Quantum theory of electronic friction

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Electronic friction is an important energy loss channel for atoms and molecules scattering off, reacting, or simply vibrating at metallic surfaces. It is usually well described by mixed classical-quantum approaches where the nuclei evolve classically according to Langevin-type equations of motion, and Born-Oppenheimer forces and friction kernels are obtained from first-principles electronic structure calculations. However, classical dynamics falls short when light atoms are involved, which is also the situation where electronic friction becomes the dominant dissipation channel and its role in the dynamics can be unambiguously assessed. Furthermore, the interplay between electronic friction and nuclear quantum effects in molecular processes at surfaces is largely unknown; in fact, it is not even clear how to include electronic friction in a quantum setting. Here we fill this gap by developing a fully quantum theory of electronic friction at $T = 0\,\mathrm{K}$. The electronic bath is considered to be entirely general and can be made of interacting electrons, potentially in a strongly correlated state. The derived friction kernel agrees with a recently obtained mixed quantum-classical result [Dou, Miao, and Subotnik, Phys. Rev. Lett. **119**, 046001 (2017)], except for a pseudomagnetic contribution in the latter that is removed here. The ensuing equation of motion for the nuclear wave function is a nonlinear Schrödinger equation with a frictional vector potential that depends on the past wave function behavior. The equation becomes local-in-time in the typical situation where the electrons respond rapidly on the slow timescale of the nuclear dynamics (Markov limit) and generalizes previously known Schrödinger-Langevin equations to coordinate-dependent, tensorial friction kernels.

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I. INTRODUCTION

When molecules interact with metal surfaces they induce electronic excitations in the substrate, in addition to the usual phonon excitations, and may give rise to intriguing phenomena, including electron transfer processes and generation of chemically induced currents [1–4]. If electron excitation remains of limited extent, it reduces to a frictional force of electronic origin that acts on the molecular degrees of freedom, in addition to the usual Born-Oppenheimer forces that arise in an adiabatic dynamics. This is a situation that is usually well described by combining a classical, Langevin-type description of the nuclear dynamics with a quantum treatment of the electronic problem that relies on the first-principles computation of the forces and of the friction kernel [5–7]. This so-called "Born-Oppenheimer dynamics with electronic friction" approach has been applied to a variety of problems [7–15] and is nowadays a standard tool to investigate the dynamics of molecules at metal surfaces [15,16].

Electronic friction has a long history [16]. Head-Gordon and Tully (HGT) [17] were the first to derive the frictional forces that electrons exert on a set of (classically) moving nuclei. They wrote the friction kernel in the form

$$\gamma_{kj}^{\mathrm{HGT}} = \pi\hbar \sum_{ab} \langle a|\partial_k h|b\rangle \langle b|\partial_j h|a\rangle \, \delta(\epsilon_a - \epsilon_F)\delta(\epsilon_b - \epsilon_F), \tag{1}$$

where a, b label single-particle states, k, j label nuclear degrees of freedom, h is the one-particle Hamiltonian, and ϵ_F is the Fermi energy. This result was obtained at zero temperature in the independent electron approximation and found to be consistent with earlier results on vibrational relaxation at metal surfaces [18–20]. It was also rederived using different methodologies, including influence functionals [21] and nonequilibrium Green's functions [22] (see Ref. [16] for a comprehensive account). Later works addressed the issue of nonthermal, yet steady-state, electronic baths (e.g., in current-carrying metals) [23,24] and of electron-electron interactions [25,26], and showed the importance of going beyond a mean-field treatment of the electronic dynamics [26]. In particular, Dou, Miao, and Subotnik (DMS), using a mixed quantum-classical approach, derived a completely general friction kernel that is valid out of equilibrium and applies equally well to independent or interacting electrons [26]. DMS wrote the electronic friction tensor, in the Markov limit, as

$$\gamma_{kj}^{\mathrm{DMS}} = -\int_0^\infty \mathrm{tr}_e[(\partial_k H_{\mathrm{el}})e^{-\frac{i}{\hbar}H_{\mathrm{el}}\tau}(\partial_j \rho)e^{+\frac{i}{\hbar}H_{\mathrm{el}}\tau}]d\tau, \tag{2}$$

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where ρ is the steady-state electron density operator, $H_{\rm el}$ is the electronic Hamiltonian, possibly including interactions between electrons, and tr_e denotes the trace over the electronic degrees of freedom.

However, none of the above works addressed the nuclei quantum mechanically and thus leave open the question whether the electronic frictional regime is compatible with a full quantum description of the electronic-nuclear system—i.e., whether a "Born-Oppenheimer quantum dynamics with electronic friction" exists—and, eventually, how a quantum description of the nuclei can accommodate an electronic friction term. This is a significant shortcoming since electronic friction becomes the dominant energy loss channel right when a quantum description is mandatory, i.e., for light atoms that are hardly able to excite the substrate phonons. Furthermore, the proper application of the adiabatic approximation introduces, in addition to the usual Born-Oppenheimer forces, two gauge fields [27]—a pseudoelectric and a pseudomagnetic field that reflect the geometric properties of the electronic eigenspaces when viewed as functions of the nuclear degrees of freedom. It is not clear whether and how these gauge fields disappear when the electron dynamics is taken into account, even in the frictional limit considered here.

In this work, the above issues are solved by devising a full quantum description of the dynamics of the combined electronic-nuclear system. To this end we shall adopt a representation of the exact wave function that closely resembles the adiabatic one, and derive from it, under suitable conditions, the frictional response of the electronic degrees of freedom to the (quantum) nuclear dynamics. Importantly, we shall show how the adiabatic Hamiltonian has to be modified to include friction in the nuclear dynamics, and how the equation of motion for the nuclear wave function is turned into a nonlinear equation of the Schrödinger-Langevin type. The procedure is entirely general and not limited to the electronic-nuclear problem. We shall expand on this issue in a forthcoming publication.

