

# Quantum Drude friction for time-dependent density functional theory

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Friction is a desired property in quantum dynamics as it allows for localization, prevents backscattering, and is essential in the description of multistage transfer. Practical approaches for friction generally involve memory functionals or interactions with system baths. Here, we start by requiring that a friction term will always reduce the energy of the system; we show that this is automatically true once the Hamiltonian is augmented by a term of the form  $\int a(\mathbf{q}; n_0) \times [\partial \mathbf{j}(\mathbf{q}, t) / \partial t] \cdot \mathbf{J}(\mathbf{q}) d\mathbf{q}$ , which includes the current operator times the derivative of its expectation value with respect to time, times a local coefficient; the local coefficient will be fitted to experiment, to more sophisticated theories of electron-electron interaction and interaction with nuclear vibrations and the nuclear background, or alternately, will be artificially constructed to prevent backscattering of energy. We relate this term to previous results and to optimal control studies, and generalize it to further operators, i.e., any operator of the form  $\int a(\mathbf{q}; n_0) [\partial c(\mathbf{q}, t) / \partial t] \cdot C(\mathbf{q}) d\mathbf{q}$  (or a discrete sum) will yield friction. Simulations of a small jellium cluster, both in the linear and highly nonlinear excitation regime, demonstrate that the friction always reduces energy. The energy damping is essentially double exponential; the long-time decay is almost an order of magnitude slower than the rapid short-time decay. The friction term stabilizes the propagation (split-operator propagator here), therefore increasing the time-step needed for convergence, i.e., reducing the overall computational cost. The local friction also allows the simulation of a metal cluster in a uniform jellium as the energy loss in the excitation due to the underlying corrugation is accounted for by the friction. We also relate the friction to models of coupling to damped harmonic oscillators, which can be used for a more sophisticated description of the coupling, and to memory functionals. Our results open the way to very simple finite grid description of scattering and multistage conductance using time-dependent density functional theory away from the linear regime, just as absorbing potentials and self-energies are useful for noninteracting systems and leads.

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## I. INTRODUCTION

Time-dependent density functional theory<sup>1</sup> (TDDFT), in its general form which includes time-dependent current-density functional theory<sup>2-4</sup> (TDCDFT) is quickly becoming a tool of choice to study excited state and dynamics of electrons (see, e.g., Refs. 5-9). While most studies are based on linear response in frequency space,<sup>10</sup> real-time approaches (e.g., Refs. 11 and 12) are gaining in importance. Most studies use adiabatic functionals, where the functional depends on the instantaneous value of the density and current, and there has been a development of sophisticated memory functionals<sup>13-19</sup> to go beyond that, often at increased costs.

In practice, going beyond adiabatic potentials is mostly due to the need to include energy-absorbing and phase-disturbing processes; a separate issue is multiharmonic effects. Of these, energy-absorbing processes are the most important in many practical studies. For example, the TDDFT/TDCDF description of transport over a barrier, between molecules, or in a narrow channel hinges on the ability to damp the energy of electrons once they react, to avoid backscattering effects. Physically, damping of the energy is due the electron-electron collision or interaction with

phonons, and the practical question is how to describe the effect of these in a physically reasonable but computationally cheap fashion. This will be especially important as computer power grows, and one will turn to using TDDFT in complicated multistep transport environments, where some energies are removed in each stage but the wavefunction continues to propagate.

An analogy with two fields is useful: linear wavefunction dynamics and classical dynamics. For linear wavepackets a similar question arises: How to remove a wavepacket once it reaches the end of a grid? One can use the formal optical potentials of the system, but often these are as difficult to obtain as solving the complete problem. Instead, for many applications it is best to employ absorbing potentials,<sup>20-22</sup> i.e., negative-imaginary (or complex) potentials that rise gradually to remove wavefunctions once they reach the end of the grids<sup>20</sup> to mimic the effect of the true scattering off by the wavefunction.

Absorbing potentials are nontrivial to integrate fully with density functional TDDFT models since the removal of a charge causes Coulombic charging effects on the system. For transport between leads over a single barrier this problem is reasonably solved by employing leads that do not have electron-electron interactions, so that the Hamiltonian

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there is linear and charging effects are unimportant;<sup>23</sup> there are many alternate methods, such as stochastic fields in the leads,<sup>24</sup> Lagrange multipliers,<sup>25</sup> etc. Still, it is desirable to have a general time-dependent approach for friction, which is at the same as computationally efficient as adiabatic TD-DFT calculations, and which can be applied to finite systems or ones with asymptotes, or to single-stage and multistage systems.

For inspiration, we take a clue from classical dynamics. There, the effect of friction is generally trivially simple: Include a Drude term (damping of the velocity) which removes energy continuously. Our object is therefore to develop a Drude-like artificial term, which will be fitted to experiment or to more sophisticated calculations. The main requirement on this term is that it continuously removes energy from the system. This is completely analogous to negative-imaginary absorbing potentials, which by construction, continuously remove density—except that here the goal is to remove energy, not density.

Section II shows this goal is easily obtained if we add the Hamiltonian a term of the form:  $a(\mathbf{q}; n_0) \times [\partial \mathbf{j}(\mathbf{q}, t) / \partial t] \cdot \mathbf{J}(\mathbf{q})$ , i.e., a position-dependent coefficient that will depend on the underlying parameters such as the ground-state density, times the current operator multiplied by the derivative of the expectation value of the current. This term, which is vaguely reminiscent of the force times velocity energy dissipation term in classical mechanics, automatically yields energy damping so that the friction goal is easily achieved.

Section III brings the many analogies of this term to previous work and generalizes it. The present work is completely analogous to control algorithms that seek to apply an external field that enhances internal energy.<sup>26</sup> The proposed term is very general, and it is shown that any set of operators, such as total or local dipole, kinetic energy, local kinetic energy, etc., could be applied instead of the current operator. Further, we demonstrate the analogy to the results of the interaction of the quantum system to a damped classical bath; the interaction produces a memory functional that could be related, with appropriate parameters, to the local term advocated here. Finally, we explain the relation to present TDDFT memory functionals, and show that the energy damping requirement can be satisfied for more general memory functionals with positive kernels

Section IV details the methodology of the friction calculation, and shows it to be efficient and linearly scaling. Simulations of a model system (excited electrons in jellium) are reviewed in Sec. V. Section VI concludes, with outlook for future work.

## II. FORMALISM

### A. Current-based friction

Given a quantum system, we assume that it is acted on by a Hamiltonian through a static part,  $H_0$ , and a time-dependent part

$$H = H_0 + H_{EM} + H_f(t). \quad (1)$$

Here, we first introduced the usual interaction with an external field (typically electromagnetic) that drives the system and will give, remove or generally exchange energy with it. The last part,  $H_f$ , will be due to the friction.

