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## Perspective: How to understand electronic friction

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Electronic friction is a correction to the Born-Oppenheimer approximation, whereby nuclei in motion experience a drag in the presence of a manifold of electronic states. The notion of electronic friction has a long history and has been (re-)discovered in the context of a wide variety of different chemical and physical systems including, but not limited to, surface scattering events, surface reactions or chemisorption, electrochemistry, and conduction through molecular-(or nano-) junctions. Over the years, quite a few different forms of electronic friction have been offered in the literature. In this perspective, we briefly review these developments of electronic friction, highlighting the fact that we can now isolate a single, unifying form for (Markovian) electronic friction. We also focus on the role of electron-electron interactions for understanding frictional effects and offer our thoughts on the strengths and weaknesses of using electronic friction to model dynamics in general. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5035412>

### I. INTRODUCTION: MOLECULE-METAL INTERFACES

What is electronic friction? Electronic friction is the naive damping force that nuclei experience when they move near or within a manifold of metallic electrons. Whenever a heavy and slow nucleus moves, that movement disrupts the electrostatic equilibrium of the electrons in the solid and, assuming that the electrons respond quickly, the electrons then apply a force acting back upon the nucleus.<sup>1</sup> This feedback on the nucleus can be approximated as a frictional damping plus a random force. As a result, the trajectory of a nucleus ( $\mathbf{R}$ ) follows a Langevin equation,

$$-m_{\alpha}\ddot{\mathbf{R}}_{\alpha} = -\bar{\mathbf{F}}_{\alpha} + \sum_{\nu} \gamma_{\alpha\nu}\dot{\mathbf{R}}_{\nu} - \zeta_{\alpha}(t). \quad (1)$$

Here,  $\alpha$  and  $\nu$  are index nuclear degrees of freedom (DoFs),  $\bar{\mathbf{F}}_{\alpha}$  is the mean force,  $\gamma_{\alpha\nu}$  is the (Markovian) friction tensor, and  $\zeta_{\alpha}(t)$  denotes a random force.

Now, there is a very long history to this notion of electronic friction in the chemical physics literature. Although electronic friction has usually been considered in the specific context of molecules on metal surfaces,<sup>2–13</sup> as will be shown below, the concept of electronic friction goes much deeper and lies at the heart of chemical physics: electronic friction represents the first order correction to the Born-Oppenheimer approximation in the presence of a manifold of fast relaxing electronic states. Given this fundamental nature of electronic friction, one must find it strange that the notion of electronic friction has not permeated the chemical physics community. For instance, electronic friction is not discussed in any elementary quantum mechanics textbook that we are aware of (e.g., Refs. 14–16). Perhaps more dramatically, according to Google Scholar, Tully’s seminal work on surface hopping (“*Molecular dynamics with electronic transitions*”<sup>17</sup>) has been cited 2370 times as of 2017, while the key Head-Gordon and Tully (HGT) paper on electronic friction (“*Molecular dynamics with electronic frictions*”<sup>18</sup>) has been cited only 220 times.

In our minds, we can think of two explanations for this discrepancy: (i) On the one hand, perhaps chemists are less interested in solids and surfaces (where electronic friction is valid) and more interested in the gas phase or aqueous solution (where electronic friction is not valid). (ii) On the other hand, with a very diverse literature to choose from in the areas of surface science,<sup>19–23</sup> scattering reactions,<sup>24–28</sup> molecular electronics,<sup>29–35</sup> electrochemistry,<sup>36–38</sup> and recently quantum thermodynamics<sup>39–41</sup> (see also Sec. I B), it would also seem possible that there has been some confusion in the theoretical community regarding the exact meaning of electronic friction and how electronic friction can be applied effectively. Obviously, we cannot address concern (i) given above. Thus, the goal of this perspective is to address concern (ii): below, we wish to provide a new graduate student with a foothold into the field of nonadiabatic dynamics at metal surfaces while highlighting the strengths and weaknesses of the electronic friction approach.

#### A. Standard properties of a friction tensor

Before we address the exact mathematical definition of electronic friction, we want to remind the reader of a few salient details regarding friction of any kind. First, in the condensed phase, friction comes about when any one set of dynamical variables (“the system”) interacts with another, usually a larger set of dynamic variables (“the bath”). If the bath relaxes quickly, the friction becomes Markovian. For most standard treatments of nuclear friction in the condensed phase, the bath is chosen to be a set of harmonic oscillators so that an explicit friction tensor can be calculated analytically.<sup>42,43</sup> Similarly, in the case of electronic friction, Head-Gordon and Tully derived the friction tensor by mapping the electronic DoFs into harmonic oscillators<sup>44,45</sup> and then calculating the feedback of these electronic DoFs onto a nearby nuclear system. Thus, like any other Markovian friction, *electronic* friction captures the

response of a fast and large set of bath DoFs acting upon the slow dynamics of a small subsystem.