The article is organized as follows. In Sec. II we revisit the adiabatic approximation from the perspective of the variational quantum dynamics, where the gauge fields arise naturally from the form of the variational ansatz. The pseudomagnetic field is well known, and it has been thoroughly investigated because of its relation to the adiabatic geometric phase, the celebrated Berry's phase [28]. On the other hand, the pseudoelectric field has received much less attention and its meaning is far less obvious. We shall show that, by recasting the adiabatic problem into a variational problem, it is possible to give a clear interpretation of the latter in terms of the local-in-time-error (LITE) [29,30] that accompanies the variational solution. The latter is shown to be closely related to a quantum metric of the variational manifold.

In Sec. III we analyze the exact quantum dynamics at $T = 0\,\mathrm{K}$ of the combined electronic-nuclear system using the exact factorization of the wave function [31,32]. We rederive the key equations of motion for the nuclear and electronic wave functions by using a projection-operator technique that emphasizes their gauge transformation properties, thereby allowing one to single out distinct, physically meaningful contributions to the dynamics. We shall show that the electronic dynamics introduces a dynamic correction to the pseudomagnetic and pseudoelectric fields which make them vanish when averaged over the nuclear state. This leaves only one genuine, nonadiabatic contribution to the dynamics, in addition to the usual mean-field, Born-Oppenheimer-like potential. We shall show that the disappearance of the pseudoelectric force expresses conservation of a quantum metric—i.e., the vanishing of the covariant derivative of a metric tensor—which is a simple generalization of the above adiabatic metric. This appears consistent since the quantum metric and the related pseudoelectric field measure the error in the adiabatic approximation, while the dynamics considered here is exact. Likewise, the vanishing of the pseudomagnetic force signals the quenching of geometric phase effects that, in fact, should disappear when the dynamics is far from the adiabatic regime.

In Sec. IV we analyze the case of an electronic bath that relaxes quickly on the timescale relevant for the nuclear motion, and derive an electronic-friction kernel that describes the corresponding electronic-friction dynamical regime. In the Markov limit of a memoryless friction, where the electronic system returns instantaneously to its ground state, we shall show that the pseudoelectric and pseudomagnetic fields are fully restored, thereby making geometric phase effects potentially observable. This is the quantum-dynamics-with-electronic-friction regime, in which the electrons are "factored out" of the dynamical problem and only the evolution of the nuclear wave function is required. We shall show that the equation of motion of the latter is a nonlinear equation of Schrödinger-Langevin type, and obtain the corresponding effective Hamiltonian. In the simplest situation of a uniform isotropic friction kernel this bridges the theory with previous, "nonorthodox" quantum models of dissipation, namely, the Kostin equation [33], here reobtained from a microscopic model. Traditional arguments against these models (e.g., their nonlinearity) are here settled from the outset by noticing that the nuclear wave function does *not* represent the wave function of a closed system, rather it is a marginal probability amplitude of a subsystem. The theory is formulated for general memory kernels (requiring the wave function history) and only later specialized to the Markov case. Hence it is suitable, at least in principle, to address issues like the importance of the memory in the friction kernel [12]. Furthermore, no assumptions are made on the electronic bath, and the theory applies equally well to independent electrons and to interacting electrons in a strongly correlated state. The impact of the electronic state on the dynamical behavior of the nuclei has just begun to be explored [26], and the present theory sets a framework to extend these investigations to a regime where the nuclei need to be treated as quantum objects.

We briefly summarize our findings and draw some conclusions in Sec. V. The accompanying Letter [34] focuses on more physical aspects of the problem and provides a first application to a model problem. This shows that the proposed approach represents a viable way to account for electronic friction in a fully quantum setting for the nuclear dynamics.

II. ADIABATIC APPROXIMATION

As mentioned in the Introduction, we set out by revisiting the quantum adiabatic approximation from the perspective of

variational quantum dynamics. We start by considering the case where the slow variables $\mathbf{x} \in \mathcal{M}$ act as mere external parameters that are under the control of the experimenter. Here $\mathcal{M}$ is supposed to be a smooth differential manifold, equipped with an atlas, whose generic coordinate chart $\varphi: \mathcal{M} \supseteq \mathcal{U} \to \mathbb{R}^n$ defines the components x^i of $\mathbf{x} \in \mathcal{M}$ and the holonomic basis $\{\mathbf{e}_i \equiv \partial_i\}_{i=1}^n$ in the tangent bundle $T\mathcal{M}$ (along with its dual $\{dx^i\}_{i=1}^n$ in $T^*\mathcal{M}$). The Hamiltonian of the quantum system depends smoothly on $\mathbf{x}$, $H \equiv H(\mathbf{x})$, and $\mathcal{V}_\mathbf{x}$ is its eigenspace for the eigenvalue of interest, here taken be nondegenerate (although this property is not essential for most of the derivations). By attaching the eigenspace $\mathcal{V}_\mathbf{x}$ to each point $\mathbf{x}$ of the manifold $\mathcal{M}$ one defines a vector bundle, commonly denoted as $\pi: E \to \mathcal{M}$, where π is the fundamental projection on the base space $\mathcal{M}$, i.e., $\pi^{-1}(\mathbf{x}) = \mathcal{V}_\mathbf{x}$ identifies the fiber above $\mathbf{x}$. In our problem, the variables $\mathbf{x}$ are meant to be the nuclear degrees of freedom, and the quantum system is the electronic subsystem. The discussion of this subsection is instrumental for the situation most interesting for our purposes, which is the one in which the $\mathbf{x}$'s become dynamical variables and hence get subjected to the system response. We shall show how the local-in-time error [29] in these two distinct situations—i.e., $\mathbf{x}$ as external parameters vs dynamical variables—relate to each other, and later make the connection with the more common nonadiabatic transition probabilities.