The simplest form for the friction operator,  $H_f$ , will be in a form mimicking an external field, or similarly, an interaction with an external bath. As the simplest choice (with others discussed later in the paper) we obtain friction by adding to the Hamiltonian an operator proportional to the current

$$H_f(t) = \int \mathbf{J}(\mathbf{q}) \cdot \mathbf{A}(\mathbf{q}, t) d^3\mathbf{q}. \quad (2)$$

Here,  $\mathbf{J}(\mathbf{q})$  is the current operator associated with location  $\mathbf{q}$ , i.e.,

$$\mathbf{J}(\mathbf{q}) = \frac{\mathbf{p} \delta(\mathbf{x} - \mathbf{q}) + \delta(\mathbf{x} - \mathbf{q}) \mathbf{p}}{2m}, \quad (3)$$

or more generally,

$$\mathbf{J}(\mathbf{q}) = i[H, \theta(\mathbf{x} - \mathbf{q})], \quad (4)$$

where  $\mathbf{x}$  is the coordinate in the system,  $m$  is the mass of the particle, and we introduced the momentum and the step functions. We use a notation  $\mathbf{A}(\mathbf{q}, t)$  for the scaled friction field, i.e., the field which multiplies the current operator. This notation is used since  $\mathbf{A}(\mathbf{q}, t)$  is obviously analogous to an electromagnetic potential.

The criterion for the friction field that we adopt is exceedingly simple: In the absence of a true external driving field (i.e., in the absence of an external electromagnetic field), the currents in the system should decay. Note that this criterion could be criticized since it allows the system, in principle, to settle into a stationary excited state rather than to the ground state; this is because in a stationary state the currents vanish. In practice we found, at least in the simple system studied, that the system eventually settles into a ground state. In other systems, frequent applications of a weak nonperiodic perturbation should be sufficient to excite the system away from any stationary excited state, and then friction can reduce its energy to go to the ground state.

The derivative of the energy of the system with respect to time is [when  $H_f(t)=0$ ]

$$\frac{d\langle H_0 \rangle}{dt} = \frac{d\langle H \rangle}{dt} - \frac{d\langle H_f \rangle}{dt}, \quad (5)$$

where the expectation value is defined as usual as

$$\langle A \rangle = \langle \Psi(t) | A | \Psi(t) \rangle, \quad (6)$$

and we introduce the wavefunction of the system, fulfilling

$$i \frac{\partial \Psi}{\partial t} = H \Psi. \quad (7)$$

Using the Hellman–Feynman theorem

$$\frac{d\langle H \rangle}{dt} = \left\langle \frac{\partial H}{\partial t} \right\rangle = \left\langle \frac{\partial H_f}{\partial t} \right\rangle = \left\langle \int \mathbf{J}(\mathbf{q}) \cdot \frac{\partial \mathbf{A}(\mathbf{q}, t)}{\partial t} d^3 \mathbf{q} \right\rangle, \quad (8)$$

so

$$\left\langle \frac{\partial H}{\partial t} \right\rangle = \int \mathbf{j}(\mathbf{q}, t) \cdot \frac{\partial \mathbf{A}(\mathbf{q}, t)}{\partial t} d^3 \mathbf{q}, \quad (9)$$

where we defined the local current function

$$\mathbf{j}(\mathbf{q}, t) = \langle \mathbf{J}(\mathbf{q}) \rangle = \langle \Psi(t) | \mathbf{J}(\mathbf{q}) | \Psi(t) \rangle. \quad (10)$$

Combining Eqs. (5) and (9) yields

$$\frac{d\langle H_0 \rangle}{dt} = \int \mathbf{j}(\mathbf{q}, t) \cdot \frac{\partial \mathbf{A}(\mathbf{q}, t)}{\partial t} d^3 \mathbf{q} - \frac{d}{dt} \int \mathbf{j}(\mathbf{q}, t) \cdot \mathbf{A}(\mathbf{q}, t) d^3 \mathbf{q}, \quad (11)$$

i.e.,

$$\frac{d\langle H_0 \rangle}{dt} = - \int \frac{\partial \mathbf{j}(\mathbf{q}, t)}{\partial t} \cdot \mathbf{A}(\mathbf{q}, t) d^3 \mathbf{q}. \quad (12)$$

A very simple prescription then follows: In order to ensure that the energy monotonically decreases, it is sufficient to define the field coupling to the current operator as proportional to the derivative of the current with respect to time,

$$\mathbf{A}(\mathbf{q}, t) = a(\mathbf{q}; n_0) \frac{\partial \mathbf{j}(\mathbf{q}, t)}{\partial t}, \quad (13)$$

where we define the friction coefficient function, which needs to be non-negative

$$a(\mathbf{q}; n_0) \geq 0, \quad (14)$$

and its strength determines the amount of friction in each region; this yields the final expression

$$H_f(t) = \int a(\mathbf{q}; n_0) \frac{\partial \mathbf{j}(\mathbf{q}, t)}{\partial t} \cdot \mathbf{J}(\mathbf{q}) d^3 \mathbf{q}. \quad (15)$$

Note that this expression is both Hermitian and one body. Also, the general units of the coupling constant are time  $\times$  volume/mass.

The value of the friction coefficient function will be determined by other means, such as linear-response studies, fitting to experiment, etc. The dependence on the underlying density is not known, but most likely will not be strictly local, i.e., if  $\mathbf{q}$  refers to a position coordinate, the friction coefficient at  $\mathbf{q}$  should depend on the ‘‘typical,’’ (i.e., locally averaged) density in the vicinity of  $\mathbf{q}$ . To simplify the notation, the  $n_0$  dependence is not explicitly denoted below. Also note that the final application of the formalism is not limited to linear response, and even for very large amplitude motions friction will lead to continuous reduction in energy, as shown in the results section.

In Eq. (14) we treat the friction function as a scalar; however, for nonhomogeneous system it could also be a tensor,  $a_{ij}(\mathbf{q})$ , and the only requirements then will be that the eigenvalues of the tensor be non-negative. To conclude this section, the main result is that a Hamiltonian with a guaranteed dissipation will be

$$H = H_0 + \int a(\mathbf{q}) \frac{\partial \mathbf{j}(\mathbf{q}, t)}{\partial t} \cdot \mathbf{J}(\mathbf{q}) d\mathbf{q}. \quad (16)$$

Formally, the proof in the previous section was for a traditional linear time-independent Hamiltonian, so it needs to be extended when used with TDDFT (and TDCDFT). The extension is trivial, as shown in the Appendix.

## B. Potential derived friction

It is also possible to use a local potential for friction, in the form

$$H_f''(t) = \int \hat{n}(\mathbf{x}) V(\mathbf{x}, t) d^3 \mathbf{x}, \quad (17)$$

which gives

$$\frac{d\langle H_0 \rangle}{dt} = - \int \frac{\partial n(\mathbf{x}, t)}{\partial t} V(\mathbf{x}, t) d^3 \mathbf{x}, \quad (18)$$

so that

$$V(\mathbf{x}, t) = - a''(\mathbf{x}) \frac{\partial n(\mathbf{x}, t)}{\partial t} \quad (19)$$

will guarantee that the energy at least does not increase as a function of time, and as long as there are density fluctuations, the density will decrease. Note that previous studies of memory functionals in TDDFT have also derived a memory potential that depends on the rate of change of the density.

