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**Electron and Energy Transfer Dynamics in Homogeneous and Inhomogeneous Environments**

**Joseph Subotnik**  
**TRUSTEES OF THE UNIVERSITY OF PENNSYLVANIA**

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**Final Report**

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## ABSTRACT

The PI's current AFOSR/PECASE grant (FA9950-13-1-0157, 2013-2018) has resulted in 26 publications with a direct impact on the field of electronic relaxation, especially electron and energy transfer in solution and at metal surfaces.

For the case of chemical dynamics in solution, the PI has made significant strides in developing a simple and reliable surface-hopping picture for photoexcited dynamics, whereby one can model nuclear vibrations stochastically (depending on the instantaneous charge state). The PI has shown that this intuitive picture of photochemistry can be justified by comparison with the quantum-classical Liouville equation, with the proviso that decoherence is correctly taken into account. Moreover, the PI performed the first simulations of energy transfer using *ab initio* electronic structure theory, investigating how triplets transfer between aromatic donors and acceptors.

For the case of chemical dynamics at a metal-molecule interface, the PI demonstrated a surprising agreement between surface hopping and electronic friction. Furthermore, the PI derived a universal form of electronic friction that acts as a universal correction to the standard Born-Oppenheimer approximation. As such, the PI made fundamental progress in understanding one of the most important tenets of chemistry (the Born-Oppenheimer approximation) and has offered a new approach for a quantitative algorithm.

# Final Report for “Electron and Energy Transfer Dynamics in Homogeneous and Inhomogeneous Environments”, AFOSR FA9950-13-1-0157

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## Results from Previous Work

The PI’s current AFOSR/PECASE grant (FA9950-13-1-0157, 2013-present), has resulted in 26 publications<sup>1–26</sup> with a direct impact on the field of nonadiabatic dynamics, both in solution and at metal surfaces. We now review our main results. Our work on surface hopping for finite systems – especially photo-excited molecules in solution – was recently reviewed in *Annual Reviews of Physical Chemistry*.<sup>2</sup>

### 0.1 The Foundations of Surface Hopping

As it was originally formulated<sup>27</sup>, Tully’s surface hopping algorithm was guessed (rather than derived); in other words, using his physical intuition, Tully made an ansatz as to how to run stochastic nuclear trajectories so as to extract quantum mechanical observables. Tully<sup>27</sup> argued that, in practice, the algorithm seemed to offer good results compared with exact quantum dynamics (for classical nuclear motion), which has been confirmed in some recent calculations by Chen and Reichman<sup>28</sup>. Nevertheless, Tully’s specific algorithm was never related back to the formal Schrodinger equation, which has been one formal difficulty as far as fixing up the well-known decoherence failures of the algorithm.<sup>29–40</sup>

With this background in mind, in Ref.<sup>3</sup>, our group took a key step forward by showing the approximations necessary to derive Tully’s surface-hopping formalism. In particular, our approach was:

1. We constructed the partial Wigner transform  $A_{ij}(\vec{R}, \vec{P})$ <sup>41,42</sup> for an FSSH simulation; here,  $\vec{R}$  and  $\vec{P}$  are the position and momenta of the nuclei. For the case of only two electronic states (1 and 2), we evaluated three phase-space densities:

- $A_{ii}(\vec{R}, \vec{P})$ : the phase space density for the nuclear population, assuming the electrons are in state  $i = 1$  or  $2$ .
- $A_{12}(\vec{R}, \vec{P})$ : the phase space density for the nuclei, assuming the electrons are in a coherence between states 1 and 2; this density is complex (as opposed to real).

These phase-space densities are plotted in Fig. 1 for one model problem.

2. We compared the FSSH equation of motion against the quantum classical Liouville equation (QCLE):

$$\frac{\partial \hat{A}(\vec{R}, \vec{P}, t)}{\partial t} = -\frac{i}{\hbar} \left[ \hat{H}_{el}(\vec{R}), \hat{A}(t) \right] + \frac{1}{2} \left\{ \hat{H}_{el}(\vec{R}), \hat{A}(t) \right\} - \frac{1}{2} \left\{ \hat{A}(t), \hat{H}_{el}(\vec{R}) \right\} \quad (1)$$

where  $\{, \}$  is the classical Poisson bracket. The QCLE<sup>41,43</sup> approximates exact quantum mechanics by cutting off the nuclear equation of motion at order  $\hbar$ , in accord with the notion of classical nuclei, and is exact for certain Hamiltonians (e.g., the spin-boson model).

