Universality of electronic friction: Equivalence of von Oppen's nonequilibrium Green's function approach and the Head-Gordon–Tully model at equilibrium

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For a molecule moving near a single metal surface at equilibrium, following von Oppen and coworkers [N. Bode, S. V. Kusminskiy, R. Egger, and F. von Oppen, Beilstein J. Nanotechnol. **3**, 144 (2012)] and using a nonequilibrium Green's-function (NEGF) approach, we derive a very general form of electronic friction that includes non-Condon effects. We then demonstrate that the resulting NEGF friction tensor agrees exactly with the Head-Gordon–Tully model, provided that finite temperature effects are incorporated correctly. The present results are in agreement with our recent claim that there is only one *universal* electronic friction tensor arising from the Born-Oppenheimer approximation [W. Dou, G. Miao, and J. E. Subotnik, Phys. Rev. Lett. **119**, 046001 (2017)].

I. INTRODUCTION

The dynamics of molecules near metal surfaces underlie many interesting phenomena in the area of electrochemistry [1–6] and molecular electronics [7–13]. While these dynamics can be directly related to straightforward scattering processes of gas molecules on metal surfaces [14–17] and chemisorption and dissociation [18–20], one must always remember that these dynamics can also display surprising behavior [21–27]. Due to electron transfer processes between molecule and metal, the charge state of the molecule need not be static and thus the Born-Oppenheimer approximation can break down [28,29]. Compared with more conventional nonadiabatic effects for molecules in the gas phase or solution [30–38], such nonadiabaticity at a metal surface is extremely challenging because the metal presents a continuous manifold of electron states (rather than a handful) [39–44].

The simplest way to model the nonadiabaticity at a metal surface is the electronic friction model. In the limit of fast electronic dynamics, where electron transfer occurs very quickly, the nuclei move effectively on an average potential energy surface while also experiencing friction and a fluctuating force. In the literature, quite a variety of friction models have been derived using different methods, some systematic and some *ad hoc*. Techniques for deriving friction include path integrals [45], nonequilibrium Green's functions (NEGFs) and scattering approaches [46–48], influence functionals [49,50], Meyer-Miller (MM) mappings [51,52], quantum-classical Liouville equation projections [53], as well as simple Fermi's "golden rule" arguments [54,55]. The final expression for electronic friction can also be expressed in a variety of different forms, i.e., in the time or energy domains [51,56], in terms of Green's functions (GFs) or scattering matrices [46,47], in diabatic or adiabatic basis representations (e.g., Kohn-Sham orbitals) [50,52,57,58], or in the form of response (correlation) functions or derivative couplings [45,52,59,60], etc.

Among these different forms for electronic friction, probably the mostly commonly used expression was given by Head-Gordon and Tully (HGT) in 1995 [52]. The HGT friction model has been successfully used to calculate the time scale for vibrational relaxation, and has been implemented in *ab initio* electronic structure theory [61]. The original HGT model is based on a MM mapping in the adiabatic basis combined with Ehrenfest dynamics. While the original article was restricted to zero temperature, very recently, as argued in Ref. [55] and confirmed in Ref. [53], the fluctuating force and other finite temperature effects can also be included [54].

Apart from the HGT expression, another important (and very different) type of electronic friction has been given by von Oppen and coworkers, using a NEGF and scattering matrix formalism [47]. This approach has certain advantages relative to the HGT approach. In particular, through this approach Langevin dynamics are more rigorously derived with the proper random force; the approximation can also be systematically verified. Moreover, the friction can be applied to the nonequilibrium case, resulting in, for instance, current induced friction. However, the derivation is rather complicated for those without expertise in nonequilibrium field theory, especially when non-Condon effects are incorporated [56]. Furthermore, both the HGT and von Oppen NEGF models effectively assume noninteracting electrons, where electron-electron (el-el) correlation is missing; el-el interactions can give very new and interesting physics at low temperature [26,53,62].

Finally, a third form for electronic friction can also be found in the literature: the friction can be expressed in terms of response or correlation functions [45,53,59]. Indeed, the HGT form for electronic friction can be rewritten in the form of Fermi's "golden rule" rate, i.e., second-order perturbation theory [55], which is equivalent to a correlation function expression. More generally, el-el interactions can also be incorporated into the friction tensor when expressed with correlation functions (as was argued by d'Agliano *et al.* long ago [59]).