The potential-derived friction will be effective only in regions where there are longitudinal currents. In regions where the currents are purely transverse so that  $\nabla \cdot \mathbf{j}(\mathbf{x}, t) = 0$ , there will be no dissipation since by the continuity equation, we can write

$$V(\mathbf{x}, t) = a''(\mathbf{x}) \nabla \cdot \mathbf{j}(\mathbf{x}, t). \quad (20)$$

This raises an interesting physical point, noted in memory-functional studies; in simulations of metallic systems through a jellium, potential-derived friction will only work at the surface of the metal, where the density oscillates. Within a potential-based prescription for a memory functional or friction, this problem is remedied (see Ref. 16 and references therein) through the modification of a jellium background to make it nonhomogeneous (e.g., by explicit local atomic pseudopotentials). In the Drude current-friction formalism as in Eq. (13), this problem does not occur and the friction will implicitly account for any inhomogeneity in the underlying potential, while retaining formally the uniform potential description since friction occurs whenever the current changes in time, even where it is homogeneous.

## C. General friction

It is obvious that any other family of one-body operator, in addition to the current and the density, could be used for friction; given a set of one-body operators  $\mathbf{Z}(\mathbf{q})$ , a friction Hamiltonian associated with it will be

$$H_{\text{fric}} = \int \mathbf{D}(\mathbf{q}, t) \cdot \mathbf{Z}(\mathbf{q}) d\mathbf{q}. \quad (21)$$

Here,  $\mathbf{q}$  is a general coordinate that parametrizes the operator  $\mathbf{Z}(\mathbf{q})$ ; in the discussion above, the physical coordinate was used but we could have equally well used other coordinates such as the three-dimensional momentum.  $D(\mathbf{q}, t)$  is the associated friction field, which analogously to the previous discussion, needs to be of the form

$$D(\mathbf{q}, t) = a(\mathbf{q}) \frac{d\mathbf{z}(\mathbf{q}, t)}{dt}, \quad (22)$$

where

$$\mathbf{z}(\mathbf{q}, t) = \langle \mathbf{Z}(\mathbf{q}) \rangle. \quad (23)$$

We use boldface quantities to indicate that the friction operator and associated field could be a general tensor (i.e., scalars, vectors, two-index tensors, etc.); the friction coefficients,  $a(\mathbf{q})$ , could analogously be scalars or non-negative-definite tensors.

Furthermore, instead of using a continuous coordinate  $\mathbf{q}$  we could even use a discrete sum, i.e., we can write

$$H_{\text{fric}} = \sum_j \mathbf{D}_j(t) \cdot \mathbf{Z}_j, \quad (24)$$

with  $D_j(t) = a_j d\mathbf{z}_j(t)/dt$ , such global operators could be, for example, the total dipole, current, quadruple, etc., of the system, rather than the local ones. The use of global operators is then completely analogous to the methods used in controlling molecular motion.

### III. ANALOGIES

There are several analogies and correlatives to expression (13), which we discuss below.

#### A. Analogy to control

The friction expressions, Eqs. (12) and (13), are analogous to an expression derived (see e.g., Ref. 26) for optimal control of molecular motion, where the electric field generally couples to a dipole; there, the goal is generally opposite, i.e., increase excitation. The associated field in that case is electrical, is constant over space (as it needs to be for realistic experiments of control of molecules), and couples to the total dipole of the system so that

$$H_{\text{control}}(t) = -\mu(t) \cdot \mathbf{E}(t), \quad (25)$$

where

$$\mu(t) \equiv \int n(\mathbf{x}, t) \mathbf{x} d^3\mathbf{x}, \quad (26)$$

and we introduced the density operator. The energy absorption is then

$$\frac{d\langle H_0 \rangle}{dt} = \frac{d\mu(t)}{dt} \cdot \mathbf{E}(t), \quad (27)$$

i.e., continuous energy absorption will occur when the external field is proportional to (minus) the time derivative of the dipole of the system

$$\mathbf{E}_{\text{optimal}} = -c \frac{d\mu(t)}{dt}. \quad (28)$$

Similar expressions for control of other observables are straightforwardly obtained.

#### B. Analogy to system-bath studies

The friction Hamiltonian derived above can be motivated by relating it to a system-bath description, in which there are a set of classical oscillators at every point  $\mathbf{q}$  (i.e., typically for every grid point). Specifically, consider a system interacting with a classical-bath Hamiltonian

$$H(\mathbf{q}, \{\mathbf{R}_n\}, \{\mathbf{P}_n\}) = H_0 + \int \left( \sum_n \alpha_n(\mathbf{q}) \mathbf{R}_n(\mathbf{q}) \mathbf{J}(\mathbf{q}) + \sum_n \frac{\mathbf{P}_n(\mathbf{q})^2}{2M} + \frac{M\omega_n^2 \mathbf{R}_n(\mathbf{q})^2}{2} \right) d\mathbf{q}. \quad (29)$$

The interaction here is through coupling to the current operator rather than to the position. Also, we introduced the bath coordinates, momenta, mass and frequency, and a coupling coefficient that is dependent on the coordinate of the quantum system. The harmonic oscillators in the description can represent interaction with a lattice or interactions with electron-hole excitations.

One missing ingredient is a counterterm of the form  $\mathbf{J}(\mathbf{q})^2$ , which prevents a runoff of the total energy to very negative values if the oscillators are damped; instead, however, we assume that the bath itself is subject to a friction term, which is Drude-like but affects both the coordinates and momenta of the harmonic oscillators. This is equivalent to requiring that these oscillators are attached to an even larger zero-temperature bath. Specifically, we write the equation of motion for the oscillators with a Drude terms added

$$\begin{aligned} \frac{d\mathbf{R}_n}{dt} &= \frac{\mathbf{P}_n}{M} - \gamma_n \mathbf{R}_n, \\ \frac{d\mathbf{P}_n}{dt} &= -\nabla_{\mathbf{R}_n} \langle H \rangle - M\omega_n^2 \mathbf{R}_n - \gamma_n \mathbf{P}_n \\ &= -\int \alpha_n(\mathbf{q}) \mathbf{j}(\mathbf{q}, t) d\mathbf{q} - M\omega_n^2 \mathbf{R}_n - \gamma_n \mathbf{P}_n, \end{aligned} \quad (30)$$

while the quantum dynamics will be of the form

$$i \frac{d|\Psi(t)\rangle}{dt} = \left( H_0 + \int \mathbf{A}_{\text{HO}}(\mathbf{q}, t) \cdot \mathbf{J}(\mathbf{q}) d\mathbf{q} \right) |\Psi(t)\rangle, \quad (31)$$

where

$$\mathbf{A}_{\text{HO}}(\mathbf{q}, t) \equiv \sum_n \alpha_n(\mathbf{q}) \mathbf{R}_n(\mathbf{q}, t), \quad (32)$$

and we ignored in this relation the contribution of the energy of the harmonic oscillator terms (the  $A_2$ -type terms).

