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Citation: The Journal of Chemical Physics **145**, 054102 (2016); doi: 10.1063/1.4959604
View online: http://dx.doi.org/10.1063/1.4959604
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A many-body states picture of electronic friction: The case of multiple orbitals and multiple electronic states

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(Received 15 May 2016; accepted 13 July 2016; published online 1 August 2016)

We present a very general form of electronic friction as present when a molecule with multiple orbitals hybridizes with a metal electrode. To develop this picture of friction, we embed the quantum-classical Liouville equation (QCLE) within a classical master equation (CME). Thus, this article extends our previous work analyzing the case of one electronic level, as we may now treat the case of multiple levels and many electronic molecular states. We show that, in the adiabatic limit, where electron transitions are much faster than nuclear motion, the QCLE-CME reduces to a Fokker-Planck equation, such that nuclei feel an average force as well as friction and a random force—as caused by their interaction with the metallic electrons. Finally, we show numerically and analytically that our frictional results agree with other published results calculated using non-equilibrium Green's functions. Numerical recipes for solving this QCLE-CME will be provided in a subsequent paper. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4959604]

I. INTRODUCTION

The non-adiabatic dynamics of coupled electron-nuclear motion have gained a lot of interest recently, as such motions fundamentally underlie many chemical reactions, transition state theory, photochemistry, and many other processes. Due to the breakdown of the Born-Oppenheimer approximation,[1] propagating non-adiabatic dynamics is still challenging theoretically and computationally.[2]

With only a few electronic states, there are nowadays a few semiclassical dynamics methods available.[3–9] Among the many possible algorithms, surface hopping, Ehrenfest dynamics, and multiple spawning are used widely for both realistic and model systems.[3,10–19] Direct propagation of the Quantum-Classical Liouville Equation (QCLE)[20,21] is yet another option, though numerical instabilities can be problematic. As will be important below, the QCLE can be derived either directly from a Wigner transformation of a Liouville equation or from a linearized influence functional formalism.[22] Recent work has shown a connection between Tully's surface hopping algorithm and the QCLE.[23]

Now, at a molecule-metal interface, with a manifold of electronic degrees of freedom (DoFs), the coupled electron-nuclear motion is obviously more tricky and there are far fewer dynamical options; some of the schemes described above carry over easily and some do not. On the one hand, for mean-field dynamics, it is known that the simplest way to model the effects of a metal surface on the motion of a nearby molecule is the incorporation of "electronic" friction, as has been derived independently by Head-Gordon/Tully,[24,25] Brandbyge *et al.*,[26,27] Mozyrsky *et al.*,[28] and von Oppen *et al.*[29] On the other hand, an extension of traditional surface hopping has also been proposed to include many electronic DoFs through the Independent-Electron Surface Hopping (IESH) formalism.[30,31] More recently, a classical master equation (CME) approach has been derived, which represents in a sense another (different) extension of surface hopping to describe coupled electron-nuclear at a molecule-metal interface.[32–38]

Last year, in Ref. 35, we considered in detail the case of a molecule with two different charge states in the adiabatic limit where electron transitions occur much faster than nuclear motion. In that adiabatic limit, as shown in Ref. 35, we showed that a CME/surface hopping approach correctly reduces to Langevin dynamics with the correct electronic friction (agreeing with von Oppen and Tully), provided that the effects of level broadening effect are not very large. See Appendix C for a brief review. Galperin and Nitzan[37] have also studied the connection between surface hopping and electronic friction from the framework of nonequilibrium Green's functions for the case of one molecular orbital and two electronic states.

In the present paper, we will now extend the results of Ref. 35 to the case of many electronic orbitals. Our approach is as follows: First, we will embed a molecular system in the Hamiltonian of a metallic bath (leading to a CME) and second we will take the Wigner transform of the system (which leads to the QCLE). The resulting QCLE-CME hybrid is suitable for describing the coupled electron-nuclear motion near metal surfaces when considering multiple molecular DoFs (electronic and nuclear) in the molecule. Finally, in the adiabatic limit, we will show how to transform the QCLE-CME into a Fokker-Planck equation, where the friction and random force can be expressed in a compact form. Our final form of the friction nearly agrees with von Oppen results (both numerically and analytically) in the limit of weak broadening.

Before proceeding, we note that the QCLE-CME hybrid equation below incorporates a great many non-adiabatic effects and should be a very powerful master equation for future simulations. In a follow-up paper, we will provide a numerical recipe for propagating QCLE-CME dynamics with a surface hopping algorithm.

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The remainder of this paper is organized as follows. In Sec. II, we derive the QCLE-CME to describe coupled electron-nuclear dynamics near metal surfaces, followed by a transformation to a FP equation. In Sec. III, this QCLE-CME is compared with another CME based on a reduced density matrix description of all electronic DoFs (denoted CME-1RDM). In Sec. IV we compare our friction results with previously published results. We conclude in Sec. V.

Notation. Our notation will be as follows: A "hat" denotes an operator, e.g., $\hat{O}$, which can be nuclear or electronic (or both) in nature. The subscript "el" signifies an exclusively electronic operator, that will usually depend parametrically on some nuclear coordinate, e.g., the partially Wignerized density matrix $\hat{\rho}_{el} = \hat{\rho}_{el}(\mathbf{X},\mathbf{P})$. Bold face denotes vectors, e.g., $\mathbf{X}$ denotes the coordinates of the nuclei in configuration space. The greek letters α and β index nuclear vectors and roman letters $(n,m,k,\ldots)$ index electronic orbitals.

II. THEORY: QCLE-CME

To derive a general form of electronic friction, we begin by decomposing the total Hamiltonian $\hat{H}_{tot}$ into a system Hamiltonian $\hat{H}_s$, a bath Hamiltonian $\hat{H}_b$, and the interaction Hamiltonian $\hat{H}_v$ (coupling the system and bath),

$$\hat{H}_{tot} = \hat{H}_s + \hat{H}_v + \hat{H}_b. \tag{1}$$

Here, $\hat{H}_s$ describes a molecule (i.e., our system) which consists of many electrons that can hop between molecule and metal with orbital creation/annihilation operators $\hat{d}_m^+/\hat{d}_n$. These electrons are coupled to nuclear motion as follows:

$$\hat{H}_s = \sum_{mn} h_{mn}(\hat{\mathbf{X}})\hat{d}_m^+\hat{d}_n + \sum_{\alpha}\frac{\hat{P}_\alpha^2}{2M_\alpha} + U(\hat{\mathbf{X}}). \tag{2}$$

$\hat{H}_b$ describes a metal surface (i.e., our bath) which is a manifold of non-interacting electronic orbitals $(\hat{c}_k^+, \hat{c}_k)$,

$$\hat{H}_b = \sum_k \epsilon_k \hat{c}_k^+\hat{c}_k. \tag{3}$$

The interaction $\hat{H}_v$ between the system and bath is defined to be bilinear,

$$\hat{H}_v = \sum_{km} V_{km}(\hat{c}_k^+\hat{d}_m + \hat{d}_m^+\hat{c}_k). \tag{4}$$

For the system-bath couplings, we will assume the wide-band approximation, such that the hybridization function $\Gamma_{mn}(\epsilon)$ is independent of ϵ,

$$\Gamma_{mn}(\epsilon) \equiv 2\pi\sum_k V_{km}V_{kn}\delta(\epsilon-\epsilon_k) = \Gamma_{mn}. \tag{5}$$

A. Born-Markovian approximation for weak system-bath couplings

For a tractable approach, we apply the Born-Markovian approximation to the system-bath couplings, such that the equation of motion (EOM) for the system density matrix can be written as

$$\frac{\partial}{\partial t}\hat{\rho}_I = -\hat{\hat{\mathcal{L}}}_I\hat{\rho}_I. \tag{6}$$

We have written the above equation in the interaction picture, where an operator $\hat{O}$ (in Schrodinger picture) evolves as $\hat{O}_I(t) = e^{i(\hat{H}_s+\hat{H}_b)t/\hbar}\hat{O}e^{-i(\hat{H}_s+\hat{H}_b)t/\hbar}$. The Born-Markovian approximation assumes weak system-bath couplings and an uncorrelated system-bath density matrix in the kernel's dynamics. The superoperator $\hat{\hat{\mathcal{L}}}_I$ can be written explicitly as

$$\hat{\hat{\mathcal{L}}}_I\hat{\rho}_I = \frac{1}{\hbar^2}\int_0^\infty d\tau tr_b[\hat{H}_{Iv}(t),[\hat{H}_{Iv}(t-\tau),\hat{\rho}_I(t)\bigotimes\hat{\rho}_b^{eq}]], \tag{7}$$

where $\hat{\rho}_b^{eq}$ is the equilibrium density matrix of the bath. tr_b denotes tracing over the bath DoFs. Equation (6) is often denoted as a "Redfield Equation."[39]

If we transform Eq. (6) back into the Schrodinger picture $\hat{\rho} = e^{-i\hat{H}_s t/\hbar}\hat{\rho}_I e^{i\hat{H}_s t/\hbar}$, the Redfield equations become

$$\frac{\partial}{\partial t}\hat{\rho} = -\frac{i}{\hbar}[\hat{H}_s,\hat{\rho}] - \hat{\hat{\mathcal{L}}}_{bs}\hat{\rho}, \tag{8}$$

where $\hat{\hat{\mathcal{L}}}_{bs}$ now is given by

$$\hat{\hat{\mathcal{L}}}_{bs}\hat{\rho} = \frac{1}{\hbar^2}\int_0^\infty d\tau e^{-i\hat{H}_s t/\hbar}tr_b\left([\hat{H}_{Iv}(t),[\hat{H}_{Iv}(t-\tau),e^{i\hat{H}_s t/\hbar}\hat{\rho}(t)e^{-i\hat{H}_s t/\hbar}\bigotimes\hat{\rho}_b^{eq}]]\right)e^{i\hat{H}_s t/\hbar}. \tag{9}$$

B. A partial Wigner transform

In order to take the classical limit for the nuclei, we apply a partial Wigner transform to the equation of motion of $\hat{\rho}$ (Eq. (8)), where the partial Wigner transform of the density matrix is defined as

$$\hat{\rho}_{el}(\mathbf{X},\mathbf{P}) \equiv (2\pi\hbar)^{-3N}\int d\mathbf{Y}\langle\mathbf{X}-\mathbf{Y}/2|\hat{\rho}|\mathbf{X}+\mathbf{Y}/2\rangle e^{i\mathbf{P}\cdot\mathbf{Y}/\hbar}, \tag{10}$$

and the partial Wigner transform of an Operator $\hat{O}$ is

$$\hat{O}_{el}(\mathbf{X},\mathbf{P}) \equiv \int d\mathbf{Y}\langle\mathbf{X}-\mathbf{Y}/2|\hat{O}|\mathbf{X}+\mathbf{Y}/2\rangle e^{i\mathbf{P}\cdot\mathbf{Y}/\hbar}. \tag{11}$$

