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Current-Induced Forces for Nonadiabatic
Molecular Dynamics

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Abstract

We present general first principles derivation of expression for current-induced forces. The expression is applicable in nonequilibrium molecular systems with arbitrary intra-molecular interactions and for any electron-nuclei coupling. It provides a controlled consistent way to account for quantum effects of nuclear motion around classical trajectory, accounts for electronic non-Markov character of the friction tensor, and opens way to treatments beyond strictly adiabatic approximation. We show connection of the expression with previous studies, and discuss effective ways to evaluate the friction tensor.

Introduction

Nonadiabatic molecular dynamics (NAMD) is a fundamental problem related to breakdown of the usual timescale separation (the Born-Oppenheimer approximation) between electron and nuclear dynamics. The NAMD plays an important role in many processes, ranging from chemistry\(^1,2\) and photochemistry\(^3\) to spectroscopy\(^4-7\) and nonradiative electronic relaxation,\(^8\) and from electron and proton transfer\(^9-11\) to coherent control\(^12\) and photo-induced energy transfer.\(^13,14\) Significance of the problem stems from both complexity of its fundamental theoretical description, and applicational importance for development of optoelectronic\(^15,16\) and optomechanical\(^17\) molecular devices.

A crucial part of formulating nuclear dynamics is definition of nuclear forces induced by the electronic subsystem.\(^18-20\) A number of recent studies have discussed ways to account for “the electronic friction” in the dynamics.\(^21-30\) Majority of the works employ intuitive reasoning in their formulations,\(^23-30\) some of them are also confined to only non-interacting and/or equilibrium electronic systems.\(^23-28,30\)

A consistent derivation of nuclear forces was presented in the literature within path integral formulation employing the Feynman-Vernon influence functional\(^31-33\) or utilizing scattering theory.\(^34\) The derivations lead to the Langevin equation driven by a set of forces:
friction, non-conservative, renormalization, and the Berry phase. However, the studies are restricted to non-interacting electronic systems and to linear coupling between nuclear and electronic degrees of freedom. All the aforementioned works consider only extremely slow nuclear dynamics. Recently, more general considerations started to appear. However, they are also restricted to purely classical nuclei and quasiparticle based description of electronic system.

Here we discuss a derivation of nuclear forces for nonadiabatic nuclear dynamics, which accounts for nonequilibrium character of an open molecular system, arbitrary intra-molecular interactions, and general coupling between electronic and nuclear degrees of freedom. The approach utilizes many-body electronic states of the molecule as a basis. This yields a possibility to access information on state-specific contributions to the forces, which makes our consideration potentially useful in construction of advanced surface hopping schemes. Moreover, the consideration opens a way to go beyond extremely slow limit of nuclear motion. While focus of the paper is on molecular junctions, presented derivation is applicable to any open molecular system (e.g., molecules chemisorbed on surfaces, molecules in thermal environment, etc.).

Structure of the paper is as follows: first we introduce a model and present the general derivation. After that, utilizing the Zubarev’s method of nonequilibrium statistical operator we show how our general derivation is reduced to previous studies indicating corresponding approximations. We then propose an efficient way to simulate the forces in nonequilibrium interacting molecular systems employing nonequilibrium Hubbard Green functions. In particular, we show how the celebrated result of Head-Gordon and John Tully for electronic friction appears as a part of our general expression in the quasiparticle limit and at equilibrium. We illustrate our consideration with a numerical simulations for a non-interacting model, where comparison of our general scheme to the known exact results is possible. Finally, we summarize our findings and indicate directions of further research.
Figure 1: Nuclear coordinates on time-ordered, $x(t)$, and anti-time ordered, $y(t)$, branches of the Keldysh contour.
Theory

We consider dynamics of a molecule $M$ adsorbed on a surface(s) $K$. Hamiltonian of the system is separated into the nuclear kinetic and potential energies, and the electron Hamiltonian which depends on the nuclear coordinates $\hat{q}$

$$\hat{H} = \sum_{\alpha} \frac{\hat{p}_{\alpha}^2}{2} + \hat{V}(\hat{q}) + \hat{H}_e(\hat{q})$$ (1)

$\hat{H}_e(\hat{q})$ consists of the molecular $\hat{H}_M(\hat{q})$ and contacts $\hat{H}_K$ parts, and the coupling $\hat{V}_K(\hat{q})$ between them

$$\hat{H}_e(\hat{q}) = \hat{H}_M(\hat{q}) + \sum_K \left( \hat{H}_K + \hat{V}_K(\hat{q}) \right)$$ (2)

Contacts $K$ are modeled as reservoir(s) of free electrons, each at its own equilibrium. Molecular part $\hat{H}_M(\hat{q})$ can include any intra-molecular interactions (e.g., electron-electron repulsion) and is represented in the basis of many-body electronic states $\{|S\rangle\}$ of the molecule. Explicit expressions are

$$\hat{H}_M = \sum_{S_1, S_2} |S_1\rangle H_{S_1S_2}(\hat{q}) \langle S_2|; \quad \hat{H}_K = \sum_{k \in K} \varepsilon_k \hat{c}_k^\dagger \hat{c}_k;$$

$$\hat{V}_K = \sum_{k \in K} \sum_{S_1, S_2} \left( V_{k(S_1,S_2)}(\hat{q}) \hat{c}_k^\dagger |S_1\rangle \langle S_2| + H.c. \right)$$ (3)

Here $\hat{c}_k^\dagger$ ($\hat{c}_k$) creates (annihilates) electron in state $k$ of contact $K$, $S_1$ and $S_2$ indicate a pair of molecular many-body states which belong to the same charging block ($N_{S_1} = N_{S_2}$) in $\hat{H}_M$ and to charging blocks different by one electron ($N_{S_1} + 1 = N_{S_2}$) in $\hat{V}_K$ ($N_S$ is number of electrons in state $|S\rangle$). Note that although $\hat{H}_M$ is written in the diabatic basis, the derivation below is not restricted to this particular choice. Note also that the general derivation does not assume on any particular form of the electronic Hamiltonian, so that (3) becomes important only when discussing connection of our consideration to previous works.

\footnote{Additional baths (e.g., thermal bath) can be introduced into consideration in straightforward manner.}
Effective evolution for the nuclear density matrix is obtained by tracing the density matrix over electron degrees of freedom

\[ \hat{\rho}_{\text{vib}} \equiv \text{Tr}_e\{\hat{\rho}\} \] 

(4)

Assuming the initial density matrix being direct product of nuclear and electron density matrices, \( \hat{\rho}^{(0)} = \hat{\rho}_{\text{vib}}^{(0)} \otimes \hat{\rho}_{\text{el}}^{(0)} \), nuclear effective evolution can be represented in terms of the Feynman-Vernon functional \( F_{35} \)

\[ \rho_{\text{vib}}(x_2, y_2) = \int dx_1 \int dy_1 \mathcal{K}(x_2, y_2; x_1, y_1) \rho_{\text{vib}}(x_1, y_1) \] 

(5)

\[ \mathcal{K}(x_2, y_2; x_1, y_1) = \int_{(x_1, y_1)}^{(x_2, y_2)} D(x, y) e^{i \left( S_{\text{vib}}(x) - S_{\text{vib}}(y) \right)} F(x, y) \] 

(6)

\[ F(x, y) = \left\langle T_C e^{-i \int_C dt H_e(q(t))} \right\rangle \equiv e^{i S_{\text{eff}}(x, y)} \] 

(7)