A. Slow variables as external parameters

When the slow variables $\mathbf{x}$ are regarded as parameters that are under the control of the experimenter, the Hamiltonian governing the evolution of the system has a predefined time dependence $H(t) = H(\mathbf{x}(t))$ for any given path $[0, T] \ni t \to \mathbf{x}(t)$ of the parameters. The adiabatic approximation for the nth state can be recast as a variational approximation to the problem

$$i\hbar \frac{d}{dt} |\Psi_t\rangle = H(t) |\Psi_t\rangle \quad |\Psi_0\rangle = |u_n(\mathbf{x}(0))\rangle$$

by introducing a time-dependent variational manifold $\mathcal{V}(t) \equiv \mathcal{V}_{\mathbf{x}(t)}$ and a trivial, complex-analytic representation of the wave function. For instance, for a nondegenerate eigenspace, the variational ansatz takes the form $|\Psi_t\rangle = C\,|u_n(\mathbf{x}(t))\rangle$, where C is the only (complex) variational parameter of the problem and $|u_n(\mathbf{x})\rangle \in \mathcal{V}_\mathbf{x}$ is a normalized eigenvector of $H(\mathbf{x})$, chosen smoothly over the manifold patches. The Dirac-Frenkel condition [35] amounts to

$$P(i\hbar\partial_t - H)\,|\Psi_t\rangle = 0, \tag{3}$$

where P is the instantaneous eigenprojector and $Q = 1 - P$ its orthogonal complement. Equivalently, upon using $Q\,|\dot\Psi_t\rangle \equiv \dot P\,|\Psi_t\rangle$, we can rewrite the time derivative of the wave function, $|\dot\Psi_t\rangle$, as

$$i\hbar\,|\dot\Psi_t\rangle = H_{PP}(t)\,|\Psi_t\rangle + i\hbar\dot P\,|\Psi_t\rangle\,, \tag{4}$$

where the first term on the right-hand side (r.h.s.) is a proper dynamical term (here $H_{PP} \equiv PHP$) and the second term describes the dynamics of the variational manifold. The latter is supposed to be "much smaller" than the first if the adiabatic approximation is expected to be accurate in the long run. This term has a purely geometric nature, since in reduced time units $s = t/T$ it is the same irrespective of the slowness of the adiabatic process,

$$i\hbar\frac{d}{ds}|\Psi\rangle = TH_{PP}\,|\Psi\rangle + i\hbar\frac{dP}{ds}\,|\Psi\rangle\,,$$

i.e., irrespective of how large T is for the given transformation along the path $\mathbf{x}(t)$. Importantly, however "small" the $\dot P$ term is, it is crucial for the adiabatic dynamics since it keeps the state vector on the (moving) eigenspace: without such a term, the time derivative on the left-hand side would be constrained to the instantaneous eigenspace of the Hamiltonian, hence $|\Psi\rangle$ could not follow the evolution in time of the latter. Furthermore, by generating the geometric phase, this term provides the correct phase change during the adiabatic evolution. As a matter of fact, the presence of $\dot P$ in the variational equation of motion, Eq. (4), makes it equivalent to a parallel transport condition (see Appendix A).

For the purpose of introducing the LITE [29,30] in the considered variational approximation, Eq. (4) is conveniently transformed into an effective Schrödinger equation $i\hbar\,|\dot\Psi_t\rangle = H_n\,|\Psi_t\rangle$. The corresponding self-adjoint effective Hamiltonian takes the form

$$H_n = H_{PP} + i\hbar[\dot P, P]$$

as follows from $P\dot P\,|\Psi_t\rangle \equiv 0$, upon noticing the identities $P\dot PP = Q\dot PQ = 0$. The LITE is a quantum distance [30] that measures, in the short run, how much the physical state described by the variational solution deviates from the exact one. In the case of a complex-analytic parametrization the variational equation of motion is generated by a "variational Hamiltonian," here H_n above, and the LITE takes the form $\varepsilon = \hbar^{-1}\|(H - H_n)\Psi\|$, for a normalized $|\Psi\rangle$. Hence,

$$\varepsilon = \hbar^{-1}||Q(H - i\hbar\dot P)\Psi|| \equiv ||\dot P\Psi||, \tag{5}$$

where in the last step use has been made of the fact that $|\Psi\rangle$ is an instantaneous eigenstate of the Hamiltonian H. We thus see that this error is a purely geometrical property, meaning that for a given infinitesimal displacement in parameter space it does *not* depend on the slowness of the evolution,

$$\varepsilon^2 dt^2 = \sum_{jk} \langle\Psi|(\partial_j P)(\partial_k P)|\Psi\rangle\, dx^j dx^k,$$

where $\partial_j \equiv \partial/\partial x^j$ has been introduced. In fact, for a nondegenerate eigenspace the LITE is a property of the vector bundle

$$\varepsilon^2 = \sum_{jk} \langle\partial_j u_n|Q|\partial_k u_n\rangle\, V^j V^k = \sum_{jk} g_{jk} V^j V^k, \tag{6}$$

as can be seen upon introducing a "frame" $|u_n(\mathbf{x})\rangle$ for any $\mathbf{x} \in \mathcal{M}$, and noticing that $(\partial_j P)\,|u_n\rangle = Q\,|\partial_j u_n\rangle$ [or more directly from Eq. (5), upon observing that $||\dot P\Psi|| = ||\dot P u_n||$]. Here $V^j = \dot x^j$ is the jth component of the parameter velocity vector and norm conservation ($|C|^2 \equiv 1$ at any time) has been used to write the error in terms of properties of the frame. In the above equation, only the symmetric components of $q_{jk} = \langle\partial_j u_n|Q|\partial_k u_n\rangle$ matter, but it is useful to introduce the rank-2 covariant tensor q

$$q = \sum_{jk} \langle\partial_j u_n|Q|\partial_k u_n\rangle\, dx^j dx^k, \tag{7}$$

known as quantum geometric tensor [28,36], and define g to be its symmetric part (the g_{jk}'s above are then the components on the direct-product basis $dx^j dx^k$). This symmetric (real) part g represents a quantum metric (a Fubini-Study metric [36]) on the tangent bundle, i.e., an inner product for tangent vectors that is (smoothly) defined for any $\mathbf{x} \in \mathcal{M}$ and that is sensitive to the attached quantum states in a gauge invariant way. Accordingly, ε above can also be viewed as the magnitude of the velocity—as measured by this metric—along the variational trajectory, namely, $\varepsilon \equiv \sqrt{g(\mathbf{V}, \mathbf{V})}$. Appendix B summarizes the properties of the Fubini-Study metric and its relation with the LITE.