As usual,[20] the partial Wigner transform of the commutator in Eq. (8) yields a quantum-classical Liouville equation (QCLE),

$$-\frac{i}{\hbar}[\hat{H}_s,\hat{\rho}]_{el} \to -\frac{i}{\hbar}[\hat{H}_s^{el}(\mathbf{X},\mathbf{P}),\hat{\rho}_{el}(\mathbf{X},\mathbf{P})] + \{\hat{H}_s^{el}(\mathbf{X},\mathbf{P}),\hat{\rho}_{el}(\mathbf{X},\mathbf{P})\}_a. \tag{12}$$

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After the Wigner transform, $\hat{H}_s^{el}$ is of the same form as $\hat{H}_s$ (in Eq. (2)), but we replace the nuclear operators $(\hat{\mathbf{X}},\hat{\mathbf{P}})$ with the classical parameters $(\mathbf{X},\mathbf{P})$,

$$\hat{H}_s^{el}(\mathbf{X},\mathbf{P}) = \sum_{mn} h_{mn}(\mathbf{X})\hat{d}_m^+\hat{d}_n + \sum_\alpha \frac{P_\alpha^2}{2M_\alpha} + U(\mathbf{X}). \quad (13)$$

In Eq. (12), $\{\cdot,\cdot\}_a$ is defined as

$$\{\hat{O}_1,\hat{O}_2\}_a = \frac{1}{2}\{\hat{O}_1,\hat{O}_2\} - \frac{1}{2}\{\hat{O}_2,\hat{O}_1\}, \quad (14)$$

where $\{\cdot,\cdot\}$ is the usual Poisson bracket

$$\{\hat{O}_1,\hat{O}_2\} = \sum_\alpha \frac{\partial\hat{O}_1}{\partial X_\alpha}\frac{\partial\hat{O}_2}{\partial P_\alpha} - \frac{\partial\hat{O}_1}{\partial P_\alpha}\frac{\partial\hat{O}_2}{\partial X_\alpha}. \quad (15)$$

Thus,

$$\{\hat{H}_s^{el},\hat{O}\}_a = -\sum_\alpha \frac{P_\alpha}{M_\alpha}\frac{\partial\hat{O}}{\partial X_\alpha} + \frac{1}{2}\sum_\alpha\left(\frac{\partial\hat{H}_s^{el}}{\partial X_\alpha}\frac{\partial\hat{O}}{\partial P_\alpha} + \frac{\partial\hat{O}}{\partial P_\alpha}\frac{\partial\hat{H}_s^{el}}{\partial X_\alpha}\right). \quad (16)$$

When we apply the partial Wigner transforms (Eqs. (10) and (11)) to the Redfield operator $\hat{\hat{\mathcal{L}}}_{bs}$ in Eq. (8), we keep only those terms up to the zeroth order in the gradient expansion.[40] In other words, we replace the Wigner transform of the product by the product of the Wigner transforms $(\hat{O}_1\hat{O}_2)_{el} = \hat{O}_1^{el}\hat{O}_2^{el}$, such that

$$(\hat{\hat{\mathcal{L}}}_{bs}\hat{\rho})_{el}(\mathbf{X},\mathbf{P}) \to \hat{\hat{\mathcal{L}}}_{bs}^{el}(\mathbf{X})\hat{\rho}_{el}(\mathbf{X},\mathbf{P}). \quad (17)$$

To be clear, let us write out $\hat{\hat{\mathcal{L}}}_{bs}^{el}(\mathbf{X})\hat{\rho}_{el}(\mathbf{X},\mathbf{P})$ explicitly,

$$\hat{\hat{\mathcal{L}}}_{bs}^{el}\hat{\rho}_{el} = \frac{1}{\hbar^2}\int_0^\infty d\tau e^{-i\hat{H}_s^{el}t/\hbar} tr_b\left([\hat{H}_{Iv}^{el}(t),[\hat{H}_{Iv}^{el}(t-\tau),e^{i\hat{H}_s^{el}t/\hbar}\hat{\rho}_{el}(t)e^{-i\hat{H}_s^{el}t/\hbar}\bigotimes\hat{\rho}_b^{eq}]]\right)e^{i\hat{H}_s^{el}t/\hbar}, \quad (18)$$

where we have defined $\hat{H}_{Iv}^{el}(t) \equiv e^{i(\hat{H}_s^{el}+\hat{H}_b)t/\hbar}\hat{H}_v e^{-i(\hat{H}_s^{el}+\hat{H}_b)t/\hbar}$.

After a Wigner transform has been performed, $\hat{H}_s^{el}$ depends only on $\mathbf{X}$ and $\mathbf{P}$ as parameters, and one can easily evaluate Eq. (18) and write down $\hat{\hat{\mathcal{L}}}_{bs}^{el}(\mathbf{X})$ explicitly (see Appendix A). Moreover, since the free potential $U(\mathbf{X})$ and kinetic energy terms in $\hat{H}_s^{el}$ (Eq. (13)) commute with any operators in Eq. (18), we note that the dependence of $\hat{\hat{\mathcal{L}}}_{bs}^{el}$ on $\mathbf{X}$ arises only through $h_{mn}(\mathbf{X})$.

Finally, the EOM for $\hat{\rho}_{el}$ becomes

$$\frac{\partial}{\partial t}\hat{\rho}_{el}(\mathbf{X},\mathbf{P},t) = \{\hat{H}_s^{el}(\mathbf{X}),\hat{\rho}_{el}(\mathbf{X},\mathbf{P},t)\}_a - \hat{\hat{\mathcal{L}}}_{el}(\mathbf{X})\hat{\rho}_{el}(\mathbf{X},\mathbf{P},t), \quad (19)$$

or more simply, if we drop the parametric dependence on $(\mathbf{X},\mathbf{P})$ for a moment,

$$\frac{\partial}{\partial t}\hat{\rho}_{el}(t) = \{\hat{H}_s^{el},\hat{\rho}_{el}(t)\}_a - \hat{\hat{\mathcal{L}}}_{el}\hat{\rho}_{el}(t).$$

Here, for every position $\mathbf{X}$, we have defined $\hat{\hat{\mathcal{L}}}_{el}(\cdot) \equiv \hat{\hat{\mathcal{L}}}_{bs}^{el}(\cdot) + \frac{i}{\hbar}[\hat{H}_s^{el},\cdot]$. Because all of the relevant terms involve commutators, it is straightforward to see that $tr_e\hat{\hat{\mathcal{L}}}_{el}(\cdot) = 0$, where tr_e represents a trace over the system electronic DoFs. Furthermore, as above, it is easy to see that $\hat{\hat{\mathcal{L}}}_{el}$ depends only on $\mathbf{X}$ (and not on $\mathbf{P}$, i.e., $\hat{\hat{\mathcal{L}}}_{el} = \hat{\hat{\mathcal{L}}}_{el}(\mathbf{X})$) and that all dependence on $\mathbf{X}$ arises through $h_{mn}(\mathbf{X})$.

Eq. (19) is our starting point for studying friction: it is a combination of the QCLE and CME for describing classical nuclear motion with electron transitions for molecules near metal surfaces; henceforward, we will abbreviate this equation as the QCLE-CME. To further analyze Eq. (19), we consider below the slow motion of nuclei (as compared with electron transitions). We remind the reader that the discussion below is completely analogous to the analysis in Ref. 35, even though the math is necessarily more complicated.

C. Stationary states

To proceed further, we define $\hat{\sigma}_{eq}^{el}(\mathbf{X})$ to be the local equilibrium distribution satisfying $\hat{\hat{\mathcal{L}}}_{el}(\mathbf{X})\hat{\sigma}_{eq}^{el}(\mathbf{X}) = 0$, with normalization condition $tr_e\hat{\sigma}_{eq}^{el} = 1$ for all $\mathbf{X}$. Recall that the dependence of $\hat{\sigma}_{eq}^{el}$ on $\mathbf{X}$ arises only through $h_{mn}(\mathbf{X})$. We now define $A(\mathbf{X},\mathbf{P},t) \equiv tr_e\hat{\rho}_{el}(\mathbf{X},\mathbf{P},t)$ to be total probability density in phase space at position $(\mathbf{X},\mathbf{P})$. The difference between $\hat{\rho}_{el}$ and $A\hat{\sigma}_{eq}^{el}$ is defined as $\hat{B}_{el}$,

$$\hat{\rho}_{el}(\mathbf{X},\mathbf{P},t) \equiv A(\mathbf{X},\mathbf{P},t)\hat{\sigma}_{eq}^{el}(\mathbf{X}) + \hat{B}_{el}(\mathbf{X},\mathbf{P},t). \quad (20)$$

With Eq. (19), the coupled EOM for A and $\hat{B}_{el}$ is (for brevity, we temporarily omit the dependence on variables $\mathbf{X},\mathbf{P}$)

$$\begin{aligned}\frac{\partial}{\partial t}A &= tr_e\{\hat{H}_s^{el},A\hat{\sigma}_{eq}^{el}\}_a + tr_e\{\hat{H}_s^{el},\hat{B}_{el}\}_a \\ &= -\sum_\alpha\frac{P_\alpha}{M_\alpha}\frac{\partial A}{\partial X_\alpha} + \sum_\alpha tr_e\left(\frac{\partial\hat{H}_s^{el}}{\partial X_\alpha}\hat{\sigma}_{eq}^{el}\right)\frac{\partial A}{\partial P_\alpha} \\ &\quad + \sum_\alpha tr_e\left(\frac{\partial\hat{H}_s^{el}}{\partial X_\alpha}\frac{\partial\hat{B}_{el}}{\partial P_\alpha}\right), \quad (21)\end{aligned}$$

$$\begin{aligned}\frac{\partial}{\partial t}\hat{B}_{el} &= \{\hat{H}_s^{el},\hat{B}_{el}\}_a - \hat{\sigma}_{eq}^{el}tr_e\{\hat{H}_s^{el},\hat{B}_{el}\}_a - \hat{\hat{\mathcal{L}}}_{el}\hat{B}_{el} \\ &\quad + \{\hat{H}_s^{el},A\hat{\sigma}_{eq}^{el}\}_a - \hat{\sigma}_{eq}^{el}tr_e\{\hat{H}_s^{el},A\hat{\sigma}_{eq}^{el}\}_a. \quad (22)\end{aligned}$$

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D. The approximation of slow nuclei