Here \( x \equiv x(t) \) and \( y \equiv y(t) \) are respectively nuclear coordinates on the time-ordered and anti-time-ordered branches of the Keldysh contour at time \( t \), \( \int_{(x_1, y_1)}^{(x_2, y_2)} D(x, y) \ldots \) is integral over nuclear paths \( x(t) \) and \( y(t) \) from time \( t_1 \) to \( t_2 \), \( x(t_i) \equiv x_i \) and \( y(t_i) \equiv y_i \) \( (i = 1, 2) \), \( \mathcal{K}(x_2, y_2; x_1, y_1) \) is the nuclear propagation kernel, \( \rho_{\text{vib}}(x_i, y_i) = \langle x_i | \hat{\rho}_{\text{vib}}(t_i) | y_i \rangle \), \( S_{\text{vib}}(x) \) and \( S_{\text{vib}}(y) \) are the actions of free nuclear evolution on forward and backward branches of the contour, e.g.

\[ S_{\text{vib}}(x) = \int_{t_1}^{t_2} dt L(x, \dot{x}) \equiv \int_{t_1}^{t_2} dt \left( \sum_{\alpha} \frac{x_{2\alpha}^2}{2} - V(x) \right) \] 

(8)

and \( T_C \) is the contour ordering operator (see Fig. 1). Here and below \( \langle \ldots \rangle = \text{Tr}_e[\ldots \hat{\rho}_{\text{el}}^{(0)}] \) is quantum mechanical and statistical average over only electronic degrees of freedom and \( q \equiv q(t) \) will denote pair of nuclear coordinates, \( q = (x, y) \), at time \( t \).

Now we want to derive expression for the effective action \( S_{\text{eff}} \), Eq. (7). To do so we separate the classical, \( Q_\alpha \), and quantum, \( \xi_\alpha \), nuclear dynamics by transferring to the Wigner
coordinates (see Fig. 1)
\[ Q_\alpha = \frac{x_\alpha + y_\alpha}{2}, \quad \xi_\alpha = x_\alpha - y_\alpha \] (9)
and rewrite the Hamiltonian in the form of zero-order classical nuclear evolution plus quantum perturbation
\[ \hat{H}_e(q(\tau)) = \hat{H}_e(Q(\tau)) + \hat{V}_e(q(\tau)) \] (10)
where \( \hat{V}_e(q(\tau)) \equiv \hat{H}_e(q(\tau)) - \hat{H}_e(Q(\tau)) \). Here \( \tau \) is the contour variable, so that \( \hat{H}_e(q(\tau)) \) indicates that at time \( t \) corresponding to the contour variable \( \tau \) we consider Hamiltonian to be defined respectively by coordinates \( x(t) \) or \( y(t) \) of the nuclei on the forward or backward branch of the contour; \( \hat{H}_e(Q(\tau)) \) depends on coordinates \( Q(t) \) on both branches.

Employing the linked cluster procedure\(^{31,36}\) we replace \( \hat{V}_e(q(\tau)) \) by \( \lambda \hat{V}_e(q(\tau)) \) to get
\[ S_{eff}(x, y) = -\int_0^1 d\lambda \int_C d\tau \langle \hat{V}^I_e(q(\tau)) \rangle_c \] (11)
Here superscript \( H \) shows that the operator is in the Heisenberg picture, i.e. electronic system evolution is governed by the full Hamiltonian \( \hat{H}_e(q(\tau)) \), Eq. (10), and subscript \( c \) indicates that one has to consider only connected diagrams.

So far consideration is exact. Now we perform expansion of (11) in \( \lambda \hat{V}_e(q(\tau)) \). We justify the expansion in ‘quantumness’ of the nuclei by noting that for purely classical nuclei, \( x = y \), the functional (7) is unity\(^{37}\) and that for relatively slow nuclear motion deviation from the classical trajectory is small. Expanding (11) up to first order in \( \lambda \hat{V}_e(q(\tau)) \) and evaluating integral in \( \lambda \) yields
\[ S_{eff}(x, y) \approx -\left\langle \int_C d\tau \hat{V}^I_e(q(\tau)) \right\rangle_c \] (12)
\[ + \frac{i}{2} \left\langle T_C \int_C d\tau_1 \int_C d\tau_2 \hat{V}^I_e(q(\tau_1)) \hat{V}^I_e(q(\tau_2)) \right\rangle_c \]
where superscript \( I \) shows that the operator is in the interaction picture, i.e. its evolution is defined by Hamiltonian \( \hat{H}_e(Q(\tau)) \). In (12) first row corresponds to first order and second
to second order of the cumulant expansion. Employing the Langreth rules\textsuperscript{38} to project (12) onto the real time axis and expanding $\hat{V}_e(q(\tau))$ up to second order in the quantum coordinates $\xi_\alpha$ leads to

$$S_{\text{eff}}(x, y) \approx -\sum_\alpha \int dt \xi_\alpha(t) \left\langle \partial_\alpha \hat{H}_e^I(Q(t)) \right\rangle_c$$

$$+ \frac{i}{2} \sum_{\alpha, \beta} \int dt_1 \int dt_2 \xi_\alpha(t_1) \Pi_{\alpha\beta}(t_1, t_2) \xi_\beta(t_2)$$

where

$$\left\langle \partial_\alpha \hat{H}_e^I(Q(t)) \right\rangle_c \equiv \text{Tr}_e \left\{ \partial_\alpha \hat{H}_e(Q(t)) \hat{\rho}_{\text{el}}(t) \right\}_c$$

$$\Pi_{\alpha\beta}(t_1, t_2) = \frac{1}{2} \left\langle \left\{ \partial_\alpha \hat{H}_e^I(Q(t_1)); \partial_\beta \hat{H}_e^I(Q(t_2)) \right\} \right\rangle_c$$

Here $\partial_\alpha \hat{H}_e^I(Q(t))$ indicates interaction picture for operator $\partial_\alpha \hat{H}_e(Q(t))$, $\{ \ldots; \ldots \}$ is anti-commutator,

$$\hat{\rho}_{\text{el}}(t) = \hat{U}(t, t_0) \hat{\rho}_{\text{el}}^{(0)} \hat{U}^\dagger(t, t_0)$$

is the time evolved electronic density matrix,

$$\hat{U}(t_1, t_2) = T \exp \left[ -i \int_{t_1}^{t_2} dt \hat{H}_e(Q(t)) \right]$$

is the electronic evolution operator under classical nuclear driving, $T$ is time-ordering operator, and $\hat{H}_e(Q(t))$ is the electronic Hamiltonian in the Schrödinger picture build for nuclear frame $Q(t)$. Note that additional quantum contributions to the resulting expression can be obtained by performing expansion of (11) to higher orders in $\lambda \hat{V}_e(q(\tau))$. Below we only consider result of the first order expansion, Eq.(13).
Using (13) in (6) yields

\[\mathcal{K}(Q_2, \xi_2; Q_1, \xi_1) = \int D(Q, \xi) \exp \left[ i\xi_2 \dot{Q}_2 - i\xi_1 \dot{Q}_1 \right] \times \]

\[\exp \left[ i \sum_{\alpha} \int dt \xi_{\alpha}(t) \left( L_{\alpha}(t) + i \sum_{\beta} \int dt' \Pi_{\alpha\beta}(t, t') \frac{\xi_{\beta}(t')}{2} \right) \right] \]

where

\[L_{\alpha}(t) = -\ddot{Q}_{\alpha}(t) - \partial_{\alpha} V(Q(t)) - \langle \partial_{\alpha} \hat{H}_e^I(Q(t)) \rangle \]

is the Lagrangian.