Now, despite the presence of so many different approaches to electronic friction, to date, unfortunately, there have been very few studies comparing the different formal expressions. Furthermore, there has been no conclusion in the literature as to the differences between these friction tensors. For instance, on the one hand, are there perhaps different forms for electronic friction, just as there are many slightly different master equations [53,63–67]? When studying rate crossings near a metal surface, Smith and Hynes derived a non-Markovian friction tensor and argued that this friction tensor was "quite

distinct [from the HGT] Markovian electronic friction, acting on a particle impinging from the gas phase on a metallic surface" [51]. Or perhaps, on the other hand, are the different forms for electronic friction just a matter of notation?

In a recent letter, we have argued that there is a unique, universal electronic friction tensor [53] that is valid in and out of equilibrium, with or without el-el interactions:

$$\gamma_{\alpha\nu}(\mathbf{R}) = \int_0^\infty dt \, \mathrm{tr}_e[\delta \hat{f}_\alpha(\mathbf{R}) e^{-i\hat{H}(\mathbf{R})t/\hbar} \partial_\nu \hat{\rho}_{ss}(\mathbf{R}) e^{i\hat{H}(\mathbf{R})t/\hbar}]. \quad (1)$$

Here $\delta \hat{f}_\alpha = -\partial_\alpha \hat{H} + \mathrm{tr}_e(\partial_\alpha \hat{H} \hat{\rho}_{ss})$ is the random force, $\hat{H}$ is the electronic Hamiltonian, and $\hat{\rho}_{ss}$ is the steady-state electronic density matrix (all parametrized at position $\mathbf{R}$). tr_e implies tracing over the many-body electronic eigenstate states. At equilibrium, where $\hat{\rho}_{ss}$ is a Boltzmann average ($\hat{\rho}_{ss}(\mathbf{R}) = e^{-\beta \hat{H}(\mathbf{R})}/Z$), Ref. [53] proves that the friction tensor can be recast into the form of a correlation function of the random force:

$$\gamma_{\alpha\nu} = \frac{\beta}{2} \int_0^\infty dt \, \mathrm{tr}_e[\delta \hat{f}_\alpha e^{-i\hat{H}t/\hbar} (\delta \hat{f}_\nu \hat{\rho}_{ss} + \hat{\rho}_{ss} \delta \hat{f}_\nu) e^{i\hat{H}t/\hbar}]. \quad (2)$$

Equation (2) agrees with the results of d'Agliano *et al.* [59] and Daligault and Mozyrsky [45]. Furthermore, without el-el interaction, Ref. [53] also demonstrates that Eq. (2) can be further reduced to the HGT model [Eq. (25)].

With this background in mind, in the present paper, our goal is to take one more step forward towards consolidating electronic friction models. In particular, our goal is to prove that the electronic friction as calculated with NEGFs (following von Oppen and coworkers [47]) is in complete agreement with the HGT model [52] *at equilibrium* (which in turn agrees with the universal friction tensor in Ref. [53]). Note that we do not consider electron-electron interactions in this paper (because von Oppen's NEGF treatment assumes independent electrons). While we have previously shown agreement between von Oppen and HGT for a one-level problem [56], our earlier approach was not direct and could not be easily extended to the case of many system (molecular) orbitals with or without non-Condon effects. In the current paper, however, we claim that this agreement can be proven quite generally.

We organize this paper as follows. In Sec. II, using a NEGF approach in order to connect with von Oppen's formalism, we derive a Langevin equation for a noninteracting electronic system. In Sec. III, we apply our results to a model of a molecule (system) with many orbitals in contact with a bath of metallic electrons at equilibrium. Here, we demonstrate that the NEGF formalism is entirely equivalent to the HGT model, even when we include non-Condon effects, whereby metal-molecule couplings may fluctuate with nuclear motion. In Sec. IV, we discuss a key nuance which must be properly addressed when performing an NEGF gradient expansion with non-Condon effects. We conclude in Sec. V.

Regarding notations, below we use a hat to denote electronic operators. α and ν index nuclear degrees of freedom (DOFs) with position and momentum vectors $\mathbf{R}$ and $\mathbf{P}$. p and q index electronic orbitals in general. m and n index the electronic orbitals in the system (molecule), whereas k and k' index the orbitals in the bath (metal). $\hat{H}$ denotes the electronic Hamiltonian, including the pure nuclear potential $U_0(\mathbf{R})$. The total Hamiltonian is represented by $\hat{H}_{\mathrm{tot}}$, i.e., the electronic Hamiltonian plus the nuclear kinetic energy.