Finally, to conclude our frictional model, we must make the approximation that the nuclei move slowly compared with electronic motion, such that we can disregard the first 3 terms in Eq. (22), and approximate $\hat{\hat{\mathcal{L}}}_{el}\hat{B}_{el}$ as[41]

$$\begin{aligned}\hat{\hat{\mathcal{L}}}_{el}\hat{B}_{el} &= \{\hat{H}_s^{el}, A\hat{\sigma}_{eq}^{el}\}_a - \hat{\sigma}_{eq}^{el} tr_e\{\hat{H}_s^{el}, A\hat{\sigma}_{eq}^{el}\}_a \\ &= -\sum_\beta \frac{P_\beta}{M_\beta}\frac{\partial \hat{\sigma}_{eq}^{el}}{\partial X_\beta} A \\ &\quad + \frac{1}{2}\sum_\beta \Big(\frac{\partial \hat{H}_s^{el}}{\partial X_\beta}\hat{\sigma}_{eq}^{el} + \hat{\sigma}_{eq}^{el}\frac{\partial \hat{H}_s^{el}}{\partial X_\beta}\Big)\frac{\partial A}{\partial P_\beta} \\ &\quad - \sum_\beta tr_e\Big(\frac{\partial \hat{H}_s^{el}}{\partial X_\beta}\hat{\sigma}_{eq}^{el}\Big)\frac{\partial A}{\partial P_\beta}\hat{\sigma}_{eq}^{el}. \end{aligned} \tag{23}$$

Note that both sides of the above equation are traceless. With this condition, we can solve for $\hat{B}_{el}$ by formally inverting the supermatrix $\hat{\hat{\mathcal{L}}}_{el}$. Plugging the solution back into Eq. (21), we get a Fokker-Planck (FP) equation for pure nuclear motion,

$$\begin{aligned}\frac{\partial}{\partial t}A &= -\sum_\alpha \frac{P_\alpha}{M_\alpha}\frac{\partial A}{\partial X_\alpha} - \sum_\alpha F_\alpha \frac{\partial A}{\partial P_\alpha} \\ &\quad + \sum_{\alpha,\beta}\gamma_{\alpha\beta}\frac{\partial}{\partial P_\alpha}\Big(\frac{P_\beta}{M_\beta}A\Big) + \sum_{\alpha,\beta} D_{\alpha\beta}\frac{\partial^2 A}{\partial P_\alpha \partial P_\beta}. \end{aligned} \tag{24}$$

Here F_α, $\gamma_{\alpha\beta}$, $D_{\alpha\beta}$ are the mean force, friction, and correlation of the random force, respectively,

$$F_\alpha(\mathbf{X}) = -tr_e\Big(\frac{\partial \hat{H}_s^{el}}{\partial X_\alpha}\hat{\sigma}_{eq}^{el}\Big), \tag{25}$$

$$\gamma_{\alpha\beta}(\mathbf{X}) = -tr_e\Big(\frac{\partial \hat{H}_s^{el}}{\partial X_\alpha}\hat{\hat{\mathcal{L}}}_{el}^{-1}\frac{\partial \hat{\sigma}_{eq}^{el}}{\partial X_\beta}\Big), \tag{26}$$

$$\begin{aligned}D_{\alpha\beta}(\mathbf{X}) &= \frac{1}{2}tr_e\Big(\frac{\partial \hat{H}_s^{el}}{\partial X_\alpha}\hat{\hat{\mathcal{L}}}_{el}^{-1}\Big(\frac{\partial \hat{H}_s^{el}}{\partial X_\beta}\hat{\sigma}_{eq}^{el} \\ &\quad + \hat{\sigma}_{eq}^{el}\frac{\partial \hat{H}_s^{el}}{\partial X_\beta} - 2tr_e\Big(\frac{\partial \hat{H}_s^{el}}{\partial X_\beta}\hat{\sigma}_{eq}^{el}\Big)\hat{\sigma}_{eq}^{el}\Big)\Big). \end{aligned} \tag{27}$$

The Langevin equation that corresponds to the FP equation in Eq. (24) is

$$M_\alpha \ddot{X}_\alpha = F_\alpha(\mathbf{X}) - \sum_\beta \gamma_{\alpha\beta}(\mathbf{X})\dot{X}_\beta + \delta F_\alpha(t). \tag{28}$$

Here δF_α is a random force with a correlation function that is Markovian

$$\langle \delta F_\alpha(t)\delta F_\beta(t')\rangle = 2D_{\alpha\beta}(\mathbf{X})\delta(t-t'). \tag{29}$$

Eqs. (24)-(27) are the main results of this paper. There are a few important points to address below.

E. The fluctuation-dissipation theorem

For one electronic bath, if $\hat{H}_s^{el}(\mathbf{X})$ is diagonal at all $\mathbf{X}$ in some fixed diabatic basis, the fluctuation-dissipation theorem is automatically satisfied, i.e., $D_{\alpha\beta}(\mathbf{X}) = kT\gamma_{\alpha\beta}(\mathbf{X})$. To prove this statement, we note that the solution to $\hat{\hat{\mathcal{L}}}_{el}(\mathbf{X})\hat{\sigma}_{eq}^{el}(\mathbf{X}) = 0$ is $\hat{\sigma}_{eq}^{el}(\mathbf{X}) = e^{-\hat{H}_s^{el}(\mathbf{X})/kT}/Z(\mathbf{X})$ (where $Z(\mathbf{X}) \equiv tr_e e^{-\hat{H}_s^{el}(\mathbf{X})/kT}$), no matter whether $\hat{H}_s^{el}$ is diagonal or not (see Appendix A for a proof). If $\hat{H}_s^{el}(\mathbf{X})$ is diagonal, the following equation is also true:

$$\begin{aligned}&\frac{\partial}{\partial X_\beta}e^{-\hat{H}_s^{el}(\mathbf{X})/kT} \\ &\quad = -\frac{kT}{2}\left(\frac{\partial \hat{H}_s^{el}}{\partial X_\beta}e^{-\hat{H}_s^{el}(\mathbf{X})/kT} + e^{-\hat{H}_s^{el}(\mathbf{X})/kT}\frac{\partial \hat{H}_s^{el}}{\partial X_\beta}\right). \end{aligned} \tag{30}$$

The fluctuation-dissipation theorem can then be verified by plugging $\hat{\sigma}_{eq}^{el}(\mathbf{X}) = e^{-\hat{H}_s^{el}(\mathbf{X})/kT}/Z(\mathbf{X})$ into Eqs. (26) and (27) and using Eq. (30). More generally, if $\hat{H}_s^{el}(\mathbf{X})$ is not diagonal, Eq. (30) is correct to order of $\hbar$,[21] such that the fluctuation-dissipation theorem is satisfied to order $\hbar$.

F. Energy conservation and the symmetry of the friction

One question of interest is whether the mean force (Eq. (25)) is conservative or not. While this question is tricky to answer in general,[29] we can show easily that at equilibrium (i.e., in the case of one electronic bath), if the system Hamiltonian is diagonal in some fixed diabatic basis, then the mean force is conservative. To prove this statement, we must show that the curl of the mean force is equal to 0,

$$\frac{\partial F_\alpha}{\partial X_\beta} - \frac{\partial F_\beta}{\partial X_\alpha} = tr_e\Big(\frac{\partial \hat{H}_s^{el}}{\partial X_\beta}\frac{\partial \hat{\sigma}_{eq}^{el}}{\partial X_\alpha}\Big) - tr_e\Big(\frac{\partial \hat{H}_s^{el}}{\partial X_\alpha}\frac{\partial \hat{\sigma}_{eq}^{el}}{\partial X_\beta}\Big) \stackrel{?}{=} 0. \tag{31}$$

As mentioned above, at equilibrium, $\hat{\sigma}_{eq}^{el}(\mathbf{X}) = e^{-\hat{H}_s^{el}(\mathbf{X})/kT}/Z(\mathbf{X})$. Thus, if $\hat{H}_s^{el}$ is diagonal—such that we can apply Eq. (30)—one can easily verify Eq. (31). More generally, the mean force will always be conservative at equilibrium, even if the system Hamiltonian is not diagonal. See the supplementary material for details.

Another question of interest is whether the friction (Eq. (26)) is symmetric in terms of the nuclear coordinates α and β. In general, the exact friction is guaranteed to be symmetric by time-reversal symmetry.[42,43] While our derived friction is not symmetric, for a system Hamiltonian that is diagonal in some fixed basis, there are two cases for which the friction will be symmetric: (i) if we operate in the Redfield regime (where $\Gamma_{mn} \ll kT$) or (ii) if we make the so-called secular approximation. See Sec. III for more details.

III. A MASTER EQUATION BASED ON THE ELECTRONIC ONE PARTICLE REDUCED DENSITY MATRIX (CME-1RDM)

As stated above, Eqs. (24)-(27) are the main results of this paper. That being said, these equations may well appear difficult to interpret because we cannot write down an explicit form for the inverse of the Redfield operator, $\hat{\hat{\mathcal{L}}}_{el}^{-1}$. To that end, using a different approach, we will now derive a second master equation, for which some analytical results can be obtained in the limit that the system Hamiltonian is diagonal in some diabatic basis. By doing so, we will connect our results to

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other results from a well-established non-equilibrium Green's function formalism.[29]

The ansatz is to work directly with the one particle reduced density matrix, rather than the many-body eigenstates of the system. The former approach is less general than the latter approach, but should work well if there are no electron-electron interactions. The reader can safely skip this section if the results are not relevant to his or her research interests and proceed directly to Sec. IV.