To obtain the stochastic Langevin equation starting from expression for the nuclear propagation kernel (18) we employ a heuristic derivation. For more detailed discussion one can consult Ref.\textsuperscript{39} Using the Hubbard-Startonovich transformation

\[\det A \exp \left[ \sum_{i,j} \xi_i A_{ij} \xi_j \right] = \int D(f) \exp \left[ - \sum_{i,j} f_i A_{ij}^{-1} f_j + \sum_i (f_i \xi_i + \xi_i f_i) \right] \]

we decouple last (quadratic) term in Eq.(18). This yields for the kernel

\[\mathcal{K}(x_2, y_2; x_1, y_1) \sim \int D(Q, \xi, f) \exp \left[ i\xi_2 \dot{Q}_2 - i\xi_1 \dot{Q}_1 \right] \]

\[\times \exp \left[ - i \sum_{\beta} \int dt \xi_{\alpha}(t) \left( L_{\alpha}(t) - f_{\alpha}(t) \right) \right] \]

\[\times \exp \left[ - \frac{1}{2} \sum_{\alpha,\beta} \int dt_1 \int dt_2 f_{\alpha}(t_1) \Pi_{\alpha\beta}^{-1}(t_1, t_2) f_{\beta}(t_2) \right] \]

Integrating out quantum variables \(\xi_{\alpha}(t)\) yields delta function \(\delta(L - f)\). This finally leads to

\[\ddot{Q}_{\alpha}(t) = -\partial_{\alpha} V(Q(t)) - \langle \partial_{\alpha} \hat{H}_e^I(Q(t)) \rangle + f_{\alpha}(t) \]
where $f_\alpha(t)$ is stochastic force which satisfies

$$\langle f_\alpha(t_1) f_\beta(t_2) \rangle = \Pi_{\alpha\beta}(t_1, t_2) \quad (23)$$

Eq. (22) is the stochastic Langevin equation for the classical nuclear dynamics driven by the quantum electronic bath. The latter is characterized by Eqs. (14), (15), and (23).

Note that without timescale separation between electron and nuclear dynamics Eq. (22) does not contain electronic friction. To introduce the latter one has assume fast electron and slow nuclear degrees of freedom. We suggest a general rigorous approach to introduce the separation by utilizing the Zubarev’s method of the nonequilibrium statistical operator (NESO). Within the NESO the electronic density operator $\hat{\rho}_{el}(t)$, Eq.(16), is expressed in terms of the relevant distribution $\hat{\rho}_{rel}(t)$ as

$$\hat{\rho}_{el}(t) = \hat{\rho}_{rel}(t) - \int_{-\infty}^{t} dt' e^{-\delta(t-t')} \hat{U}(t, t') \times \left\{ \frac{\partial}{\partial t'} \hat{\rho}_{rel}(t') + i \left[ \hat{H}_e(Q(t')), \hat{\rho}_{rel}(t') \right] \right\} \hat{U}^\dagger(t, t') \quad (24)$$

where $\delta \rightarrow +0$. Note that employing (24) yields a completely general way to introduce timescale separation applicable to (22) or any higher order expansion (in quantum character of nuclei) of the propagation kernel (6) which is applicable for any electron-nuclei coupling.

**Discussion**

Now we compare our general derivation with previous studies of the electronic friction and suggest ways for effective evaluation of the friction tensor in interacting nonequilibrium molecular systems. We assume initial state of the system to be in infinite past and, in accordance with previous studies, below we mostly confine our consideration to strictly adiabatic nuclei, when quantum electronic system adjusts to new positions of nuclei instantaneously, so that nonequilibrium electronic baths utilized for derivation of nuclear forces are electronic.
steady states corresponding to a fixed nuclear framework.

**Friction tensor.** In the limit of extremely slow nuclear driving the relevant distribution \( \hat{\rho}_{\text{rel}}(t) \) becomes identical with steady-state electron distribution \( \rho_{\text{ss}}^t \) for nuclear frame \( Q(t) \):

\[
\hat{\rho}_{\text{rel}}(t) \approx \rho_{\text{ss}}^t, \tag{25}
\]

so that \( [\hat{H}_e(Q(t)); \hat{\rho}_{\text{rel}}(t)] \approx 0 \) and \( \partial_t \hat{\rho}_{\text{rel}}(t) \approx \sum_\beta \partial_\beta \rho_{\text{ss}}^t \dot{Q}_\beta(t) \). Using (25) in (14) yields

\[
\left\langle \partial_\alpha \hat{H}_e(Q(t)) \right\rangle_c \approx \text{Tr}_e \left\{ \partial_\alpha \hat{H}_e(Q(t)) \hat{\rho}_{\text{ss}}^t \right\} - \sum_\beta \int_{-\infty}^{t} dt' e^{-\delta(t-t')} \dot{Q}_\beta(t') \times \text{Tr}_e \left\{ \partial_\alpha \hat{H}_e(Q(t)) \hat{U}(t, t') \partial_\beta \hat{\rho}_{\text{ss}}^t \hat{U}^\dagger(t, t') \right\}_c \tag{26}
\]

Substituting this result into (22) leads to Langevin equation in the form

\[
\ddot{Q}_\alpha(t) = - \partial_\alpha V_{\text{eff}}(Q(t)) - \sum_\beta \int_{-\infty}^{t} dt' \gamma_{\alpha\beta}(t, t') \dot{Q}_\beta(t') + f_\alpha(t) \tag{27}
\]

where

\[
\partial_\alpha V_{\text{eff}}(Q(t)) \equiv \partial_\alpha V(Q(t)) + \text{Tr}_e \left\{ \partial_\alpha \hat{H}_e(Q(t)) \hat{\rho}_{\text{ss}}^t \right\} \tag{28}
\]

\[
\gamma_{\alpha\beta}(t_1, t_2) \equiv -\theta(t_1 - t_2) e^{-\delta(t_1-t_2)} \times \text{Tr}_e \left\{ \partial_\alpha \hat{H}_e(Q(t_1)) \hat{U}(t_1, t_2) \partial_\beta \hat{\rho}_{\text{ss}}^t \hat{U}^\dagger(t_1, t_2) \right\}_c \tag{29}
\]

are the effective (renormalized) nuclear force and the friction tensor, respectively. Note that Markov version of equation (27), which disregards nuclear motion at timescales of electronic correlations, was suggested in Refs. 29,30.
**Fluctuation-dissipation theorem.** At equilibrium, when nuclei do not move at the timescale of electron correlation,

\[ \hat{\rho}_{ss} \rightarrow \hat{\rho}_{eq} = \frac{e^{-\hat{H}_e(Q)/k_B T}}{\text{Tr}_e \{ e^{-\hat{H}_e(Q)/k_B T} \}} \]  

(30)

Employing the Sneddon’s formula,\(^{42}\) Eq.(29) becomes

\[
\gamma_{\alpha\beta}(t_1 - t_2) = \frac{1}{k_B T} \theta(t_1 - t_2) \int_0^1 dx \langle \partial_\alpha \hat{H}_e^I(t_1) \partial_\beta \hat{H}_e^I(t_2 + i\hbar x/k_B T) \rangle_c 
\]

(31)

\[
= \frac{1}{k_B T} \theta(t_1 - t_2) \int_0^1 dx \langle \partial_\beta \hat{H}_e^I(t_2 - i\hbar x/k_B T) \partial_\alpha \hat{H}_e^I(t_1) \rangle_c 
\]

