

Born-Oppenheimer Dynamics, Electronic Friction, and the Inclusion of Electron-Electron Interactions

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(Received 13 March 2017; revised manuscript received 4 May 2017; published 25 July 2017)

We present a universal expression for the electronic friction as felt by a set of classical nuclear degrees of freedom (DOFs) coupled to a manifold of quantum electronic DOFs; no assumptions are made regarding the nature of the electronic Hamiltonian and electron-electron repulsions are allowed. Our derivation is based on a quantum-classical Liouville equation for the coupled electronic-nuclear motion, followed by an adiabatic approximation whereby electronic transitions are assumed to equilibrate faster than nuclear movement. The resulting form of friction is completely general, but does reduce to previously published expressions for the quadratic Hamiltonian (i.e., Hamiltonians without electronic correlation). At equilibrium, the second fluctuation-dissipation theorem is satisfied and the frictional matrix is symmetric. To demonstrate the importance of electron-electron correlation, we study electronic friction within the Anderson-Holstein model, where a proper treatment of electron-electron interactions shows signatures of a Kondo resonance and a mean-field treatment is completely inadequate.

DOI: 10.1103/PhysRevLett.119.046001

Introduction.—The Born-Oppenheimer (BO) approximation is probably the most important framework underlying modern physics and chemistry. According to the BO approximation, for a system of nuclei and electrons, we split up the total Hamiltonian into the nuclear kinetic energy (\hat{T}_{nuc}) and the electronic Hamiltonian \hat{H} :

$$\hat{H}_{\text{tot}} = \hat{T}_{\text{nuc}} + \hat{H}, \quad (1)$$

$$\hat{H} = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{nn} + \hat{V}_{en}. \quad (2)$$

The electronic Hamiltonian \hat{H} includes the electronic kinetic energy \hat{T}_e , electron-electron repulsion (\hat{V}_{ee}), nucleus-nucleus repulsion (\hat{V}_{nn}), and nucleus-electron attraction (\hat{V}_{en}). According to the BO approximation, we diagonalize \hat{H} and propagate all nuclear motion along a single eigenvalue of \hat{H} , which is called an adiabatic state; for a large system in the condensed phase, that special state is usually chosen to be the ground state.

When applying the BO approximation, one must use caution because the BO approximation is strictly valid only when nuclear motion is infinitesimally slow, and there are very well known instances where the BO approximation breaks down; see, e.g., the recent work of Wodtke on vibrational relaxation and electron transfer at metal surfaces [1,2]. Furthermore, nonadiabatic effects in molecular electronics are known to account for a huge number of interesting phenomena including heating [3,4], instability [5,6], and inelastic scattering effects [7,8]. Thus, for many experiments, theory must go beyond the BO approximation.

The goal of the present Letter is to show that, each and every time one invokes the BO approximation in the condensed phase—provided there is a continuous manifold of electronic states that relax quickly—there is a single,

unique Fokker-Planck equation guiding the nuclear dynamics [9]. In other words, if one is considering a system with a manifold of electronic states and one wishes to treat the nuclei classically, BO dynamics should always be propagated with a well-defined frictional damping term and corresponding random force. The universal expressions for such a friction and random force are presented below and should be applicable to many dynamical scenarios: e.g., nuclei scattering off metal surfaces [10], atoms vibrating within metal surfaces [11], molecules relaxing when tethered to photoexcited metals [12], and molecules stretching and contracting when experiencing a current (and sitting between two metal contacts) [13,14].

Previous results.—The notion that the BO approximation can sometimes lead to friction is not new. In particular, such a friction was identified long ago in the context of molecular motion at metal surfaces, where a manifold of electronic states is clearly present and can lead to so-called “electronic friction.”

