(x) \equiv V_i(x) + \int_{x_0}^x dx' (n(E(x')) - f(E(x'))) \frac{dE(x')}{dx'} \quad (10)$$

See Figure 1a for a plot of these potentials.

As shown in ref 3, these BCME (diabatic) dynamics are equivalent to EF (adiabatic) dynamics along BPMF (eq 4) but with unbroadened friction (eq 9). Empirically, to date, we have found that BCME dynamics successfully interpolate between SH (in the limit of small Γ) and BFP dynamics (in the limit of large Γ).^{3,37}

One historical note is perhaps appropriate. In 2002, Mohr and Schmickler conjectured a different surface-hopping scheme⁴³ to extrapolate between the adiabatic and nonadiabatic limits. According to their scheme, one runs nuclear dynamics on a mean-field potential followed by collapsing events to a diabatic potential energy surface. Thus, the Mohr–Schmickler proposed dynamics were in the spirit of what Prezhdov–Rosky⁴⁴ and Hack–Truhlar⁴⁵ conjectured for Tully’s normal fewest-switches surface-hopping algorithm⁴¹ in solution. Although we do not believe these approaches can be justified rigorously, the methods clearly have a physical motivation and the similarity between these approaches is itself noteworthy.

2.2. Rate Constant. We will now investigate the rate of escape for a particle which is subject to Langevin dynamics with an external non-electronic source of nuclear friction ($\gamma_n \neq 0$); the particle must emerge from one diabatic PES (V_0 in eq 1) into another diabatic PES (V_1). We start with parabolic PESs:

$$V_0(x) = \frac{1}{2}m\omega^2 x^2 \quad (11a)$$

$$V_1(x) = \frac{1}{2}m\omega^2(x - g)^2 + \Delta G^0 \quad (11b)$$

The reorganization energy E_r is defined to be $E_r \equiv 1/2m\omega^2 g^2$. For comparison, there are three relevant analytical rate theories.

First, in the limit of small Γ , the Marcus rate of electron transfer is³⁹

$$k_{1 \rightarrow 0} = \int_{-\infty}^{\infty} d\epsilon \frac{\Gamma(\epsilon)}{\hbar} (1 - f(\epsilon)) \frac{e^{-(E_r - \Delta G^0 + \epsilon)/4E_r k_b T}}{\sqrt{4\pi E_r k_b T}} \quad (12a)$$

$$k_{0 \rightarrow 1} = \int_{-\infty}^{\infty} d\epsilon \frac{\Gamma(\epsilon)}{\hbar} f(\epsilon) \frac{e^{-(E_r + \Delta G^0 - \epsilon)/4E_r k_b T}}{\sqrt{4\pi E_r k_b T}} \quad (12b)$$

Here, ΔG^0 is the free energy difference between the occupied impurity state (denoted as “1”) and the unoccupied impurity state (denoted as “0”). Equation 12 can be derived through many different pathways, either starting with Fermi’s Golden Rule or using Redfield theory.⁸

Second, in the limit of large Γ , all dynamics are adiabatic along a BPMF (eq 4). Provided that electronic friction is small (see eq 7), one can use straightforward adiabatic transition state theory (TST) for the rate:

$$k_{\text{TST}} = \kappa \frac{\omega}{2\pi} e^{-\beta U^{(b)\ddagger}} \quad (13)$$

Here, $U^{(b)\ddagger}$ is the barrier height in eq 4, and κ is a transmission function that must be calculated ($\kappa \leq 1$).

Third, for an analytic rate expression that interpolates between the Marcus nonadiabatic rate (at small Γ) and the adiabatic rate (at large Γ), one option is to invoke Landau–Zener theory (which can be applied in the nonadiabatic and adiabatic limits). However, because the system is coupled to a continuum of electron bath states, Landau–Zener theory must necessarily require a sum-overstates approach (which must be done carefully; see ref 12 for a good discussion). This will be the subject of another report. Another interpolation scheme is the Zusman approach,^{5,6,46,47} which is roughly as follows:

$$k_{\text{Zusman}}^{-1} = k_{\text{Marcus}}^{-1} + k_{\text{TST}}^{-1} \quad (14)$$

3. RESULTS AND DISCUSSION

3.1. Parabolic Diabats. Results for the parabolic PESs defined in eq 11 are plotted in Figure 1. Rates were obtained by fitting diabatic population to an exponential as a function of time. We observe that as Γ increases from small to large, the rate changes from (i) linear in Γ (which agrees with Marcus theory, eq 12), (ii) followed but a slight leveling off, and then (iii) eventually followed by another nearly exponential rise (which agrees with transition state theory, eq 13). These features have been predicted earlier by Schmickler and Mohr:⁴³ as we increase Γ , the escape rate increases for small Γ because one increases the probability for an electron to hop, while, for large Γ , the rate increases because the adiabatic barrier decreases. See ref 12. for a nice discussion of this physics. A similar phenomenon is also seen for the ET rate of a standard two level system in solution.^{48–50} Note that our prescribed BCME (eq 10) agrees with this interpretation and interpolates correctly from the CME to BFP, giving us a very simple picture of the correct semiclassical trajectories.