We will follow Ref. 44, working with the Hamiltonian

$$\hat{H} = \sum_{mn} h_{mn}\hat{d}_m^+\hat{d}_n + \sum_{km}(V_{km}\hat{c}_k^+\hat{d}_m + \hat{d}_m^+\hat{c}_k) + \sum_k \epsilon_k \hat{c}_k^+\hat{c}_k. \tag{32}$$

The one particle reduced density matrix is

$$\sigma_{mn} = \langle \hat{d}_m^+\hat{d}_n\rangle. \tag{33}$$

With knowledge of the commutators,

$$[\hat{d}_m^+, \hat{H}] = -\sum_a h_{am}\hat{d}_a^+ - \sum_k V_{km}\hat{c}_k^+, \tag{34}$$

$$[\hat{d}_n, \hat{H}] = \sum_a h_{na}\hat{d}_a + \sum_k V_{kn}\hat{c}_k, \tag{35}$$

$$[\hat{c}_k^+, \hat{H}] = -\epsilon_k\hat{c}_k^+ - \sum_a V_{ka}\hat{d}_a^+, \tag{36}$$

$$[\hat{c}_k, \hat{H}] = \epsilon_k\hat{c}_k + \sum_a V_{ka}\hat{d}_a, \tag{37}$$

we can evaluate the EOM for σ_{mn}, $\langle \hat{c}_k^+\hat{d}_n\rangle$ and $\langle \hat{d}_m^+\hat{c}_k\rangle$,

$$\begin{aligned} i\hbar\dot{\sigma}_{mn} &= -\sum_a h_{am}\sigma_{an} + \sum_a \sigma_{ma}h_{na} \\ &\quad - \sum_k V_{km}\langle \hat{c}_k^+\hat{d}_n\rangle + \sum_k V_{kn}\langle \hat{d}_m^+\hat{c}_k\rangle, \end{aligned} \tag{38}$$

$$\begin{aligned} i\hbar\partial_t\langle \hat{c}_k^+\hat{d}_n\rangle &= -\epsilon_k\langle \hat{c}_k^+\hat{d}_n\rangle - \sum_a V_{ka}\sigma_{an} + \sum_a h_{na}\langle \hat{c}_k^+\hat{d}_a\rangle \\ &\quad + \sum_{k'} V_{k'n}\langle \hat{c}_k^+\hat{c}_{k'}\rangle, \end{aligned} \tag{39}$$

$$\begin{aligned} i\hbar\partial_t\langle \hat{d}_m^+\hat{c}_k\rangle &= \epsilon_k\langle \hat{d}_m^+\hat{c}_k\rangle + \sum_a V_{ka}\sigma_{ma} - \sum_a h_{am}\langle \hat{d}_a^+\hat{c}_k\rangle \\ &\quad - \sum_{k'} V_{k'm}\langle \hat{c}_{k'}^+\hat{c}_k\rangle. \end{aligned} \tag{40}$$

To get a closed EOM for σ_{mn}, we approximate $\langle \hat{c}_k^+\hat{c}_{k'}\rangle = f(\epsilon_k)\delta_{k,k'}$, where f is the Fermi function. If we further assume that $\hat{h}$ is diagonal ($h_{mn} = h_{mm}\delta_{mn}$), then the final result can be written explicitly. After a Fourier transformation of Eqs. (39) and (40), we get

$$\begin{aligned} &(\hbar\omega + (\epsilon_k - h_{nn}))\langle \hat{c}_k^+\hat{d}_n\rangle(\omega) \\ &\quad = -\sum_a V_{ka}\sigma_{an}(\omega) + V_{kn}f(\epsilon_k)2\pi\delta(\omega), \end{aligned} \tag{41}$$

$$\begin{aligned} &(\hbar\omega - (\epsilon_k - h_{mm}))\langle \hat{d}_m^+\hat{c}_k\rangle(\omega) \\ &\quad = \sum_a V_{ka}\sigma_{ma}(\omega) - V_{km}f(\epsilon_k)2\pi\delta(\omega). \end{aligned} \tag{42}$$

Plugging the above equations into the Fourier transform of Eq. (38), we find

$$\begin{aligned} \hbar\omega\sigma_{mn}(\omega) &= -(h_{mm} - h_{nn})\sigma_{mn}(\omega) + \sum_{ka} V_{km}V_{ka}\sigma_{an}(\omega)\frac{1}{\hbar\omega + (\epsilon_k - h_{nn}) + i\eta} \\ &\quad + \sum_{ka} V_{kn}V_{ka}\sigma_{ma}(\omega)\frac{1}{\hbar\omega - (\epsilon_k - h_{mm}) + i\eta} \\ &\quad - \sum_k V_{km}V_{kn}2\pi\delta(\omega)f(\epsilon_k)\frac{1}{\hbar\omega + (\epsilon_k - h_{nn}) + i\eta} \\ &\quad - \sum_k V_{km}V_{kn}2\pi\delta(\omega)f(\epsilon_k)\frac{1}{\hbar\omega - (\epsilon_k - h_{mm}) + i\eta}. \end{aligned} \tag{43}$$

Here, η is a positive infinitesimal. In the limit of the wideband approximation, we then arrive at the EOM for σ_{mn} (after a Fourier transform back to real time),

$$\begin{aligned} \dot{\sigma}_{mn} &= \frac{i}{\hbar}(h_{mm} - h_{nn})\sigma_{mn} - \frac{1}{2\hbar}\sum_a \Gamma_{ma}\sigma_{an} \\ &\quad - \frac{1}{2\hbar}\sum_a \Gamma_{an}\sigma_{ma} + \frac{1}{2\hbar}\Gamma_{mn}(f(h_{nn}) + f(h_{mm})). \end{aligned} \tag{44}$$

We will denote Eq. (44) as a CME-1RDM. Equation (44) has a simple equilibrium solution, $\sigma_{mn}^{eq} = f(h_{mm})\delta_{mn}$. We can rewrite the above equation in a matrix form,

$$\dot{\hat{\sigma}} = -\hat{\hat{L}}_C(\hat{\sigma} - \hat{\sigma}^{eq}). \tag{45}$$

Here $\hat{\hat{L}}_C$ can be written explicitly,

$$\begin{aligned} (L_C)_{mnab} &= -\frac{i}{\hbar}(h_{ma}\delta_{nb} - h_{bn}\delta_{ma}) \\ &\quad + \frac{1}{2\hbar}(\Gamma_{ma}\delta_{nb} + \Gamma_{bn}\delta_{ma}). \end{aligned} \tag{46}$$

Or, $\hat{\hat{L}}_C(\cdot) = -\frac{i}{\hbar}[\hat{h}, \cdot] + \frac{1}{2\hbar}[\hat{\Gamma}, \cdot]_+$, where $[\cdot,\cdot]_+$ is an anti-commutator. At this point, if nuclear motion couples with the

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electronic Hamiltonian $\hat{H}$ (Eq. (32)) such that h_{mn} depends on the nuclear position $\mathbf{X}$, the EOM for the nuclei becomes

$$-m_\alpha \ddot{X}_\alpha = \frac{\partial U(\mathbf{X})}{\partial X_\alpha} + \sum_{mn} \frac{\partial h_{mn}(\mathbf{X})}{\partial X_\alpha} \hat{d}_m^+ \hat{d}_n, \tag{47}$$

where $U(\mathbf{X})$ is the free potential of the nuclei. In the spirit of a mean field approximation,[29] we can replace $\hat{d}_m^+ \hat{d}_n$ with its average $\sigma_{mn} = \langle \hat{d}_m^+ \hat{d}_n \rangle$. Furthermore, to first order in the velocity of the nuclear motion, we approximate Eq. (45) as

$$\hat{\sigma} = \hat{\sigma}^{eq} - \sum_\beta \dot{X}_\beta \hat{\hat{L}}_C^{-1} \frac{\partial \hat{\sigma}^{eq}}{\partial X_\beta}. \tag{48}$$

Plugging Eq. (48) into Eq. (47), the first term on the right hand side of Eq. (48) gives a mean force, while the second term gives a velocity ($\dot{X}_\beta$) dependent force with a frictional coefficient $\gamma_{\alpha,\beta}$,

$$\gamma_{\alpha,\beta} = -tr_e\Big(\frac{\partial \hat{h}}{\partial X_\alpha} \hat{\hat{L}}_C^{-1} \frac{\partial \hat{\sigma}^{eq}}{\partial X_\beta}\Big). \tag{49}$$

When there are no electron-electron interactions, Eq. (49) should be identical with Eq. (26); both results arise from second order perturbation theory. In fact, in Appendix B we show that the Redfield operator for the CME-1RDM can be derived from the QCLE-CME.

A. Secular approximation

According to Eq. (49), we must invert a superoperator in order to evaluate the electronic friction (just as found in Eq. (26)); thus, we have not apparently made any progress in gaining intuition. However, in this present case—where we consider the 1-RDM—we can make one further, natural approximation: the secular approximation. In doing so, we assume that only the diagonal elements of $\hat{\sigma}$ can be nonzero. Equation (45) reduces to

$$\dot{\sigma}_{mm} = -\frac{\Gamma_{mm}}{\hbar}(\sigma_{mm} - f(h_{mm})). \tag{50}$$

Similar to the argument above, we find a friction of the form

$$\gamma_{\alpha,\beta} = -\sum_m \frac{\partial h_{mm}}{\partial X_\alpha} \frac{\hbar}{\Gamma_{mm}} \frac{\partial f(h_{mm})}{\partial X_\beta}. \tag{51}$$

B. Symmetry of the friction

Working within a secular approximation, we can easily show that Eq. (51) is symmetric between nuclei α, β. That being said, the more general expressions for friction (Eqs. (26) and (49)) are not totally symmetric. However, we will now show that, in the Redfield limit where $kT \gg \Gamma_{mn}$, symmetry is maintained.

To prove this claim, We first need to evaluate the inverse of the superoperator $\hat{\hat{L}}_C$,

$$\hat{\hat{L}}_C \hat{Y} = \frac{1}{2\hbar}(\hat{\Gamma} - i2\hat{h})\hat{Y} + \frac{1}{2\hbar}\hat{Y}(\hat{\Gamma} + i2\hat{h}) = \frac{\partial \hat{\sigma}^{eq}}{\partial X_\beta}. \tag{52}$$

The above equation has a formal solution,

$$\hat{Y} = \hat{\hat{L}}_C^{-1} \frac{\partial \hat{\sigma}^{eq}}{\partial X_\beta} = 2\hbar \int_0^\infty d\lambda e^{-(\hat{\Gamma} - i2\hat{h})\lambda} \frac{\partial \hat{\sigma}^{eq}}{\partial X_\beta} e^{-(\hat{\Gamma} + i2\hat{h})\lambda}, \tag{53}$$

which can be verified by plugging the above equation into Eq. (52) and integrating by parts. Since $\hat{h}$ is diagonal (in some diabatic basis), with $\hat{\sigma}^{eq} = f(\hat{h})$, we have

$$\frac{\partial \hat{\sigma}^{eq}}{\partial X_\beta} = -\frac{1}{kT} \frac{e^{-\hat{h}/2kT}}{1 + e^{-\hat{h}/kT}} \frac{\partial \hat{h}}{\partial X_\beta} \frac{e^{-\hat{h}/2kT}}{1 + e^{-\hat{h}/kT}}. \tag{54}$$

If we assume that $kT \gg \Gamma_{mn}$ (i.e., the Redfield limit), such that $[\hat{h}/kT, \hat{\Gamma}] \approx 0$, the friction in Eq. (49) can be written as

$$\gamma_{\alpha,\beta} = \frac{2\hbar}{kT} \int_0^\infty d\lambda tr_e \times \Big(\frac{\partial \hat{h}}{\partial X_\alpha} \frac{e^{-(\hat{\Gamma} - i2\hat{h})\lambda - \hat{h}/2kT}}{1 + e^{-\hat{h}/kT}} \frac{\partial \hat{h}}{\partial X_\beta} \frac{e^{-(\hat{\Gamma} + i2\hat{h})\lambda - \hat{h}/2kT}}{1 + e^{-\hat{h}/kT}}\Big). \tag{55}$$