One early derivation of electronic friction is due to Head-Gordon and Tully (HGT) [15,16], who followed the dynamics of electrons and nuclei with Ehrenfest dynamics. At zero temperature, and without any electron-electron interactions in the Hamiltonian, they derived the following functional form for the electronic friction:

$$\gamma_{\alpha\nu} = \pi\hbar \sum_{pq} \langle \phi_p | \partial_\alpha \hat{V}_{\text{SCF}} | \phi_q \rangle \langle \phi_q | \partial_\nu \hat{V}_{\text{SCF}} | \phi_p \rangle \times \delta(\epsilon_F - \epsilon_q) \delta(\epsilon_F - \epsilon_p). \quad (3)$$

Here, ϵ_p and ϕ_p are, respectively, the energies and orbitals that diagonalize \hat{V}_{SCF} , the one-electron self-consistent

potential. ϵ_F is the Fermi level, and the α (or ν) indices label the nuclear degrees of freedom (DOFs). To date, this mean-field form of electronic friction has been applied to many systems using *ab initio* electronic structure theory (e.g., density-functional theory) [17–23], and Langevin dynamics on a metal surface with density-functional theory potentials has become a standard tool.

We emphasize, however, that Eq. (3) is based on the assumption of independent (either free or mean-field) electrons at equilibrium (i.e., with only one metallic lead). That being said, this form for electronic friction is consistent with the one-dimensional rates for vibrational relaxation previously published by Persson and Hellsging [24,25] and others [26,27]. Several other research groups have also identified the same effective friction tensor [28] using different methodologies, some using influence functionals [29] and some using nonequilibrium Green's functions [30,31]. The effects of non-Condon terms have also been considered [32–34] at finite temperature.

More recently, von Oppen and co-workers have provided an explicit form for the electronic friction using a non-equilibrium Green's function and scattering matrix approach [35] plus an explicit adiabatic expansion in terms of nuclear velocity. The resulting expression is valid both in and out of equilibrium, e.g., for a molecule sitting between two metals with a current running through it. However, again one must assume either a quadratic Hamiltonian without electron-electron repulsion [35] or a mean-field electronic Hamiltonian [36]. (In a forthcoming article, we will show that the von Oppen and HGT expressions are identical at equilibrium [37].)

In the end, many distinct approaches for electronic friction can be found in the literature, most assuming electrons at equilibrium and almost all assuming noninteracting electrons. However, for a realistic description of molecular electronic structure, even if we ignore the effects of an external voltage, it is well known that one cannot waive away electron-electron interactions [38]. Despite decades of work on electronic friction, we believe the most general expression for electronic friction (that includes electron-electron correlation) arguably still belongs to Suhl and co-workers [39]. In Ref. [39], the authors conjectured (without proof) a form for electronic friction that does actually include electron-electron correlation (see below). A few years ago, Daligault and Mozyrsky [40] successfully derived Suhl's conjecture at equilibrium with a proper random force for the first time, although they did not investigate electron-electron interactions explicitly. Most importantly, we emphasize that Refs. [39,40] are limited to an electronic system in equilibrium.

Outline.—Given (i) how many important effects break the BO approximation, (ii) how little attention has been paid to the effects of electron-electron correlation on the friction tensor [41–43], and (iii) how many experiments routinely apply voltages to metals with molecules nearby, the goal of the present Letter is to derive one universal

expression for electronic friction (with a random force) that is valid both with and without electron-electron interactions and in and out of equilibrium. We will also show that this universal friction reduces to the HGT model for the case of a quadratic Hamiltonian (i.e., free electrons) at equilibrium. At equilibrium, our final expression matches Suhl's expression [39,40] and can be understood easily through the lens of linear response and correlation functions. However, we emphasize that, in contrast with Refs. [39,40], our derived Fokker-Planck equation is valid out of equilibrium so that the effects of nonequilibrium initial conditions can be analyzed. We will show that the second fluctuation-dissipation theorem is satisfied only at equilibrium.

Lastly, to demonstrate just why electron-electron interactions are so important for nonadiabatic effects, we will study the electronic friction tensor for the Anderson-Holstein model in the limit of reasonably large U . Here, we will show that a mean-field treatment of electron-electron interactions [as in Eq. (3)] can yield a qualitatively incorrect picture of electronic friction. Given the current push to extend correlated electronic structure methods (beyond mean-field theory) to extended systems [44,45], the present Letter should be immediately useful for describing coupled nuclear-electron motion in the condensed phase.