The Zusman rates are shown in Figure 1c and agree fairly well with our BCME results. This near agreement is perhaps surprising because Zusman theory can be derived^{5,6,46,47} for a two-state spin-boson model, whereas the physics here involve a continuum of electronic states (rather than two). For instance, note that electronic transitions can be delocalized according to the surface-hopping protocol (eq 3), whereas ET is assumed to happen only at the diabatic crossing point according to Zusman theory. From the agreement in Figure 1c, we hypothesize that, even for the AH model, ET between diabats must occur mostly at the crossing point (where the Fermi function switches quickly from 0 to 1).

3.2. Electronic Friction For Small Γ . The most surprising feature of Figure 1 is the behavior of FP/BFP at small Γ . As stated above, we do not expect FP dynamics to be correct for $\Gamma \ll \omega$ (at least in vacuum).³⁰ That being said, note that FP dynamics agree with CME and Marcus theory. In fact, we now prove a near equivalence (which will be valid for escape rates over large barriers).

First, we rewrite Marcus’s nonadiabatic theory of ET (eq 12) as an integral over the real space of the oscillator:³⁹

$$k_{0 \rightarrow 1} = \int_{-\infty}^{\infty} dx \frac{\Gamma}{\hbar} f(E(x)) \frac{e^{-\beta V_0(x)}}{Z_0} \quad (15)$$

Here, Z_0 is the partition function for $V_0(x)$; for the harmonic case in Figure 1, $Z_0 = \sqrt{2\pi/(\beta m\omega^2)}$. According to eq 6, eq 15 can be written as

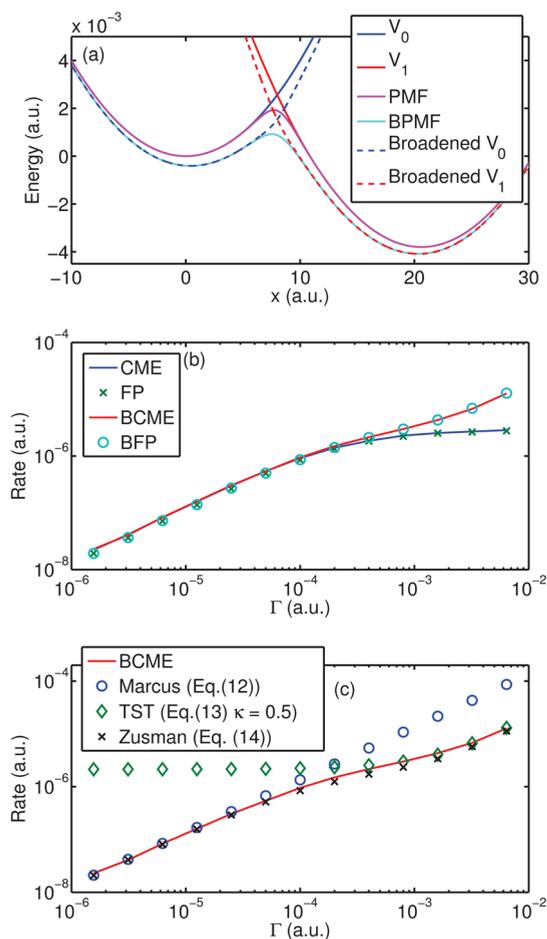


Figure 1. (a) Shifted, diabatic harmonic PESs defined in eq 11. The potential of mean force (PMF, eq 6), broadened PMF (BPFM, eq 4), and broadened diabatic PESs (eq 10) for $\Gamma = 0.0016$ au are also shown. (b) Rates of reaction as a function of Γ for the four dynamics algorithms. The parameters are (all in atomic units): mass $m = 2000$, $\omega = 0.0002$, $g = 20.6097$, $\Delta G^\circ = -0.0038$, and nuclear friction $\gamma_n = 2m\omega = 0.8$. The temperature is 300 K (so $k_b T = 9.5 \times 10^{-4}$ au). The barrier height for the unbroadened surfaces is 0.00256 au. The CME must be valid for small Γ , and BFP must be valid for large Γ . Note that BCME and BFP work across the full range of Γ . (c) Rate as a function of Γ according to standard rate theories. The transmission coefficient κ in eq 13 is fit to be $\kappa = 0.5$.