II. NONEQUILIBRIUM GREEN'S FUNCTION

A. Equation of motion

We consider coupled electron-nuclear motion, where the total Hamiltonian $\hat{H}_{\mathrm{tot}}$ can be divided into the electronic Hamiltonian $\hat{H}$, and nuclear kinetic energy:

$$\hat{H}_{\mathrm{tot}} = \hat{H} + \sum_\alpha \frac{P_\alpha^2}{2m^\alpha}. \quad (3)$$

The electronic Hamiltonian $\hat{H}$ consists of a manifold of electrons that is quadratic (in electronic orbitals p and q) plus a nuclear potential energy $U_0(\mathbf{R})$:

$$\hat{H} = \sum_{pq} \mathcal{H}_{pq}(\mathbf{R}) \hat{d}_p^\dagger \hat{d}_q + U_0(\mathbf{R}). \quad (4)$$

Without loss of generality, we restrict ourselves to the case of a real-valued $\mathcal{H}$ matrix below. Here, we re-emphasize that we are treating a noninteracting electronic (or Hartree-Fock or mean-field) Hamiltonian. (For a very general treatment that includes electron-electron interactions, see Ref. [53].)

We consider the classical dynamics of the nuclei, such that the equation of motion (EOM) for the nuclei is given by the Newtonian equation

$$m^\alpha \ddot{R}^\alpha = -\partial_\alpha \hat{H} = -\partial_\alpha U_0 - \sum_{pq} \partial_\alpha \mathcal{H}_{pq} \langle \hat{d}_p^\dagger \hat{d}_q \rangle + \delta \hat{f}_\alpha \quad (5)$$

where we have defined the random force $\delta \hat{f}_\alpha$:

$$\delta \hat{f}_\alpha = -\sum_{pq} \partial_\alpha \mathcal{H}_{pq} (\hat{d}_p^\dagger \hat{d}_q - \langle \hat{d}_p^\dagger \hat{d}_q \rangle). \quad (6)$$

Our goal is to transform Eq. (5) into a Langevin equation. To achieve this purpose, we define the lesser and retarded GFs, respectively:

$$\tilde{G}_{qp}^<(t_1, t_2) = \frac{i}{\hbar} \langle \hat{d}_p^\dagger(t_2) \hat{d}_q(t_1) \rangle_{\mathbf{R}(t_1)}, \quad (7)$$

$$\tilde{G}_{qp}^R(t_1, t_2) = -\frac{i}{\hbar} \theta(t_1 - t_2) \langle \{\hat{d}_q(t_1), \hat{d}_p^\dagger(t_2)\} \rangle_{\mathbf{R}(t_1)}. \quad (8)$$

Since the electronic Hamiltonian $\hat{H}$ is quadratic, and the nuclei are prescribed by $\mathbf{R}(t_1)$ and not $\mathbf{R}(t_2)$, the EOM for $\tilde{G}^R$ is given by

$$-i\hbar \partial_{t_2} \tilde{G}^R(t_1, t_2) = \delta(t_1 - t_2) + \tilde{G}^R(t_1, t_2) \mathcal{H}. \quad (9)$$

B. Gradient expansion: Mean force and friction

To proceed, it will be convenient to work in the Wigner representation, where the Wigner transformation is defined as

$$\tilde{G}^R(t, \epsilon) = \int d\tau \, e^{i\epsilon\tau/\hbar} \tilde{G}^R(t + \tau/2, t - \tau/2). \quad (10)$$

For a convolution, $D(t_1, t_2) = \int dt_3 \, B(t_1, t_3) C(t_3, t_2)$, the Wigner transformation can be expressed with a "Moyel

operator" as

$$D^W(t,\epsilon) = \exp\left[\frac{i\hbar}{2}\left(\partial_\epsilon^A \partial_t^B - \partial_\epsilon^B \partial_t^A\right)\right]B^W C^W$$
$$\approx B^W C^W + \frac{i\hbar}{2}\partial_\epsilon B^W \partial_t C^W - \frac{i\hbar}{2}\partial_\epsilon C^W \partial_t B^W. \quad (11)$$

The approximation made in the above equation is known as a gradient expansion in some fields of physics (and an $\hbar$ expansion in others).