3. We showed that, with large enough temperatures and an appropriate decoherence correction, FSSH nearly matches the QCLE and can therefore be partially justified.
4. We note, however, that a rigorous decoherence correction requires interacting trajectories (rather than the usual noninteracting trajectories). Nevertheless, with a formal expression for the correct decoherence correction, one gains a great deal of intuition for how to construct approximate corrections<sup>29-40</sup>. In particular, our derivation established the correctness of the Rossky-Truhlar approach of including decoherence through a term proportional to the difference in forces  $\vec{F}_{11} - \vec{F}_{22}$ <sup>31,32,44</sup>. Moreover, we were also able to compare the formal decoherence correction with an approximate, parameter-free augmented FSSH (A-FSSH) decoherence expression<sup>45,46</sup>. We note that, through a previous AFSOR grant (2011-2014, FA9950-13-1-0157), we showed how that decoherence can be absolutely crucial modeling photo-induced condensed phase dynamics; for instance, without decoherence, FSSH will not necessarily recover Marcus theory.<sup>46,47</sup>

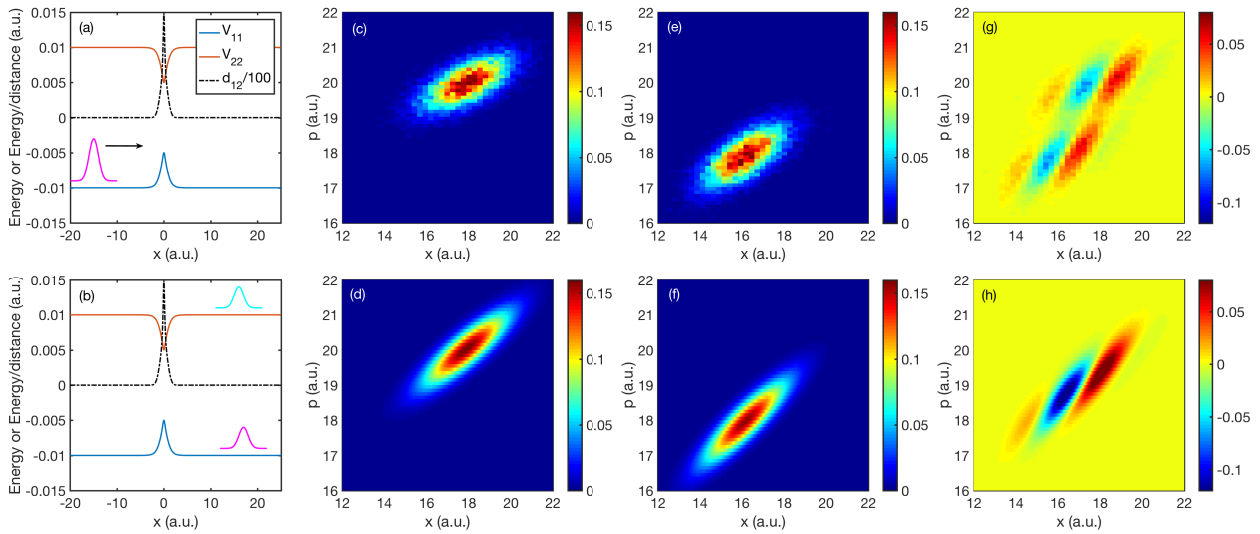


Figure 1: Understanding Tully’s FSSH algorithm through a partial Wigner transform. (a) The setup for Tully model problem #1: A nuclear wavepacket (in pink) approaches an avoided crossing from the left coming in along the lower adiabat ( $V_{11}$  in blue). This wavepacket can either remain on the lower adiabat or jump to the upper adiabat ( $V_{22}$  in red). The derivative coupling  $d_{12}$  is plotted in black. (b) The wavepackets on the lower and upper adiabatic surfaces are slightly separated at a later time. (c) – (h): The partial Wigner transforms for the system at that later time. (c)  $A_{11}^{FSSH}$ , (d)  $A_{11}^{exact}$ , (e)  $A_{22}^{FSSH}$ , (f)  $A_{22}^{exact}$ , (g)  $\text{Real}((A_{12}^{FSSH}))$ , (h)  $\text{Real}((A_{12}^{exact}))$ . Note that surface hopping calculations do recapitulate partial Wigner transforms for the populations on surfaces 1 and 2: this agreement endorses surface-hopping as an approximate solution to the QCLE. That being said, there are errors in the 1-2 coherences, which present a difficulty for the surface-hopping ansatz when analyzing spectroscopy.<sup>13</sup>