$$\begin{aligned}
 k_{0 \rightarrow 1} &= \int_{-\infty}^{\infty} dx \frac{\Gamma}{\hbar} f(E(x))(1 - f(E(x))) \frac{e^{-\beta U(x)}}{Z_0} \\
 &= \int_{-\infty}^{\infty} dx \frac{\Gamma}{\hbar} \left(\frac{-df(E(x))}{dx} \right) \left(\beta \frac{dE(x)}{dx} \right)^{-1} \frac{e^{-\beta U(x)}}{Z_0} \\
 &\approx \int_{-\infty}^{\infty} dx \frac{\Gamma}{\hbar} \delta(x - x_B) \left(\beta \left| \frac{dE(x)}{dx} \right| \right)^{-1} \frac{e^{-\beta U(x)}}{Z_0} \\
 &= \frac{\Gamma}{\beta \hbar} \left| \frac{dE(x)}{dx} \right|_{x=x_B}^{-1} \frac{e^{-\beta U(x_B)}}{Z_0}
 \end{aligned} \tag{16}$$

Here, we have used the large barrier approximation so the derivative of Fermi function is approximated as a Dirac δ function. x_B is the coordinate of the diabatic crossing point.

Equation 16 was obtained long ago by Morgan and Wolynes,⁵¹ Ulstrup,⁵² and Levich.⁵³

Second, we treat FP dynamics with electronic friction. Note that, as $\Gamma \rightarrow 0$, the electronic friction (eqs 9 to 7) becomes infinite. According to Kramer's theory⁸ of the adiabatic rate constant in the overdamped limit, the rate can be written as

$$\begin{aligned}
 k &= \left[\int_{-\infty}^{x_B} dx e^{-\beta U(x)} \int_x^{\infty} dx' \beta \gamma_e e^{\beta U(x')} \right]^{-1} \\
 &= \left[\int_{-\infty}^{x_B} dx e^{-\beta U(x)} \int_x^{\infty} dx' \frac{\beta^2 \hbar}{\Gamma} \right. \\
 &\quad \left. \times f(E(x'))(1 - f(E(x')) \left(\frac{dE(x')}{dx'} \right)^2 e^{\beta U(x')} \right)^{-1} \\
 &= \left[\int_{-\infty}^{x_B} dx e^{-\beta U(x)} \int_x^{\infty} dx' \frac{\beta \hbar}{\Gamma} \left(\frac{-df(E(x'))}{dx'} \right) \frac{dE(x')}{dx'} e^{\beta U(x')} \right]^{-1}
 \end{aligned} \tag{17}$$

Converting df/dx to a δ function again,⁵⁴

$$\begin{aligned}
 k &\approx \left[\int_{-\infty}^{x_B} dx e^{-\beta U(x)} \int_x^{\infty} dx' \frac{\beta \hbar}{\Gamma} \delta(x' - x_B) \left| \frac{dE(x')}{dx'} \right| e^{\beta U(x')} \right]^{-1} \\
 &= \left[\int_{-\infty}^{x_B} dx e^{-\beta U(x)} \frac{\beta \hbar}{\Gamma} \left| \frac{dE(x)}{dx} \right|_{x=x_B} e^{\beta U(x_B)} \right]^{-1} \\
 &\approx \frac{1}{Z_0} \frac{\Gamma}{\hbar \beta} \left| \frac{dE(x)}{dx} \right|_{x=x_B}^{-1} e^{-\beta U(x_B)}
 \end{aligned} \tag{18}$$

In the last line, we have approximated $\int_{-\infty}^{x_B} \exp(-\beta U(x))$ as Z_0 , again based on the large barrier approximation.

From the manipulations above, it is clear that eq 16 and eq 18 are identical, so that FP and Marcus theory should be roughly equivalent for small Γ when there is a large barrier preventing any escape from one diabatic well and an external source of nuclear friction ($\gamma_n \neq 0$). Thus, adiabatic dynamics can seemingly recover nonadiabatic features.