Let us now show that $\gamma_{\alpha,\beta} = \gamma_{\beta,\alpha}$. To simplify the formulae, we denote $\mathcal{U} \equiv \frac{e^{-(\hat{\Gamma} - i2\hat{h})\lambda - \hat{h}/2kT}}{1 + e^{-\hat{h}/kT}}$.[45] We note $\mathcal{U}^+ = \mathcal{U}^*$. Using the cyclic properties of the trace, we find

$$\begin{aligned}
\gamma_{\alpha,\beta}^* &= \frac{2\hbar}{kT} \int_0^\infty d\lambda tr_e\Big(\Big(\frac{\partial \hat{h}}{\partial X_\alpha} \mathcal{U} \frac{\partial \hat{h}}{\partial X_\beta} \mathcal{U}^+\Big)^+\Big) \\
&= \frac{2\hbar}{kT} \int_0^\infty d\lambda tr_e\Big(\mathcal{U} \frac{\partial \hat{h}}{\partial X_\beta} \mathcal{U}^+ \frac{\partial \hat{h}}{\partial X_\alpha}\Big) \\
&= \frac{2\hbar}{kT} \int_0^\infty d\lambda tr_e\Big(\frac{\partial \hat{h}}{\partial X_\alpha} \mathcal{U} \frac{\partial \hat{h}}{\partial X_\beta} \mathcal{U}^+\Big) = \gamma_{\alpha,\beta}
\end{aligned} \tag{56}$$

so that $\gamma_{\alpha\beta}$ is necessarily real. Similarly,

$$\begin{aligned}
\gamma_{\alpha,\beta}^* &= \frac{2\hbar}{kT} \int_0^\infty d\lambda tr_e\Big(\Big(\frac{\partial \hat{h}}{\partial X_\alpha} \mathcal{U} \frac{\partial \hat{h}}{\partial X_\beta} \mathcal{U}^+\Big)^*\Big) \\
&= \frac{2\hbar}{kT} \int_0^\infty d\lambda tr_e\Big(\frac{\partial \hat{h}}{\partial X_\alpha} \mathcal{U}^+ \frac{\partial \hat{h}}{\partial X_\beta} \mathcal{U}\Big) \\
&= \frac{2\hbar}{kT} \int_0^\infty d\lambda tr_e\Big(\frac{\partial \hat{h}}{\partial X_\beta} \mathcal{U} \frac{\partial \hat{h}}{\partial X_\alpha} \mathcal{U}^+\Big) = \gamma_{\beta,\alpha}.
\end{aligned} \tag{57}$$

Thus, we have proven that, in the Redfield limit, our friction is symmetric. This result should hold both for Eq. (49) and, because of the connection established in Appendix B, also for Eq. (26) (the QCLE-CME friction).

IV. RESULTS

Eqs. (26) and (49) are not the first published, many-orbital expressions for electronic friction. For the Hamiltonian in Eqs. (1)-(4), Ref. 29 gives an alternative expression for electronic friction using a non-equilibrium Green's function,

$$\gamma_{\alpha,\beta} = \hbar \int \frac{d\epsilon}{2\pi} tr_e \times \Big(\hat{G}^< \frac{\partial \hat{h}}{\partial X_\alpha} \partial_\epsilon \hat{G}^R \frac{\partial h}{\partial X_\beta} - \hat{G}^< \frac{\partial \hat{h}}{\partial X_\beta} \partial_\epsilon \hat{G}^A \frac{\partial \hat{h}}{\partial X_\alpha}\Big), \tag{58}$$

where $\hat{h}$ is the matrix form of h_{mn} in Eqs. (13) and (32). To evaluate Eq. (58), we need the retarded Green's function $\hat{G}^R$, whose inverse can be written as

$$(G^{R^{-1}})_{mn} = \epsilon\delta_{mn} - h_{mn} + i\Gamma_{mn}/2. \tag{59}$$

For the case of one metal surface, the lesser Green's function is $G_{mn}^< = -i2\mathrm{Im}(G_{mn}^R) f(\epsilon)$, where $f(\epsilon) = \frac{1}{1+\exp(\epsilon/kT)}$ is the Fermi function.

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Let us now compare our results versus Green's function results both analytically and empirically.

A. Analytical comparison

The different frictional expressions can be easily compared in the special case that the system Hamiltonian is diagonal ($h_{mn} = h_{mm}\delta_{mn}$) and we invoke the secular approximation.

Within the secular approximation, we neglect the off-diagonal terms in the Green's function results, so that Eq. (59) can be inverted as (provided h_{mn} is diagonal),

$$(G^R)_{mn} = \frac{1}{\epsilon - h_{mm} + i\Gamma_{mm}/2}\delta_{mn}. \tag{60}$$

The friction (Eq. (58)) can then be evaluated,

$$\gamma_{\alpha,\beta} = -\frac{\hbar}{2}\sum_m \int \frac{d\epsilon}{2\pi}\left(\frac{\Gamma_{mm}}{(\epsilon - h_{mm})^2 + (\Gamma_{mm}/2)^2}\right)^2 \times \partial_\epsilon f(\epsilon)\frac{\partial h_{mm}}{\partial X_\alpha}\frac{\partial h_{mm}}{\partial X_\beta}. \tag{61}$$

In the limit of $kT \gg \Gamma_{mm}$, when we can disregard the effects of broadening, $\Gamma_{mm}\left(\frac{\Gamma_{mm}}{(\epsilon - h_{mm})^2 + (\Gamma_{mm}/2)^2}\right)^2 \to 4\pi\delta(\epsilon - h_{mm})$ and Eq. (61) reduces to Eq. (51).

Note that, for completeness, for the special case of a one-level system, we provide all relevant equations in Appendix C (that also addresses the effect of broadening on the friction).

B. Numerical comparison

An analytical comparison of density matrix approaches versus Green's function approaches is difficult beyond the secular approximation and/or in the case of a nondiagonal Hamiltonian. Thus, we have found numerical comparisons to be very useful.

To compare our results with the Green's function results, we choose a two-level electronic system coupled with a harmonic oscillator

$$\hat{H}_s^{el} = E_1(x)\hat{d}_1^+\hat{d}_1 + E_2(x)\hat{d}_2^+\hat{d}_2 + V(\hat{d}_1^+\hat{d}_2 + \hat{d}_2^+\hat{d}_1) + \frac{1}{2}m\omega^2 x^2 + \frac{p^2}{2m}. \tag{62}$$

This system is subsequently coupled to one metal surface. For the exact form of system-bath couplings, we take the wide-band approximation, such that $\Gamma_{mn} \equiv 2\pi\sum_k V_{km}V_{kn}\delta(\epsilon - \epsilon_k)$ is independent of energy for all electronic orbitals n and m. We investigate our results for two models

1. $E_1(x) = gx\sqrt{2m\omega/\hbar}$, $E_2(x) = 0$, $\Gamma_{11} = \Gamma_{21} = \Gamma_{12} = 0$, $\Gamma_{22} = \Gamma$, $V \neq 0$.
2. $E_1(x) = gx\sqrt{m\omega/2\hbar} - \sqrt{m\omega g^2x^2/2\hbar + \Delta^2}$, $E_2(x) = gx\sqrt{m\omega/2\hbar} + \sqrt{m\omega g^2x^2/2\hbar + \Delta^2}$, $V = 0$, $\Gamma_{11} = \Gamma_{22} = \Gamma$, $\Gamma_{12} = \Gamma_{21} = -\Gamma$.

Note that, for model #2, the system $\hat{H}_s^{el}$ can be diagonalized in a diabatic basis but for model #1, the system $\hat{H}_s^{el}$ is non-diagonal in every diabatic basis. If we want to diagonalize the system Hamiltonian of model #1 in a position dependent adiabatic basis, we would need to introduce derivative couplings and the mathematics would get necessarily more involved. The forms of the supermatrix $\hat{\tilde{\mathcal{L}}}_{bs}^{el}$ for both cases are given in Appendix A.

1. Non-diagonal system Hamiltonian

In Fig. 1, we compare our results (Eq. (26), which we denote as QCLE-CME) with the Green's function results (GF, Eq. (58)) for model #1. For small Γ (Fig. 1(a)), we see good agreement between the two answers. As we leave the Redfield regime (Fig. 1(b), $\Gamma > kT$), the difference between the GF and QCLE-CME results becomes larger, where we now find that usually the QCLE-CME result has sharper dips or peaks. As mentioned above, we are reasonably certain that all differences between the QCLE-CME and GF results in Fig. 1 are due to a lack of broadening in the QCLE-CME.

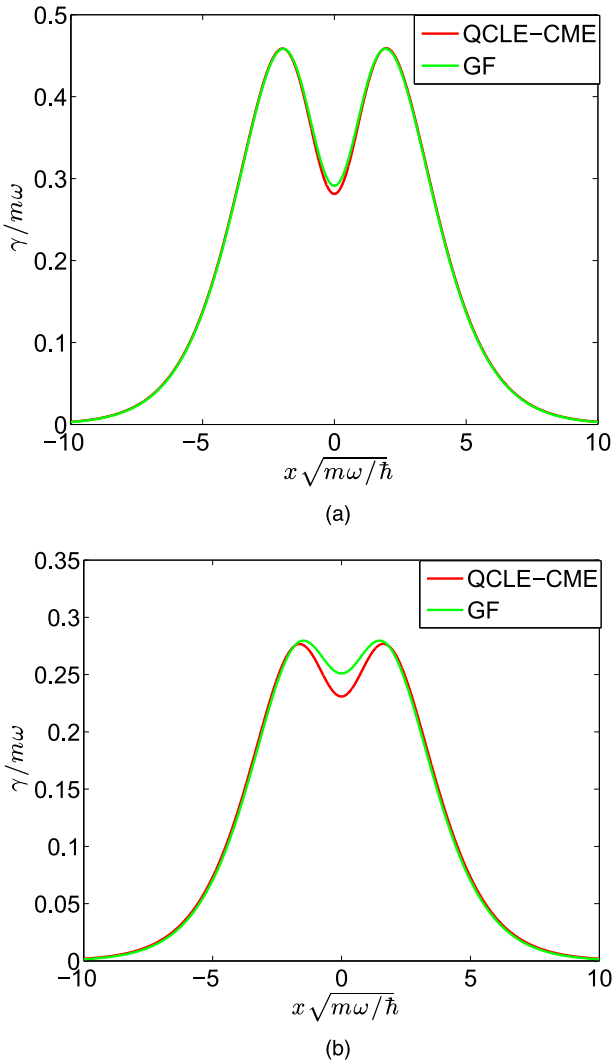


FIG. 1. Electronic friction as a function of x for model #1, with a non-diagonal $\hat{H}_s^{el}$. (a) In the Redfield regime (small Γ), our QCLE-CME result (Eq. (26)) agrees with the Green's function (GF) result (Eq. (58)) very well. (b) For larger Γ, the QCLE-CME and GF results agree less well, where we find that usually the QCLE-CME result has sharper dips or peaks due to a lack of broadening. $kT = 0.01$, $\hbar\omega = 0.003$, $g = 0.0075$, $V = 0.01$. (a) $\Gamma = 0.01$. (b) $\Gamma = 0.02$.