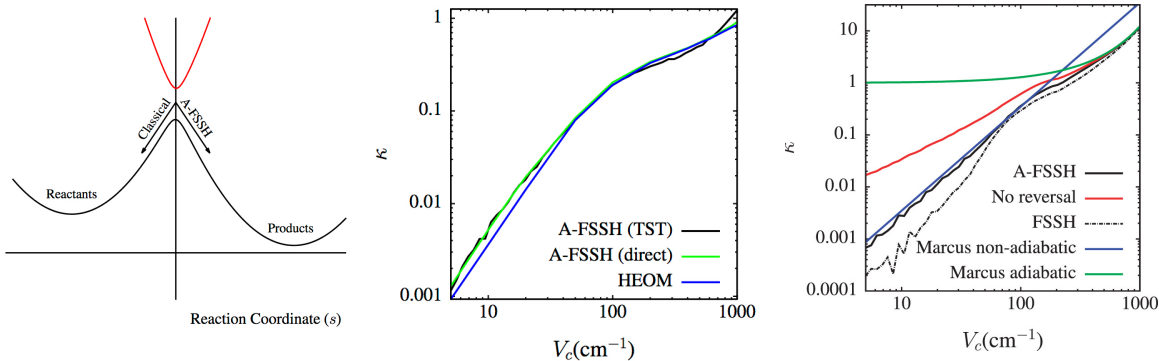
## 0.2 Transition State Theory and Surface Hopping

While the work above<sup>3</sup> puts FSSH on firmer theoretical ground, there is one unavoidable difficulty associated with the FSSH algorithm: the algorithm is not time-reversible<sup>14</sup>. One consequence of this failure is the fact that, according to FSSH, the entropy of the total universe is not conserved.<sup>48</sup> Nevertheless, as Ref.<sup>24</sup> shows, FSSH does usually recover the correct value of the entropy of the electronic subsystem; although the entropy of the nuclear subsystem was not investigated, FSSH presumably recovers this correct value as well. Thus, in the spirit of Boltzmann’s H-theorem<sup>49</sup>, FSSH does correctly predict the increase for the universe as measured by the relative entropy increase for each subsystem.

Now, a lack of time reversibility has one consequence in practice: calculating the rates of rate, thermal (as opposed to photo-induced) electron and energy transfer events is not very straightforward with FSSH. After all, if we start with a trajectory at the transition state, in order to calculate a rate, we must: (a) propagate the trajectories forwards in time to make sure they reach the product and (b) propagate the trajectories backwards in time to make sure they reach the reactant basin<sup>50–52</sup>. Obviously, forward propagation is easy with FSSH; however, as just mentioned, propagating trajectories backwards in time is difficult because of the stochastic nature of FSSH dynamics.

Several years ago, Hammes-Schiffer and Tully suggested one approach to overcome this problem of backward propagation<sup>53,54</sup>: namely, one could propagate artificial trajectories backwards in time (starting from the transition state) and then propagate trajectories forwards in time (and add in the correct weights). This approach will recover the true FSSH result assuming that one samples over all artificial trajectories backwards in time; in practice, the cost is only 2-3 times a standard calculation but, concomitantly, there is no means to incorporate decoherence. Thus, in Ref.<sup>7</sup>, we proposed an extension of the Hammes-Schiffer/Tully scheme that did allow for the inclusion of decoherence events (and with zero additional computational cost). Effectively, our heuristic approach was based on backwards propagation on one adiabat and forwards propagation on multiple adiabats. In Fig. 2, we show how our transition state theory matched up with Marcus theory and higher level exactly quantum mechanics<sup>55-58</sup>; the strong agreement is a powerful endorsement of FSSH as a tool for modeling long-time nonadiabatic dynamics for systems with a finite number of electronic states.

Figure 2: (*left*) A schematic diagram highlighting how we calculate nonadiabatic rates with a combination of transition state theory (TST) and augmented surface hopping dynamics (A-FSSH) (from Ref.<sup>7</sup>): trajectories are run backwards classically (which ignores branching and decoherence) and run forwards with surface hopping dynamics (which includes branching and decoherence). (*middle*) A-FSSH results for the spin-boson model; we plot the electron transfer transmission factor ( $\kappa$ ) as a function of the diabatic coupling ( $V_c$ ). Despite the many approximations in our algorithm, note that our TST surface hopping results do agree with direct A-FSSH calculations as well as exact hierarchical equation of motion (HEOM), which is a strong endorsement of our heuristic approach. (*right*) Here, without friction, we compare the A-FSSH transmission factor versus classical Marcus theory in the nonadiabatic and adiabatic limits. Note that A-FSSH interpolates correctly between the two different limits, outperforming FSSH (which ignores decoherence) and again endorsing the TST-AFSSH approach. Note also another discovery of Ref.<sup>7</sup>: surface hopping results without velocity reversal upon a forbidden hop can yield quite erroneous answers.



### 0.3 A Classical Master Equation for Nonadiabatic Dynamics at Metal Surfaces

Tully’s FSSH is not the only stochastic surface-hopping approach for treating electron transfer. For a molecule near a metal surface, in the limit of weak molecule-metal coupling, there is another flavor of surface hopping known as a classical master equation surface hopping (CMESH)<sup>21,22,59</sup>. For these dynamics, and unlike Tully’s FSSH dynamics, no coherence is ever propagated because the molecule is literally changing charge state and exchanging electrons with a metal. Instead,

according to simplest CME, if the molecule is uncharged, the nuclei evolve on a single diabatic surface ( $V_0(R)$ ), while hops to a charged diabatic surface ( $V_1(R)$ ) are prescribed in a Markovian sense based upon the lifetime of the molecule ( $\Gamma(R)$ ) – and the latter must be either known or calculated at each geometry. This motion on different diabatic states is akin to so-called DIMET dynamics<sup>60,61</sup> in surface femtochemistry.