The solution of the classical equations for driven Harmonic oscillators is straightforward to derive, and eventually yields



$$\mathbf{A}_{\text{HO}}(\mathbf{q}, t) = \int_{-\infty}^t \mathbf{j}(\mathbf{q}, t') \cdot \mathbf{M}(\mathbf{q}, t - t') dt', \quad (33)$$

where the memory is

$$\mathbf{M}(\mathbf{q}, t - t') = \sum_n \frac{|\alpha_n(\mathbf{q})|^2}{M\omega_n} \sin(\omega_n(t - t')) e^{-\gamma_n(t-t')}. \quad (34)$$

The remainder of the derivation is very heuristic. Since each oscillator moves with a specific frequency, it essentially interacts with the component of the current that has the same frequency; we therefore approximate the total current as a sum of individual components

$$\mathbf{j}(\mathbf{q}, t') \approx \sum_n \mathbf{j}_n(\mathbf{q}; t) \cos(\omega_n(t - t')) + \frac{\mathbf{j}'_n(\mathbf{q}; t)}{\omega_n} \sin(\omega_n(t - t')), \quad (35)$$

where  $\mathbf{j}_n, \mathbf{j}'_n$  are coefficients that are assumed to be a slowly varying function of time so that

$$\frac{d\mathbf{j}(\mathbf{q}, t)}{dt} \approx \sum_n \mathbf{j}'_n(\mathbf{q}; t). \quad (36)$$

Plugging the expansion into Eq. (33) yields, for small Drude friction,

$$\mathbf{A}_{\text{HO}}(\mathbf{q}, t) = \sum_n \frac{|\alpha_n(\mathbf{q})|^2 \mathbf{j}'_n(\mathbf{q})}{\omega_n^2 \gamma_n M}, \quad (37)$$

so that if the couplings are approximately proportional to frequency, we can replace the coupling part by the average, i.e.,

$$\mathbf{A}_{\text{HO}}(\mathbf{q}, t) \approx a(\mathbf{q}) \frac{d\mathbf{j}(\mathbf{q}, t)}{dt}, \quad (38)$$

which has the desired form of a derivative of the current with respect to time, where

$$a(\mathbf{q}) = \frac{1}{M} \left\langle \frac{|\alpha_n(\mathbf{q})|^2}{\gamma_n \omega_n^2} \right\rangle. \quad (39)$$

This shows that the friction term we introduced is related to system-bath studies, and even gives an estimate on the magnitude of the coupling.

### C. Analogy to memory-dependent and frequency-dependent functionals

Finally we note the analogy to TDDFT/TDCDFT memory functionals (see, e.g., Refs. 13, 14, 16–19, and 27). A typical memory current-based functional will depend on the density or current at earlier times, but the specifics of the memory functional will vary. There has been much activity in this field, with the overall goal of taking linear-response frequency-dependent interaction and converting it into linear-response and beyond-linear memory functionals. Some of the derived ones depend on, for example, the time-dependent density derivative in earlier times [e.g., Eq. (29) in Ref. 16] which will have, for a short-time kernel, a limit of the potential the derivative of the density with respect to time.

For linear-response frequency-dependent studies, the derivative of the current with respect to time is reminiscent of the frequency term in TDCDFT, for example, the viscoelastic field in Ref. 28, which however, relates to the gradients of the velocity field rather than the velocity field itself, as it is in the present simplified Drude treatment. Further, we have not aimed at Lagrangian-type Galilean invariance for the simplified friction.

Finally, it is easy to extend the Drude formula to a subset of general memory functionals, i.e., if we are given a memory functional which has the form

$$H_f = \int \frac{\partial \mathbf{z}(\mathbf{q}, t - t')}{\partial t} \cdot \mathbf{a}(\mathbf{q}, t - t') \cdot \mathbf{z}(\mathbf{q}, t) dt', \quad (40)$$

i.e., the friction function becomes a kernel. Then, using similar analysis, it is easy to show that the energy dissipation is

$$\frac{d\langle H_0 \rangle}{dt} = - \int \frac{\partial \mathbf{z}(\mathbf{q}, t)}{\partial t} \cdot \mathbf{a}(\mathbf{q}, t - t') \cdot \frac{\partial \mathbf{z}(\mathbf{q}, t')}{\partial t} d^3 \mathbf{q} dt'. \quad (41)$$

If the friction kernel damps rapidly enough we can average the energy dissipation over a finite time range, which will be significantly bigger than the fall-off time of the friction function. Then, the typical energy loss in such a range will be

$$\Delta \langle H_0 \rangle \cong + \int \omega^2 \mathbf{z}^*(\mathbf{q}, \omega) \cdot \mathbf{a}(\mathbf{q}, \omega) \cdot \mathbf{z}(\mathbf{q}, \omega) d^3 \mathbf{q} d\omega. \quad (42)$$

Here,  $\mathbf{z}(\mathbf{q}, \omega)$  is the Fourier transform of a smoothed  $\mathbf{z}(\mathbf{q}, t)$  in the finite time range. The energy loss will be manifestly negative if each eigenvalue of the tensor  $\mathbf{a}(\mathbf{q}, \omega)$  [or for a scalar friction, if each of  $a(\mathbf{q}, \omega)$ ] has a negative real part, i.e., if  $\mathbf{a}(\mathbf{q}, t - t')$  is a negative definite kernel. Such a friction will not lead to automatic energy loss at short times, but will be guaranteed to damp energy over times that are significantly larger than the falloff of the friction kernel.

### D. Global versus local friction

The use of friction which is local in time and space is, of course, a simplification. There could be cases where we expect the energy to increase in time and to be different for different subsystems, or to require detailed memory. Nevertheless, the use of a local friction still allows for quantum effects such as energy exchange between subsystems (energy that will be removed continuously, depending on the strength of the damping). As a practical tool, local friction is expected to work best for metallic jelliumlike systems, while for more coherent cases such as quantum systems with a few degrees of freedom, we expect that it may be better to damp global operators such as the kinetic energy and the total current, rather than local operators. This is analogous to classical mechanics where Drude friction is an approximation but is very useful. For practical case of transport and for use as artificial damping of reflected waves, a local damping (in space and time) should be sufficient.