Second, beyond the generic definition of the friction mentioned above, we remind the reader that any correct theory of electronic friction must obey certain symmetry requirements, especially the following:

1. The friction tensor must be positive definite at equilibrium, i.e., for any set of velocities  $\dot{R}_\alpha$  (and  $\dot{R}_\nu$ ), the inequality  $\sum_{\alpha,\nu} \dot{R}_\alpha \gamma_{\alpha\nu} \dot{R}_\nu \geq 0$  must hold.<sup>46</sup> Obviously, without positivity, a friction tensor can enhance (as opposed to damp) nuclear motion, resulting in instability. Such motion cannot be physical at equilibrium.<sup>47</sup>
2. Beyond positivity, at equilibrium, another requirement is that the friction tensor  $\gamma_{\alpha\nu}$  ought to be symmetric between the nuclear DoFs  $\alpha$  and  $\nu$ .<sup>48,49</sup> As is well known in statistical mechanics, the symmetry of the friction tensor is guaranteed by the time-reversibility of the all dynamical equations (e.g., Newton's laws, the Schrödinger equation, etc).<sup>50,51</sup>

## B. A plethora of theoretical approaches

A few additional words are also now appropriate regarding the vast history of electronic friction. Interestingly, many of the key features of electronic friction were first explored long ago by Suhl and co-workers,<sup>52</sup> who used a “bootstrap” approach to (correctly) conjecture a potential electronic friction tensor (that is valid at equilibrium); the random force was not addressed.

In the wake of the seminal work of Suhl on electronic friction, over the last 40 years, many different research groups have advanced the field in different ways and through different approaches. Here are a few of the key contributors (though this list is not exhaustive):

- Persson and Persson<sup>53</sup> investigated vibrational relaxation at zero temperature and identified the appropriate golden rule rate (FGR).
- Head-Gordon and Tully repeated the FGR calculations of Persson and Persson and found that the FGR rate could be connected to a multi-dimensional electronic friction tensor.<sup>18,54</sup> The authors postulated that a random force should accompany electronic friction at finite temperature.
- Brandbyge *et al.* used an influence functional approach to investigate a Newns model and gave a compact form for the one-dimensional frictional force acting on a given vibration.<sup>55</sup> This result was extended to multiple-dimensions and the non-equilibrium case later.<sup>56</sup>
- Hynes and co-workers studied the rate of electron transfer for electrochemical problems and identified a memory kernel for the frictional force.<sup>36</sup>
- Using a linearized path-integral approach (similar to Brandbyge *et al.*<sup>55</sup>), Mozyrsky and Delligault gave the first full-fledged derivation of electronic friction including electron-electron (el-el) interactions and they isolated the appropriate random force. Their results

were completely general at equilibrium (i.e., without any steady-state current).<sup>57</sup>

- von Oppen and co-workers used non-equilibrium Green's functions (and a scattering matrix approach) to study molecular conductors and calculated electronic friction tensors and random forces both in and out of equilibrium; however, their results were limited to non-interacting electrons.<sup>58,59</sup>
- Very recently, our research group has studied electronic friction in the context of master equations.<sup>60,61</sup>

## II. ELECTRONIC FRICTION AS A CORRECTION TO THE BORN-OPPENHEIMER APPROXIMATION

Historically, the approaches listed above were used to model quite different chemical and physical phenomena (vibrational relaxation, electron transfer rates, etc.). And to our knowledge, until recently, these different forms for electronic friction were never fully compared or contrasted, and there was no general consensus as to whether these different approaches yielded the same physical insights. For instance, in Ref. 36, Hynes studied a curve-crossing problem near a metal surface and concluded that the relevant form of friction was very different from the HGT friction.

Recently, however, we have argued that, in fact, all of the above results can be derived from a single, unique, and universal electronic friction tensor (at least in the Markovian limit).<sup>1,62,63</sup> Given how easy it is to derive such a result, we will now offer the reader a simple, heuristic way to calculate the appropriate electronic friction tensor and random force. Note that the approach taken below is not a “rigorous” derivation but rather a sketch of a proof with the correct physical intuition. A more rigorous derivation can be found in Ref. 1, which follows the quantum-classical Liouville equation (QCLE)<sup>64–66</sup> and relies on the separation of time scales (in the same spirit as a Mori-Zwanzig projection<sup>50,67,68</sup>).