Taking Fourier transform of \(\gamma_{\alpha\beta}(t_1 - t_2)\) and evaluating integral in \(x\) leads to two equivalent expressions corresponding to two lines in (31)

\[
\gamma_{\alpha\beta}(E) = +i \int \frac{d\omega}{2\pi} \frac{J_{\alpha\beta}(\omega)}{E - \omega + i\delta} \frac{1 - e^{-\hbar\omega/k_B T}}{\hbar\omega} 
\]

(32)

\[
= -i \int \frac{d\omega}{2\pi} \frac{J_{\alpha\beta}(\omega)}{E - \omega + i\delta} \frac{1 - e^{-\hbar\omega/k_B T}}{\hbar\omega} 
\]

where

\[
J_{\alpha\beta}(\omega) = \int dt_1 \int dt_2 e^{i\omega(t_1 - t_2)} \langle \partial_\alpha \hat{H}_e(t_1) \partial_\beta \hat{H}_e(t_2) \rangle_c 
\]

(33)

and where in the derivation of (32) we used\(^40\)

\[
J_{\beta\alpha}(-\omega) = J_{\alpha\beta}(\omega) e^{-\hbar\omega/k_B T} 
\]

(34)

Two equivalent expressions in (31) lead to \(\gamma_{\alpha\beta}(t_1 - t_2) = \gamma_{\alpha\beta}^*(t_1 - t_2)\) and hence

\[
\gamma_{\alpha\beta}^*(E) = \gamma_{\alpha\beta}(-E) 
\]

(35)
Thus, using (32) and taking into account relation (35) leads to

$$2 \text{Re} \gamma_{\alpha \beta}(E) \equiv \gamma_{\alpha \beta}(E) + \gamma_{\alpha \beta}(-E) = J_{\alpha \beta}(E) \frac{1 - e^{-E/k_B T}}{E}$$

(36)

At the same time, Fourier transform of (15) is

$$\Pi_{\alpha \beta}(E) = 1 + \frac{e^{-E/k_B T}}{2} J_{\alpha \beta}(E)$$

(37)

where we again used (34). Finally, using (36) in (37) leads to the fluctuation-dissipation theorem

$$\Pi_{\alpha \beta}(E) = E \text{Re} \gamma_{\alpha \beta}(E) \coth \frac{E}{2k_B T}.$$ 

(38)

which at high temperatures reduces to its classical version

$$\Pi_{\alpha \beta}(E) = 2k_B T \text{Re} \gamma_{\alpha \beta}(E)$$

(39)

**Additive electronic Hamiltonian.** A number of studies\(^{21,22,31,32}\) considered electronic Hamiltonian (2) consisting of zero-order coordinate-independent part and electron-nuclear coupling depending on nuclear coordinates

$$\hat{H}_e(q) = \hat{H}_e^{(0)} + \hat{H}_e^{(1)}(q)$$

(40)

We now consider how their results can be obtained from our general scheme. To show the connection we have to assume weak electron-nuclear coupling \(\hat{H}_e^{(1)}(q)\) (this assumption is an inherent part of previous considerations). Employing the assumption we can expand the evolution operator \(\hat{U}\) up to linear order in \(\hat{H}_e^{(1)}\) as

$$\hat{U}(t_1, t_2) \approx \hat{U}_0(t_1, t_2) - i \int_{t_2}^{t_1} dt' \hat{U}_0(t_1, t') \hat{H}_e^{(1)}(Q(t')) \hat{U}_0(t', t_2)$$

(41)
where \( \hat{U}_0(t_1, t_2) = \exp \left[ -i \hat{H}_e^{(0)}(t_1 - t_2) \right] \).

Substituting the expansion into (14) and keeping only terms up to second order in \( \hat{H}_e^{(1)} \) leads to

\[
\langle \partial_\alpha \hat{H}_e^I(Q(t)) \rangle_c \approx \langle \partial_\alpha \hat{H}_e^{(1)I}(Q(t)) \rangle + \int dt' \Pi_\alpha^r(t, t')
\]

(42)

\[
\Pi_\alpha^r(t, t') \equiv -i \theta(t - t') \langle [\partial_\alpha \hat{H}_e^{(1)I}(Q(t)), \hat{H}_e^{(1)I}(Q(t'))] \rangle_c
\]

(43)

Here superscript \( I \) indicates interaction picture with respect to Hamiltonian \( \hat{H}_e^{(0)} \). As previously, first term on the right in (42) renormalizes the nuclear potential, while second term accounts for the electronic friction. Utilizing second order expansion in \( \hat{H}_e^{(1)} \) also in (15) (i.e. using \( \hat{U}_0 \) in place of \( \hat{U} \) in the expression) generalizes non-interacting considerations of Refs. 21, 22, 31, 32 to the case of interacting nonequilibrium systems.

To detail the connection we consider non-interacting electronic Hamiltonian of Ref. 32

\[
\hat{H}_M(\hat{q}) = \sum_{ij} \left( H_{ij}^0 + \sum_\alpha M_{ij}^\alpha \hat{q}_\alpha \right) \hat{c}_i^\dagger \hat{c}_j
\]

(44)

instead of general form (3) in (15) and (43). This leads to expressions for dissipation and fluctuation in terms of two-particle Green functions. Applying the Wick’s theorem\(^{43}\) immediately yields results of the work

\[
\Pi_\alpha^r(t_1, t_2) = i\theta(t_1 - t_2)
\]

\[
= \frac{1}{2} \text{Tr} \left[ M^\alpha G^<(t_1, t_2) M^\beta G^>(t_2, t_1) \right] - M^\alpha G^>(t_1, t_2) M^\beta G^<(t_2, t_1)
\]

\[
\Pi_{\alpha\beta}(t_1, t_2) = \frac{1}{2} \text{Tr} \left[ M^\alpha G^>(t_1, t_2) M^\beta G^<(t_2, t_1) \right] + M^\alpha G^<(t_1, t_2) M^\beta G^>(t_2, t_1)
\]

Here trace is over molecular orbitals and \( G^{/>/<} \) are the greater/lesser projections of the single-
particle Green function \( G_{ij}(\tau_1, \tau_2) \equiv -i \langle T_c \hat{c}_i(\tau_1) \hat{c}^\dagger_j(\tau_2) \rangle \), friction tensor \( \Pi'_{\alpha\beta}(t_1, t_2) \) originates from (43), and evolution of electron creation and annihilation operators \( \hat{c}^\dagger_j(\tau_2) \) and \( \hat{c}_i(\tau_1) \) is governed by \( \hat{H}^{(0)}_e \) of (44).

Previously introduced in the literature standard friction, nonconservative, renormalization and the Berry phase forces are related to our electronic friction as follows. Expressions for the friction, Eq. (29) or (43), have generic form \( F(t, t') = \theta(t - t') f(t, t') \). At steady state, when \( f(t, t') = f(t - t') \), Fourier transform of \( F(t, t') \) is

\[
F(E) = -i PP \int \frac{d\omega}{2\pi} \frac{f(\omega)}{E - \omega} + \pi f(E)
\]

where \( PP \) is the principle part. The standard friction is identified with \( \pi \text{Im} f(E) \), the nonconservative force is given by \( \pi \text{Re} f(E) \), the renormalization contribution comes from \( PP \int \frac{d\omega}{2\pi} \text{Im} f(\omega) \), and the Berry phase force is associated with \( PP \int \frac{d\omega}{2\pi} \text{Re} f(\omega) \) (see Ref. 32 for details).