Theory.—Consider the very general Hamiltonian in Eqs. (1) and (2) and let us make a temperature-dependent BO approximation, whereby we assume that the nuclei are propagated along a Boltzmann average of the Born-Oppenheimer adiabatic surfaces:

$$F_\alpha = -\text{tr}_e(\partial_\alpha \hat{H} \hat{\rho}_{ss}). \quad (4)$$

Here, $\hat{\rho}_{ss}$ is a steady-state electronic density matrix. At equilibrium and in the limit of zero temperature, $\hat{\rho}_{ss} = |g\rangle\langle g|$ and the force F_α is simply the ground-state force, which is the more standard BO approximation. tr_e implies tracing over all electronic DOFs.

As shown in Sec. I of the Supplemental Material [46], starting with the quantum-classical Liouville equation [47,48] and assuming that electronic motion is much faster than nuclear motion, we derive a Fokker-Planck equation for the nuclear motion in the same spirit as a Mori-Zwanzig projection [49–54]. We denote the nuclear phase space density as $\mathcal{A}(\mathbf{R}, \mathbf{P})$. The explicit Fokker-Planck equation reads

$$\begin{aligned} \partial_t \mathcal{A} = & -\sum_\alpha \frac{P_\alpha}{m_\alpha} \partial_\alpha \mathcal{A} - \sum_\alpha F_\alpha \frac{\partial \mathcal{A}}{\partial P_\alpha} \\ & + \sum_{\alpha\nu} \gamma_{\alpha\nu} \frac{\partial}{\partial P_\alpha} \left(\frac{P_\nu}{m_\nu} \mathcal{A} \right) + \sum_{\alpha\nu} \bar{D}_{\alpha\nu}^s \frac{\partial^2 \mathcal{A}}{\partial P_\alpha \partial P_\nu}. \end{aligned} \quad (5)$$

Thus, all BO trajectories should be Langevin dynamics with an electronic friction and a random force:

$$-m_\alpha \ddot{R}_\alpha = -F_\alpha + \sum_\nu \gamma_{\alpha\nu} \dot{R}_\nu - \zeta_\alpha. \quad (6)$$

The electronic friction has the following simple form in the time domain (expressed in terms of correlation functions)

$$\gamma_{\alpha\nu} = - \int_0^\infty dt \text{tr}_e (\partial_\alpha \hat{H} e^{-i\hat{H}t/\hbar} \partial_\nu \hat{\rho}_{ss} e^{i\hat{H}t/\hbar}) \quad (7)$$

or the following form in the energy domain (expressed in terms of Green's functions)

$$\gamma_{\alpha\nu} = -\hbar \int_{-\infty}^\infty \frac{d\epsilon}{2\pi} \text{tr}_e (\partial_\alpha \hat{H} \hat{G}^R(\epsilon) \partial_\nu \hat{\rho}_{ss} \hat{G}^A(\epsilon)). \quad (8)$$

Here, we have defined the many-body (as opposed to one-body) retarded and advanced Green's functions $\hat{G}^{R/A}(\epsilon) = (\epsilon - \hat{H} \pm i\eta)^{-1}$. These expressions prove that the friction must always be real, $\gamma_{\alpha\nu} = \gamma_{\alpha\nu}^\dagger$.

For the random force, at steady state and in the Markovian limit, we find

$$\begin{aligned} \bar{D}_{\alpha\nu}^S &= \frac{1}{2} \int_0^\infty dt \text{tr}_e (e^{i\hat{H}t/\hbar} \delta \hat{F}_\alpha e^{-i\hat{H}t/\hbar} (\delta \hat{F}_\nu \hat{\rho}_{ss} + \hat{\rho}_{ss} \delta \hat{F}_\nu)), \\ \delta \hat{F}_\alpha &\equiv -\partial_\alpha \hat{H} + \text{tr}_e (\partial_\alpha \hat{H} \hat{\rho}_{ss}) \end{aligned} \quad (9)$$

so that

$$\frac{1}{2} [\langle \zeta_\alpha(t) \zeta_\nu(t') \rangle + \langle \zeta_\nu(t) \zeta_\alpha(t') \rangle] \equiv \bar{D}_{\alpha\nu}^S \delta(t-t'). \quad (10)$$

Note $\bar{D}_{\alpha\nu}^S$ is always real and symmetric. Here, we assume that the electronic Hamiltonian \hat{H} is real valued.