Let  $\rho_{00}(\vec{R}, \vec{P})$  (or  $\rho_{11}(\vec{R}, \vec{P})$ ) be the probability that the molecule sits at  $(\vec{R}, \vec{P})$  in phase space and is uncharged (or charged). Mathematically, as derived initially by von Oppen *et al*<sup>59</sup>, the simplest CME takes the form:

$$\frac{\partial \rho_{00}(\vec{R}, \vec{P}, t)}{\partial t} = \sum_{\alpha} \frac{\partial V_0}{\partial R_{\alpha}} \frac{\partial \rho_{00}(t)}{\partial P_{\alpha}} - \frac{P_{\alpha}}{m_{\alpha}} \frac{\partial \rho_{00}(t)}{\partial R_{\alpha}} - \frac{\Gamma}{\hbar} f(E(R)) \rho_{00}(t) + \frac{\Gamma}{\hbar} (1 - f(E(R))) \rho_{11}(t) \quad (2)$$

$$\frac{\partial \rho_{11}(\vec{R}, \vec{P}, t)}{\partial t} = \sum_{\alpha} \frac{\partial V_1}{\partial R_{\alpha}} \frac{\partial \rho_{11}(t)}{\partial P_{\alpha}} - \frac{P_{\alpha}}{m_{\alpha}} \frac{\partial \rho_{11}(t)}{\partial R_{\alpha}} + \frac{\Gamma}{\hbar} f(E(R)) \rho_{00}(t) - \frac{\Gamma}{\hbar} (1 - f(E(R))) \rho_{11}(t) \quad (3)$$

Here, the fermi function  $f(z)$  enters because any charge injection into a metal must enter above the fermi level, and hence the energy difference between the two molecular charge states ( $E(R) \equiv V_1 - V_0$ ) must always be compared against the fermi level of the metal. In Ref.<sup>21</sup>, we showed that Eqns. 2-3 in fact reach the correct equilibrium (without any external friction). We also verified in Ref.<sup>22</sup> that these equations are completely compatible with Marcus theory.

## 0.4 A New Understanding of Electronic Friction

Perhaps the most important component of research funded under FA9950-13-1-0157 has been our investigation of electronic friction. Electronic friction is a key phenomenon that arises when molecules exchange energy with a continuum of electronic levels and changes in nuclear position cause disruptions in the electronic distribution of the metal. With weak enough electron-phonon coupling and slow enough nuclear motion, these disruptions can be quantified through electronic friction parameters. Generally speaking, the domain of validity for electronic friction is unknown<sup>26</sup>, and almost<sup>62,63</sup> all models of electronic friction heretofore have been evaluated with mean-field or non-interacting electrons<sup>64-70</sup>. With these limitations in mind, we have now taken three keys steps towards improving our working knowledge of electronic friction.

**(i) A Comparison of Electronic Friction with Marcus Theory** One of the most surprising results from our previous research is presented in Ref.<sup>26</sup>. Here we show the non-intuitive fact that, even though electronic friction should be applicable in the *adiabatic* limit (with small electron phonon couplings), in fact electronic friction actually recapitulates the Marcus’s *nonadiabatic* theory of metal-molecule electron transfer. This agreement can be shown analytically<sup>26</sup> and in Fig. 3(b) we visualize numerical data from Ref.<sup>26</sup>. Effectively, from our numerical and analytical results, we may conclude that the domain of validity for electronic friction is non-intuitive; all we can discern is that electronic friction will fail if excited state dynamics are important. See Fig. 3(e, f).

**(ii) A Universal Derivation of Electronic Friction** Models of electronic friction have been traditionally derived using either Green’s functions (and a so-called “gradient expansion”)<sup>66-68</sup>, path integrals<sup>71</sup>, or a Meyer-Miller transformation<sup>72</sup> followed by some form of perturbation theory<sup>64</sup>. While Ref.<sup>64</sup> was restricted to zero temperature and equilibrium, Refs.<sup>66-68</sup> were derived at finite temperature and in/out of equilibrium conditions. In both cases, one assumes non-interacting electrons within a metal and single electron transfer between molecule and metal.