We consider a very general Hamiltonian, where the total Hamiltonian can be split into the nuclear kinetic energy ( $\hat{T}_{nuc}$ ) and the electronic Hamiltonian  $\hat{H}$ ,

$$\hat{H}_{tot} = \hat{T}_{nuc} + \hat{H}, \quad (2)$$

$$\hat{H} = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{en} + \hat{V}_{nn}. \quad (3)$$

Here, the electronic Hamiltonian  $\hat{H}$  consists of the electronic kinetic energy operator  $\hat{T}_e$ , the electron-electron interaction operator  $\hat{V}_{ee}$ , the electron-nuclei interaction operator  $\hat{V}_{en}$ , and the nuclei-nuclei interaction operator  $\hat{V}_{nn}$ .

In semi-classical dynamics, nuclear trajectories ( $R_\alpha, P_\alpha$ ) follow Newton's equations and the electronic density matrix ( $\hat{\rho}$ ) follows the von Neumann-Liouville equation,

$$-m_\alpha \ddot{R}_\alpha = \partial_\alpha \hat{H}, \quad (4)$$

$$\frac{d}{dt} \hat{\rho} = -\hat{\mathcal{L}} \hat{\rho}. \quad (5)$$

Here, we have denoted  $\partial_\alpha \equiv \frac{\partial}{\partial R_\alpha}$  and  $\hat{\mathcal{L}}$  is the standard Liouvillian superoperator,  $-\hat{\mathcal{L}}(\cdot) = -\frac{i}{\hbar} [\hat{H}, \cdot]$ . The electronic density matrix  $\hat{\rho}$  satisfies  $tr_e(\hat{\rho}) = 1$ , where  $tr_e$  implies tracing over all electronic DoFs. Equations (4) and (5) are formally operator equations (note that Eq. (4) is the Heisenberg equation of

motion if we interpret  $R_\alpha$  as an operator  $\hat{R}_\alpha$ , but we wish to solve for the nuclear DoFs at the level of classical mechanics, and so we have substituted  $R_\alpha$  for  $\hat{R}_\alpha$  in Eq. (4).

Note that Eq. (4) is different from traditional Ehrenfest dynamics, where the force is the average force  $-tr_e(\partial_\alpha \hat{H} \hat{\rho})$ . In order for Langevin dynamics (with an associated random force) to be appropriate, one must go beyond mean-field dynamics and account for the fluctuations in the force. Thus, we define the random force  $\delta \hat{F}_\alpha$  as the difference between the force operator and the average force:  $\delta \hat{F}_\alpha = -\partial_\alpha \hat{H} + tr_e(\partial_\alpha \hat{H} \hat{\rho})$ . We can now rewrite Eq. (4) as

$$-m_\alpha \ddot{R}_\alpha = tr_e(\partial_\alpha \hat{H} \hat{\rho}) - \delta \hat{F}_\alpha. \quad (6)$$

Our goal is to evaluate and refashion Eq. (6) where, as we can see, the left hand side (LHS) is a classical quantity and the right hand side (RHS) is an electronic operator.

We begin by considering the first term on the RHS of Eq. (6), using Eq. (5) to analyze the density matrix  $\hat{\rho}$ . We note that the total derivative with respect to time [ $\frac{d}{dt}$  in Eq. (5)] is equal to the partial derivative with respect to time  $\frac{\partial}{\partial t}$  plus a driving term due to nuclear motion:  $\frac{d}{dt} = \frac{\partial}{\partial t} + \sum_\nu \dot{R}_\nu \partial_\nu$ . In this way, we realize that the time evolution of the electronic density can be divided into two separate time scales: the time scale for electronic relaxation and the time scale for nuclear motion. Without any nuclear motion (i.e.,  $\dot{R}_\nu = 0$ ), the electrons admit a steady state density matrix  $\hat{\rho}_{ss}$  satisfying  $-\hat{\mathcal{L}}\hat{\rho}_{ss} = 0$ , which implies  $\frac{\partial}{\partial t}\hat{\rho}_{ss} = 0$ . The time scale for electronic relaxation ( $\tau$ ) is defined by the condition that for any  $\hat{\rho}$ ,  $e^{-\hat{\mathcal{L}}\tau}\hat{\rho} \approx \hat{\rho}_{ss}$  (or  $e^{-\hat{\mathcal{L}}\tau}(\hat{\rho} - \hat{\rho}_{ss}) \approx 0$ ).