Equations (7)–(10) are completely general: they express the friction and random force that correspond to the BO approximation, in or out of equilibrium. Note that Eqs. (7)–(9) require taking a full electronic trace, whereas Eq. (3) is expressed in terms of single electronic orbitals. In Sec. V of the Supplemental Material [46], we prove that Eq. (7) in fact reduces to Tully's expression (3) at equilibrium if there are no electron-electron interactions. At this point, there is no simple relationship between $\gamma_{\alpha\nu}$ and $\bar{D}_{\alpha\nu}^S$.

Equilibrium, the second fluctuation-dissipation theorem, and the symmetry of the friction.—At equilibrium, the steady-state electronic density matrix is $\hat{\rho}_{ss} = e^{-\hat{H}/k_B T} / Z$, where Z is the corresponding normalization factor or partition function: $Z = \text{tr}_e (e^{-\hat{H}/k_B T})$. In Sec. II of the Supplemental Material [46], we show that

$$\gamma_{\alpha\nu} = \frac{1}{k_B T} \bar{D}_{\alpha\nu}^S. \quad (11)$$

Thus, the second fluctuation-dissipation theorem is satisfied at equilibrium. Since $\bar{D}_{\alpha\nu}^S$ is symmetric, $\gamma_{\alpha\nu}$ is also symmetric along α and ν at equilibrium.

Anderson-Holstein model.—To establish the importance of electron-electron interactions, we will now calculate the electronic friction for the Anderson-Holstein model,

$$\hat{H}_{\text{AH}} = \hat{H}_A + \hat{H}_{\text{osc}}, \quad (12)$$

$$\begin{aligned} \hat{H}_A &= E(x) \sum_\sigma \hat{d}_\sigma^+ \hat{d}_\sigma + U \hat{n}_\uparrow \hat{n}_\downarrow + \sum_{k\sigma} \epsilon_k \hat{c}_{k\sigma}^+ \hat{c}_{k\sigma} \\ &+ \sum_{k\sigma} V_k (\hat{d}_\sigma^+ \hat{c}_{k\sigma} + \hat{c}_{k\sigma}^+ \hat{d}_\sigma), \end{aligned} \quad (13)$$

$$\hat{H}_{\text{osc}} = \frac{1}{2} \hbar \omega (x^2 + p^2). \quad (14)$$

Physically, the Anderson-Holstein model represents an electronic impurity d sitting near a metal surface and coupled to a vibrating oscillator (x). The impurity can be filled with an electron of up or down spin, and so $\sigma = \uparrow, \downarrow$ indicates spin. The oscillator is a vibrational degree of freedom and feels a different force depending on the occupation of the impurity, $E(x) \equiv E_d + \sqrt{2}gx$. Note we have defined x and p to be in dimensionless units.

To understand how the motion of the oscillator is perturbed by the fluctuating charge of the impurity, we will calculate the electronic friction. Of course, to apply Eq. (7), we must diagonalize \hat{H}_A , which will be done via a numerical renormalization group (NRG) calculation [55]. We take the wide band approximation, such that the hybridization function $\Gamma \equiv 2\pi \sum_k V_k^2 \delta(\epsilon - \epsilon_k)$ is assumed to be independent of energy. We leave all details of the calculation to Secs. III and IV of the Supplemental Material [46], and show the results below.

In Fig. 1(a), we compare the electronic friction as calculated from NRG theory versus the electronic friction as calculated with mean-field theory (MFT), Eq. (3), which is commonly used to treat the Anderson model [36]. We study the case of a large repulsion U . Whereas NRG theory predicts two peaks in the electronic friction—where there is a resonance of electron attachment or detachment with the Fermi level of the metal ϵ_F (i.e., $E_d + \sqrt{2}gx = 0$ and $E_d + \sqrt{2}gx + U = 0$, where we have set $\epsilon_F = 0$)—MFT predicts only a very broad plateau in friction. We have attempted to reconstruct these two peaks by manipulating the multiple (broken-symmetry) mean-field solutions of the Anderson-Holstein model, but we have so far been unable to qualitatively match the correct answer.