One of the key results of under AFOSR grant FA9950-13-1-0157 has been a novel derivation of electronic friction without any of the limitations described above: in other words, the most general form of electronic friction that allows interacting electrons, in/out of equilibrium, and finite temperature.<sup>73</sup> In particular, we have shown that there is only one universal friction and random force applicable to any system with nuclei and electrons, and this friction and random force applies whenever the Born-Oppenheimer treatment separates nuclear motion from electronic motion. Suppose, as usual, that the Hamiltonian can be written as the sum of an electronic Hamiltonian  $\hat{H}_{el}(\vec{R})$  (which depends parametrically on the nuclear coordinates  $\vec{R}$ ) and the kinetic energy of the nuclei,  $\mathbf{T}_n$ ,  $\hat{\mathbf{H}} = \hat{H}_{el}(\vec{R}) + \mathbf{T}_n$ . The universal, broadened potential of mean force adiabatic surface  $V_{BPMF}$ , friction  $\gamma_{\alpha\nu}$ , and damping force correlation function  $D_{\alpha\nu}$  satisfy:

$$\frac{\partial V_{BPMF}}{\partial R_\alpha}(\vec{R}) = -\text{tr}_e \left( \frac{\partial \hat{H}_{el}(\vec{R})}{\partial R_\alpha} \hat{\rho}_{ss} \right) \quad (4)$$

$$\gamma_{\alpha\nu}^{exact} = - \int_0^\infty \text{tr}_e \left( \frac{\partial \hat{H}_{el}(\vec{R})}{\partial R_\alpha} e^{-i\hat{H}_{el}t} \frac{\partial \hat{\rho}_{ss}(\vec{R})}{\partial R_\nu} e^{i\hat{H}_{el}t} \right) dt \quad (5)$$

$$D_{\alpha\nu}^{exact} = \frac{1}{2} \int_0^\infty \text{tr}_e \left( e^{i\hat{H}_{el}t} \delta F_\alpha e^{-i\hat{H}_{el}t} \left( \delta F_\nu \hat{\rho}_{ss}(\vec{R}) + \hat{\rho}_{ss}(\vec{R}) \delta F_\nu \right) \right) dt \quad (6)$$

$$\delta F_\alpha \equiv -\frac{\partial \hat{H}_{el}(\vec{R})}{\partial R_\alpha} + \text{tr}_e \left( \frac{\partial \hat{H}_{el}(\vec{R})}{\partial R_\alpha} \hat{\rho}_{ss} \right) \quad (7)$$

Here,  $\hat{\rho}_{ss}(\vec{R})$  is the steady-state electronic density matrix parametrized by nuclear coordinate. At equilibrium, we expect  $\hat{\rho}_{ss}(\vec{R}) = \exp(-\beta \hat{H}_{el}(\vec{R}))/Z$  where  $Z = \text{tr}_e \left( \exp(-\beta \hat{H}_{el}(\vec{R})) \right)$ , and so we find that  $\gamma$  and  $D$  are simply integrals of time-correlation functions, exactly in the spirit of linear-response theory<sup>74</sup>. Moreover, at equilibrium, the friction  $\gamma_{\alpha\nu}$  is positive and symmetric, and the fluctuation-dissipation theorem holds<sup>75</sup>.

We emphasize that Eqns. 4-7 represent very fundamental quantities: these are the corrections that will *always* accompany any Born-Oppenheimer dynamics in the condensed phase (with many electronic states). We are now working on understanding the implications of these results in detail.

**(ii) A Derivation of Electronic Friction from Perturbation Theory** While Eqs. 4-7 are succinct results, they do require some (approximate) diagonalization of the electronic Hamiltonian which can be difficult. Another important result from AFOSR grant FA9950-13-1-0157 has been our demonstration that, for large enough metal-molecule coupling, even a CME is compatible with an electronic friction. For the case of the CME in Eqn. 2-3, one can show the necessary transformation quite explicitly. Namely, we transform from the phase space density of the different diabats ( $\rho_{00}(\vec{R}, \vec{P})$  and  $\rho_{11}(\vec{R}, \vec{P})$ ) to the total density  $A(\vec{R}, \vec{P})$  and the fluctuations away from equilibrium  $B(\vec{R}, \vec{P})$ :

$$A(\vec{R}, \vec{P}) \equiv \rho_{00}(\vec{R}, \vec{P}) + \rho_{11}(\vec{R}, \vec{P}) \quad (8)$$

$$B(\vec{R}, \vec{P}) \equiv \left( 1 - f(E(\vec{R})) \right) \rho_{11}(\vec{R}, \vec{P}) - f(E(\vec{R})) \rho_{00}(\vec{R}, \vec{P}) \quad (9)$$

Assuming that the fluctuations relax quickly, at equilibrium, the quantity  $A$  approximately satisfies<sup>18</sup> a Fokker-Planck (FP) equation moving along an adiabatic, potential of mean-force surface