Now with nonzero nuclear motion, we can write the total electronic density  $\hat{\rho}$  as a combination of the steady state solution  $\hat{\rho}_{ss}$  plus a correction term  $\Delta\hat{\rho}$  (due to nuclear motion),

$$\hat{\rho} = \hat{\rho}_{ss} + \Delta\hat{\rho}. \quad (7)$$

If we plug Eq. (7) into Eq. (5) and use the properties of the steady state solution we find

$$\frac{\partial}{\partial t}\Delta\hat{\rho} = -\hat{\mathcal{L}}\Delta\hat{\rho} - \sum_\nu \dot{R}_\nu \partial_\nu \hat{\rho}. \quad (8)$$

At this point, we make the key adiabatic approximation that the nuclear motion is slow compared to the electronic dynamics. As a result,  $\Delta\hat{\rho}$  is small and we can approximate  $\partial_\nu \hat{\rho}$  by  $\partial_\nu \hat{\rho}_{ss}$  in the above equation. With proper initial conditions (assuming that at  $t = 0$ , the electronic system remains at steady state so that  $\Delta\hat{\rho} = 0$ ), we can solve

$$\Delta\hat{\rho} = -\sum_\nu \int_0^t \dot{R}_\nu(t') e^{-\hat{\mathcal{L}}(t-t')} \partial_\nu \hat{\rho}_{ss} dt'. \quad (9)$$

Here  $e^{-\hat{\mathcal{L}}t}(\cdot) = e^{-i\hat{H}t/\hbar}(\cdot)e^{i\hat{H}t/\hbar}$  is the Liouvillian propagator. If we plug Eqs. (7) and (9) back into Eq. (6), we arrive at an equation of Langevin form for the nuclei,

$$-m_\alpha \ddot{R}_\alpha = -\bar{F}_\alpha + \sum_\nu \int_0^t \tilde{\gamma}_{\alpha\nu}(t, t') \dot{R}_\nu(t') dt' - \delta \hat{F}_\alpha, \quad (10)$$

where the mean force  $\bar{F}_\alpha$ , friction kernel  $\tilde{\gamma}_{\alpha\nu}(t, t')$ , and random force  $\delta \hat{F}_\alpha$  are given, respectively, by

$$\bar{F}_\alpha = -tr_e(\partial_\alpha \hat{H} \hat{\rho}_{ss}), \quad (11)$$

$$\tilde{\gamma}_{\alpha\nu}(t, t') = -tr_e(\partial_\alpha \hat{H} e^{-\hat{\mathcal{L}}(t-t')} \partial_\nu \hat{\rho}_{ss}), \quad (12)$$

$$\delta \hat{F}_\alpha = -\partial_\alpha \hat{H} + tr_e(\partial_\alpha \hat{H} \hat{\rho}_{ss}). \quad (13)$$

In Eq. (13), when evaluating the random force  $\delta \hat{F}_\alpha$ , we have replaced  $\hat{\rho}$  by  $\hat{\rho}_{ss}$ , which is consistent with the adiabatic approximation (slow nuclear motion). We now turn our attention to the random force  $\delta \hat{F}_\alpha$  in Eq. (10), which is still an electronic operator. This operator can be approximately replaced by a random number if we understand the corresponding statistics. For that purpose, we need to evaluate the corresponding correlation function. For the proposed, semi-classical dynamics, we assume that the appropriate correlation function is simply the symmetrized product,

$$D_{\alpha\nu}^S(t, t') = \frac{1}{2} tr_e(\delta \hat{F}_\alpha(t)(\delta \hat{F}_\nu(t') \hat{\rho}_{ss} + \hat{\rho}_{ss} \delta \hat{F}_\nu(t'))) \quad (14a)$$

$$= \frac{1}{2} tr_e(\delta \hat{F}_\alpha e^{-\hat{\mathcal{L}}(t-t')} (\delta \hat{F}_\nu \hat{\rho}_{ss} + \hat{\rho}_{ss} \delta \hat{F}_\nu)). \quad (14b)$$

Here, again,  $\hat{\rho}_{ss}$  has been used to evaluate the correlation function (in the adiabatic limit).<sup>69</sup> In Eq. (14a), we have also used a notation appropriate for the Heisenberg picture,  $\delta \hat{F}_\alpha(t) = e^{i\hat{H}t/\hbar} \delta \hat{F}_\alpha e^{-i\hat{H}t/\hbar}$ . With such a notation (and noting  $tr_e(\partial_\nu \hat{\rho}_{ss}) = 0$ ), Eq. (12) can be rewritten as

$$\tilde{\gamma}_{\alpha\nu}(t, t') = tr_e(\delta \hat{F}_\alpha(t-t') \partial_\nu \hat{\rho}_{ss}). \quad (15)$$

Note that in classical dynamics, all variables are real, and the symmetrized correlation function in Eq. (14a) is guaranteed to be real by construction.<sup>70</sup> Note also that such a symmetric correlation function can be derived more rigorously from the quantum-classical Liouville equation (QCLE).<sup>1</sup>

Finally, to evolve the Langevin dynamics in practice, the random force  $\delta \hat{F}_\alpha$  can be realized by generalizing a random number  $\zeta_\alpha$ , whose statistics satisfy<sup>71</sup>

$$\langle \zeta_\alpha(t) \rangle = 0, \quad (16)$$

$$\frac{1}{2} \langle \zeta_\alpha(t) \zeta_\nu(t') + \zeta_\nu(t) \zeta_\alpha(t') \rangle = D_{\alpha\nu}^S(t, t'). \quad (17)$$

Thus, we have presented a closed Langevin equation for modeling electronic friction.