## IV. METHODOLOGY

The practical application of the friction formalism is slightly complicated by the dependence on the derivative of

the current with respect to time in Eq. (16), as well as the use of the current operator. We found that the following prescription for a real-time propagator works quite well. A set of  $L$  time-dependent orbitals is propagated as

$$|\psi_l(t+dt)\rangle = e^{-iH_0(dt/2)} U_F(dt) e^{-iH_0(dt/2)} |\psi_l(t)\rangle, \quad (43)$$

where the friction-related short-time propagator is

$$U_F(dt) = \exp\left(-i \int a(\mathbf{q}) \frac{d\mathbf{j}(\mathbf{q},t)}{dt} \cdot \mathbf{J}(\mathbf{q}) d\mathbf{q} dt\right), \quad (44)$$

and its action is explained in Eqs. (46)–(51) and especially in Eq. (50) below.

The nonfriction part of the Hamiltonian is straightforwardly evaluated by the usual split-operator approach

$$e^{-iH_0(dt/2)} |\psi_l(t)\rangle = e^{-iV(dt/4)} e^{-iK(dt/2)} e^{-iV(dt/4)} |\psi_l(t)\rangle, \quad (45)$$

where  $K$  is the kinetic Hamiltonian, and  $V(\mathbf{x})$  is the total potential which depends on the density, including electron nuclear, direct, exchange, correlation, and any interaction with an external electromagnetic field. An obvious point is that  $V(\mathbf{x})$  will depend, in DFT, on the density and therefore on the orbitals. Therefore, the potentials that will be applied in the first and second  $H_0$  term will be different, as the orbitals change after the application of the first  $\exp(-iH_0 dt/2)$  term and the friction term.

Action by the friction term,  $U_F(dt) e^{-iH_0(dt/2)} |\psi_l(t)\rangle$ , is simple. Given  $|\chi_l(t)\rangle \equiv \exp(-iH_0 dt/2) |\psi_l(t)\rangle$ , we calculate

$$\mathbf{j}(\mathbf{q},t) = \sum_l \langle \chi_l(t) | \mathbf{J}(\mathbf{q}) | \chi_l(t) \rangle, \quad (46)$$

and estimate the current from

$$\frac{d\mathbf{j}(\mathbf{q},t)}{dt} \cong \frac{\mathbf{j}(\mathbf{q},t) - \mathbf{j}(\mathbf{q},t-dt)}{dt}, \quad (47)$$

from which the friction evolution is calculated,

$$U_F(dt) |\chi_l(t)\rangle \equiv |\chi_l(t)\rangle - idt \int a(\mathbf{q}) \frac{d\mathbf{j}(\mathbf{q},t)}{dt} \cdot \mathbf{J}(\mathbf{q}) |\chi_l(t)\rangle d\mathbf{q}. \quad (48)$$

The propagation requires the action of the current operator on the orbital, which is done by

$$\begin{aligned} \langle \mathbf{x} | \mathbf{J}(\mathbf{q}) | \chi_l(t) \rangle &= \frac{\langle \mathbf{x} | \mathbf{p} \delta + \delta \mathbf{p} | \chi_l(t) \rangle}{2m} \\ &= \frac{\langle \mathbf{x} | \mathbf{p} | \mathbf{q} \rangle \langle \mathbf{q} | \chi_l \rangle + \delta(\mathbf{x} - \mathbf{q}) \langle \mathbf{q} | \mathbf{p} \chi_l \rangle}{2m}, \end{aligned} \quad (49)$$

leading to the desired expression for the action of the friction operator

$$\begin{aligned} \langle \mathbf{x} | U_F(dt) | \chi_l(t) \rangle &\equiv \chi_l(\mathbf{x},t) - i \frac{dt}{2m} \langle \mathbf{x} | \mathbf{p} \eta_l \rangle \\ &\quad - i \frac{dt}{2m} a(\mathbf{x}) \frac{d\mathbf{j}(\mathbf{x},t)}{dt} \langle \mathbf{x} | \mathbf{p} \chi_l \rangle, \end{aligned} \quad (50)$$

where we defined the auxiliary function

$$\eta_l(\mathbf{q},t) \equiv a(\mathbf{q}) \frac{d\mathbf{j}(\mathbf{q},t)}{dt} \chi_l(\mathbf{q},t). \quad (51)$$

For simplicity, the action of the momentum is calculated in the friction term in the final expression [Eq. (50)] by a five-point derivative formula (with periodic boundary conditions) for each spatial direction; this is separate from the calculation of the kinetic term, which is easiest done by a fast-Fourier transform (FFT) approach. Overall, the calculation of the friction term is therefore linear in the total number of grid points and orbitals. Similar sparse equations will be developed for a basis-set description. We found generally that the use of the friction operator does not require reduction of the time step, in spite of the seemingly very low order accuracy (in  $dt$ ) of the expressions for the derivative of the current and for the action of  $U_F$ , Eqs. (47) and (48).

Finally, we note that the split-operator approach we used may not be the most optimal, and further optimization in the order of the terms may yield improvements of factor  $\sim 2-4$  in speed; e.g., it may be simpler to split the current propagator to a product of many short-time propagators, and change the order, e.g., in the form

$$U(dt) \approx U_F\left(\frac{dt}{2M}\right)^M U_0(dt) U_F\left(\frac{dt}{2M}\right)^M, \quad (52)$$

where  $U_0 = \exp(-iH_0 dt)$  is the nonfriction part of the Hamiltonian, and  $M$  should be 1–10, with the value chosen by optimization for overall efficiency. This will be checked in future papers.

## V. SIMULATIONS

To test the approach, we tested a simple system of spherical Jellium with a smooth falloff

$$n_J(\mathbf{r}) = \frac{n_0}{1 + \exp\left(\frac{r-r_0}{\beta}\right)}, \quad (53)$$

where the jellium's maximum density, fall-off width, and radius are  $n_0=0.008\,842$ ,  $r_0=8.1$ , and  $\beta=0.5$  (all in a.u.), respectively. The total number of occupied spatial orbitals is denoted as  $N$ ; we used  $N=10$ , with two electrons per orbital. The jellium parameters were fixed so that the total jellium charge is  $2N$ , so the system is neutral.

We used a standard DFT-local density approximation potential

$$V = V_{eN} + V_{ee} + V_{xc}, \quad (54)$$

where the electron-electron and exchange-correlation terms depend on time implicitly through their dependence on the electron density, defined as

$$n(\mathbf{x},t) = 2 \sum_{n=1}^N |\phi_n(\mathbf{x},t)|^2. \quad (55)$$

The one nontrivial point in the preparation is the application of a shift. Specifically, in the preparation of the ground-state system we shift the jellium density away from the origin, and therefore the associated electronic density is also shifted. The

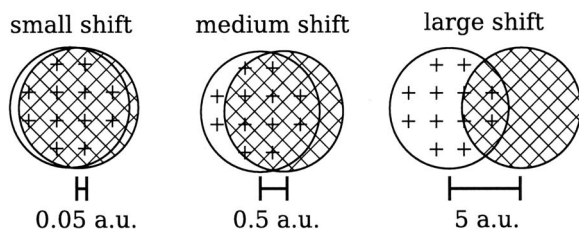


FIG. 1. Illustration of the various electron density shifts (cross hatching) from the jellium background. Not to scale.

jellium density appears only through its effects on the electron-nuclear Coulomb potential, so it is best to do the shift in the Fourier space, i.e., the electron-nuclear potential during the preparation of the ground state is

$$V_{eN,\text{shifted}}(\mathbf{r}) = \int \frac{4\pi}{k^2} n_j(\mathbf{k}) e^{i\mathbf{k}\cdot(\mathbf{r}-\delta\mathbf{x})} d^3\mathbf{k}, \quad (56)$$

where  $\delta\mathbf{x}$  is the shift and the integral is evaluated as usual by a fast-Fourier summation.