$V^{PMF}$

$$\frac{\partial V_{PMF}}{\partial R_\alpha}(\vec{R}) = -\frac{\partial V_1(\vec{R})}{\partial R_\alpha} f(E(\vec{R})) - \frac{\partial V_0(\vec{R})}{\partial R_\alpha} (1 - f(E(\vec{R}))) \quad (10)$$

with friction of the form:

$$\gamma_{\alpha\nu}^{CME} = \frac{\hbar}{\Gamma} \frac{1}{kT} f(E(\vec{R})) (1 - f(E(\vec{R}))) \frac{\partial E}{\partial R_\alpha} \frac{\partial E}{\partial R_\nu} \quad (11)$$

We have shown<sup>17,18</sup> that the friction  $\gamma^{CME}$  in Eqn. 11 approximately agrees with the exact friction  $\gamma^{exact}$  in Eqn. 5 but with the caveat that the former ignores so-called “broadening” and can only be valid for small  $\Gamma$ . Nevertheless, from Eq. 11, we gain a very intuitive picture of friction: because the friction is proportional to  $f(1 - f)$ , we see that the friction will strongly peak around those areas of configuration spaces whether  $f(E(\vec{R})) \approx \frac{1}{2}$ . Or, in words, the friction is largest when the energy difference between charged and neutral states of the molecule line up perfectly with the fermi function of the metal, so that molecules becomes charged and uncharged rapidly in time and thus experience a drag plus random force in their motion. For a picture, see Fig. 3. This intuition picture of friction carries over to the case of more than two electronic states<sup>17</sup>.

## 0.5 A Broadened Classical Master Equation for Both Adiabatic and Nonadiabatic Dynamics at Metal Surfaces

Above, we have discussed two distinct dynamical theories of electron transfer at metal surfaces with two different domains of validity: CME dynamics (which are valid for small metal-molecule couplings) and Fokker-Planck (FP) dynamics with electronic friction (which are valid if the nuclear motion is slow enough). Moreover, we have also discussed how these methods should be consistent with each other if the metal molecule coupling is not too large and the nuclear motion is not too fast: without broadening, Eqn. 5 and Eqn. 11 do agree with each other.<sup>17,18</sup> This raises the question of whether or not these different theories can be merged or extrapolated into one grand theory with near universal applicability.

Indeed, in Ref.<sup>16</sup>, we showed that at least one universal extrapolation is possible. For the case of only two electronic states of the molecule (charged and uncharged), the simplest means to achieve such an extrapolation is by defining “broadened diabatic surfaces”,  $\tilde{V}_0(\vec{R})$  and  $\tilde{V}_1(\vec{R})$ :

$$n(E) \equiv \int_{-\infty}^{\infty} \frac{d\epsilon}{2\pi} \frac{\Gamma}{(\epsilon - E)^2 + \Gamma^2/4} f(\epsilon) \quad (12)$$

$$\tilde{V}_i(\vec{R}) \equiv V_i(\vec{R}) + \int_{\vec{R}_0}^{\vec{R}} \left( n(E(\vec{R}')) - f(E(\vec{R}')) \right) \frac{\partial E(\vec{R}')}{\partial \vec{R}'} \cdot d\vec{R}' \quad i = 0, 1 \quad (13)$$

Henceforward, the use of Eqns. 2,3,12,13, with the substitution of  $\tilde{V}_0(\vec{R})$  and  $\tilde{V}_1(\vec{R})$  for  $V_0(\vec{R})$  and  $V_1(\vec{R})$  will be referred to as a broadened classical master equation (BCME).

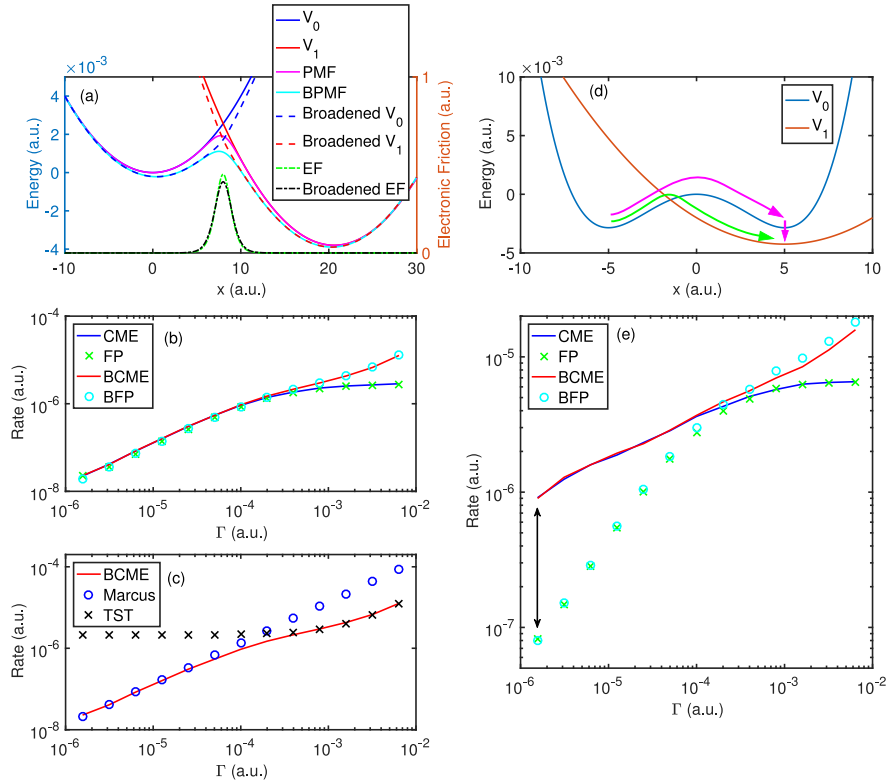
Broadening is the phenomenon whereby a charged molecule will lose charge (sometimes exponentially quickly) to a metal nearby; such an exponential feature cannot be captured correctly by second-order perturbation theory in the metal-molecule couplings (which requires that  $\Gamma \ll kT$ ), and therefore broadening is not present in the CME. In practice, broadening effects can be very large for molecules near metal surface. For instance, chemically speaking, broadening includes all hybridization of molecules to surfaces, and thus broadening must enter all heterogeneous inner sphere electrochemistry. For many molecules on metal surfaces,  $\Gamma$  can be on the order