**Effective evaluation of the friction tensor.** We now discuss effective ways to evaluate current-induced forces in interacting molecular junctions in situations when molecule-contacts couplings are relatively weak although not negligible. As demonstrated in our previous publications,\(^{44-46}\) methods of the nonequilibrium atomic limit (formulated in the basis of many-body states of the molecule) may be a convenient alternative to the standard (orbital based) treatments of electronic degrees of freedom. In particular, recently introduced by us nonequilibrium diagrammatic technique for the Hubbard Green functions\(^{47,48}\) may be beneficial also for evaluation of the friction tensor.

Deferring study of nonadiabatic effects on the timescale of electronic correlations to future research, we focus on the additive electronic Hamiltonian (40) with the nuclear coordinate dependence confined only to the molecular Hamiltonian \( \hat{H}_M \). In this case the dissipation
Figure 2: (a) Two-sites two-modes non-interacting junction model. (b) Second order diagram utilized in simulation of the Hubbard Green function (47). Directed single and double lines represent bare and dressed electron locator, respectively; circles indicate pricked vertices (see Refs. 47,48 for details).
term, Eq. (43), is

$$
\Pi_\alpha(t_1, t_2) = \sum_{S_1, S_2, S_3, S_4} \partial_\alpha H_{S_1 S_2}(Q) H_{S_3 S_4}^* (Q) \\
\times D_{S_1 S_2, S_3 S_4}(t_1, t_2)
$$

where $D^r$ is the retarded projection of the single-particle Hubbard Green function

$$
D_{S_1 S_2, S_3 S_4}(\tau_1, \tau_2) = -i \langle T_c \hat{X}_{S_1 S_2}(\tau_1) \hat{X}_{S_3 S_4}^* (\tau_2) \rangle_e
$$

Here $\hat{X}_{S_1 S_2}(\tau)$ ($\hat{X}_{S_1 S_2} \equiv |S_1\rangle \langle S_2|$) is the Hubbard (projection) operator, $\tau_1,2$ are the contour variables and $T_c$ is the contour ordering operator. The Green function (47) can be evaluated utilizing nonequilibrium diagrammatic technique of Ref.47. Note that while friction is expressed in terms of the single-particle Hubbard Green function, similar orbital based treatment inevitably leads to appearance of the two-particle Green function. Its evaluation (in the presence of interactions) is a complicated numerical task already at equilibrium.29 Note also that the Hubbard GFs treat formally exactly all electron correlations within the molecule and account for correlations between the molecule and contacts in an ordered manner of the diagrammatic perturbation theory (i.e. all diagrams of a particular order are summed in the expansion).

**Generalized version of Head-Gordon and Tully friction tensor.**

Here we discuss generalization of Head-Gordon and Tully friction tensor49 to open nonequilibrium molecular systems. For simplicity and in agreement with consideration in Ref.,49 we consider non-interacting model (44). As shown above, frictional force in the stochastic
Liouville equation takes the form

\[- \sum_{\beta} \int_{-\infty}^{+\infty} dt' \Pi_{\alpha\beta}^e(t - t') Q_\beta(t') \]

\[\equiv - \sum_{\beta} \sum_{S_1, S_2, S_3, S_4} \partial_\alpha H^e_{S_1 S_2}(Q) \partial_\beta H^e_{S_4 S_3}(Q) \]

\[\times \int_{-\infty}^{t} dt' D^e_{S_1 S_2, S_3 S_4}(t, t') Q_\beta(t') \quad (48)\]

For simplicity, let consider two-level model (see Fig. 2a). Within the model each of the states \(S_i\) (\(i = 1, 2, 3, 4\)) in the sum above can be either state with single electron populating eigenstate \(E_1\) (state \(a\)) or state with single electron populating eigenstate \(E_2\) (state \(b\)) in the single electron subspace of the many-body molecular basis.

We claim that from all contributions in (48), only two (first with \(S_1 = S_3 = a\) and \(S_2 = S_4 = b\); second with \(S_1 = S_3 = b\) and \(S_2 = S_4 = a\)) are related to Head-Gordon and Tully result. Thus, generalized version of Head-Gordon and Tully friction tensor is

\[- \sum_{\beta} \int_{-\infty}^{t} dt' \left[ \partial_\alpha H^e_{ab}(Q) \partial_\beta H^e_{ba}(Q) D^e_{ab, ab}(t, t') \right.\]

\[\left. + \partial_\alpha H^e_{ba}(Q) \partial_\beta H^e_{ab}(Q) D^e_{ba, ba}(t, t') \right] Q_\beta(t') \quad (49)\]

where

\[D^e_{S_1 S_2, S_3 S_4}(t, t') = - i \theta(t - t') \langle \left[ \hat{X}_{S_1}(t); \hat{X}_{S_3}^\dagger(t') \right] \rangle_e \quad (50)\]

is retarded projection of the Hubbard Green function (47).

In quasiparticle limit, when hybridization with baths can be disregarded and thus evolution of the Hubbard operators in (50) is governed solely by molecular electronic Hamiltonian,

\[\hat{X}_{S_1 S_2}(t) = \hat{X}_{S_1 S_2} e^{i \omega_{S_1 S_2} t} \quad (\omega_{S_1 S_2} \equiv E_{S_1} - E_{S_2}) \quad (51)\]
Green functions in (49) become

\[ \mathcal{D}^{r}_{ab,ab}(t,t') = -i\theta(t-t')[P_a - P_b]e^{-i\omega_{ba}(t-t')} \]  

(52)

\[ \mathcal{D}^{r}_{ba,ba}(t,t') = -i\theta(t-t')[P_b - P_a]e^{+i\omega_{ba}(t-t')} \]  

(53)

Here \( P_S \equiv \langle \hat{X}_{SS} \rangle_e \) is probability for the system to be in state \( S \).

Following Ref. 49 we assume that at time \( t_0 \) (taken to be \(-\infty\) in our consideration; assumed to be 0 in Ref. 49) \( P_a = 1 \) and \( P_b = 0 \). Then after substituting (52) and (53) into (49), we get

\[ 2 \sum_{\beta} \partial_{\alpha} H^e_{ab}(Q) \partial_{\beta} H^e_{ba}(Q) \int_{-\infty}^{t} dt' \sin \left[ \omega_{ba}(t-t') \right] Q_{\beta}(t') \]  

(54)

Taking the integral by parts and neglecting surface term we get

\[ -2 \sum_{\beta} \partial_{\alpha} H^e_{ab}(Q) \partial_{\beta} H^e_{ba}(Q) \int_{-\infty}^{t} dt' \cos \left[ \frac{\omega_{ba}(t-t')}{\omega_{ba}} \right] \frac{\dot{Q}_{\beta}(t')}{\omega_{ba}} \]  

(55)

Finally, noting that

\[ \partial_{\alpha} H^e_{ab}(Q) = \omega_{ab} d_{\alpha}^{\mu} \]  

(56)

where \( d_{\alpha}^{\mu} \) is nonadiabatic coupling, we arrive at Head-Gordon and Tully expression for friction tensor (compare to Eqs. (19) and (20) in Ref. 49).

Note that original Head-Gordon and Tully result is derived from consideration of an isolated molecule (no baths). Note also that the friction kernel in Ref. 49 is of the second order in non-adiabatic transfer element, which implies two important assumptions: a. electron-nuclei coupling is small and b. decoherence rate in ground and excited electronic states is big. Our numerical example below demonstrates failure of the assumptions for a model of open molecular system.