We used  $16^3$  grid points with a grid size of 2 a.u. The ground-state density and potential were obtained using imaginary-time propagation of  $H_0$  with the shifted electron-nuclear potential, first with a coarse time step of 0.5 a.u. followed by a refined step of 0.025 a.u. Throughout the imaginary-time propagation, the total density was kept normalized (this is equivalent to using the correct chemical potential in the propagation). The total binding energy of the system is 1.3 a.u. Following the ground-state preparation we remove the shift [i.e., recalculate Eq. (56) without a shift]; this creates a dipole excitation in the system as the electron cloud is shifted relative to the Jellium.

Finally, we let the system evolve under the full Hamiltonian including the friction field, using Eq. (43) and record the energy and dipole moment. Generally, we used  $dt=0.025-0.05$  a.u., and verified numerical convergence; even for the largest shift a time step of  $dt=0.05$  a.u. was sufficient to essentially converge the dipole moment, provided there was adequate damping. To ensure accurate FFT results, we evolved the systems in time for at least 3500 a.u., such that (except in the zero friction case) the dipole signals decayed to nearly zero.

Three shifts of the electron cloud with respect to the jellium background were applied: 0.05, 0.5, and 5 a.u. (see Fig. 1). The first is extremely small so linear response is valid, and the medium excitation is also essentially linear. The largest shift, however, corresponds to a huge excitation, as the electron and nuclear clouds hardly overlap. The total energy in the latter case is positive as the excitation energy is 5.2 a.u., i.e., about four times the total binding energy so that without friction the system would have quickly ionized.

We applied a friction coupling,  $a(\mathbf{q})$ , which is constant in space. In future studies we will adopt the results of memory functionals to include density dependence; clearly, a physical realization will have less friction away from the jellium. Several values were studied, ranging up to 200 a.u. As discussed below (also see Fig. 7), this range of values leads to a Drude time parameter of about 3–9 fs (for the short-time damping), appropriate for typical metals. The rea-

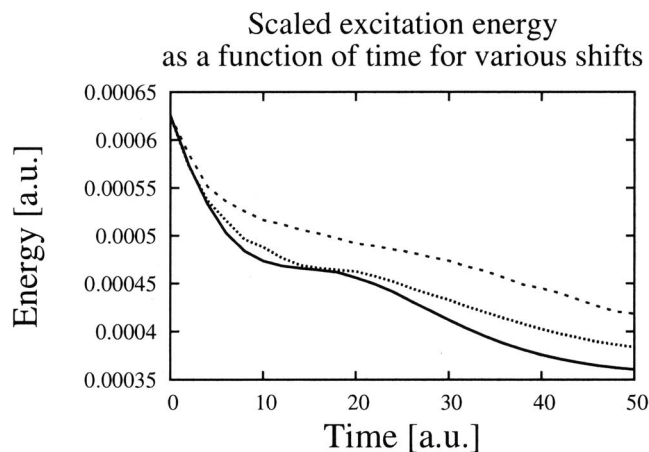


FIG. 2. Scaled excitation energies for short times for the three electron density shifts (solid: 0.05 a.u., fine dashed: 0.5 a.u., and coarse dashed: 5 a.u.) A constant friction coupling was used,  $a(\mathbf{q})=a=100$  a.u. The Drude friction rapidly removes energy from the system. For clarity, the 5 a.u. shift and 0.5 a.u. energies were divided by 8706 and 100, respectively. The corresponding Drude time parameters are 6, 7, and 9 fs.

son for such a large numerical value for  $a$  is that is multiplied by the derivative of the current, which in a.u. is small due both to the small jellium density and also due to the dependence on the oscillation frequency (around 0.06 a.u.) squared

Figures 2 and 3 show the excitation energies for all three shifts as a function of time, and demonstrate that the Drude friction removes energy steadily from the system. Initially (Fig. 2) the energy removal is very rapid, but it then settles (Fig. 3) to a lower rate. The corresponding Drude time parameter,  $\tau$ , is straightforward to calculate from the energy decay curves. The Drude time parameter is defined from

$$\frac{dj}{dt} \propto -\frac{j}{\tau}. \quad (57)$$

Assuming that energy decays exponentially with a decay constant  $\Gamma$ ,  $E(t) \propto e^{-\Gamma t}$ , and since the energy is proportional to the square of the current  $E \propto |j|^2$ , it follows that

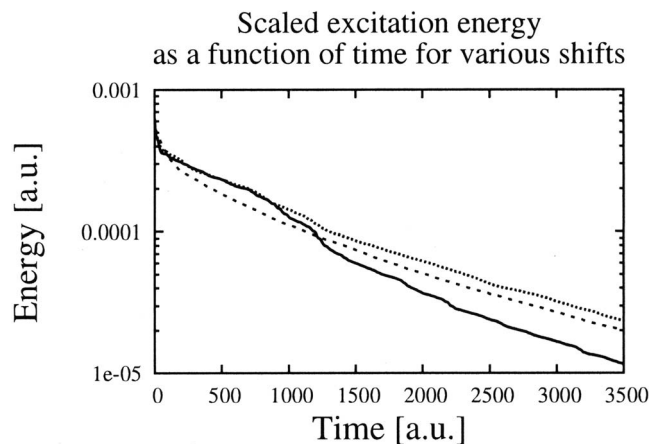


FIG. 3. Analogous to Fig. 2 but shown for longer times. The corresponding long-time Drude parameters for large, medium, and small shifts are 70, 81, and 83 fs for the small, medium, and large shifts, respectively.