3.3. Quartic versus Quadratic Diabatic Potentials.

Before concluding, we must emphasize that, for small Γ , even though FP and Marcus theory may agree for the case of large barriers, neither of these models needs to be correct and neither one will necessarily agree with the correct CME dynamics. Consider Figure 2 and the corresponding diabatic PESs:

$$V_0(x) = a(x^4 - bx^2) \tag{19a}$$

$$V_1(x) = \frac{1}{2}m\omega^2(x - g)^2 + E_d \tag{19b}$$

Initially, we imagine the particle is equilibrated in the left basin of V_0 and we fit the average position of the nucleus to get the rate constant. Now, unlike Figure 1, the FP and CME rate constants are very different for small Γ (as highlighted with the arrow in Figure 2b). This discrepancy comes from the fact that, according to the mean-field based algorithms (FP and BFP), there is only one channel for the barrier crossing (the green arrow in Figure 2a). However, according to the surface-hopping algorithms (CME and BCME), there are two channels through which the particle can escape the basin on the left: either a direct hop from V_0 to V_1 at the crossing point (the green arrow) or motion over the barrier on V_0 followed by subsequent relaxation on V_0 and later on a hop down to V_1 (the purple arrows). Thus, it is not simply slow motion or a large barrier per se that justifies EF dynamics; in general, an

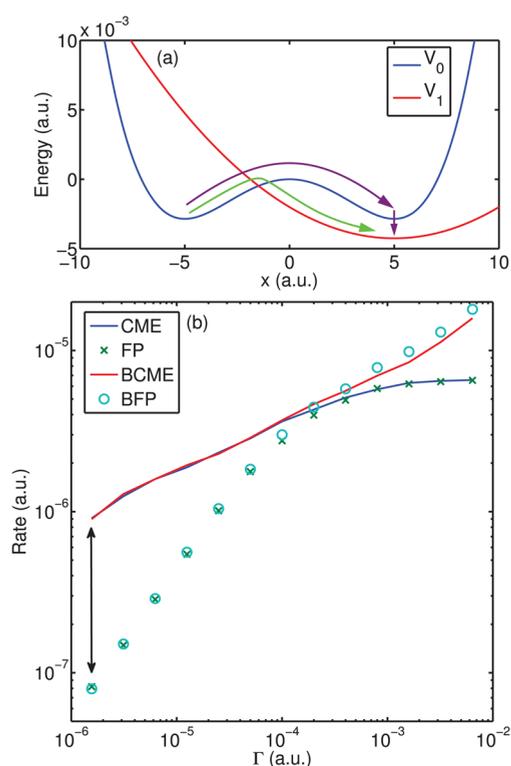


Figure 2. (a) Anharmonic, diabatic PESs defined in eq 19. (b) The rates of reaction as a function of Γ . The parameters for the PES are (all in atomic units): $m = 2000$, $a = 4.56 \times 10^{-6}$, $b = 50$, $\omega = 0.0003$, $g = 5$, $E_d = -0.00425$ and nuclear friction $\gamma_n = 2.7$. The temperature is $300K$ (so $k_b T = 9.5 \times 10^{-4} a.u.$). The unbroadened barrier height for the two paths denoted by green and purple arrows are $0.002375 a.u.$ and $0.00285 a.u.$, respectively. The CME must be valid for small Γ and BFP must be valid for large Γ . Note that surface-hopping based algorithms (CME and BCME) capture ground state dynamics (green arrow in (a)) and excited state dynamics (purple arrows), whereas mean-field based algorithms (FP and BFP) capture only the former. This leads to large differences for small Γ , as highlighted with the black arrow in (b).

electronic friction model will fail whenever excited state dynamics are important.

4. CONCLUSIONS

To conclude, we have calculated the rates of activated barrier crossings with SH, FP, BFP, and BCME dynamics for the AH model. We summarize our findings:

- As one should have expected from perturbation theory, SH dynamics work well (only) when Γ is small.
- More interestingly, if we merely broaden the diabatic PESs, our resulting BCME dynamics capture the correct rates in both the small and large Γ limits. In fact, because of the algorithm's simplicity, we hypothesize that BCME trajectories should be trustworthy more generally.
- Perhaps most surprisingly, we have shown that BFP dynamics are also meaningful both in the large and small Γ limits, assuming parabolic diabats and large barriers. Indeed, eqs 16–18 above prove that, for electronic transitions with large nuclear barriers and only one possible escape channel, Marcus theory is effectively consistent with Kramer's theory in the limit of small Γ (and large, overdamped electronic friction). This finding contradicts our intuition that EF dynamics should be correct only when $\Gamma > \omega$ ³⁰ and raises the question of,

what are the exact conditions necessary for EF dynamics to be valid?⁵⁵

Figure 2 is arguably the most important figure in this article. The figure reminds us that if there are any excited state dynamics at all, electronic friction must fail. And in practice, it may well be very hard to rule out such dynamical processes, especially in multidimensional problems. These findings should be useful in the context of electrochemistry and surface physics, where there is a continuous transition from outer to inner sphere ET, and inexpensive dynamical models are sorely needed.