After applying the Wigner transform and the gradient expansion to the EOM of $\tilde{G}^R(t_1,t_2)$ [Eq. (9)], we find

$$\tilde{G}^R\epsilon - \tilde{G}^R\mathcal{H} = 1 + \frac{i\hbar}{2}\partial_\epsilon\tilde{G}^R\partial_t\mathcal{H} + \frac{i\hbar}{2}\partial_t\tilde{G}^R. \quad (12)$$

At this point, we note that we are looking for a general friction tensor, i.e., a tensor that multiplies the velocity $\dot{\mathbf{R}}$. Because we will eventually replace $\partial_t = \sum_\nu \dot{R}^\nu \partial_\nu$, it is clear that, for all terms where there is already one factor of ∂_t, we may safely replace $\tilde{G}^R$ with the frozen G^R. We define the frozen GF:

$$G^R(\mathbf{R},\epsilon) = [\epsilon - \mathcal{H}(\mathbf{R}) + i\eta]^{-1}. \quad (13)$$

Here G^R represents the responses of an electron achieving instantaneous equilibration with the electronic Hamiltonian $\mathcal{H}$ (which will eventually be modulated by some nuclear motion). Substitution of the frozen Green's function for the full Green's function leads to

$$\tilde{G}^R(G^R)^{-1} \approx 1 + \frac{i\hbar}{2}\partial_\epsilon G^R\partial_t\mathcal{H} + \frac{i\hbar}{2}\partial_t G^R. \quad (14)$$

Note that $\partial_\epsilon G^R = -G^R G^R$, $\partial_t G^R = G^R\partial_t\mathcal{H}G^R$, as well as $\partial_t\mathcal{H} = \sum_\nu \dot{R}^\nu \partial_\nu\mathcal{H}$. Therefore, Eq. (14) can be solved as

$$\tilde{G}^R \approx G^R + \frac{i\hbar}{2}\sum_\nu \dot{R}^\nu(\partial_\epsilon G^R\partial_\nu\mathcal{H}G^R - G^R\partial_\nu\mathcal{H}\partial_\epsilon G^R). \quad (15)$$

At this point, we have a straightforward adiabatic first-order correction to the frozen retarded GF. This correction can be transformed back into the time domain as follows:

$$\tilde{G}^R(t_1,t_2) \approx G^R(t_1,t_2)$$
$$+ \frac{i\hbar}{2}\sum_\nu \dot{R}^\nu \int dt_3\,\partial_\epsilon G^R(t_1,t_3)\partial_\nu\mathcal{H}G^R(t_3,t_2)$$
$$- \frac{i\hbar}{2}\sum_\nu \dot{R}^\nu \int dt_3\, G^R(t_1,t_3)\partial_\nu\mathcal{H}\partial_\epsilon G^R(t_3,t_2). \quad (16)$$

Here we have used the backwards Wigner transformation. For instance, $\partial_\epsilon G^R(t_1,t_2)$ is defined as

$$\partial_\epsilon G^R(t_1,t_2) \equiv \int \frac{d\epsilon}{2\pi\hbar} e^{-i\epsilon(t_1-t_2)/\hbar}\partial_\epsilon G^R\left(\frac{t_1+t_2}{2},\epsilon\right). \quad (17)$$

Note that the correction of the full Green's function takes the form of a time convolution in real time. If this convolution is extended to a convolution on the Keldysh contour, we may now reproject onto the real time domain for the lesser GF. Using

the standard projection rules for the NEGF [68], we find

$$\tilde{G}^<(t_1,t_2) \approx G^<(t_1,t_2)$$
$$+ \frac{i\hbar}{2}\sum_\nu \dot{R}^\nu \int dt_3\,\partial_\epsilon G^<(t_1,t_3)\partial_\nu\mathcal{H}G^A(t_3,t_2)$$
$$+ \frac{i\hbar}{2}\sum_\nu \dot{R}^\nu \int dt_3\,\partial_\epsilon G^R(t_1,t_3)\partial_\nu\mathcal{H}G^<(t_3,t_2)$$
$$- \frac{i\hbar}{2}\sum_\nu \dot{R}^\nu \int dt_3\, G^<(t_1,t_3)\partial_\nu\mathcal{H}\partial_\epsilon G^A(t_3,t_2)$$
$$- \frac{i\hbar}{2}\sum_\nu \dot{R}^\nu \int dt_3\, G^R(t_1,t_3)\partial_\nu\mathcal{H}\partial_\epsilon G^<(t_3,t_2). \quad (18)$$

Finally, if we again perform a Wigner transformation, we recover

$$\tilde{G}^< \approx G^< + \frac{i\hbar}{2}\sum_\nu \dot{R}^\nu(\partial_\epsilon G^<\partial_\nu\mathcal{H}G^A - G^R\partial_\nu\mathcal{H}\partial_\epsilon G^<$$
$$+ \partial_\epsilon G^R\partial_\nu\mathcal{H}G^< - G^<\partial_\nu\mathcal{H}\partial_\epsilon G^A). \quad (19)$$