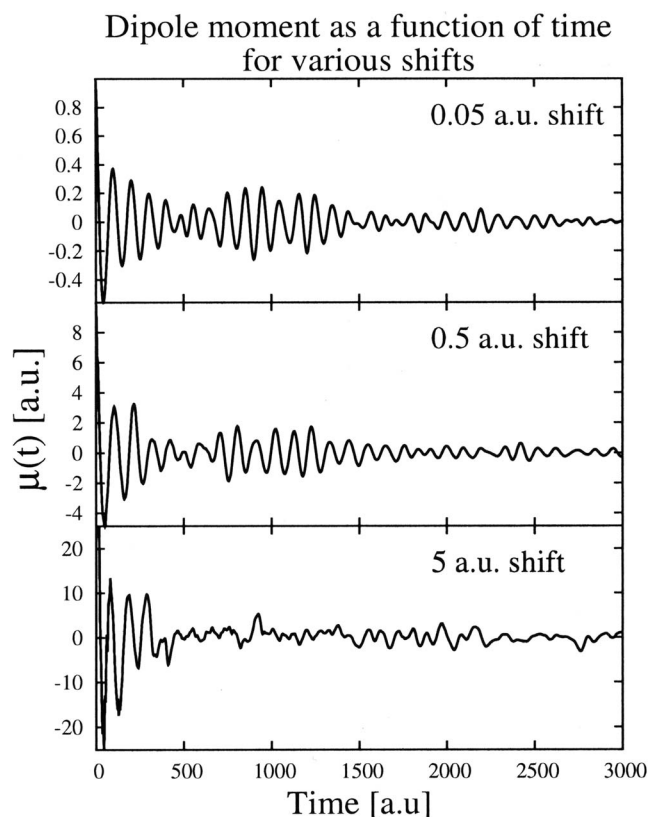


FIG. 4. Dipole moment as a function of time for fixed friction coupling of  $a=100$  a.u. and three shift values. There are strong recurrences in the small and medium (0.05 and 0.5 a.u., respectively) shifts due to interaction between nearby excited states (c.f. Fig. 6).

$$\tau = \frac{2}{\Gamma}, \quad (58)$$

where  $\Gamma$  is most readily calculated from the slope of  $\ln[E(t)]$  versus  $t$ .

The damping has a different rate at short and long times so we fitted it by two exponentials. In Figure 3, which shows the short-time damping, the exponential decay constants for the three shifts (small, medium, and large) are  $\Gamma=6.9 \times 10^{-4}$ ,  $6.0 \times 10^{-4}$ , and  $5.8 \times 10^{-4}$  a.u., respectively, which are equivalent to Drude time parameters of 70, 81, and 83 fs. Similarly, the effective coupling at short times, as shown in Fig. 3, is about an order of magnitude larger so the Drude parameter at short times were 9, 7, and 6 fs.

Figure 4 shows the dipole moment as a function of time for the three cases. There is an interesting recurrence as a function of time, which is especially evident for the weak and medium shifts; this recurrence is a true quantum effect as observed by comparing to a friction-free simulation, which shows overall oscillations (Fig. 5). These oscillations are due to two nearby excited states, as shown in the absolute value of the Fourier transform of  $\mu(t)$  (Fig. 6), which compares the excitation spectra with and without friction. To converge the no-friction result, the signal was damped by a weak exponential decay  $[(\exp(-t/1000 \text{ fs}))]$  and for consistency, such a damping was also applied to the finite friction case even though it is not required there due to the natural falloff of the dipole. For a given  $a(\mathbf{q})$  the friction is less

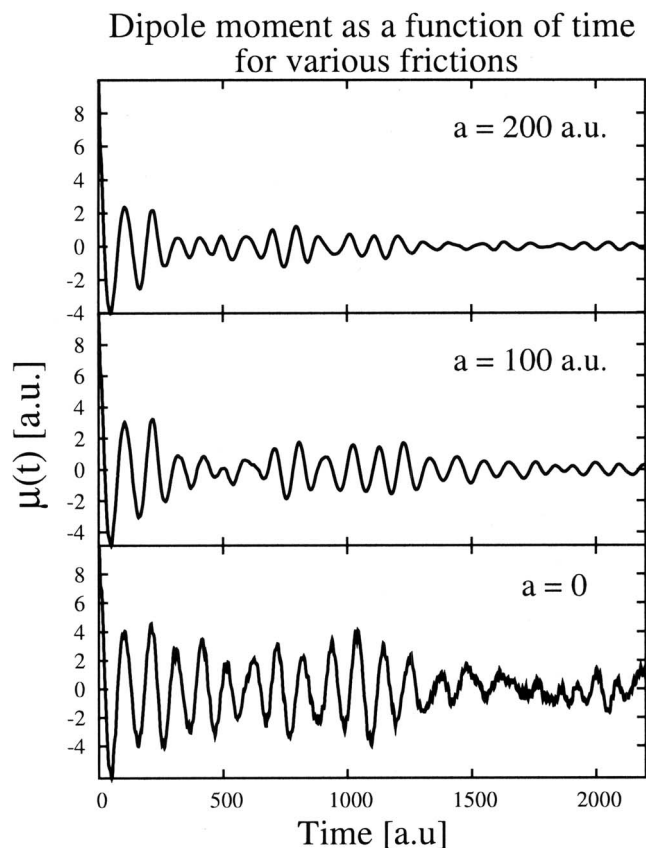


FIG. 5. Dipole moment as a function of time for a fixed 0.05 a.u. shift and various values of the friction coupling. For the largest damping the quantum recurrences are strongly damped.

effective at lower frequencies so it is clear that the overall Drude-like time parameter will be larger (i.e., less damping) for the higher excitation case, as was evident in the slopes of the energy versus time curves in Fig. 3 and the resultant values of  $\tau$ .

To better understand the correlation between the friction parameter  $a(\mathbf{q})$  and the Drude-like time parameter  $\tau$ , we var-

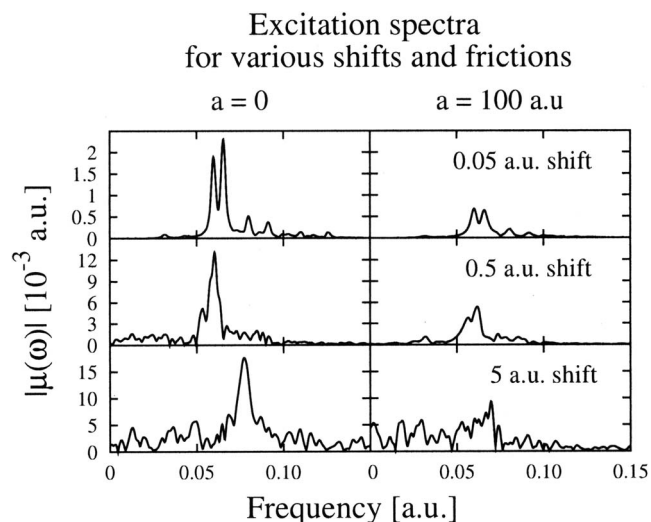


FIG. 6. Excitation spectra for the shifted-jellium system with no friction (left) and a friction coupling constant of  $a(\mathbf{q})=100$  a.u. (right) for three values of electron density shift.