## A. Markovian approximation

In practice, Eq. (10) can be further simplified in the Markovian limit, when the decay of the memory kernel is faster than nuclear motion:  $\int_0^t \tilde{\gamma}_{\alpha\nu}(t, t') \dot{R}_\nu(t') dt' \rightarrow \gamma_{\alpha\nu} \dot{R}_\nu(t)$  and  $D_{\alpha\nu}^S(t, t') \rightarrow 2\bar{D}_{\alpha\nu}^S \delta(t-t')$ . Eq. (10) now reduces to Eq. (1) with

$$\begin{aligned} \gamma_{\alpha\nu} &= -\int_0^\infty tr_e(\partial_\alpha \hat{H} e^{-\hat{\mathcal{L}}t} \partial_\nu \hat{\rho}_{ss}) dt \\ &= \int_0^\infty tr_e(\delta \hat{F}_\alpha(t) \partial_\nu \hat{\rho}_{ss}) dt, \end{aligned} \quad (18)$$

$$\bar{D}_{\alpha\nu}^S = \frac{1}{2} \int_0^\infty tr_e(\delta \hat{F}_\alpha(t)(\hat{\rho}_{ss} \delta \hat{F}_\nu(0) + \delta \hat{F}_\nu(0) \hat{\rho}_{ss})) dt. \quad (19)$$

Note that the time scale for the decay of the memory kernel is exactly the same as the time scale for electronic relaxation, such that the Markovian approximation is indeed consistent with the adiabatic approximation (i.e., fast electronic

dynamics compared with slow nuclear motion). After all,  $\tilde{\gamma}_{\alpha\nu}(t, t')$  in Eq. (12) will equal zero when  $e^{-\hat{L}(t-t')} \partial_\nu \hat{\rho}_{ss} = 0$ . In other words, if we define a fictitious density operator  $\hat{\rho} = \hat{\rho}_{ss} + \dot{R}_\nu \partial_\nu \hat{\rho}_{ss}$ , then the memory kernel decays at time  $\tau$  where  $e^{-\hat{L}\tau} \hat{\rho} \approx \hat{\rho}_{ss}$ , which is precisely the time scale for electronic relaxation.

## B. Equilibrium vs. non-equilibrium conditions and the fluctuation dissipation theorem

To compute  $\gamma_{\alpha\nu}$  (and  $\bar{D}_{\alpha\nu}^S$ ) in Eqs. (18) and (19), we require the steady state  $\hat{\rho}_{ss}$ . In the case of one electronic bath, the steady state solution is simply the equilibrium one,  $\hat{\rho}_{ss} = \exp(-\hat{H}/kT)/Z$  ( $Z = \text{tr}_e(\exp(-\hat{H}/kT))$ ), such that the second fluctuation-dissipation theorem is satisfied (see the supplementary material in Ref. 1), i.e.,

$$\bar{D}_{\alpha,\nu}^S = kT\gamma_{\alpha\nu}. \quad (20)$$

Note that  $\bar{D}_{\alpha,\nu}^S$  is positive definite and symmetric between  $\alpha$  and  $\nu$  [at least for real valued  $\hat{H}$ ; see Eq. (19)] such that the frictional tensor is also positive definite and symmetric. Therefore, the nuclear DoFs will reach a thermal equilibrium with the same temperature as the electrons.

Note also that, at equilibrium, the mean force  $\bar{F}_\alpha$  [in Eq. (11)] is conservative:  $\partial_\nu \bar{F}_\alpha = \partial_\alpha \bar{F}_\nu$  (for a proof, see the supplementary material of Ref. 61). With such a conservative mean force, we can define the potential of the mean force,

$$U_{pmf}(\mathbf{R}) = - \int_{\mathbf{R}_0}^{\mathbf{R}} \bar{\mathbf{F}} \cdot d\mathbf{R}. \quad (21)$$

The integral in Eq. (21) is done along any path from a reference position  $\mathbf{R}_0$  to the position  $\mathbf{R}$ .<sup>72</sup>