of an electron volt (which is obviously much greater than room temperature). Thus, broadening must be accounted for in realistic simulations in order to retrieve, for example, accurate barrier heights. Luckily, using the transformation in Eqns 8-9, one can show that the BCME dynamics along broadened diabats do evolve on the correctly broadened potential energy surface. See Fig. 3.

The set of broadened classical master equations in Eqns. 2,3,12,13 is perhaps the most important result of our research program funded under AFOSR grant FA9950-13-1-0157: this set of equations will allow us to study both inner sphere and outer sphere electron transfer at a metal surface (and the transition between the two) using only one universal set of equations. Thus, for example, this protocol will allow in the future to study the scattering of molecules off of metals surfaces for which there is transient electron transfer (which is sometimes called the Gadzik mechanism<sup>76</sup>).

In Fig. 3, we show the electron transfer rate according to the BCME as a function of metal-molecule coupling  $\Gamma$ , from the limit of nonadiabatic electron transfer (small  $\Gamma$ ) to the limit of adiabatic electron transfer (large  $\Gamma$ ). This shape for transfer rate versus metal-molecule coupling has been identified previously by Schmickler<sup>77,78</sup>. Note that the BCME recovers the correct result in both cases. Furthermore, in Fig. 3, we also show results from a model problem with two pathways between charge states, where only the BCME can reliably recover the correct results. Altogether, every piece of data indicates that the extrapolated BCME will be a reliable and powerful tool for studying dynamics on metal surfaces.

Figure 3: (a) For a system with two possible charge states, we plot parabolic models for the diabats (reactant  $V_0$  and product  $V_1$  in Eqns. 2-3) and an approximate, adiabatic potential of mean force ( $V_{PMF}$ , Eqn. 10) (without broadening). The broadened diabats ( $\tilde{V}_0, \tilde{V}_1$  in Eqn. 13) and exact broadened potential of mean force adiabatic ( $V_{BPMF}$  in Eqn. 4) are shown as well. Note that broadening can strongly effect the size of a nuclear barrier and cannot be ignored. The approximate, unbroadened electronic friction (EF) ( $\gamma^{CME}$ , Eqn. 11) and the exact, broadened electronic friction ( $\gamma^{exact}$ , Eqn. 5) are shown in green and black, respectively, and plotted on the right-hand axis. The broadening of friction has only a small effect here. (b) Rates of reaction according to several semiclassical dynamics schemes, including classical master equation (CME) dynamics (Eqns. 2-3), Fokker-Planck (FP) dynamics on one unbroadened adiabatic surface with electronic friction (Eqn. 8-11), broadened classical master equation (BCME) dynamics (Eqns. 2,3 together with the replacements in 12,13), and broadened FP (BFP) dynamics (Eqns. 4-7). The rates are plotted as a function of the metal-molecule coupling,  $\Gamma$ . Small  $\Gamma$  is the nonadiabatic regime; larger  $\Gamma$  is the adiabatic regime; very large  $\Gamma$  is sometimes called the catalytic regime. CME dynamics must be accurate for small  $\Gamma$  and BFP dynamics must be accurate for large  $\Gamma$ . Note that, surprisingly, the BFP dynamics apparently are accurate at even small  $\Gamma$ . This fortunate coincidence is not general, as shown in (d) – (e). Here, we study a problem with non-parabolic diabats  $V_0$  and  $V_1$  with multiple reaction pathways; in such a case, electronic friction fails at small  $\Gamma$  and only the BCME can be valid because excited state dynamics enter. (c). We compare BCME results versus adiabatic transition state theory (TST) and nonadiabatic Marcus theory. Note that BCME correctly extrapolates between the two limits. Altogether, this data strongly endorses the BCME approach for studying nonadiabatic dynamics on metal surfaces. All data from Ref.<sup>26</sup>.