Using Eq. (5), we can now identify the correct friction coefficient,

$$\gamma_{\alpha\nu} = \hbar\int\frac{d\epsilon}{2\pi}\text{tr}(\partial_\alpha\mathcal{H}\partial_\epsilon G^<\partial_\nu\mathcal{H}G^A - \partial_\alpha\mathcal{H}G^R\partial_\nu\mathcal{H}\partial_\epsilon G^<), \quad (20)$$

as well as a mean force:

$$F_\alpha = i\int\frac{d\epsilon}{2\pi}\text{tr}(\partial_\alpha\mathcal{H}G^<). \quad (21)$$

Thus, we have derived several terms in the desired Langevin equation:

$$m^\alpha\ddot{R}^\alpha = -\partial_\alpha U_0 + F_\alpha - \sum_\nu \gamma_{\alpha\nu}\dot{R}^\nu + \delta\hat{f}_\alpha. \quad (22)$$

C. Equilibrium

Equation (20) is a general form for friction valid in or out of equilibrium. At equilibrium, this expression can be simplified further using the following relationships:

$$G^< = i2\pi\mathcal{P}f, \quad (23)$$

$$\mathcal{P} = -\frac{1}{\pi}\text{Im}G^R = \delta(\epsilon - \mathcal{H}). \quad (24)$$

Here f is the Fermi function, $f(\epsilon) = (e^{\beta\epsilon} + 1)^{-1}$ ($1/\beta \equiv k_B T$). We also have the universal relationship, $G^A = (G^R)^\dagger$. Using these relationships and integration by parts, Eq. (20) can be further rewritten as

$$\gamma_{\alpha\nu} = -\pi\hbar\int d\epsilon\,\text{tr}(\partial_\alpha\mathcal{H}\mathcal{P}\partial_\nu\mathcal{H}\mathcal{P})\partial_\epsilon f. \quad (25)$$

The exact form of Eq. (25) was not derived by von Oppen and coworkers [47], but this result does agree with the HGT model [52]. Similarly, the mean force at equilibrium reads

$$F_\alpha = -\int d\epsilon\,\text{tr}(\partial_\alpha\mathcal{H}\mathcal{P})f. \quad (26)$$

To make the Langevin equation [Eq. (22)] closed, we must now evaluate the correlation function of the random force $\delta\hat{f}_\alpha$.

D. Correlation of the random force

We now evaluate the correlation of the random force. While Ref. [53] provides a complete non-Markovian correlation function, here we consider only the Markovian correlation function:

$$\langle \delta \hat{f}_\alpha(t) \delta \hat{f}_\nu(t') \rangle = D_{\alpha\nu} \delta(t - t'). \tag{27}$$

This Markovian assumption is consistent with an adiabatic approximation (where electrons move much faster than nuclei).

Since the electronic Hamiltonian $\hat{H}$ is quadratic, Wick's theorem can be applied:

$$\langle \delta \hat{f}_\alpha(t) \delta \hat{f}_\nu(t') \rangle = \hbar^2 \sum_{p'q'pq} \partial_\alpha \mathcal{H}_{p'q'} \tilde{G}^>_{q'p}(t,t') \partial_\nu \mathcal{H}_{pq} \tilde{G}^<_{qp'}(t',t). \tag{28}$$

In the limit of fast electronic motion and relaxation, we replace the adiabatic GF $(\tilde{G})$ by the corresponding frozen GF (G), such that

$$D_{\alpha\nu} = \hbar^2 \int d\tau \, \mathrm{tr}[\partial_\alpha \mathcal{H} G^>(\tau) \partial_\nu \mathcal{H} G^<(-\tau)]$$

$$= \hbar \int \frac{d\epsilon}{2\pi} \, \mathrm{tr}[\partial_\alpha \mathcal{H} G^>(\epsilon) \partial_\nu \mathcal{H} G^<(\epsilon)]. \tag{29}$$

Equation (29) is valid in or out of equilibrium. At equilibrium, similar to Eq. (23), we have

$$G^> = -i2\pi(1 - f)\mathcal{P}. \tag{30}$$

Now the correlation function of the random force reads

$$D_{\alpha\nu} = 2\pi\hbar \int d\epsilon \, \mathrm{tr}(\partial_\alpha \mathcal{H} P \partial_\nu \mathcal{H} P) f(1 - f). \tag{31}$$

If we compare Eq. (31) with the friction in Eq. (25), and note that at equilibrium $\partial_\epsilon f = -\beta f(1 - f)$, we see that the second fluctuation-dissipation theorem is satisfied $(D_{\alpha\nu} = 2k_B T \gamma_{\alpha\nu})$ at equilibrium. Therefore, after equilibration, the nuclei will always reach the same temperature as the (electronic) metal surface.