We conclude this section by noticing that, on the other hand, the antisymmetric (imaginary) part of the quantum geometric tensor is related to Berry's curvature. In a single equation we have

$$q = g - \frac{i}{2} d\omega, \tag{8}$$

where d denotes the exterior derivative and ω is the differential form $\omega = \sum_j A_j dx^j$. Here $A_j = i \langle u_n | \partial_j u_n \rangle \in \mathbb{R}$ subsumes the Berry's connection

$$T_{\mathbf{x}}\mathcal{M} \times \mathcal{V}_{\mathbf{x}} \ni (\mathbf{X}, |\psi\rangle) \to \nabla_{\mathbf{X}} |\psi\rangle = \sum_j X^j P |\partial_j \psi\rangle , \tag{9}$$

as becomes evident when acting on the chosen frame, $\nabla_{\mathbf{X}} |u_n\rangle = -i(\sum_j X^j A_j) |u_n\rangle$, and using the Leibniz rule for arbitrary vectors $|\psi\rangle = c |u_n\rangle$. In the above decomposition of the quantum geometric tensor, one can make explicit the relation with Berry's curvature, namely, $d\omega = \sum_{jk} B_{jk} dx^j dx^k$, where $B_{jk} \equiv \partial_j A_k - \partial_k A_j$ are the components of the curvature tensor for the present problem.

On comparing Eq. (9) with Eq. (5) one notices that while the Berry's connection projects the state-vector variations on the fiber bundle, the LITE quantifies their changes in the normal bundle. The simple and well-known case of the Bloch sphere illustrates well the meaning of the related tensors, $d\omega$ and g, respectively. The sphere is the appropriate parameter space to describe the adiabatic dynamics of a spin-1/2 in a magnetic field (but also the projective Hilbert space of a two-state system). The spherical coordinates then specify the direction of the magnetic field and the vector $|\psi\rangle = \cos(\theta/2) |\alpha\rangle + e^{i\phi} \sin(\theta/2) |\beta\rangle$ uniquely identifies the adiabatic space with definite, positive projection along the field axis [37]. The corresponding quantum geometric tensor is easily found to be $q = \frac{1}{4}[d\theta^2 + \sin^2\theta d\phi^2] \pm \frac{i}{4} \sin\theta (d\theta \wedge d\phi)$ for the positive and negative projection and describes the usual metric of the Riemann sphere of radius 1/2, with a curvature $d\omega = -2\mathrm{Im} q = \mp \frac{d\Omega}{2}$, where $d\Omega$ is the infinitesimal solid angle and $\wedge$ denotes the wedge product.

B. Slow variables as dynamical variables

If the slow variables are considered as dynamical variables, the electron-nuclear wave function is written as

$$|\Psi\rangle = \int d\mathbf{x} \psi(\mathbf{x}) |u_n(\mathbf{x})\rangle |\mathbf{x}\rangle . \tag{10}$$

The variational manifold is again complex and application of the variational principle reduces to the Dirac-Frenkel condition [29],

$$\int d\mathbf{x}' d\mathbf{x} \delta\psi^*(\mathbf{x}') \langle u_n(\mathbf{x}'), \mathbf{x}' | [i\hbar\partial_t - H] |u_n(\mathbf{x}), \mathbf{x}\rangle \psi(\mathbf{x}) = 0.$$

Here

$$\langle u_n(\mathbf{x}'), \mathbf{x}' | H | u_n(\mathbf{x}), \mathbf{x}\rangle = \delta(\mathbf{x} - \mathbf{x}') \big[\langle \hat{T} \rangle_n + E_n(\mathbf{x}) \big],$$

where $E_n(\mathbf{x})$ is the Born-Oppenheimer potential energy surface and $\langle \hat{T} \rangle_n$ is the coordinate representation of the nuclear kinetic energy operator averaged over the electronic state,

$$\langle \hat{T} \rangle_n = \langle u_n(\mathbf{x}) | \hat{T} | u_n(\mathbf{x}) \rangle .$$

Setting

$$H_n = \langle T \rangle_n + E_n(\mathbf{x}), \tag{11}$$

the variational equation of motion takes the form of a Schrödinger equation for the nuclear wave function

$$H_n \psi = i\hbar \frac{\partial \psi}{\partial t}$$

with an effective Hamiltonian specific to the electronic state under consideration. The main difference with respect to the common Born-Oppenheimer Hamiltonian lies in the nuclear kinetic energy operator which gets dressed by the electronic motion: this dressing is the way the gauge fields originate from the geometric properties of the adiabatic approximation. In this context, it may be worth noticing that the above equation of motion, differently from the Born-Oppenheimer evolution, correctly conserves energy

$$\frac{d}{dt} \langle \Psi | H | \Psi \rangle = 0$$

due to its variational origin, and this occurs upon including the above mentioned gauge fields.

Let us now examine the dressed kinetic energy operator. We assume that T takes the form

$$\hat{T} = \frac{1}{2} \sum_{jk} \xi^{jk} \hat{p}_j \hat{p}_k,$$

where $\xi^{jk} = \xi^{kj}$ is the inverse mass tensor, here taken to be coordinate independent. A simple calculation gives

$$\langle \hat{p}_j \hat{p}_k \rangle_n = (\hat{p}_j - \hbar A_j)(\hat{p}_k - \hbar A_k) + \hbar^2 q_{jk},$$

where A_j and q_{jk} have been introduced above [38], hence

$$\langle \hat{T} \rangle_n = \frac{1}{2} \sum_{jk} \xi^{jk} \hat{\pi}_j \hat{\pi}_k + \phi \tag{12}$$

with

$$\hat{\pi}_j = \hat{p}_j - \hbar A_j \quad \phi = \frac{\hbar^2}{2} \sum_{jk} \xi^{jk} g_{jk}. \tag{13}$$