Beyond the formation of two peaks, an even more interesting feature arises from NRG theory at still lower temperatures, where Kondo physics now shows a signature. In Fig. 1(b), we now show that, below $T = 1 \times 10^{-4}$, the electronic friction exhibits two additional peaks for a total of *four* peaks. Previously, in Ref. [42], Plihal and Langreth argued that such new peaks might arise from Kondo resonances. In other words, we might expect to find peaks in electronic friction at those positions in space for which the Kondo temperature is equal to the system temperature. Here, we define the Kondo temperature to be $T_K(x) = D \exp[-2\pi|E(x)||E(x) + U|/U/\Gamma]$, where D is the bandwidth. Thus, for Fig. 1(c), we plot both $T_K(x)$ and the actual $T(x)$, i.e., the temperature at which one finds (with NRG theory) a peak in friction at position x . Note that, as the data show, the relevant Kondo temperature T_K is close to the physical temperature T , though the agreement is not perfect.

Let us now establish, however, that Ref. [42] [which is based on the noncrossing approximation and the case of infinite U] may not be entirely applicable for our data. First,

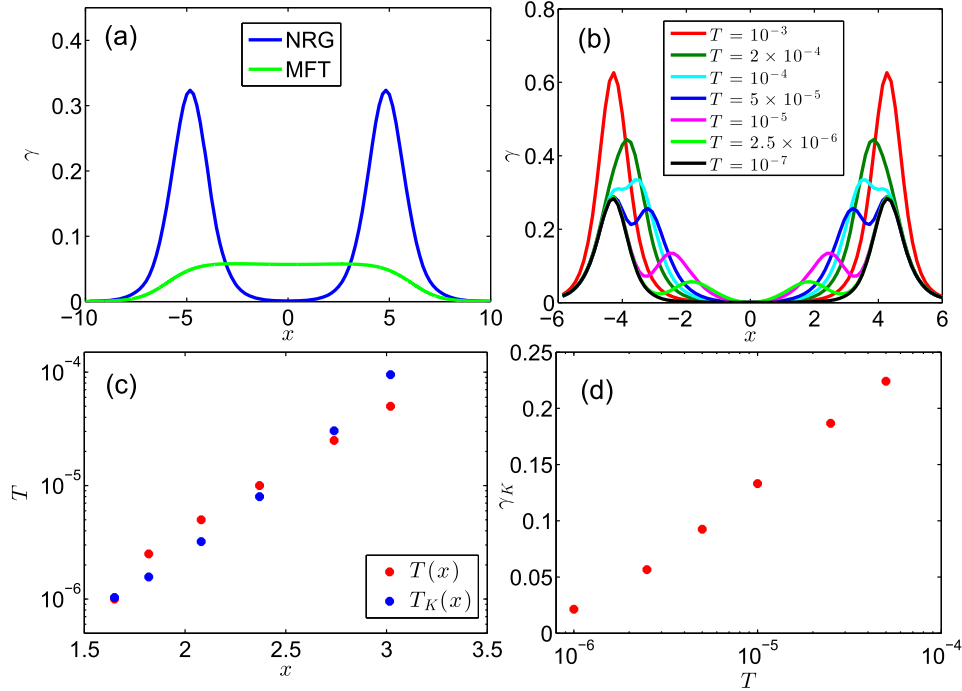


FIG. 1. (a) Electronic friction as a function of position x according to both NRG and MFT [36,56] calculations at temperature $T = 0.005$. Note that MFT fails to recover two peaks in the friction. (b) Electronic friction according to NRG theory at low temperature; note that the two peaks in friction become four peaks in friction at low temperature. (c) The Kondo temperature $T_K(x)$ as a function of position and the physical temperature $T(x)$ for which we find a peak in friction at position x . Note that these two temperatures are in rough agreement, as predicted by Langreth [42]. (d) The height of the Kondo peak γ_K as a function of temperature; note that these peaks decrease exponentially and vanish at zero temperature, in disagreement with Ref. [42]. Other parameters are $U = 0.1$, $\Gamma = 0.01$, $E_d = -0.05$, $g = 0.0075$, bandwidth $D = 1$. We have set $k_B = \hbar = 1$.