**Numerical example.** We now present a numerical example for a two-sites two-
vibrational modes non-interacting junction model (see Fig. 2a). While the model has been considered previously within the standard NEGF, we consider its results to be important because this is the simplest non-trivial model for which exact results for electronic friction (although limited to second order expansion in weak electron-nuclei interaction) are available in the literature so far. We stress that up to now there is no exact derivation of electronic friction for interaction systems; we are the first to present such derivation for open nonequilibrium systems. Thus, at the moment meaningful comparison is possible only for non-interacting electronic systems. Applications of our scheme to more realistic systems is a goal for future research.

For the model presented in Fig. 2a, the Hamiltonian (40) takes the form

\[ H_e^{(0)} = \sum_{m=1,2} \epsilon_m \hat{d}_m^\dagger \hat{d}_m - t(\hat{d}_1^\dagger \hat{d}_2 + H.c.) \]

\[ + \sum_{k \in L,R} \varepsilon_k \hat{c}_k^\dagger \hat{c}_k + \sum_{\ell \in L} (V_{\ell 1} \hat{c}_{\ell}^\dagger \hat{d}_1 + H.c.) + \sum_{r \in R} (V_{r 2} \hat{c}_r^\dagger \hat{d}_2 + H.c.) \]

\[ H_e^{(1)}(Q) = m_1(\hat{d}_1^\dagger \hat{d}_2 + H.c.)Q_1 + m_2(\hat{d}_1^\dagger \hat{d}_1 - \hat{d}_2^\dagger \hat{d}_2)Q_2 \]

Here \( \hat{d}_m^\dagger \) (\( \hat{d}_m \)) creates (annihilates) electron in orbital \( m \) (\( m = 1,2 \)). For this form of the Hamiltonian (43) yields friction tensor \( \Pi_{\alpha \beta}(t,t') = -i \theta(t-t') \langle [\partial_\alpha \hat{H}_e^{(1)}(Q); \partial_\beta \hat{H}_e^{(1)}(Q)] \rangle_c \).

To make comparison with Ref.\(^{32}\) easier, we simulate \( \Lambda(E) \) function, which is related to the friction tensor as \( \Pi_{\alpha \beta}(t,t') = \theta(t-t') 2\pi i \Lambda_{\alpha \beta}(t,t') \).

We compare the NEGF results for current-induced forces (exact for the model) with the Hubbard NEGF simulations. The Green function (47) was simulated within second order diagrammatic perturbation theory (see Ref.\(^{47}\) for details). Parameters of the simulation are \( T = 300 \) K, \( \epsilon_1 = -\epsilon_2 \equiv \epsilon_0 = 0.1 \) eV, \( t = 0.2 \) eV, \( \Gamma = 1 \) eV, and \( m_1 = m_2 = 0.01 \) eV/AMU\(^{1/2}\) Å. Fermi energy is taken as origin, \( E_F = 0 \). Simulations are performed for bias \( V = 1 \) V; \( \mu_{L,R} = \pm|e|V/2 \).

Figure 3 shows elements of \( \Lambda_{\alpha \beta}(E) \) as obtained from the NEGF and Hubbard NEGF
Figure 3: Friction tensor $\Lambda(E)$ for the noninteracting junction model (Fig. 2a). Results of the NEGF calculation (solid line, red) are compared with the Hubbard NEGF (dashed line, blue) and nonequilibrium generalization of the Head-Gordon and Tully electronic friction (dotted line, black). See text for parameters.
Figure 4: Element $\Lambda_{11}(E)$ of the friction tensor for the noninteracting junction model (Fig. 2a). Simulations are performed for (a) $\Gamma = 0.5$ eV, (b) $\Gamma = 0.2$ eV, (c) $\Gamma = 0.05$ eV, and (d) $\Gamma = 0.01$ eV. Results of the NEGF calculation (solid line, red) are compared with the Hubbard NEGF (dashed line, blue) and nonequilibrium generalization of the Head-Gordon and Tully electronic friction (dotted line, black). Other parameters are as in Fig. 3.
Figure 5: The Berry phase force relative to the average friction. (a) Results of the NEGF calculation (solid line, red) are compared with the Hubbard NEGF (dashed line, blue). Numbers indicate position of the level $\epsilon_0$. (b) Map of the ratio vs. energy and position of the level. Parameters are as in Fig. 3.
simulations. It is interesting to note that although system-bath coupling $\Gamma$ is not small and while the Hubbard NEGF is perturbative in system-bath coupling strength expansion, Hubbard simulations follow exact (for the model) NEGF results very closely. Similar accuracy in a wide range of parameters was noted in our recent publication. We attribute the effect to similarity of diagrammatic techniques for the two Green functions.

We now compare the results with a generalized version of the Head-Gordon and Tully friction tensor. As expected, at non-negligible system-bath coupling this form of the tensor fails to reproduce correct behavior (see Fig. 3). Figure 4 shows one element of the friction tensor calculated employing the NEGF simulations (exact for the model; solid line, red), the Hubbard NEGF results (applicable also in interacting systems; dashed line, blue) and the generalized version of the Head-Gordon and Tully friction tensor (dotted line, black) for several system-bath coupling strengths $\Gamma$. Naturally, with decrease in the system-bath coupling $\Gamma$ the Head-Gordon and Tully result becomes more accurate (especially at the energies corresponding to transitions between molecular eigenstates).

Figure 5 demonstrates relative importance of the Berry phase force. Also here, the Hubbard NEGF calculations closely follow exact (for the model) NEGF results. As was first indicated in Ref., the Berry force is pronounced at energies corresponding to transitions between molecular many-body states. Its significance decreases with separation between the transition energy and chemical potential.

**Non-Condon effects in current-induced forces.** Finally, we present short discussion of non-Condon effects in current-induced forces. We postpone detailed study to future publications. Effective evaluation of nuclear coordinate dependence in the molecule-contacts coupling, Eq.(2), in interacting systems can utilize decoupling between molecular and contacts electronic degrees of freedom. For example, the non-Condon effects due to coupling-coupling correlation are given approximately by the following expressions, again
involving only single-particle Hubbard Green functions (47)

\[
\Pi_\alpha(t_1, t_2) = 2 \text{Im} \theta(t_1 - t_2) (59)
\]

\[
\times \text{Tr} \left[ \Sigma^{(\alpha)}(t_1, t_2) D^<(t_2, t_1) - \Sigma^{(\alpha)}(t_1, t_2) D^>(t_2, t_1) \right]
\]

\[
\Pi_{\alpha\beta}(t_1, t_2) = \text{Tr} \left[ \Sigma^{(\alpha\beta)}(t_1, t_2) D^<(t_2, t_1) \right.
\]

\[
+ \Sigma^{(\alpha\beta)}(t_1, t_2) D^>(t_2, t_1) \left. \right] (60)
\]

Here trace is over single-electron transitions between many-body states of the molecule and \(\Sigma^{(\alpha)}>/<\) and \(\Sigma^{(\alpha\beta)}>/<\) are the greater/lesser projections of self-energies due to molecule-contacts coupling.