Clearly, the dressed operator contains terms analogous to a vector (A_j) and a scalar (ϕ) electromagnetic potential and these modify the nuclear dynamics, when the comparison is made with the simpler Born-Oppenheimer dynamics. To see the effect of the gauge fields we start by noticing that the

$\hat{\pi}_k$'s are the operators for the mechanical momenta, since the nuclear velocity takes the form

$$\hat{v}^j = \frac{i}{\hbar}[\langle H\rangle_n, \hat{x}^j] = \sum_k \xi^{jk}\hat{\pi}_k.$$

These mechanical momentum operators do not commute with each other, but rather satisfy the gauge invariant commutation relation

$$[\hat{\pi}_i, \hat{\pi}_j] = i\hbar^2 B_{ij}.$$

Here the gauge freedom is the arbitrariness in the choice of the electronic frame: a gauge transformation $|u_n\rangle \to e^{-i\varphi}|u_n\rangle$ amounts to adding the exact 1-form $d\varphi$ to ω without altering the scalar potential and, at the same time, to adding a phase factor to the nuclear wave function [39], $\psi \to e^{+i\varphi}\psi$. The force is then obtained by the rate of variation of the particle's mechanical momentum,

$$\begin{aligned}\dot{\hat{\pi}}_k &= \frac{i}{\hbar}[\langle H\rangle_n, \hat{\pi}_k] \\ &= \frac{i}{\hbar}\left[\frac{1}{2}\sum_{ij}\xi^{ij}\hat{\pi}_i\hat{\pi}_j + E_n + \phi, \hat{\pi}_k\right]\end{aligned}$$

and takes the form

$$F_k = -\partial_k E_n - \partial_k\phi + \frac{\hbar}{2}\sum_j(\hat{v}^j B_{kj} + B_{kj}\hat{v}^j).$$

That is, $F_k = F_k^{\rm BO} + F_k^{\rm el} + F_k^{\rm mag}$, where the first term represents the Born-Oppenheimer force

$$F_k^{\rm BO} = -\frac{\partial E_n(\mathbf{x})}{\partial x^k},$$

while the latter two form an effective Lorentz force comprising both an electric component

$$F_k^{\rm el} = -\frac{\hbar^2}{2}\sum_{ij}\xi^{ij}\frac{\partial g_{ij}}{\partial x^k}$$

arising from the Fubini-Study metric tensor and a magnetic force

$$F_k^{\rm mag} = \frac{\hbar}{2}\sum_j(\hat{v}^j B_{kj} + B_{kj}\hat{v}^j)$$

due to Berry's curvature. Indeed, in the simple three-dimensional case, upon setting $\hbar B_{xy} = H_z$, $\hbar B_{xz} = -H_y$, and $\hbar B_{yz} = H_x$, one recovers the correct quantum mechanical expression of the Lorentz force acting on a unit charge due to the presence of the magnetic field $\mathbf{H} = H_x\mathbf{e}_x + H_y\mathbf{e}_y + H_z\mathbf{e}_z$, namely, $\mathbf{F}^{\rm mag} = \frac{1}{2}[\hat{\mathbf{v}}\wedge\mathbf{H} - \mathbf{H}\wedge\hat{\mathbf{v}}]$.

As is well known, the two components above behave very differently from each other: the pseudomagnetic field may vanish almost everywhere yet give rise to observable effects, similarly to what happens in the Aharonov-Bohm effect [27], while the pseudoelectric field is ubiquitous (i.e., it does not vanish unless the adiabatic error is uniform over the configuration space sampled by the nuclei) but typically of secondary importance and seldom considered in practice. Remarkably, though, they both arise from one and the same object, namely, the quantum geometric tensor.

Here we are especially interested in the LITE in this "dynamic" adiabatic approximation. As shown in Ref. [29], we need the time derivative of the whole wave function in the "standard" dynamical gauge where the state vector evolves according to a zero-averaged Hamiltonian. That is, $\langle\Psi|\dot{\Psi}^+\rangle \equiv 0$ if we use the superscript "+" to denote the trajectory $|\Psi\rangle = |\Psi(t)\rangle$ in this gauge. We need in particular the squared norm of the time derivative, which reads as

$$\hbar^2||\dot{\Psi}^+||^2 = \int d\mathbf{x}\psi^*(\mathbf{x})\{\langle\hat{T}\rangle_n + [E_n(\mathbf{x}) - \bar{E}]\}^2\psi(\mathbf{x}),$$

where $\langle T\rangle_n$ is the dressed kinetic energy operator of Eq. (12) and $\bar{E} = \langle\Psi|H|\Psi\rangle$ is the average total energy. We also need the energy variance

$$\Delta E^2 = \int d\mathbf{x}\psi^*(\mathbf{x})\,\langle\{\hat{T} + [H_{\rm el}(\mathbf{x}) - \bar{E}]\}^2\rangle_n\,\psi(\mathbf{x})$$

and the result

$$\begin{aligned}&\langle\{\hat{T} + [H_{\rm el}(\mathbf{x}) - \bar{E}]\}^2\rangle_n \\ &\quad = \langle\hat{T}^2\rangle_n + [E_n(\mathbf{x}) - \bar{E}]^2 + 2{\rm Re}[\langle\hat{T}\rangle_n[E_n(\mathbf{x}) - \bar{E}]].\end{aligned}$$

Hence, upon taking the difference of the two expressions, we find for the LITE the following expression:

$$\varepsilon^2 = \frac{1}{\hbar^2}\int d\mathbf{x}\psi^*(\mathbf{x})\big[\langle\hat{T}^2\rangle_n - \langle\hat{T}\rangle_n^2\big]\psi(\mathbf{x}), \tag{14}$$

which shows explicitly the crucial role played by the nuclear kinetic energy fluctuations in the adiabatic approximation.