For the case of non-equilibrium conditions (e.g., in the presence of an electronic current between two metals), the mean force is not necessarily conservative.<sup>59,73,74</sup> Furthermore, out of equilibrium, the second fluctuation-dissipation theorem is not satisfied such that electronic friction is not necessarily positive definite nor symmetric, resulting in (current induced) heating or instability effects.<sup>56,59,75</sup>

## III. STANDARD EXAMPLE: ONE ORBITAL ON A METAL SURFACE

While the mathematics above may appear daunting, in fact, to gain intuition for the expressions above, there is one very simple case that offers the correct physical insight with minimal effort. Consider a single (molecular) level coupled to a manifold of electronic states (in the metal),<sup>8,55,76–79</sup>

$$\begin{aligned} \hat{H} = & \epsilon_d(x) \hat{d}^+ \hat{d} + \sum_k V_k (\hat{d}^+ \hat{c}_k + \hat{c}_k^+ \hat{d}) \\ & + \sum_k \epsilon_k \hat{c}_k^+ \hat{c}_k + U_0(x). \end{aligned} \quad (22)$$

Here  $\epsilon_d(x)$  is the energy level of the molecule, which depends on nuclear geometry  $x$ .  $\epsilon_k$  is the energy level of orbital  $k$  in the metal.  $U_0$  is a purely nuclear potential. Depending on whether the level in the molecule ( $d$ ) is empty or occupied, we have two diabatic potentials:  $U_0(x)$  and  $U_1(x) = U_0(x) + \epsilon_d(x) - \epsilon_F$  ( $\epsilon_F$  is the fermi energy). Within the spirit of the

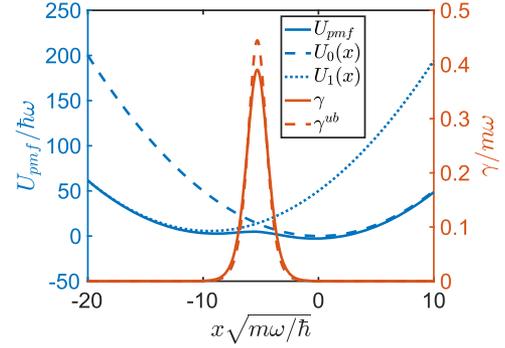


FIG. 1. Electronic friction as a function of position  $x$  for the model in Eq. (22). Note that the electronic friction shows a peak at the position where the two diabatic potentials cross [ $U_0(x) = U_1(x)$  or  $\epsilon_d = \epsilon_F$ ], i.e., where electrons are able to jump back and forth between the molecule and metal. The electronic friction without broadening [ $\gamma^{ub}$ , Eq. (24)] has a slightly sharper peak than the exact friction [ $\gamma$ , Eq. (23)]. We also plot the potential of mean force  $U_{pmf}$  from Eq. (21) (see Ref. 82). Parameters are as follows:  $\Gamma = 0.03$ ,  $kT = 0.015$ ,  $\hbar\omega = 0.003$ ,  $g = 0.02$ , and  $\epsilon_0 = 0.15$  (we set  $\epsilon_F = 0$ ).

wide-band approximation, we define  $\Gamma = 2\pi \sum_k V_k^2 \delta(\epsilon - \epsilon_k)$  to characterize the electronic coupling between the molecule and metal. For such a model, with one nuclear DoF, the friction tensor [Eq. (18)] reduces to a single number and can be written as<sup>80</sup>

$$\gamma = -\frac{\hbar}{2} \left( \frac{\partial \epsilon_d}{\partial x} \right)^2 \int \frac{d\epsilon}{2\pi} \left( \frac{\Gamma}{(\epsilon - \epsilon_d)^2 + (\Gamma/2)^2} \right)^2 \frac{\partial f(\epsilon)}{\partial \epsilon}, \quad (23)$$

where  $f(\epsilon) = 1/(\exp(\epsilon - \epsilon_F)/kT + 1)$  is the fermi function. Note that when  $\Gamma$  is smaller than  $kT$ , the above equation reduces to

$$\gamma^{ub} = \frac{\hbar}{\Gamma} \left( \frac{\partial \epsilon_d}{\partial x} \right)^2 \frac{f(\epsilon_d)(1 - f(\epsilon_d))}{kT}. \quad (24)$$