\[
\Sigma^{(\alpha)}_{S_1S_2S_3S_4}(\tau_1, \tau_2) = \sum_k \partial_\alpha V_{S_1S_2,k}(Q) g_k(\tau_1, \tau_2) V_{k,S_3S_4}(Q) (61)
\]

\[
\Sigma^{(\alpha\beta)}_{S_1S_2S_3S_4}(\tau_1, \tau_2) = \sum_k \partial_\alpha V_{S_1S_2,k}(Q) g_k(\tau_1, \tau_2) \partial_\beta V_{k,S_3S_4}(Q) (62)
\]

and \(g_k(\tau_1, \tau_2) \equiv -i \langle T_c \hat{c}_k(\tau_1) \hat{c}_k^\dagger(\tau_2) \rangle\) is Green function of free electrons in state \(k\) of contacts. Similar evaluation of molecule-coupling cross terms will result in multi-time Hubbard correlation functions. Diagrammatic technique allows pretty accurate evaluation of the latter as well.\(^{48}\)

**Conclusion**

We presented general derivation of current-induced forces for nonadiabatic nuclear dynamics and compared it to previous works. Our derivation opens a way to go beyond the usually assumed extremely slow nuclear dynamics and yields electronic state-specific contributions to the forces. Thus, resulting expressions for the forces are applicable also in intermediate
regime and can be utilized for construction of advanced surface-hopping schemes. The derivation is completely general in a sense that it is applicable in equilibrium and nonequilibrium molecular systems which may be open or closed, with or without intra-molecular interactions (e.g., electron-electron repulsion) taken into account, and for any electron-nuclear coupling. The derivation is based on a standard cumulant expansion performed in difference of nuclear quantum and classical versions of electronic Hamiltonian. That is, the derivation is a first principles consideration, which in principle allows for consistent extension of the treatment into higher orders of deviations from classical behavior accounting for nuclear quantum effects around classical trajectory. Established connection with the Zubarev’s method of nonlinear statistical operator opens a practical way for considerations beyond strictly adiabatic limit. Results of previous works are shown to follow from our derivation as particular limiting cases. We also discussed effective ways of evaluating friction tensor in interacting nonequilibrium systems. In particular, we show that recently introduced by us nonequilibrium diagrammatic technique for the Hubbard Green functions may be a convenient tool for evaluation of the friction tensor. For example, usual expressions for the tensor in interacting systems require consideration of the two-particle Green function; the same consideration requires evaluation of only the single-particle Hubbard Green function. The celebrated Head-Gordon and Tully expression for electronic friction is shown to be a quasiparticle equilibrium limit of part of our general expression for the frictions tensor. We discussed generalization of the Head-Gordon and Tully result to nonequilibrium situations and showed that the expression works only for isolated systems or situations with extremely small system-bath couplings. For non-negligible couplings, Head-Gordon and Tully expression for the friction tensor fails to reproduce correct tensor behavior. In this case one needs to account for additional correlations which are included in our expression for the tensor. We stress that main goal of this study is to demonstrate a consistent general derivation and its connection to previous considerations. Application of the methodology to actual calculations and elucidation of the role of nonadiabatic driving and quantum nuclear effects are the goals for future research.
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References

(1) Jiang, B.; Alducin, M.; Guo, H. Electron-Hole Pair Effects in Polyatomic Dissociative Chemisorption: Water on Ni(111). *J. Phys. Chem. Lett.* 2016, 7, 327–331.

(2) Ouyang, W.; Saven, J. G.; Subotnik, J. E. A Surface Hopping View of Electrochemistry: Non-Equilibrium Electronic Transport through an Ionic Solution with a Classical Master Equation. *J. Phys. Chem. C* 2015, 119, 20833–20844.

(3) Lei, Y.; Wu, H.; Zheng, X.; Zhai, G.; Zhu, C. Photo-Induced 1,3-cyclohexadiene Ring Opening Reaction: Ab Initio On-the-Fly Nonadiabatic Molecular Dynamics Simulation. *J. Photochem. Photobiol. A* 2016, 317, 39 – 49.

(4) Bennett, K.; Kowalewski, M.; Mukamel, S. Nonadiabatic Dynamics May Be Probed through Electronic Coherence in Time-Resolved Photoelectron Spectroscopy. *J. Chem. Theory Comput.* 2016, 12, 740–752.

(5) Petit, A. S.; Subotnik, J. E. Appraisal of Surface Hopping as a Tool for Modeling Condensed Phase Linear Absorption Spectra. *J. Chem. Theory Comput.* 2015, 11, 4328–4341.

(6) Petit, A. S.; Subotnik, J. E. Calculating Time-Resolved Differential Absorbance Spectra for Ultrafast Pump-Probe Experiments with Surface Hopping Trajectories. *J. Chem. Phys.* 2014, 141, 154108.
(7) Petit, A. S.; Subotnik, J. E. How to Calculate Linear Absorption Spectra with Lifetime Broadening Using Fewest Switches Surface Hopping Trajectories: A Simple Generalization of Ground-State Kubo Theory. *J. Chem. Phys.* 2014, 141, 014107.

(8) Long, R.; Guo, M.; Liu, L.; Fang, W. Nonradiative Relaxation of Photoexcited Black Phosphorus Is Reduced by Stacking with MoS2: A Time Domain Ab Initio Study. *J. Phys. Chem. Lett.* 2016, 7, 1830–1835.

(9) Wang, L.; Prezhdo, O. V.; Beljonne, D. Mixed Quantum-Classical Dynamics for Charge Transport in Organics. *Phys. Chem. Chem. Phys.* 2015, 17, 12395–12406.

(10) Xu, C.; Yu, L.; Zhu, C.; Yu, J.; Cao, Z. Intersystem Crossing-Branched Excited-State Intramolecular Proton Transfer for O-Nitrophenol: An Ab Initio On-the-Fly Nonadiabatic Molecular Dynamic Simulation. *Sci. Rep.* 2016, 6, 26768.

(11) Liu, X.-Y.; Chang, X.-P.; Xia, S.-H.; Cui, G.; Thiel, W. Excited-State Proton-Transfer-Induced Trapping Enhances the Fluorescence Emission of a Locked GFP Chromophore. *J. Chem. Theory Comput.* 2016, 12, 753–764.

(12) Tiwari, A. K.; Henriksen, N. E. Phase-Only Laser Control in the Weak-Field Limit: Two-Pulse Control of IBr Photofragmentation Revisited. *J. Chem. Phys.* 2016, 144, 014306.

(13) Lee, M. K.; Huo, P.; Coker, D. F. Semiclassical Path Integral Dynamics: Photosynthetic Energy Transfer with Realistic Environment Interactions. *Ann. Rev. Phys. Chem.* 2016, 67, 639–668.

(14) Krüger, B. C.; Bartels, N.; Bartels, C.; Kandratsenka, A.; Tully, J. C.; Wodtke, A. M.; Schäfer, T. NO Vibrational Energy Transfer on a Metal Surface: Still a Challenge to First-Principles Theory. *J. Phys. Chem. C* 2015, 119, 3268–3272.
(15) Ohmura, S.; Tsuruta, K.; Shimojo, F.; Nakano, A. Doping Effect on Photoabsorption and Charge-Separation Dynamics in Light-Harvesting Organic Molecule. *AIP Advances* **2016**, *6*, 015305.

(16) Nelson, T.; Fernandez-Alberti, S.; Roitberg, A. E.; Tretiak, S. Nonadiabatic Excited-State Molecular Dynamics: Modeling Photophysics in Organic Conjugated Materials. *Acc. Chem. Res.* **2014**, *47*, 1155–1164.