This expression can also be put in a form that makes explicit the contributions of electronic transitions. To this end it is worth introducing the kinetic energy operator "reduced" with respect to the electronic coordinates, $\langle\hat{T}\rangle_{nm} = \langle u_n|\hat{T}|u_m\rangle$ (the case $n = m$ reduces to the previous dressed kinetic energy operator $\langle T\rangle_n$). These operators have a Hermitian symmetry $\langle T\rangle_{nm}^\dagger = \langle T\rangle_{mn}$ (as can be readily checked by either their definition or a direct calculation) and allow us to write

$$\langle\hat{T}^2\rangle_{nn} - \langle\hat{T}\rangle_{nn}^2 = \sum_{m\neq n}\langle\hat{T}\rangle_{nm}\langle\hat{T}\rangle_{mn} \equiv \sum_{m\neq n}\langle\hat{T}\rangle_{mn}^\dagger\langle\hat{T}\rangle_{mn}.$$

In turn, upon defining

$$\varphi_{m\leftarrow n}(\mathbf{x}) = \langle\hat{T}\rangle_{mn}\,\psi(\mathbf{x}) \equiv \langle u_m|\hat{T}|u_n\rangle_{\rm el}\,\psi(\mathbf{x})$$

we have the error in terms of the contributing electronic transitions,

$$\varepsilon^2 = \frac{1}{\hbar^2}\sum_{m\neq n}\int d\mathbf{x}|\varphi_{m\leftarrow n}(\mathbf{x})|^2,$$

where

$$\begin{aligned}\nu_{m\leftarrow n}(\mathbf{x}) &= \frac{1}{\hbar^2}|\varphi_{m\leftarrow n}(\mathbf{x})|^2 \\ &= \frac{1}{\hbar^2}\psi^*(\mathbf{x})\,\langle u_n|\,\hat{T}\,|u_m\rangle\,\langle u_m|\,\hat{T}\,|u_n\rangle\,\psi(\mathbf{x})\end{aligned}$$

is a "transition probability density," which, in this form, is manifestly gauge-invariant since $\psi(\mathbf{x})\,|u_n\rangle \equiv \langle\mathbf{x}|\Psi\rangle$.

In order to make a closer comparison with the error obtained in the previous section for the "quantum-classical" adiabatic approximation, we introduce $\nu(\mathbf{x}) = \sum_{m\neq n}\nu_{m\leftarrow n}(\mathbf{x})$

and the total conditional transition probability $\Pi(\mathbf{x}) = \nu(\mathbf{x})/|\psi(\mathbf{x})|^2$ in such a way that

$$\varepsilon^2 = \int d\mathbf{x} |\psi(\mathbf{x})|^2 \Pi(\mathbf{x})$$

provided $\psi(\mathbf{x}) \neq 0$. Clearly, $\Pi(\mathbf{x})$ measures the error locally in configuration space (as well as in time), and thus describes the tendency of the system in configuration $\mathbf{x}$ to jump to an electronic state other than n. For a smooth nuclear wave function $\psi(\mathbf{x})$ and a frame $|u_n(\mathbf{x})\rangle$ in the vector bundle $\pi : E \to \mathcal{M}$ we consider $|\psi_n(\mathbf{x})\rangle = \psi(\mathbf{x})\,|u_n(\mathbf{x})\rangle$ as a smooth section of E, and the map to the normal bundle defined by $|\psi_n(\mathbf{x})\rangle \to |\varphi(\mathbf{x})\rangle = Q\hat{T}\,|\psi_n(\mathbf{x})\rangle$, which gives $\nu(\mathbf{x}) = \hbar^{-2}\langle\varphi(\mathbf{x})|\varphi(\mathbf{x})\rangle$. We find

$$\begin{aligned} Q\hat{T}\,|\psi_n(\mathbf{x})\rangle = & -i\hbar \sum_j (\hat{v}^j\psi) Q\,|\partial_j u_n\rangle \\ & - \frac{\hbar^2}{2}\psi \sum_{jk} \xi^{jk} D_{jk}\,|u_n\rangle\,, \end{aligned} \tag{15}$$

where

$$D_{jk}\,|u_n\rangle = iA_j Q\,|\partial_k u_n\rangle + iA_k Q\,|\partial_j u_n\rangle + Q\,|\partial_j\partial_k u_n\rangle\,.$$

Written in this way the map is a sum of two terms that are separately gauge-invariant: under the gauge transformation $|u_n\rangle \to |u_n\rangle\, e^{-i\varphi}$, $\psi \to \psi e^{+i\varphi}$ we have $A_i \to A_i + \partial_i\varphi$ and

$$\begin{aligned} Q\,|\partial_j u_n\rangle &\to e^{-i\varphi} Q\,|\partial_j u_n\rangle\,, \\ \hat{v}^j\psi &\to e^{i\varphi}\hat{v}^j\psi\,, \\ D_{jk}\,|u_n\rangle &= e^{-i\varphi} D_{jk}\,|u_n\rangle\,, \end{aligned}$$

as can be readily verified with a direct calculation. Stated differently, the operators $Q\partial_j$, $\hat{\pi}_j$, $\hat{v}^j$, D_{jk}, etc., are tensorial under gauge transformations. Hence, upon introducing the (gauge-tensorial) residue

$$R\,|u_n\rangle = \frac{\hbar}{2}\sum_{jk}\xi^{jk} D_{jk}\,|u_n\rangle \tag{16}$$

and the complex-valued, quantum velocity fields V^j

$$V^j = \frac{\hat{v}^j\psi}{\psi} = \frac{\psi^*\hat{v}^j\psi}{|\psi|^2}, \tag{17}$$

we find the following expression for the total conditional transition probability:

$$\begin{aligned} \Pi(\mathbf{x}) = & \sum_{jk} (V^j)^* V^k q_{jk} \\ & - i\sum_j (V^j)^*\,\langle\partial_j u_n | R u_n\rangle \\ & + i\sum_j V^j\,\langle R u_n|\partial_j u_n\rangle \\ & + \langle R u_n | R u_n\rangle\,, \end{aligned} \tag{18}$$

where the q_{jk}'s are the components of the quantum geometric tensor, Eq. (7), and the remaining scalar products contain higher derivatives of the electronic state in a gauge-invariant form. Notice that the V^j's of Eq. (17) depend on both t and $\mathbf{x}$; however, in the following, for notational convenience we shall omit this dependence unless it is necessary otherwise.