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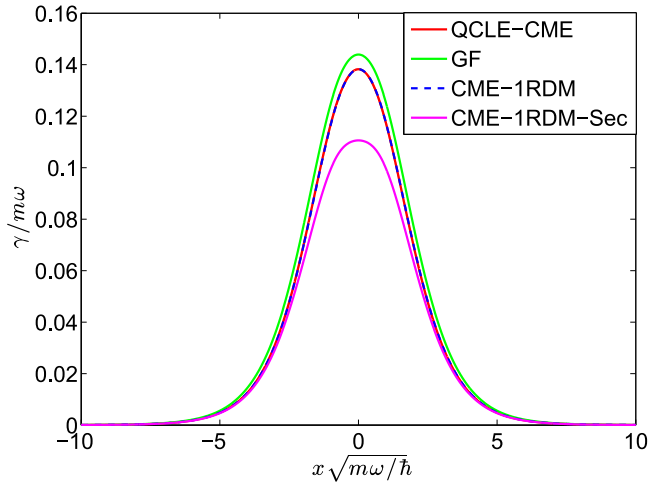


FIG. 2. Electronic friction as a function of x for model #2 where the system Hamiltonian is diagonal. Results from the QCLE-CME (Eq. (26)) and CME-1RDM (Eq. (49)) agree exactly and closely match the Green's function (GF) results (though without broadening). CME-1RDM-Sec results (Eq. (51)) perform less well, highlighting the limitations of the secular approximation, which ignores off-diagonal contributions to the electronic friction (as caused by intramolecular coherence). $kT = 0.01$, $\hbar\omega = 0.003$, $g = 0.0075$, $\Delta = 0.01$, $V = 0$, $\Gamma = 0.01$.

2. Diagonal system Hamiltonian

Results for the diagonal Hamiltonian (model #2) are plotted in Fig. 2. We plot the friction from Green's function (GF, Eq. (58)) theory versus the friction from all of the relevant flavors of density matrix theory: QCLE-CME, CME-1RDM, and CME-1RDM-Sec (i.e., CME-1RDM with the secular approximation, Eq. (51)).

Note the exact agreement between the QCLE-CME and CME-1RDM frictional results, as must be true (see Appendix B). The QCLE-CME/CME-1RDM friction closely approximates the GF result. That being said, notice that when we make the secular approximation, the quality of the result decreases noticeably. The secular approximation performs well only when the energy spacing between the adiabatic levels of the system (ignoring system-bath coupling) is much larger than Γ. This analysis is consistent with the observation that the CME-1RDM results and CME-1RDM-Sec results deviate the most around $x = 0$ where $|E_2(x) - E_1(x)|$ is smallest.

In the end, our QCLE-CME result for the electronic friction in terms of the system eigenstates (Eq. (26)) captures most of the relevant features for many-body friction (excluding broadening). In the near future, we would like to apply this frictional model to a more realistic, *ab initio* Hamiltonian, where we can also investigate the spurious asymmetry of Eq. (26). This work is ongoing.

V. CONCLUSION

We have formed a QCLE-CME hybrid set of equations to describe the electron-nuclear coupled dynamics near metal surfaces. In the adiabatic limit, where electronic transitions are much faster than nuclear motion, we arrive at a Fokker-Planck equation for pure nuclear motion, with friction and random force given explicitly. Our final model of friction mostly agrees with von Oppen's results,[29] provided that level broadening can be disregarded. However, we must emphasize that because our QCLE-CME works naturally in a basis of many-body eigenstates of the system—whereas von Oppen's approach works naturally with a one electron Hamiltonian—differences will arise when electron-electron correlation becomes important. In such a case, we expect the QCLE-CME friction in Eq. (26) will be a better prescription than the CME-1RDM or Green's function friction results. In the future, we hope to investigate these approaches with realistic *ab initio* electronic structure calculations where such electron-electron correlation effects can be explored.

SUPPLEMENTARY MATERIAL

See supplementary material for a proof of energy conservation and a guide for evaluating the Redfield relaxation operator.

ACKNOWLEDGMENTS

This material is based upon work supported by the (U.S.) Air Force Office of Scientific Research (USAFOSR) PECASE award under AFOSR Grant No. FA9950-13-1-0157.

APPENDIX A: REDFIELD OPERATOR IN THE SYSTEM EIGENBASIS

In this appendix, we show how to evaluate Eq. (18) explicitly and computate $\hat{\hat{\mathcal{L}}}^{el}_{bs}$. All manipulations will be at one point in configuration space $\mathbf{X}$, and so we drop all $\mathbf{X}$ dependence for convenience henceforward. We will use the indices N, M to denote electronic eigenstates of $\hat{H}^{el}_s$.

To begin the calculation, we note that (in the interaction picture),

$$\hat{H}^{el}_{Iv}(t) = \sum_{mk} V_{mk} e^{i\hat{H}^{el}_s t/\hbar} \hat{d}^{+}_m e^{-i\hat{H}^{el}_s t/\hbar} \hat{c}_k e^{-i\epsilon_k t/\hbar} + h.c. \tag{A1}$$

When we plug Eq. (A1) into Eq. (18), we will find 8 nonzero terms (4 terms plus their h.c.) when we disentangle the commutators. To be explicit, we show one term

$$\frac{1}{\hbar^2}\int_0^\infty d\tau \sum_{mnk} V_{mk}V_{nk} e^{-i\epsilon_k\tau/\hbar} \hat{d}^{+}_m e^{-i\hat{H}^{el}_s\tau/\hbar} \hat{d}_n e^{i\hat{H}^{el}_s\tau/\hbar} \times (1 - f(\epsilon_k))\hat{\rho}_{el}(t). \tag{A2}$$

Here, we have used $tr_b(\hat{c}_k \hat{c}^{+}_{k'} \hat{\rho}^{eq}_b) = (1 - f(\epsilon_k))\delta_{k,k'}$. To proceed, we must diagonalize the system Hamiltonian, so that we can express the NM matrix element as

$$(U^{+} e^{-i\hat{H}^{el}_s\tau/\hbar} \hat{d}_n e^{i\hat{H}^{el}_s\tau/\hbar} U)_{NM} = (U^{+}\hat{d}_n U)_{NM} e^{-i(\tilde{E}_N - \tilde{E}_M)\tau/\hbar}, \tag{A3}$$

where U and $\tilde{E}_N$ are the eigenvectors and eigenvalues of the system Hamiltonian $\hat{H}^{el}_s$. Then the integral in Eq. (A2) for the NM matrix element becomes

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$$\sum_k V_{mk}V_{nk}\int_0^\infty d\tau(1-f(\epsilon_k))e^{-i\epsilon_k\tau/\hbar} \times\left(U^+e^{-i\hat{H}_s^{el}\tau/\hbar}\hat{d}_n e^{i\hat{H}_s^{el}\tau/\hbar}U\right)_{NM} \quad (A4)$$

$$= \pi\hbar\sum_k V_{mk}V_{nk}(1-f(\epsilon_k)) \times(U^+\hat{d}_nU)_{NM}\delta(\epsilon-\tilde{E}_M+\tilde{E}_N) \quad (A5)$$

$$= \frac{\hbar}{2}\Gamma_{mn}(U^+\hat{d}_nU)_{NM}(1-f(\tilde{E}_M-\tilde{E}_N)). \quad (A6)$$

For convenience, we now define $(\tilde{\mathbb{D}}_n)_{NM}\equiv(U^+\hat{d}_nU)_{NM}(1-f(\tilde{E}_M-\tilde{E}_N))$, so that Eq. (A2) becomes (with this shorthand notation),

$$\sum_{mn}\frac{\Gamma_{mn}}{2\hbar}\hat{d}_m^+U\tilde{\mathbb{D}}_nU^+\hat{\rho}_{el}(t). \quad (A7)$$

The final form for the Redfield operator is

$$\hat{\hat{\mathcal{L}}}_{bs}^{el}\hat{\rho}_{el} = \sum_{mn}\frac{\Gamma_{mn}}{2\hbar}\hat{d}_m^+U\tilde{\mathbb{D}}_nU^+\hat{\rho}_{el}(t) + \sum_{mn}\frac{\Gamma_{mn}}{2\hbar}\hat{d}_mU\mathbb{D}_n^+U^+\hat{\rho}_{el}(t) - \sum_{mn}\frac{\Gamma_{mn}}{2\hbar}\hat{d}_m^+\hat{\rho}_{el}(t)U\mathbb{D}_nU^+ - \sum_{mn}\frac{\Gamma_{mn}}{2\hbar}\hat{d}_m\hat{\rho}_{el}(t)U\tilde{\mathbb{D}}_n^+U^+ + h.c. \quad (A8)$$

In the above equation, we have further defined $(\mathbb{D}_n^+)_{NM}\equiv(U^+\hat{d}_n^+U)_{NM}f(\tilde{E}_N-\tilde{E}_M)$, $(\mathbb{D}_n)_{NM}\equiv(U^+\hat{d}_nU)_{NM}f(\tilde{E}_M-\tilde{E}_N)$, and $(\tilde{\mathbb{D}}_n^+)_{NM}\equiv(U^+\hat{d}_n^+U)_{NM}(1-f(\tilde{E}_N-\tilde{E}_M))$.