(17) Nikiforov, A.; Gamez, J. A.; Thiel, W.; Filatov, M. Computational Design of a Family of Light-Driven Rotary Molecular Motors with Improved Quantum Efficiency. *J. Phys. Chem. Lett.* **2016**, *7*, 105–110.

(18) Bustos-Marín, R.; Refael, G.; von Oppen, F. Adiabatic Quantum Motors. *Phys. Rev. Lett.* **2013**, *111*, 060802.

(19) Hopjan, M.; Stefanucci, G.; Perfetto, E.; Verdozzi, C. Molecular Junctions and Molecular Motors: Including Coulomb Repulsion in Electronic Friction using Nonequilibrium Green’s Functions. *Phys. Rev. B* **2018**, *98*, 041405.

(20) Kantorovich, L. Nonadiabatic Dynamics of Electrons and Atoms under Nonequilibrium Conditions. *Phys. Rev. B* **2018**, *98*, 014307.

(21) Bode, N.; Kusminskiy, S. V.; Egger, R.; von Oppen, F. Scattering Theory of Current-Induced Forces in Mesoscopic Systems. *Phys. Rev. Lett.* **2011**, *107*, 036804.

(22) Bode, N.; Kusminskiy, S. V.; Egger, R. E.; von Oppen, F. Current-Induced Forces in Mesoscopic Systems: A Scattering-Matrix Approach. *Beilstein J. Nanotechnol.* **2012**, *3*, 144–162.

(23) Shenvi, N.; Tully, J. C. Nonadiabatic Dynamics at Metal Surfaces: Independent Electron Surface Hopping with Phonon and Electron Thermostats. *Faraday Discuss.* **2012**, *157*, 325–335.
(24) Falk, M. J.; Landry, B. R.; Subotnik, J. E. Can Surface Hopping sans Decoherence Recover Marcus Theory? Understanding the Role of Friction in a Surface Hopping View of Electron Transfer. *J. Phys. Chem. B* **2014**, *118*, 8108–8117.

(25) Dou, W.; Nitzan, A.; Subotnik, J. E. Frictional Effects Near a Metal Surface. *J. Chem. Phys.* **2015**, *143*, 054103.

(26) Askerka, M.; Maurer, R. J.; Batista, V. S.; Tully, J. C. Role of Tensorial Electronic Friction in Energy Transfer at Metal Surfaces. *Phys. Rev. Lett.* **2016**, *116*, 217601.

(27) Maurer, R. J.; Askerka, M.; Batista, V. S.; Tully, J. C. *Ab Initio* Tensorial Electronic Friction for Molecules on Metal Surfaces: Nonadiabatic Vibrational Relaxation. *Phys. Rev. B* **2016**, *94*, 115432.

(28) Dou, W.; Subotnik, J. E. A Many-Body States Picture of Electronic Friction: The Case of Multiple Orbitals and Multiple Electronic States. *J. Chem. Phys.* **2016**, *145*, 054102.

(29) Dou, W.; Miao, G.; Subotnik, J. E. Born-Oppenheimer Dynamics, Electronic Friction, and the Inclusion of Electron-Electron Interactions. *Phys. Rev. Lett.* **2017**, *119*, 046001.

(30) Dou, W.; Subotnik, J. E. Universality of Electronic Friction: Equivalence of von Oppen’s Nonequilibrium Green’s Function Approach and the Head-Gordon - Tully Model at Equilibrium. *Phys. Rev. B* **2017**, *96*, 104305.

(31) Brandbyge, M.; Hedegård, P.; Heinz, T. F.; Misewich, J. A.; Newns, D. M. Electronically Driven Adsorbate Excitation Mechanism in Femtosecond-Pulse Laser Desorption. *Phys. Rev. B* **1995**, *52*, 6042–6056.

(32) Lü, J.-T.; Brandbyge, M.; Hedegård, P.; Todorov, T. N.; Dundas, D. Current-Induced Atomic Dynamics, Instabilities, and Raman Signals: Quasiclassical Langevin Equation Approach. *Phys. Rev. B* **2012**, *85*, 245444.
(33) Lü, J.-T.; Christensen, R. B.; Wang, J.-S.; Hedegård, P.; Brandbyge, M. Current-Induced Forces and Hot Spots in Biased Nanojunctions. *Phys. Rev. Lett.* **2015**, *114*, 096801.

(34) Thomas, M.; Karzig, T.; Kusminskiy, S. V.; Zaránd, G.; von Oppen, F. Scattering Theory of Adiabatic Reaction Forces due to Out-Of-Equilibrium Quantum Environments. *Phys. Rev. B* **2012**, *86*, 195419.

(35) Feynman, R.; Vernon, F. The Theory of a General Quantum System Interacting with a Linear Dissipative System. *Ann. Phys.* **1963**, *24*, 118 – 173.

(36) Atland, A.; Simons B. *Condensed Matter Field Theory*; Cambridge University Press, 2010.

(37) Kamenev, A. *Field Theory of Non-Equilibrium Systems*; Cambridge University Press, 2011.

(38) Haug, H.; Jauho, A.-P. *Quantum Kinetics in Transport and Optics of Semiconductors*, second, substantially revised edition ed.; Springer: Berlin Heidelberg, 2008.

(39) Schmid, A. On a Quasiclassical Langevin Equation. *J. Low Temp. Phys.* **1982**, *49*, 609–626.

(40) Zubarev, D.; Morozov, V.; Röpke, G. *Statistical Mechanics of Nonequilibrium Processes*; Akademie Verlag: Berlin, 1996.

(41) Morozov, V. G.; Röpke, G. Many-Particle Correlations and Boundary Conditions in the Quantum Kinetic Theory. *Condensed Matter* **1998**, *1*, 797–814.

(42) Puri, R. R. *Mathematical Methods of Quantum Optics*; Springer Series in Optical Sciences; Springer: Berlin, Heidelberg, New York, 2001; Vol. 79.

(43) Fetter, A. L.; Walecka, J. D. *Quantum Theory of Many-Particle Systems*; McGraw-Hill Book Company, 1971.
(44) White, A. J.; Ochoa, M. A.; Galperin, M. Nonequilibrium Atomic Limit for Transport and Optical Response of Molecular Junctions. *J. Phys. Chem. C* **2014**, *118*, 11159–11173.

(45) Galperin, M.; Nitzan, A. Nuclear Dynamics at Molecule-Metal Interfaces: A Pseudoparticle Perspective. *J. Phys. Chem. Lett.* **2015**, *6*, 4898–4903.

(46) Galperin, M. Photonics and Spectroscopy in Nanojunctons: A Theoretical Insight. *Chem. Soc. Rev.* **2017**, *46*, 4000–4019.

(47) Chen, F.; Ochoa, M. A.; Galperin, M. Nonequilibrium Diagrammatic Technique for Hubbard Green Functions. *J. Chem. Phys.* **2017**, *146*, 092301.

(48) Miwa, K.; Chen, F.; Galperin, M. Towards Noise Simulation in Interacting Nonequilibrium Systems Strongly Coupled to Baths. *Sci. Rep.* **2017**, *7*, 9735.

(49) Head-Gordon, M.; Tully, J. C. Molecular Dynamics with Electronic Frictions. *J. Chem. Phys.* **1995**, *103*, 10137–10145.

(50) Kapral, R.; Ciccotti, G. Mixed Quantum-Classical Dynamics. *J. Chem. Phys.* **1999**, *110*, 8919–8929.
Graphical TOC Entry

\[ Q = \frac{x + y}{2} \]
\[ = x - y \]

\[ F \]