III. A MODEL WITH SYSTEM-BATH SEPARATION

Equations (25) and (31) are very general expressions which make no distinction between a system and bath, and thus might appear nonintuitive. To connect with more traditional views of electronic friction, as in Ref. [47], we now separate the total system into a molecule with orbitals (index m and n), and a metal with a manifold of electronic orbitals (index k). The system-bath (molecule-metal) coupling is taken to be linear:

$$\hat{H} = \hat{H}_s + \hat{H}_b + \hat{H}_c, \tag{32}$$

$$\hat{H}_s = \sum_{mn} h_{mn}(\mathbf{R}) \hat{b}_m^\dagger \hat{b}_n + U_0(\mathbf{R}), \tag{33}$$

$$\hat{H}_b = \sum_k \epsilon_k \hat{c}_k^\dagger \hat{c}_k, \tag{34}$$

$$\hat{H}_c = \sum_{km} V_{km}(\mathbf{R})(\hat{b}_m^\dagger \hat{c}_k + \hat{c}_k^\dagger \hat{b}_m). \tag{35}$$

Notice that, aside from the bare nuclear potential $U_0(\mathbf{R})$, the energy of the system $h_{mn}(\mathbf{R})$ and the system-bath coupling $V_{km}(\mathbf{R})$ also depend on nuclear position $\mathbf{R}$.

Now, because all of the electronic terms are quadratic, we can apply Eq. (25) to evaluate

$$\mathrm{tr}(\partial_\alpha \mathcal{H} \mathcal{P} \partial_\nu \mathcal{H} \mathcal{P}) \tag{36}$$

$$= \frac{1}{\pi^2} \sum_{mnm'n'} \partial_\alpha h_{mn} \mathrm{Im} G^R_{nn'} \partial_\nu h_{n'm'} \mathrm{Im} G^R_{m'm} \tag{37}$$

$$+ \frac{2}{\pi^2} \sum_{mnkm'} \partial_\alpha h_{mn} \mathrm{Im} G^R_{nk} \partial_\nu V_{km'} \mathrm{Im} G^R_{m'm} \tag{38}$$

$$+ \frac{2}{\pi^2} \sum_{mknm'} \partial_\alpha V_{km} \mathrm{Im} G^R_{mn} \partial_\nu h_{nm'} \mathrm{Im} G^R_{m'k} \tag{39}$$

$$+ \frac{2}{\pi^2} \sum_{mnkk'} \partial_\alpha V_{km} \mathrm{Im} G^R_{mk'} \partial_\nu V_{k'n} \mathrm{Im} G^R_{nk} \tag{40}$$

$$+ \frac{2}{\pi^2} \sum_{mnkk'} \partial_\alpha V_{km} \mathrm{Im} G^R_{mn} \partial_\nu V_{nk'} \mathrm{Im} G^R_{k'k}. \tag{41}$$

Here, we have used the imaginary part of the retarded frozen GF to replace $\mathcal{P}$, since $\mathcal{P}(\epsilon) = -\frac{1}{\pi} \mathrm{Im} G^R(\epsilon)$.

To proceed, for the noninteracting electrons, the following relationship can be applied (because of the Dyson equation):

$$G^R_{nk} = \sum_{n'} G^R_{nn'} V_{n'k} g^R_k. \tag{42}$$

g^R_k is the retarded GF for the electron in the metal,

$$g^R_k = (\epsilon - \epsilon_k + i\eta)^{-1}, \tag{43}$$

so that

$$\mathrm{Im} \sum_k G^R_{nk} \partial_\alpha V_{km'} = \mathrm{Im} \sum_{kn'} G^R_{nn'} V_{n'k} g^R_k \partial_\alpha V_{km'}. \tag{44}$$

We denote

$$2 \sum_k V_{n'k} g^R_k \partial_\alpha V_{km'} = \bar{\Sigma}^\alpha_{n'm'}. \tag{45}$$