The first term of Eq. (18) closely resembles the local-in-time error in the standard adiabatic approximation analyzed in the previous section, Eq. (6), provided V^j is interpreted as classical velocity of the jth parameter. There are notable differences, though: when turning the slow variables into quantum variables both the real (symmetric) and the imaginary (antisymmetric) parts of q_{ij} matter for the error, since

$$\sum_{jk}(V^j)^* V^k q_{jk} = \sum_{jk} K^{jk} g_{jk} + \frac{1}{2}\sum_{jk} Y^{jk} B_{jk},$$

where K^{jk} (Y^{jk}) is the real (imaginary) part of the product $(V^j)^* V^k$. It is instructive then to consider their total contribution upon integrating over configuration space, which reads as

$$\int d\mathbf{x}|\psi(\mathbf{x})|^2 \sum_{jk} K^{jk} g_{jk} = \langle\psi|\sum_{jk}\hat{v}^j g_{jk}\hat{v}^k\,|\psi\rangle_X$$

and

$$\int d\mathbf{x}|\psi(\mathbf{x})|^2 \sum_{jk} Y^{jk} B_{jk} = -i\,\langle\psi|\sum_{jk}\hat{v}^j B_{jk}\hat{v}^k\,|\psi\rangle_X\,.$$

Here the scalar product $\langle .|.\rangle_X$ is that of the Hilbert space $L^2(\mathcal{M})$ describing the nuclear degrees of freedom, and use has been made of the fact that the operator $\sum_{jk}\hat{v}^j g_{jk}\hat{v}^k$ ($\sum_{jk}\hat{v}^j B_{jk}\hat{v}^k$) is Hermitean (anti-Hermitean) on that space. Hence, overall, by considering the "classical" contribution only, we find that the LITE in the dynamic adiabatic approximation is just the expectation value of a self-adjoint quantum tensor

$$\hat{q} = \sum_{jk}\hat{v}^j\Big(g_{jk} - \frac{i}{2}B_{jk}\Big)\hat{v}^k = \sum_{jk}\hat{v}^j q_{jk}\hat{v}^k, \tag{19}$$

which is nothing but the quantum version of the quantum geometric tensor. This is a version of the tensor in which quantum operators appear in place of classical manifold parameters, and the action of the basic 1-form dx^j on a generic tangent vector $\mathbf{V} \in T_x\mathcal{M}$, i.e., $V^j = dx^j(\mathbf{V})$, is replaced by the local differential operator $\hat{v}^j$ acting on the nuclear wave function. We thus have, to leading order,

$$\varepsilon^2 \approx \langle\psi|\sum_{jk}\hat{v}^j q_{jk}\hat{v}^k\,|\psi\rangle_X\,. \tag{20}$$

On comparing with the quantum-classical adiabatic approximation, however, one should also observe that additional terms appear whose physical meaning is far less obvious.

C. Nonadiabatic transition probability

To better understand the meaning of $\Pi(\mathbf{x})$ and its contributing transitions, we now consider the situation where, during the time evolution, the LITE exceeds a given threshold, thereby suggesting the need of going beyond the adiabatic approximation. This can be accomplished dynamically by "spawning" [29] the electronic basis that forms the variational

manifold, e.g., by expanding the wave function ansatz to

$$|\Psi_t\rangle = \int d\mathbf{x}\psi_t(\mathbf{x})\,|u_n(\mathbf{x}),\mathbf{x}\rangle + \int d\mathbf{x}\phi_t(\mathbf{x})\,|u_s(\mathbf{x}),\mathbf{x}\rangle\,,$$

where $s = n \pm 1$ depending on which gap $|E_n - E_{n\pm1}|$ is the smallest. Henceforth, we shall first address the simpler situation where a single neighboring state affects the dynamics and later generalize the result to a multitude of electronic states.

At the time of spawning t_s the amplitude $\phi_t(\mathbf{x})$ must vanish and its time derivative is determined by the variational equations of motion

$$\begin{aligned} i\hbar\partial_t\psi &= (\langle T\rangle_{nn} + E_n)\psi + \langle T\rangle_{ns}\,\phi \\ i\hbar\partial_t\phi &= \langle T\rangle_{sn}\,\psi + (\langle T\rangle_{ss} + E_s)\phi, \end{aligned}$$

which give $i\hbar\partial_t\phi = \langle T\rangle_{sn}\,\psi \equiv \varphi_{s\leftarrow n}$ for $t = t_s$ (here and in the following, $\partial_t = \partial/\partial t$). Thus, the probability $\nu_{s\leftarrow n}$ represents precisely the error reduction due to electronic spawning,

$$\varepsilon^2 \to \varepsilon'^2 = \varepsilon^2 - \nu_{s\leftarrow n} \quad \text{at } t = t_s,$$

i.e., the error reduction arising from lifting the adiabatic approximation by allowing nonadiabatic transitions to the state s. On the other hand, the above equation also determines the short-time behavior of the nonadiabatic transition probability P_s to the state s as $P_s \approx \nu_{s\leftarrow n}(t - t_s)^2$ $(t \geqslant t_s)$, since $\partial_t|\phi|^2 = 0$ and $\partial_t^2|\phi|^2 = \frac{2}{\hbar^2}|\langle T\rangle_{sn}\,\psi|^2$ for $t = t_s$. This finding leads to an interesting conclusion: when a single term s dominates the sum, $\nu_{s\leftarrow n}$ is approximately the total squared error in the dynamic adiabatic approximation, and, as shown in the previous section, this is determined by the quantum geometric tensor (to leading order in the derivatives of the $|u_n\rangle$'s). Hence, turning this argument around, we see that the quantum geometric tensor also determines the early transition probability upon spawning. In other words, we have approximately, up to second order in $\delta t = t - t_s$,

$$P_s \approx \int d\mathbf{x}\sum_{jk}(\delta\hat{x}^j\psi_{t_s})^*(\mathbf{x})(\delta\hat{x}^k\psi_{t_s})(\mathbf{x})q_{jk}(\mathbf{x})$$

with $\delta\hat{x}^i := \hat{v}^i\delta t$, if the most important nonadiabatic channel were suddenly opened at time t_s.