AUTHOR INFORMATION

Corresponding Author

*E-mail: subotnik@sas.upenn.edu.

Funding

This material is based upon work supported by the (U.S.) Air Force Office of Scientific Research (USAFOSR) PECASE award under AFOSR Grant No. FA9950-13-1-0157. J.E.S. acknowledges a Camille and Henry Dreyfus Teacher Scholar Award and a David and Lucille Packard Fellowship.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

J.E.S. thanks Misha Galperin for very helpful discussions.

REFERENCES

- (1) Leggett, A. J.; Chakravarty, S.; Dorsey, A. T.; Fisher, M. P. A.; Garg, A.; Zwerger, W. *Rev. Mod. Phys.* **1987**, *59*, 1–85.
- (2) Nitzan, A. *Annu. Rev. Phys. Chem.* **2001**, *52*, 681–750.
- (3) Dou, W.; Subotnik, J. E. *J. Chem. Phys.* **2016**, *144*, 024116.
- (4) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966.
- (5) Zusman, L. *Chem. Phys.* **1980**, *49*, 295–304.
- (6) Straub, J. E.; Berne, B. J. *J. Chem. Phys.* **1987**, *87*, 6111.
- (7) Hänggi, P.; Talkner, P.; Borkovec, M. *Rev. Mod. Phys.* **1990**, *62*, 251–341.
- (8) Nitzan, A. *Chemical dynamics in condensed phases: Relaxation, transfer and reactions in condensed molecular systems*, 1st ed.; Oxford University Press: New York, 2006; p 552.
- (9) Mohr, J. H.; Schmickler, W. *Phys. Rev. Lett.* **2000**, *84*, 1051–4.
- (10) Mohr, J.; Schmickler, W.; Badiali, J. *Chem. Phys.* **2006**, *324*, 140–147.
- (11) Mishra, A. K.; Waldeck, D. H. *J. Phys. Chem. C* **2009**, *113*, 17904–17914.
- (12) Mishra, A. K.; Waldeck, D. H. *J. Phys. Chem. C* **2011**, *115*, 20662–20673.
- (13) Galperin, M.; Ratner, M. A.; Nitzan, A. *J. Chem. Phys.* **2004**, *121*, 11965.
- (14) Galperin, M.; Ratner, M. A.; Nitzan, A. *J. Phys.: Condens. Matter* **2007**, *19*, 103201.
- (15) Mii, T.; Tikhodeev, S. G.; Ueba, H. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2003**, *68*, 205406.
- (16) White, A. J.; Galperin, M. *Phys. Chem. Chem. Phys.* **2012**, *14*, 13809.
- (17) Thoss, M.; Kondov, I.; Wang, H. *Chem. Phys.* **2004**, *304*, 169–181.
- (18) Kondov, I.; Thoss, M.; Wang, H. *J. Phys. Chem. A* **2006**, *110*, 1364–1374.
- (19) Thoss, M.; Kondov, I.; Wang, H. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2007**, *76*, 153313.
- (20) Li, J.; Kondov, I.; Wang, H.; Thoss, M. *J. Phys.: Condens. Matter* **2015**, *27*, 134202.
- (21) Wilner, E. Y.; Wang, H.; Cohen, G.; Thoss, M.; Rabani, E. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2013**, *88*, 045137.