1. Equilibrium solution

At this point, we remind the reader that Eq. (A8) has a simple steady state solution to $\hat{\hat{\mathcal{L}}}_{bs}^{el}\hat{\rho}_{el}=0$, namely $\hat{\rho}_{el}=e^{-\hat{H}_s^{el}/kT}/Z$ (where Z is a normalization factor).[46] To prove this statement, we notice that $\hat{\hat{\mathcal{L}}}_{bs}^{el}\hat{\rho}_{el}=0$ is satisfied if we have

$$U\tilde{\mathbb{D}}_nU^+\hat{\rho}_{el} = \hat{\rho}_{el}U\mathbb{D}_nU^+, \quad (A9)$$

$$U\mathbb{D}_n^+U^+\hat{\rho}_{el} = \hat{\rho}_{el}U\tilde{\mathbb{D}}_n^+U^+. \quad (A10)$$

Let us focus on Eq. (A9), which is equivalent to

$$\tilde{\mathbb{D}}_nU^+\hat{\rho}_{el}U = U^+\hat{\rho}_{el}U\mathbb{D}_n. \quad (A11)$$

We can verify that $(U^+\hat{\rho}_{el}U)_{NM}=\delta_{NM}e^{-\tilde{E}_N/kT}/Z$ is the solution to Eq. (A11) by looking at the NM matrix element on both sides of Eq. (A11),

$$(U^+\hat{d}_nU)_{NM}(1-f(\tilde{E}_M-\tilde{E}_N))e^{-\tilde{E}_M/kT} = e^{-\tilde{E}_N/kT}(U^+\hat{d}_nU)_{NM}f(\tilde{E}_M-\tilde{E}_N). \quad (A12)$$

Similarly, Eq. (A10) can be also verified. Thus, $\hat{\rho}_{el}=e^{-\hat{H}_s^{el}/kT}/Z$ is indeed the steady state solution to $\hat{\hat{\mathcal{L}}}_{bs}^{el}\hat{\rho}_{el}=0$. Moreover, it is easy to see that $\hat{\rho}_{el}=e^{-\hat{H}_s^{el}/kT}/Z$ is also the solution to $\hat{\hat{\mathcal{L}}}_{el}\hat{\rho}_{el}=0$, where $\hat{\hat{\mathcal{L}}}_{el}(\cdot)\equiv\hat{\hat{\mathcal{L}}}_{bs}^{el}(\cdot)+\frac{i}{\hbar}[\hat{H}_s^{el},\cdot]$.

2. Case of two level systems

Eq. (A8) is a rather general form of the Redfield operator, which we now apply to the two-level model systems in Sec. IV. In matrix form, the system Hamiltonian is

$$H_s^{el}=\begin{pmatrix}0&&&\\&E_1&V&\\&V&E_2&\\&&&E_1+E_2\end{pmatrix}+\left(\frac{1}{2}m\omega^2x^2+\frac{p^2}{2m}\right)\hat{I}_{el}, \quad (A13)$$

where $\hat{I}_{el}$ is the electronic identity operator. The annihilation operators are

$$d_1=\begin{pmatrix}0&1&0&0\\0&0&0&0\\0&0&0&-1\\0&0&0&0\end{pmatrix}, d_2=\begin{pmatrix}0&0&1&0\\0&0&0&1\\0&0&0&0\\0&0&0&0\end{pmatrix}. \quad (A14)$$

After diagonalizing the system, the eigenvalues of H_s^{el} are denoted as $\tilde{E}_N$, $N=1,\ldots,4$, and the eigenvectors are

$$U=\begin{pmatrix}1&&&\\&\cos\theta&\sin\theta&\\&-\sin\theta&\cos\theta&\\&&&1\end{pmatrix}. \quad (A15)$$

Using Eqs. (A8)-(A15), the Redfield operator can be easily evaluated (we will leave details to the supplementary material). For simplicity, we will use the notation $f_{NM}\equiv f(\tilde{E}_N-\tilde{E}_M)$.

For model #1 in Sec. IV, we find

$$-(\mathcal{L}_{bs}^{el}\rho_{el})_{11} = -\frac{\Gamma}{\hbar}(\sin^2\theta f_{21}+\cos^2\theta f_{31})\rho_{11}^{el} + \frac{\Gamma}{\hbar}(\sin^2\theta f_{12}+\cos^2\theta f_{13})\rho_{33}^{el} + \frac{\Gamma}{2\hbar}\sin\theta\cos\theta(f_{13}-f_{12}) \times(\rho_{32}^{el}+\rho_{23}^{el}), \quad (A16)$$

$$(\mathcal{L}_{bs}^{el}\rho_{el})_{33} = -(\mathcal{L}_{bs}^{el}\rho_{el})_{11}, \quad (A17)$$

$$-(\mathcal{L}_{bs}^{el}\rho_{el})_{22} = -\frac{\Gamma}{\hbar}(\cos^2\theta f_{42}+\sin^2\theta f_{43})\rho_{22}^{el} + \frac{\Gamma}{\hbar}(\cos^2\theta f_{24}+\sin^2\theta f_{34})\rho_{44}^{el} - \frac{\Gamma}{2\hbar}\sin\theta\cos\theta(f_{43}-f_{42}) \times(\rho_{32}^{el}+\rho_{23}^{el}), \quad (A18)$$

$$(\mathcal{L}_{bs}^{el}\rho_{el})_{44} = -(\mathcal{L}_{bs}^{el}\rho_{el})_{22}. \quad (A19)$$

For the coherence term, we find

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$$-(\mathcal{L}_{bs}^{el}\rho_{el})_{23} = \frac{\Gamma}{2\hbar}\sin\theta\cos\theta\Big((f_{31}-f_{21})\rho_{11}^{el} + (f_{34}-f_{24})\rho_{44}^{el} - (f_{43}-f_{42})\rho_{33}^{el} - (f_{13}-f_{12})\rho_{22}^{el}\Big) - \frac{\Gamma}{2\hbar}\Big(\sin^2\theta f_{12} + \cos^2\theta f_{13} + \cos^2\theta f_{42} + \sin^2\theta f_{43}\Big)\rho_{23}^{el} \tag{A20}$$

and $(\mathcal{L}_{bs}^{el}\rho_{el})_{32} = (\mathcal{L}_{bs}^{el}\rho_{el})_{23}^{*}$.

For model #2, where the system Hamiltonian is already diagonal, the operator $\hat{\hat{\mathcal{L}}}_{bs}^{el}$ can be written as

$$\begin{aligned}
-(\mathcal{L}_{bs}^{el}\rho_{el})_{11} &= -(\frac{\Gamma_{11}}{\hbar}f_{21} + \frac{\Gamma_{22}}{\hbar}f_{31})\rho_{11}^{el} + \frac{\Gamma_{11}}{\hbar}f_{12}\rho_{22}^{el} + \frac{\Gamma_{22}}{\hbar}f_{13}\rho_{33}^{el} + \frac{\Gamma_{12}}{2\hbar}(f_{12}+f_{13})(\rho_{32}^{el}+\rho_{23}^{el}),\\
-(\mathcal{L}_{bs}^{el}\rho_{el})_{22} &= -(\frac{\Gamma_{11}}{\hbar}f_{12} + \frac{\Gamma_{22}}{\hbar}f_{42})\rho_{22}^{el} + \frac{\Gamma_{11}}{\hbar}f_{21}\rho_{11}^{el} + \frac{\Gamma_{22}}{\hbar}f_{24}\rho_{44}^{el} - \frac{\Gamma_{12}}{2\hbar}(f_{13}-f_{43})(\rho_{32}^{el}+\rho_{23}^{el}),\\
-(\mathcal{L}_{bs}^{el}\rho_{el})_{33} &= -(\frac{\Gamma_{11}}{\hbar}f_{43} + \frac{\Gamma_{22}}{\hbar}f_{13})\rho_{33}^{el} + \frac{\Gamma_{11}}{\hbar}f_{34}\rho_{44}^{el} + \frac{\Gamma_{22}}{\hbar}f_{31}\rho_{11}^{el} - \frac{\Gamma_{12}}{2\hbar}(f_{12}-f_{42})(\rho_{32}^{el}+\rho_{23}^{el}),\\
-(\mathcal{L}_{bs}^{el}\rho_{el})_{44} &= -(\frac{\Gamma_{11}}{\hbar}f_{34} + \frac{\Gamma_{22}}{\hbar}f_{24})\rho_{44}^{el} + \frac{\Gamma_{11}}{\hbar}f_{43}\rho_{33}^{el} + \frac{\Gamma_{22}}{\hbar}f_{42}\rho_{22}^{el} - \frac{\Gamma_{12}}{2\hbar}(f_{42}+f_{43})(\rho_{32}^{el}+\rho_{23}^{el}).
\end{aligned} \tag{A21}$$

The coherence term is

$$-(\mathcal{L}_{bs}^{el}\rho_{el})_{23} = \frac{\Gamma_{12}}{2\hbar}\Big((f_{31}+f_{21})\rho_{11}^{el} - (f_{12}-f_{42})\rho_{22}^{el} - (f_{13}-f_{43})\rho_{33}^{el} - (f_{24}+f_{34})\rho_{44}^{el}\Big) - \frac{1}{2\hbar}\Big(\Gamma_{11}f_{12} + \Gamma_{22}f_{13} + \Gamma_{22}f_{42} + \Gamma_{11}f_{43}\Big)\rho_{23}^{el}. \tag{A22}$$

Again, $(\mathcal{L}_{bs}^{el}\rho_{el})_{32} = (\mathcal{L}_{bs}^{el}\rho_{el})_{23}^{*}$.

APPENDIX B: DERIVING THE CME-1RDM FROM THE QCLE-CME

Let us now show that if the system Hamiltonian is diagonal, the QCLE-CME (Eq. (19)) can be mapped to the CME-1RDM (Eq. (44)). Without nuclear motion, the QCLE-CME (Eq. (19)) reduces to

$$\frac{\partial}{\partial t}\hat{\rho}_{el} = -\frac{i}{\hbar}[\hat{H}_s^{el}, \hat{\rho}_{el}] - \hat{\hat{\mathcal{L}}}_{bs}^{el}\hat{\rho}_{el}, \tag{B1}$$

where $\hat{\hat{\mathcal{L}}}_{bs}^{el}$ is given in Eq. (A8). If the system Hamiltonian $\hat{H}_s^{el}$ is diagonal, Eq. (A8) becomes

$$\begin{aligned}
\hat{\hat{\mathcal{L}}}_{bs}^{el}\hat{\rho}_{el} = &\sum_{mn}\frac{\Gamma_{mn}}{2\hbar}\hat{d}_m^{+}\hat{d}_n(1-f(h_{nn}))\hat{\rho}_{el}\\
&+\sum_{mn}\frac{\Gamma_{mn}}{2\hbar}\hat{d}_m\hat{d}_n^{+}f(h_{nn})\hat{\rho}_{el}\\
&-\sum_{mn}\frac{\Gamma_{mn}}{2\hbar}\hat{d}_m^{+}\hat{\rho}_{el}\hat{d}_n f(h_{nn})\\
&-\sum_{mn}\frac{\Gamma_{mn}}{2\hbar}\hat{d}_m\hat{\rho}_{el}\hat{d}_n^{+}(1-f(h_{nn})) + h.c.
\end{aligned} \tag{B2}$$

In Sec. III, we defined σ_{mn} in the CME-1RDM as $\sigma_{mn} = \langle\hat{d}_m^{+}\hat{d}_n\rangle = Tr_e(\hat{\rho}_{el}\hat{d}_m^{+}\hat{d}_n)$. Of course, $\hat{\sigma}$ is Hermitian, because $\sigma_{mn}^{*} = Tr_e(\hat{\rho}_{el}\hat{d}_m^{+}\hat{d}_n)^{+} = Tr_e(\hat{d}_n^{+}\hat{d}_m\hat{\rho}_{el}) = Tr_e(\hat{\rho}_{el}\hat{d}_n^{+}\hat{d}_m) = \sigma_{nm}$.