For $G^R_{k'k}$, again from the Dyson equation,

$$G^R_{k'k} = g^R_k \delta_{k'k} + \sum_{m'n'} g^R_{k'} V_{k'm'} G^R_{m'n'} V_{n'k} g^R_k. \tag{46}$$

We denote,

$$\sum_k \partial_\nu V_{nk} g^R_k \partial_\alpha V_{km} = \frac{1}{4} \bar{\Sigma}^{\nu,\alpha}_{nm}. \tag{47}$$

From Eq. (45) and Eq. (47), we now have,

$$\mathrm{Im} \sum_{kk'} \partial_\nu V_{nk'} G^R_{k'k} \partial_\alpha V_{km} = \frac{1}{4} \mathrm{Im} \bar{\Sigma}^{\nu,\alpha}_{nm} + \frac{1}{4} \mathrm{Im}[(\bar{\Sigma}^\nu)^T G^R_s \bar{\Sigma}^\alpha]_{nm}. \tag{48}$$

Thus, we find

$$\mathrm{tr}(\partial_\alpha \mathcal{H} \mathcal{P} \partial_\nu \mathcal{H} \mathcal{P})$$

$$= \frac{1}{\pi^2} \mathrm{tr}_s \{ [\mathrm{Im} G^R_s \, \partial_\alpha h + \mathrm{Im}(G^R_s \, \bar{\Sigma}^\alpha)]$$

$$\times [\mathrm{Im} G^R_s \, \partial_\nu h + \mathrm{Im}(G^R_s \, \bar{\Sigma}^\nu)] \}.$$

$$+ \frac{1}{2\pi^2} \mathrm{tr}_s \{ \mathrm{Im} G^R_s \mathrm{Im} \bar{\Sigma}^{\nu,\alpha} + \mathrm{Im} G^R_s \mathrm{Im}[(\bar{\Sigma}^\nu)^T G^R_s \bar{\Sigma}^\alpha]$$

$$- \mathrm{Im}(G^R_s \bar{\Sigma}^\alpha) \mathrm{Im}(G^R_s \bar{\Sigma}^\nu) \}. \tag{49}$$

Here the trace tr_s implies a summation over only the system orbitals (m and n), and G_s^R is the retarded GF for the system:

$$G_s^R = (\epsilon - h - \Sigma)^{-1}, \tag{50}$$

$$\Sigma_{mn} = \sum_k V_{mk} g_k^R V_{kn}. \tag{51}$$

We note that, from the definitions in Eqs. (45) and (51), $\partial_\alpha \Sigma_{mn} = \frac{1}{2}(\bar{\Sigma}_{mn}^\alpha + \bar{\Sigma}_{nm}^\alpha)$. The final friction is then

$$\begin{aligned}
\gamma_{\alpha v} = &-\hbar \int \frac{d\epsilon}{\pi} \text{tr}_s \Big\{ \big[\text{Im} G_s^R \, \partial_\alpha h + \text{Im}\big(G_s^R \, \bar{\Sigma}^\alpha\big)\big] \\
&\times \big[\text{Im} G_s^R \, \partial_v h + \text{Im}\big(G_s^R \, \bar{\Sigma}^v\big)\big]\Big\} \partial_\epsilon f \\
&-\hbar \int \frac{d\epsilon}{2\pi} \text{tr}_s \Big\{ \text{Im} G_s^R \text{Im} \bar{\Sigma}^{v,\alpha} + \text{Im} G_s^R \text{Im}\big[(\bar{\Sigma}^v)^T G_s^R \bar{\Sigma}^\alpha\big] \\
&- \text{Im}\big(G_s^R \bar{\Sigma}^\alpha\big) \text{Im}\big(G_s^R \bar{\Sigma}^v\big)\Big\} \partial_\epsilon f. \tag{52}
\end{aligned}$$

For the case that $\partial_\alpha V_{km} = 0$ (which is known as the Condon approximation), Eq. (52) was derived previously by von Oppen and coworkers [47]. Here, however, we have shown that the von Oppen friction results are identical to the HGT friction results [Eq. (25)]. Furthermore, in the present paper, we have now extended von Oppen's results to account for non-Condon effects, i.e., the fact that V_{km} should generally depend on **R**.