in contrast with Ref. [42], we observe that the width of the frictional Kondo peak does not decrease with temperature. Second, again in contrast with Ref. [42], we find that the frictional peaks associated with a Kondo resonance disappear as the temperature decreases to zero (rather than increase). The height of these peaks is plotted in Fig. 1(d) and appears to decrease exponentially with temperature. Future pencil and paper work will be required to understand these features.

Conclusions.—We have derived a universal expression for the electronic friction as experienced by a set of classical nuclear particles coupled to a manifold of quantum mechanical electronic DOFs. The key equations are Eqs. (7), (8), and (9). The derivation is simple and, in the same spirit as a Mori-Zwanzig projection: assuming all dynamics follow the quantum-classical Liouville equation, we simply make an adiabatic approximation and isolate fluctuations around a slow variable. Our final expression is quite general, insofar as it applies in and out of equilibrium and with an arbitrary electronic Hamiltonian; at equilibrium, our work validates the Suhl’s “bootstrap” conjecture [39].

Looking forward, Eq. (7) is demanding to apply because, without any further approximations, these equations require the full diagonalization the electronic Hamiltonian in terms of the many-body electronic states (much like the Meir-Wingreen formula [57]). However, using NRG theory,

we have now shown how to calculate electronic friction tensors exactly for small model problems. Thus, extending the work of von Oppen *et al.* [35], one can now study model Hamiltonians and learn how nuclear motion near metal surfaces will be effected by electron-electron correlation, either with or without a current through the molecule. For example, in the present Letter, we have studied the Anderson-Holstein model and have shown that the usual electronic friction expression (with mean-field theory) yields qualitatively wrong features; when we account for electronic friction, we find multiple peaks, including two associated with Kondo physics. Beyond model problems, even if we cannot use NRG theory to diagonalize the Hamiltonian, there are currently several research groups that are seeking to calculate approximate energies for extended systems beyond MFT. For instance, within the condensed matter world, there is currently a big push to calculate correlated electron attachment or detachment energies with *GW* [58] and optical excitations with the Bethe-Salper equation, all for periodic systems [45,59]. Furthermore, within the chemistry world, there has been recent work to calculate ground state coupled-cluster and excited state equation of motion coupled-cluster energies for periodic systems [44,60]. All of these methods can be used to calculate electronic friction through Eq. (8) going beyond MFT and thus improve our understanding of nuclear motion in the condensed phase.

Finally, one pressing question remains regarding the validity of electronic friction: just like the BO approximation, the adiabatic approximation that we make (in the Supplemental Material [46]) to move from Eq. (38) to Eq. (39) is uncontrolled and without a unique small parameter. On the one hand, Tully *et al.* have argued that electronic friction fails for NO scattering off of gold [61]. On the other hand, while one would certainly expect electronic friction to fail in the nonadiabatic Marcus electron transfer regime, in fact we recently showed [62] that, with just a little bit of external nuclear friction, electronic friction recovers Marcus theory. From Ref. [62], the only lesson we have so far learned is that Langevin dynamics with electronic friction will fail if truly excited state dynamics appear. In this case, one possible path forward is to include memory effects with a non-Markovian Fokker-Planck equation [9] (see Sec. VII of the Supplemental Material [46]); another approach is to employ surface hopping techniques that can include frictional effects [63–65]. In the future, it will be essential to further investigate when and how such excited state dynamics occur, and given how important electronic-electronic interactions are for identifying curve crossings, the present Letter takes an important step forward by unambiguously identifying the correct, universal electronic friction tensor accompanying all Born-Oppenheimer dynamics.

This material is based upon work supported by the (U.S.) Air Force Office of Scientific Research (USAFOSR) PECASE award under AFOSR Grant No. FA9950-13-1-0157. J. E. S. gratefully acknowledges support from the Stanford PULSE Institute and a John Simon Guggenheim Memorial fellowship.

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