To derive the CME-1RDM (Eq. (44)), we multiply Eq. (B1) by $\hat{d}_m^{+}\hat{d}_n$ on the right hand side and take the trace over the electronic DoFs,

$$\frac{\partial}{\partial t}Tr_e(\hat{\rho}_{el}\hat{d}_m^{+}\hat{d}_n) = -\frac{i}{\hbar}Tr_e([\hat{H}_s^{el},\hat{\rho}_{el}]\hat{d}_m^{+}\hat{d}_n) - Tr_e((\hat{\hat{\mathcal{L}}}_{bs}^{el}\hat{\rho}_{el})\hat{d}_m^{+}\hat{d}_n). \tag{B3}$$

To be this explicit, let us first evaluate the commutator in Eq. (B3),

$$\begin{aligned}
&Tr_e\big((\hat{H}_s^{el}\hat{\rho}_{el} - \hat{\rho}_{el}\hat{H}_s^{el})\hat{d}_m^{+}\hat{d}_n\big)\\
&= \sum_{ab}h_{ab}\big(Tr_e(\hat{d}_a^{+}\hat{d}_b\hat{\rho}_{el}\hat{d}_m^{+}\hat{d}_n) - Tr_e(\hat{\rho}_{el}\hat{d}_a^{+}\hat{d}_b\hat{d}_m^{+}\hat{d}_n)\big)\\
&= \sum_{ab}h_{ab}(\langle\hat{d}_m^{+}\hat{d}_n\hat{d}_a^{+}\hat{d}_b\rangle - \langle\hat{d}_a^{+}\hat{d}_b\hat{d}_m^{+}\hat{d}_n\rangle).
\end{aligned} \tag{B4}$$

Because the Hamiltonian is quadratic, Wick's theorem can be applied

$$\begin{aligned}
\langle\hat{d}_m^{+}\hat{d}_n\hat{d}_a^{+}\hat{d}_b\rangle &= \langle\hat{d}_m^{+}\hat{d}_n\rangle\langle\hat{d}_a^{+}\hat{d}_b\rangle + \langle\hat{d}_m^{+}\hat{d}_b\rangle\langle\hat{d}_n\hat{d}_a^{+}\rangle\\
&= \sigma_{mn}\sigma_{ab} + \sigma_{mb}(\delta_{an}-\sigma_{an})
\end{aligned} \tag{B5}$$

and

$$\langle\hat{d}_a^{+}\hat{d}_b\hat{d}_m^{+}\hat{d}_n\rangle = \sigma_{ab}\sigma_{mn} + \sigma_{an}(\delta_{mb}-\sigma_{mb}). \tag{B6}$$

Thus, the commutator in Eq. (B3) finally becomes

$$\frac{i}{\hbar}Tr_e([\hat{H}_s^{el},\hat{\rho}_{el}]\hat{d}_m^{+}\hat{d}_n) = \frac{i}{\hbar}\sum_a(\sigma_{ma}h_{an} - h_{ma}\sigma_{an}). \tag{B7}$$

Here, we have used the symmetry that $h_{mn} = h_{nm}$.

To evaluate the third term in Eq. (B3), we first rewrite $\hat{\hat{\mathcal{L}}}_{bs}^{el}\hat{\rho}_{el} = \hat{\hat{\mathcal{L}}}_1\hat{\rho}_{el} + (\hat{\hat{\mathcal{L}}}_1\hat{\rho}_{el})^{+}$, where $\hat{\hat{\mathcal{L}}}_1\hat{\rho}_{el}$ represents the first 4 terms on the right hand side of Eq. (B2), and $(\hat{\hat{\mathcal{L}}}_1\hat{\rho}_{el})^{+}$ is the Hermitian conjugate of $\hat{\hat{\mathcal{L}}}_1\hat{\rho}_{el}$. Using Wick's theorem again, one can show that

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$$Tr_e\big((\hat{\hat{\mathcal{L}}}_1\hat{\rho}_{el})\hat{d}_m^+\hat{d}_n\big) = \sum_{ab}\frac{\Gamma_{ab}}{2\hbar}\big(\delta_{an}\sigma_{mb} - \delta_{an}\delta_{mb}f(h_{bb}) + \sigma_{an}\delta_{mb}f(h_{bb}) - \sigma_{ma}\delta_{bn}f(h_{bb}) + \sigma_{ma}\sigma_{bn} - \sigma_{an}\sigma_{mb}\big)$$
$$+ \sum_{ab}\sigma_{mn}(\sigma_{ab} - \sigma_{ba})(1 - f(h_{bb})) + \sigma_{mn}(\sigma_{ab} - \sigma_{ba})f(h_{bb}). \tag{B8}$$

Using the properties of the trace, we know that $Tr_e\big((\hat{\hat{\mathcal{L}}}_1\hat{\rho}_{el})^+\hat{d}_m^+\hat{d}_n\big) = \Big(Tr_e\big((\hat{\hat{\mathcal{L}}}_1\hat{\rho}_{el})\hat{d}_n^+\hat{d}_m\big)\Big)^*$, and thus

$$Tr_e\big((\hat{\hat{\mathcal{L}}}_1\hat{\rho}_{el})^+\hat{d}_m^+\hat{d}_n\big) = \sum_{ab}\frac{\Gamma_{ab}}{2\hbar}\big(\delta_{am}\sigma_{bn} - \delta_{am}\delta_{nb}f(h_{bb}) + \sigma_{ma}\delta_{bn}f(h_{bb}) - \sigma_{an}\delta_{mb}f(h_{bb}) + \sigma_{an}\sigma_{mb} - \sigma_{ma}\sigma_{bn}\big)$$
$$+ \sum_{ab}\sigma_{mn}(\sigma_{ba} - \sigma_{ab})(1 - f(h_{bb})) + \sigma_{mn}(\sigma_{ba} - \sigma_{ab})f(h_{bb}). \tag{B9}$$

Above, we have used the fact that $\sigma^*_{mn} = \sigma_{nm}$ and the fact that Γ_{mn} is real.

Eventually, the third term in Eq. (B3) becomes (with $\Gamma_{mn} = \Gamma_{nm}$),

$$Tr_e\big((\hat{\hat{\mathcal{L}}}^{el}_{bs}\hat{\rho}_{el})\hat{d}_m^+\hat{d}_n\big) = \frac{1}{2\hbar}\sum_a\Gamma_{ma}\sigma_{an} + \frac{1}{2\hbar}\sum_a\Gamma_{an}\sigma_{ma}$$
$$- \frac{1}{2\hbar}\Gamma_{mn}(f(h_{nn}) + f(h_{mm})). \tag{B10}$$

Plugging Eqs. (B10) and (B7) into Eq. (B3), one arrives at the CME-1RDM (Eq. (44)).

APPENDIX C: ONE-LEVEL CASE

For a one-orbital system Hamiltonian, all of the results above are easily quantified and were reported in Ref. 35. The system Hamiltonian is

$$\hat{H}_s^{el} = h(\mathbf{X})\hat{d}^+\hat{d} + U(\mathbf{X}) + \sum_\alpha\frac{P_\alpha^2}{2m_\alpha}. \tag{C1}$$

Using Eq. (19), we can show that the QCLE-CME reduces to

$$\frac{\partial\rho_0^{el}}{\partial t} = -\sum_\alpha\frac{P_\alpha}{m_\alpha}\frac{\partial\rho_0^{el}}{\partial X_\alpha} + \sum_\alpha\frac{\partial U(\mathbf{X})}{\partial X_\alpha}\frac{\partial\rho_0^{el}}{\partial P_\alpha}$$
$$- \frac{\Gamma}{\hbar}f\big(h(\mathbf{X})\big)\rho_0^{el} + \frac{\Gamma}{\hbar}\Big(1 - f\big(h(\mathbf{X})\big)\Big)\rho_1^{el}, \tag{C2}$$
$$\frac{\partial\rho_1^{el}}{\partial t} = -\sum_\alpha\frac{P_\alpha}{m_\alpha}\frac{\partial\rho_1^{el}}{\partial X_\alpha} + \sum_\alpha\frac{\partial U(\mathbf{X}) + h(\mathbf{X})}{\partial X_\alpha}\frac{\partial\rho_1^{el}}{\partial P_\alpha}$$
$$+ \frac{\Gamma}{\hbar}f\big(h(\mathbf{X})\big)\rho_0^{el} - \frac{\Gamma}{\hbar}\Big(1 - f\big(h(\mathbf{X})\big)\Big)\rho_1^{el}. \tag{C3}$$

The CME-1RDM/CME-1RDM-Sec (Eqs. (44) and (50)) equations of motion are

$$\frac{\partial\sigma_1}{\partial t} = \frac{\Gamma}{\hbar}\Big(f\big(h(\mathbf{X})\big) - \sigma_1\Big). \tag{C4}$$

All three CMEs give the same friction,

$$\gamma_{\alpha,\beta} = \frac{1}{kT}\frac{\hbar}{\Gamma}f\big(h(\mathbf{X})\big)\Big(1 - f\big(h(\mathbf{X})\big)\Big)\frac{\partial h(\mathbf{X})}{\partial X_\alpha}\frac{\partial h(\mathbf{X})}{\partial X_\beta}. \tag{C5}$$

The Green's function (Eq. (58)) gives a broadened result

$$\gamma_{\alpha,\beta} = \frac{\hbar}{2}\int\frac{d\epsilon}{2\pi}\left(\frac{\Gamma}{(\epsilon - h(\mathbf{X}))^2 + (\Gamma/2)^2}\right)^2$$
$$\times\frac{f(\epsilon)\big(1 - f(\epsilon)\big)}{kT}\frac{\partial h(\mathbf{X})}{\partial X_\alpha}\frac{\partial h(\mathbf{X})}{\partial X_\beta}. \tag{C6}$$

In the limit of $kT \gg \Gamma$, when we can disregard the effects of broadening, $\Gamma\left(\frac{\Gamma}{(\epsilon - h(\mathbf{X}))^2 + (\Gamma/2)^2}\right)^2 \to 4\pi\delta\big(\epsilon - h(\mathbf{X})\big)$, and Eq. (C6) reduces to Eq. (C5).

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