Equation (24) is sometimes called the un-broadened limit.<sup>81</sup>

For the sake of concreteness, let us now assume that  $U_0$  depends quadratically on  $x$ ,  $U_0 = \frac{1}{2}m\omega^2 x^2$ , and  $\epsilon_d$  depends linearly on  $x$ ,  $\epsilon_d = gx\sqrt{2m\omega}/\hbar + \epsilon_0$ . In Fig. 1, we plot both the potential of mean force [Eq. (21) and see Ref. 82] and the electronic friction [Eqs. (23) and (24)] as a function of  $x$  for the model in Eq. (22). As one can see, the friction is proportional to  $f(\epsilon_d)(1 - f(\epsilon_d))$  [see Eq. (24)] and shows a peak at the position where  $\epsilon_d(x) = \epsilon_F$  (i.e., the fermi resonance where the two diabatic potentials  $U_0$  and  $U_1$  cross). From the electron transfer perspective, note that the condition  $\epsilon_d(x) = \epsilon_F$  implies that electrons are jumping both back and forth between the molecule and metal surface,<sup>77</sup> thus offering key dynamical insights into the meaning of a peak in the electronic friction profile.<sup>60</sup> Note that  $\gamma^{ub}$  has a sharper peak due to a lack of broadening ( $\Gamma \rightarrow 0$ ).

For the case of multiple levels (mimicking larger molecules) or the case of non-Condon couplings (where  $V_k$  depends on the position), the corresponding electronic friction often reveals a very rich structure (with multiple peaks). See Refs. 61 and 83 for details.

## IV. OPEN QUESTIONS

Electronic friction has been used to investigate a host of nonadiabatic effects on metal surfaces, including chemisorption and desorption processes.<sup>84–87</sup> One of the key successes

of the method has been the estimation of vibrational relaxation rates.<sup>88–91</sup> Notwithstanding these successes, however, several essential questions remain regarding the evaluation of the friction tensor and overall utility of electronic friction dynamics.

### A. Electronic structure calculations and the role of electron-electron correlation

When electron-electron (el-el) interactions are present, the electronic Hamiltonian cannot be diagonalized and the electronic friction tensor [Eq. (18)] cannot be evaluated exactly; approximations must be made. In practice, to date, the electronic friction tensor is usually evaluated in effective mean-field theory (MFT) [usually density functional theory (DFT), e.g., Refs. 84, 90, and 92]. Thus, in practice, one of the open questions we must face is how accurate is such a mean-field approximation. For instance, in Fig. 2, we plot the friction tensor for the Hamiltonian in Eq. (22), where we now include an el-el repulsion term  $W$  between different spins in the molecular ( $d$ ) level.<sup>1</sup> For this unique example, an exact diagonalization of such an Hamiltonian can be found with the numerical renormalization group (NRG) theory,<sup>93,94</sup> which can be used to evaluate the electronic friction in Eq. (18).<sup>1</sup> Note that, at low temperature, the exact friction tensor should have four peaks: (i) two peaks arising from Fermi resonances for different spins and (ii) two peaks arising from Kondo resonances.<sup>1,95–97</sup> By contrast, mean-field theory predicts only one broad peak (see Fig. 2). In general, the electronic friction tensor may well be a fruitful and novel means to expose a great deal of rich many body correlated physics at low temperature, and these nonadiabatic effects have not yet been fully investigated. For more details, see Ref. 1. Obviously, finding the optimal means to account for el-el interactions and learning how the electronic friction tensors report on el-el correlation are key steps for the future.

Interestingly, recent experiments have emerged demonstrating how one can isolate electronic friction from phononic friction using superconducting states. In Ref. 19, the authors directly detected a drop in the electronic friction as a metal

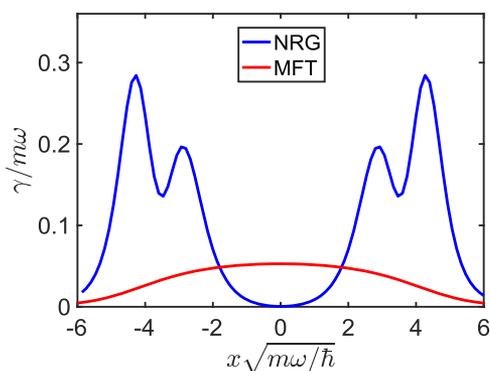


FIG. 2. For the Hamiltonian in Eq. (22) but now including electron-electron repulsion, the exact electronic friction (according to NRG) shows four peaks: (i) two outer peaks from a Fermi resonance and (ii) two inner peaks from a Kondo resonance (see Ref. 1 for detailed discussion). By contrast, electronic friction from mean-field theory (MFT) shows only one broad peak. For details, see Fig. 1 in Ref. 1 (as well as Ref. 98).

was cooled down below its superconducting transition. Since a superconductor can be viewed as a strongly correlated system with electron-electron attractions, these experiments would seem to indicate that, at least sometimes, electron-electron interactions can sometimes have enormous effects on electronic friction coefficients. These effects can and must be studied in depth in the future.