- (22) Wilner, E. Y.; Wang, H.; Thoss, M.; Rabani, E. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2014**, *89*, 205129.
- (23) Chen, J.; Su, J.; Wang, W.; Reed, M. *Phys. E* **2003**, *16*, 17–23.
- (24) Schull, T. L.; Kushmerick, J. G.; Patterson, C. H.; George, C.; Moore, M. H.; Pollack, S. K.; Shashidhar, R. *J. Am. Chem. Soc.* **2003**, *125*, 3202–3203.
- (25) Li, C.; Zhang, D.; Liu, X.; Han, S.; Tang, T.; Zhou, C.; Fan, W.; Koehne, J.; Han, J.; Meyyappan, M.; Rawlett, A. M.; Price, D. W.; Tour, J. M. *Appl. Phys. Lett.* **2003**, *82*, 645.
- (26) Galperin, M.; Ratner, M. A.; Nitzan, A. *Nano Lett.* **2005**, *5*, 125–130.
- (27) Dou, W.; Nitzan, A.; Subotnik, J. E. *J. Chem. Phys.* **2015**, *142*, 084110.
- (28) Head-Gordon, M.; Tully, J. C. *J. Chem. Phys.* **1995**, *103*, 10137.
- (29) Bode, N.; Kusminskiy, S. V.; Egger, R.; von Oppen, F. *Beilstein J. Nanotechnol.* **2012**, *3*, 144–162.
- (30) Dou, W.; Nitzan, A.; Subotnik, J. E. *J. Chem. Phys.* **2015**, *143*, 054103.
- (31) Adelman, S. A. *J. Chem. Phys.* **1976**, *64*, 2375.
- (32) Tully, J. C. *J. Chem. Phys.* **1980**, *73*, 1975.
- (33) Head-Gordon, M.; Tully, J. C. *J. Chem. Phys.* **1992**, *96*, 3939.
- (34) Brandbyge, M.; Hedegård, P.; Heinz, T. F.; Misewich, J. A.; Newns, D. M. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1995**, *52*, 6042–6056.
- (35) Mozyrsky, D.; Hastings, M. B.; Martin, I. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2006**, *73*, 035104.
- (36) Thomas, M.; Karzig, T.; Kusminskiy, S. V.; Zaránd, G.; von Oppen, F. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2012**, *86*, 195419.
- (37) Dou, W.; Subotnik, J. E. *J. Chem. Phys.* **2016**, in press (arXiv:1606.06110).
- (38) Note that the BCME using the potential in eq 10 describes only a single orbital coupled to a continuum of states. Extending the BCME to multiple orbitals coupled to a continuum of states is nontrivial. Such an extension will be studied in the future.
- (39) Dou, W.; Nitzan, A.; Subotnik, J. E. *J. Chem. Phys.* **2015**, *142*, 234106.
- (40) Elste, F.; Weick, G.; Timm, C.; von Oppen, F. *Appl. Phys. A: Mater. Sci. Process.* **2008**, *93*, 345–354.
- (41) Tully, J. C. *J. Chem. Phys.* **1990**, *93*, 1061–1071.
- (42) Galperin, M.; Nitzan, A. *J. Phys. Chem. Lett.* **2015**, *6*, 4898–4903.
- (43) Schmickler, W.; Mohr, J. *J. Chem. Phys.* **2002**, *117*, 2867.
- (44) Prezhdo, O. V.; Rossky, P. J. *J. Chem. Phys.* **1997**, *107*, 825.
- (45) Hack, M. D.; Truhlar, D. G. *J. Chem. Phys.* **2001**, *114*, 9305.
- (46) Hynes, J. T. *J. Phys. Chem.* **1986**, *90*, 3701–3706.
- (47) Morillo, M.; Cukier, R. I. *J. Chem. Phys.* **1988**, *89*, 6736.
- (48) Huo, P.; Miller, T. F.; Coker, D. F. *J. Chem. Phys.* **2013**, *139*, 151103.
- (49) Jain, A.; Subotnik, J. E. *J. Chem. Phys.* **2015**, *143*, 134107.
- (50) The physics of the AH model and the spin-boson model Hamiltonian can be very different however. For instance, note that there is no analogue of electronic friction for spin-boson Hamiltonians; for a meaningful notion of electronic friction, one requires a manifold of electronic states.
- (51) Morgan, J. D.; Wolynes, P. G. *J. Phys. Chem.* **1987**, *91*, 874–883.
- (52) Ulstrup, J. *Charge transfer processes in condensed media*; Lecture notes in chemistry; Springer-Verlag: Berlin, 1979; p 221.
- (53) Levich, V. G. *Adv. Electrochem. Eng.* **1956**, *4*, 249.
- (54) One word of caution. In eqs 16 and 18, we twice approximate $f(E(x))(1 - f(E(x)))$ as a δ function; this approximation cannot be exact given that $U(x)$ in eq 6 will not be smooth in the limit of large reorganization energies. Different manipulations can lead to slightly different prefactors, e.g., up to a factor of 2.
- (55) Note that, in Figure 1, $\gamma_n = 2m\omega$ so that ω is the correct relaxation time for the damped harmonic oscillator.