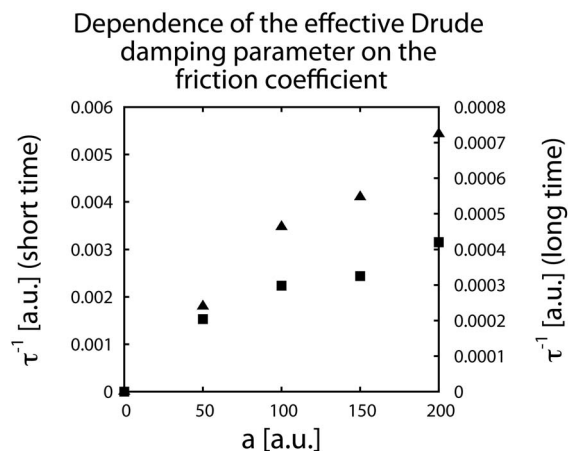


FIG. 7. Linear dependence of the Drude damping on the friction strength  $a$  for medium (0.5 a.u.) shift. The triangles refer to short-time friction, while the squares refer to the long-time friction.

ied the friction for a given shift. As shown in Fig. 7, the resulting Drude damping parameters are linear in  $a$ , for both the short- and long-time regimes. Thus, the friction coefficient can be tuned to correspond to any desired time parameter, which makes our approach suitable for modeling a wide variety of metals.

Finally, Fig. 8 shows that without the friction a very small time step is needed to prevent energy blowups. Without friction (top curve), the system is unstable for both time steps used, while friction (middle and bottom curves) stabilizes the split-operator propagation allowing the use of larger time steps (dotted lines).

## VI. CONCLUSIONS

In conclusion, we have shown that a simple prescription for quantum friction based on the requirement that the energy decays continuously gives an effective Drude damping. There are many further directions to continue this work. First, the origin of the double-exponential decay is interesting. We speculate that perhaps initially the electron motion is purely plasmonic so that a large current exists everywhere

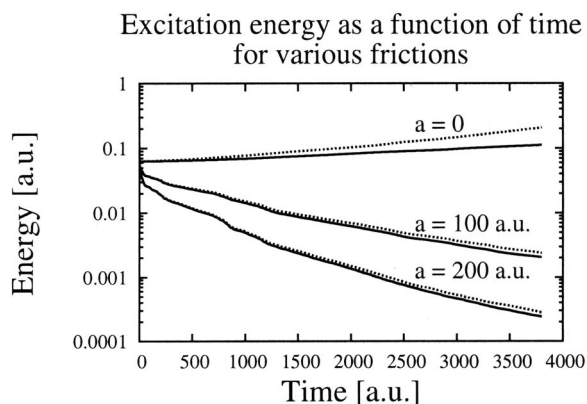


FIG. 8. Excitation energies for a medium (0.5 a.u.) shift and various values of the friction coupling constant. Solid lines are data with  $dt=0.025$  a.u. and dotted are for  $dt=0.05$  a.u. In the no-friction case, the energy quickly explodes, while for the other two cases, the Drude friction stabilizes the propagation.

and therefore the friction is very effective. At latter times the electron motion may be more of a particle-hole nature, involving possibly higher-order moments of the density matrix with small currents. If this is the case, then adding higher-order (but still one-body) friction operators may lead to further friction that is efficient even when the motion is not plasmonic; the simplest such operators will be the local kinetic energy and as an extension, the local stress tensor, in addition to the current as the friction operators, with the time dependence of the expectation values as the corresponding friction functions.

The strength of the Drude-type friction is in its simplicity. If a more precise frequency dependence is desired, then coupling to sets of harmonic oscillators is a conceivable approach, as well as the equivalent use of memory functionals. However, for limited frequency ranges or for purposes such as artificially absorbing an energy excitation in leads, a Drude description (with position-dependent coupling depending on the material and geometry) should be adequate.

The next stage in applications will be to test the method with a position-dependent friction for conductance; this will include both dc conductance where the Drude friction will be used with finite grids, multistage conductance where electrons (or excitons) will transport along several leads, in each of which there will be an amount of friction slowing them down. These will be reported in latter calculations. Finally, for multiharmonic generation or other cases where different frequencies are involved, the use of an artificial but positive definite kernel such as in Eq. (40) will be used.

## ACKNOWLEDGMENTS

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## APPENDIX: EXTENSION OF THE FRICTION PROOF TO TDDFT

Formally, the proof in Sec. II was for a traditional linear time-independent Hamiltonian, so it needs to be extended when used with TDDFT (and TDCDFT). The modified proof is trivial. We will assume that an adiabatic potential is used in TDDFT or TDCDFT. We define  $E_{KS}$  as the Kohn–Sham energy (including kinetic energy), so that we write

$$H_{KS}\phi_n \equiv \frac{\delta E_{KS}}{\delta \phi_n^*}. \quad (A1)$$

Moreover the total Hamiltonian governing the orbital motion includes the Kohn–Sham and friction contribution

$$H = H_{KS} + H_f, \quad (A2)$$

with

$$i \frac{d\phi_n}{dt} = H\phi_n \quad (A3)$$

so that

$$\begin{aligned}
\frac{dE_{\text{KS}}}{dt} &= \int \left( \frac{\delta E_{\text{KS}}}{\delta \phi_n^*} \frac{\partial \phi_n^*}{\partial t} + \frac{\delta E_{\text{KS}}}{\delta \phi_n} \frac{\partial \phi_n}{\partial t} \right) d\mathbf{x} \\
&= -i \int \left( (H_{\text{KS}} \phi_n) H \phi_n^* - (H_{\text{KS}} \phi_n^*) H \phi_n \right) d\mathbf{x} \\
&= i \langle [H, H_{\text{KS}}] \rangle = i \langle [H, H - H_f] \rangle = -i \langle [H, H_f] \rangle, \quad (\text{A4})
\end{aligned}$$

where  $\langle A \rangle \equiv \sum_n \langle \phi_n | A | \phi_n \rangle$ . Further development leads to

$$\begin{aligned}
\frac{dE_{\text{KS}}}{dt} &= - \int \sum_n \left( \phi_n^* H_f \frac{\partial \phi_n}{\partial t} + \frac{\partial \phi_n^*}{\partial t} H_f \phi_n \right) d\mathbf{x} \\
&= - \frac{d \langle H_f \rangle}{dt} + \int \sum_n \left( \phi_n^* \frac{\partial H_f}{\partial t} \phi_n \right) d\mathbf{x} \\
&= - \frac{d \langle H_f \rangle}{dt} + \left\langle \frac{\partial H_f}{\partial t} \right\rangle \\
&= - \frac{d \mathbf{j}(\mathbf{q}, t) \cdot \mathbf{A}(\mathbf{q}, t) d^3 \mathbf{q}}{dt} \\
&\quad + \left\langle \int \mathbf{J}(\mathbf{q}) \cdot \frac{\partial \mathbf{A}(\mathbf{q}, t)}{\partial t} d^3 \mathbf{q} \right\rangle \quad (\text{A5})
\end{aligned}$$

ending up exactly as in the linear-Hamiltonian case, Eq. (12).

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