Wide-band limit

To better understand the implication of the non-Condon effects, we note that in the literature the wide-band approximation is often used, such that the following purely imaginary quantities can be defined:

$$\sum_k V_{n'k} g_k^R V_{km'} = -i \Gamma_{n'm'}/2, \tag{53}$$

$$2 \sum_k V_{n'k} g_k^R \partial_\alpha V_{km'} = -i \bar{\Gamma}_{n'm'}^\alpha/2. \tag{54}$$

Here Γ_{mm} is the lifetime or hybridization of molecular orbital m on the metal surface. By definition, we have $\partial_\alpha \Gamma_{mn} = \frac{1}{2}(\bar{\Gamma}_{nm}^\alpha + \bar{\Gamma}_{mn}^\alpha)$, and $G_s^R = (\epsilon - h + i\Gamma/2)^{-1}$. If we further assume that V_{km} does not depend on k ($V_{km} = V_m$), the last term of the friction Eq. (52) vanishes (see the Supplemental Material [69]). Thus, the friction becomes:

$$\begin{aligned}
\gamma_{\alpha v} = &-\hbar \int \frac{d\epsilon}{\pi} \text{tr}_s \bigg[\bigg(\text{Im} G_s^R \, \partial_\alpha h - \frac{1}{2}\text{Re} G_s^R \, \bar{\Gamma}^\alpha\bigg) \\
&\times \bigg(\text{Im} G_s^R \, \partial_v h - \frac{1}{2}\text{Re} G_s^R \, \bar{\Gamma}^v\bigg)\bigg] \partial_\epsilon f. \tag{55}
\end{aligned}$$

Thus, we see that non-Condon effects restructure the wideband approximation so that the electronic friction will now depend on both the imaginary and real parts of the system Green's function. In general, non-Condon effects can increase or decrease friction, depending on the relative signs of the two components in Eq. (55).

IV. DISCUSSION

The results above are fairly straightforward. We have shown the following.

(i) An NEGF formalism recovers the exact same electronic friction as the Head-Gordon–Tully approach; this agreements confirms our earlier claim [53] there is only a single, universal electronic friction tensor that is relevant to semiclassical dynamics.

(ii) Non-Condon effects can be incorporated into the relevant electronic friction. In a previous paper, with only a single electronic orbital, we demonstrated that non-Condon contributions to the electronic friction can sometimes be significant [56].

At this point, before concluding, there is one key feature that ought to be addressed regarding formalisms. In the present paper, our approach was to (i) perform a gradient expansion of the full Green's function (Sec. II) and then (ii) project the full GF onto the system and system-bath coupling to learn about molecular motion on a surface. Through this procedure, we arrived at the relevant friction coefficient (Sec. III) which satisfies the second fluctuation-dissipation theorem. Now, while the formalism just described might seem obvious enough, we must emphasize that the steps taken above are not standard at all. By contrast, the more typical approach would be the opposite: (i) first focus on the system coordinates and (ii) second apply a gradient expansion in the smaller space of (system) nuclear motion. For instance, in Ref. [47], von Oppen and coworkers take the latter (not former) approach.

In our experience, we have found that these two approaches usually agree, but can disagree when non-Condon effects are present. Here, there are two data points worth mentioning. First, in Ref. [56], for the case of one system molecular orbital with non-Condon effects, we have previously performed a gradient expansion separately for the system and system-bath coupling GFs. In such a case, the resulting friction does agree with the HGT model. However, second, although we do not reproduce the derivation here, for the case of multiple system orbitals in contact with a metal with non-Condon effects, one finds that the two approaches above do *not* agree. Instead, if one invokes a naive gradient expansion which separates the system and system-bath GFs, one will recover a different friction tensor that is clearly incorrect. This incorrect friction tensor does not agree with the HGT method and does not satisfy the second fluctuation-dissipation theorem. Furthermore, this incorrect friction tensor is not symmetric along nuclear DOFs at equilibrium, whereas the correct friction tensor in this paper [Eq. (25) or (55)] is symmetric. Hence, by studying non-Condon effects, the present paper has clearly discerned how to perform a proper gradient expansion when system-bath couplings become complicated and position dependent.

V. CONCLUSIONS

In conclusion, we have extended the NEGF approach to deal with a very general Hamiltonian with many molecular orbitals sitting near a metal surface. We have derived a general form of electronic friction as felt by the system nuclei, and we have included the effects of non-Condon terms in the Hamiltonian. At equilibrium, we have shown the equivalence between a NEGF approach and the HGT model, providing strong evidence to back up our recent claim of a single, universal friction tensor arising from the Born-Oppenheimer approach

[53]. Future work will necessarily investigate the connection between Ref. [53], the HGT model, and the NEGF formalism under out-of-equilibrium conditions, i.e., for a molecule sitting between two leads with a current running through it.

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