## 0.6 Preliminary Mixed Quantum-Classical Approaches for Spectroscopy

One final area of research was pursued under AFOSR grant FA9950-13-1-0157: the semiclassical theory of condensed phase spectroscopy. Formally, in order to predict any kind of molecular absorption spectra – for which the molecule is in solution or in some other environment – one must calculate a dipole-dipole correlation function,  $\langle \hat{\mu}(0)\hat{\mu}(t) \rangle$ .<sup>79</sup> Note here that  $\hat{\mu}$  is the transition dipole between the active electronic surface and the target surface. For instance, for standard, steady state absorption spectra, the active electronic state is the ground-state ( $g$ ) and the target electronic states is an excited state ( $e$ ), and thus  $\hat{\mu} = \hat{\mu}_{eg}$ . There are similar transition dipole moments for transient absorption spectra, e.g. from initial excited states to final excited states.

Now, in general, calculating electronic spectra is difficult with semiclassical dynamics because one never knows how to propagate nuclear dynamics for a transition dipole moment. After all, for the electronic transition dipole moment  $\hat{\mu}_{eg}$ , do we run trajectories on the ground or electronic surfaces?<sup>80</sup> In Refs.<sup>1,11,13</sup>, under AFOSR funding, we tried several different approaches for resolving this problem, including (a) running trajectories on the ground state potential ( $V_g$ ), (b) running trajectories on the excited state potential ( $V_e$ ), (c) running trajectories on the average surface  $\frac{1}{2}(V_g + V_e)$ , and running one half of the trajectories on the ground plus one half on the excited surface. Furthermore, we also including surface hopping dynamics within these calculations, so that we could model how radiationless transitions affected absorption lineshapes.

After having run exhaustive calculations, we have found several good compromises between accuracy and efficiency—rather than one single, optimal algorithm—and this research is continuing in our group.

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FA9550-13-1-0157

## Principal Investigator Name

The full name of the principal investigator on the grant or contract.

Dr. Joseph Subotnik

## Program Officer

The AFOSR Program Officer currently assigned to the award

Dr. Michael Berman

## Reporting Period Start Date

03/27/2013

## Reporting Period End Date

03/31/2018

## Abstract

The PI's current AFOSR/PECASE grant (FA9950-13-1-0157, 2013-2018) has resulted in 26 publications with a direct impact on the field of electronic relaxation, especially electron and energy transfer in solution and at metal surfaces.

For the case of chemical dynamics in solution, the PI has made significant strides in developing a simple and reliable surface-hopping picture for photoexcited dynamics, whereby one can model nuclear vibrations stochastically (depending on the instantaneous charge state). The PI has shown that this intuitive picture of photochemistry can be justified by comparison with the quantum-classical Liouville equation, with the proviso that decoherence is correctly taken into account. Moreover, the PI performed the first simulations of energy transfer using ab initio electronic structure theory, investigating how triplets transfer between aromatic donors and acceptors within a series of molecules first studied by Closs et al. Altogether, this grant solved

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many problems previously identified with modern simulation approaches for nonadiabatic dynamics and produced new solutions to the problem of decoherence.

For the case of chemical dynamics at a metal-molecule interface, the PI demonstrated a surprising agreement between two standard approaches (surface hopping and electronic friction) that had not been previously compared. Furthermore, the PI derived a universal form of electronic friction that acts as a universal correction to the standard Born-Oppenheimer approximation, incorporating all previous work in the area. As such, the PI has made fundamental progress in understanding one of the oldest and most important tenets of chemistry (the Born-Oppenheimer approximation) and has offered a new approach for a quantitative algorithm.

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**New discoveries, inventions, or patent disclosures:**

**Do you have any discoveries, inventions, or patent disclosures to report for this period?**

No

**Please describe and include any notable dates**

**Do you plan to pursue a claim for personal or organizational intellectual property?**

**Changes in research objectives (if any):**

N/A

**Change in AFOSR Program Officer, if any:**

No Change

**Extensions granted or milestones slipped, if any:**

N/A

**AFOSR LRIR Number**

**LRIR Title**

**Reporting Period**

**Laboratory Task Manager**

DISTRIBUTION A: Distribution approved for public release.

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**Program Officer**

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**Research Objectives**

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**Technical Summary**

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**Funding Summary by Cost Category (by FY, \$K)**

|                      | Starting FY | FY+1 | FY+2 |
|----------------------|-------------|------|------|
| Salary               |             |      |      |
| Equipment/Facilities |             |      |      |
| Supplies             |             |      |      |
| Total                |             |      |      |

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**Report Document**

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**Report Document - Text Analysis**

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**Appendix Documents**

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## 2. Thank You

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**E-mail user**

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