### B. Domain of applicability and the Wodtke experiments

Although electronic friction can be derived assuming slow nuclear motion, the exact conditions specifying when the resulting electronic friction dynamics are applicable are not entirely clear. In many senses, this situation parallels the Born-Oppenheimer approximation itself:<sup>99</sup> even though the BO approximation can be justified assuming a very large ratio of nuclear mass to electronic mass, the approximation still clearly breaks down for relaxation through a conical intersection,<sup>100–102</sup> no matter what the nuclear mass is. In other words, there is no single small parameter that guarantees the global applicability of the Born Oppenheimer approximation independent of initial conditions. From our point of view, this complicated state of affairs finds a natural parallel near a metal surface, where many questions remain about the applicability of electronic friction.

On the one hand, as a practical matter, over the past ten years, the Wodtke group has shown that electronic friction cannot explain various nonadiabatic interactions between a diatomic and a metal surface. Through a series of remarkably exquisite experiments scattering NO off gold and silver surfaces,<sup>103–105</sup> Wodtke and co-workers have shown that, despite the energy mismatch between the NO vibration and metallic Debye frequency, there can be a huge transfer of vibrational energy nonadiabatically. Furthermore, in perhaps the most impressive set of the NO experiments, Wodtke *et al.* have shown that when a gold surface is covered with Cs atoms to lower the work function, hot electrons emerge depending on the energy of the incoming NO molecule.<sup>106–108</sup> Thus, the takeaway from Refs. 103–108 is that, for some cases, even with strong diatomic-metal interactions, the nonadiabatic interactions at metal surfaces are best considered through the lens of transient electron transfer rather than through the lens of adiabatic motion with electronic friction. For this reason, our group<sup>60,77,81,109–112</sup> and others<sup>79,113–120</sup> are now devoting a great deal of energy to develop dynamical methods for molecules at surfaces that go beyond electronic friction.

That being said, on the other hand, there are examples where electronic friction makes predictions that are far better than might be expected. For example, if we again consider a molecule near a metal surface, one estimate of the small parameter in the electronic friction expansion might be the kinetic energy of the nuclei divided by the rate of electronic relaxation ( $\Gamma$ ). With this small parameter, one would expect that the theory must fail as  $\Gamma \rightarrow 0$ . After all, in such a limit, the electron friction diverges to infinity as  $1/\Gamma$  [see Eqs. (23) and (24)] and all dynamics should therefore be expected to be meaningless. And yet, for the model in Eq. (22),

Ref. 121 shows that electronic friction in fact recapitulates the non-adiabatic Fermi golden rule as  $\Gamma \rightarrow 0$ . In fact, it turns out that this highly non-intuitive result can be understood in terms of Kramer's overdamped friction: one can show that motion on the adiabatic surface when overdamped with electron friction at the crossing point is equivalent to the Marcus theory.<sup>109,121,122</sup>

In the end, the above results raise the obvious question: when exactly will electronic friction dynamics fail? And when will electronic friction dynamics succeed? Partial answers to these questions have been given,<sup>123</sup> and more general answers will no doubt be found in the future.

### C. Non-Markovian effects

While much of the discussion above was restricted to a Markovian friction tensor, there are currently very few comparisons regarding the non-Markovian nature of the frictional tensor. In Sec. II, we identified a frictional tensor with a memory kernel. In the literature, there are different forms for the memory kernels of the electronic friction as well as correlation functions for the random force. For example, Galperin and co-workers<sup>124</sup> have recently identified a slightly different memory kernel. We believe one can slightly tune our derivation to recover the Galperin memory kernel.<sup>69</sup> Obviously, in the future, further development is needed to understand the optimal form for the memory kernel;<sup>18,36,56</sup> is there a universally best form?

Furthermore, to date, very few researchers have actually investigated the practical effects of including memory effects for electronic friction dynamics: Does including such effects in fact lead to better performance? Or do including such effects perhaps have minimal or negative effects on the dynamics? These questions can and must be answered as we look to understand the dynamics of molecules on metal surfaces.

### D. Nuclear quantum effects

Last but not least, the Langevin dynamics in Eq. (1) treat all nuclear DoFs classically. For vibrational DoFs with high frequency, however, a classical treatment may not be valid. Several research groups are now exploring practical tools for including some nuclear quantum effects for nonadiabatic dynamics in the gas phase or solution,<sup>125–132</sup> and it will be very interesting to see whether these approaches can yield new information regarding nonadiabatic dynamics at a metal surface.

## V. CONCLUSIONS AND OUTLOOK

In the end, electronic friction represents a fundamental correction to the Born-Oppenheimer theory near a metal surface, and today we know far more about nonadiabatic effects near a metal surface than we did fifty years ago. And yet, with so many open questions and so many experimental findings that cannot yet be predicted theoretically,<sup>24,103,105,106,133–135</sup> we believe that this area of theoretical chemistry represents one of the most exciting areas for future research.

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