More generally, all the above remains unaltered if the adiabatic approximation is suddenly lifted and the "spawning" process is made virtually complete, i.e., the variational constraint is suddenly removed at $t = t_s$ and the wave function is allowed to expand into the whole Hilbert space

$$\begin{aligned} |\Psi_t\rangle &= \int d\mathbf{x}\psi_t(\mathbf{x})\,|u_n(\mathbf{x}),\mathbf{x}\rangle \\ \to\ |\Psi_t\rangle &= \int d\mathbf{x}\psi_t(\mathbf{x})\,|u_n(\mathbf{x}),\mathbf{x}\rangle \\ &\quad + \sum_{m\neq n}\int d\mathbf{x}\phi_t^{(m)}(\mathbf{x})\,|u_m(\mathbf{x}),\mathbf{x}\rangle\,. \end{aligned}$$

Again, at the time of spawning, we have $\phi^{(m)} \equiv 0$ and $i\hbar\partial_t\phi^{(m)} = \langle T\rangle_{mn}\,\psi \equiv \varphi_{m\leftarrow n}$ holds for any $m \neq n$. Now the LITE is reduced exactly to zero upon spawning. and the total nonadiabatic transition probability P can be given, up to second order in δt, as

$$P \approx \int d\mathbf{x}\sum_{jk}(\delta\hat{x}^j\psi_{t_s})^*(\mathbf{x})(\delta\hat{x}^k\psi_{t_s})(\mathbf{x})q_{jk}(\mathbf{x})$$
$$\text{with } \delta\hat{x}^i := \hat{v}^i\delta t$$

under the only assumption that the terms involving the second derivatives of the electronic states are negligible. This result relates the geometric properties of the adiabatic problem to the rate of nonadiabatic transitions. In a sense, this is an obvious result since the latter transitions represent precisely the failure of the adiabatic approximation. Upon closer reflection, though, it is remarkable that the exact dynamics of the system beyond the adiabatic paradigm is determined solely by the geometric properties of the approximation.

III. EXACT FACTORIZATION OF THE WAVE FUNCTION

Next we focus on the exact factorization [31,32] of the electronic-nuclear wave function. This is an "intermediate" representation which closely resembles the adiabatic ansatz and thus represents the ideal starting point for comparing and improving the adiabatic approximation. As mentioned in the Introduction, we shall rederive the corresponding equations of motion using a projection-operator technique that emphasizes the gauge transformation properties, thereby allowing one to single out distinct, physically meaningful contributions to the dynamics.

The exact factorization of the electronic-nuclear wave function is accomplished by introducing a local basis of nuclear states $\{|\mathbf{x}\rangle\}$

$$|\Psi_t\rangle = \int d\mathbf{x}\,|\mathbf{x}\rangle\,\langle\mathbf{x}|\Psi_t\rangle_X$$

and noticing that $\langle\mathbf{x}|\Psi_t\rangle_X$ is yet a vector in the electronic Hilbert space $\mathcal{H}_{\rm el}$, that we can write as

$$\langle\mathbf{x}|\Psi_t\rangle_X = \psi_t(\mathbf{x})\,|u_t(\mathbf{x})\rangle$$

upon imposing a normalization condition and choosing a smoothly varying phase for the local electronic states $|u_t(\mathbf{x})\rangle$. This gives the wave function in the form

$$|\Psi_t\rangle = \int d\mathbf{x}\psi_t(\mathbf{x})\,|\mathbf{x}\rangle\,|u_t(\mathbf{x})\rangle\,,$$

which closely resembles the adiabatic ansatz of Eq. (10) but now with a set of time-dependent electronic states $\{|u_t(\mathbf{x})\rangle\}$ in place of the adiabatic frame $\{|u_n(\mathbf{x})\rangle\}$. Clearly, there is some freedom in choosing $|u_t\rangle$ (and correspondingly in defining the nuclear wave function ψ_t) that we may fix by imposing the arbitrary (but real) gauge term

$$A_0 = i\,\langle u|\partial_t u\rangle \tag{21}$$

in the equations of motion.

A. Equations of motion

To obtain the equations of motion for the above nuclear wave function and the electronic state we write the total Hamiltonian using the coordinate representation for the nu-

clear variables, i.e.,

$$\hat{H} = \hat{T} + H_{\rm el}(\mathbf{x}),$$

where $\hat{T}$ is the nuclear kinetic energy operator

$$\hat{T} = \frac{1}{2}\sum_{jk} \xi^{jk}\hat{p}_j\hat{p}_k \quad \text{with } \hat{p}_j = -i\hbar\partial_j$$

and $H_{\rm el}(\mathbf{x})$ is the electronic operator with the nuclei clamped at a configuration $\mathbf{x}$. From the Schrödinger equation

$$\hat{H}(\psi\,|u\rangle) = i\hbar(\partial_t\psi)\,|u\rangle + i\hbar\psi\,|\partial_t u\rangle\,,$$

we immediately obtain the equation of motion for the nuclear wave function by projecting the above equation onto $|u\rangle$

$$(\langle\hat{H}\rangle_{\rm el} - \hbar A_0)\psi = i\hbar(\partial_t\psi),$$

where $\langle\hat{H}\rangle_{\rm el} = \langle\hat{T}\rangle_{\rm el} + \langle u|H_{\rm el}|u\rangle$ contains the kinetic energy operator dressed by the time-dependent electronic state and the "Born-Oppenheimer" average energy $E_{\rm el} = \langle u|H_{\rm el}|u\rangle$. As above, $\langle\hat{T}\rangle_{\rm el}$ reads as

$$\langle\hat{T}\rangle_{\rm el} = \frac{1}{2}\sum_{jk}\xi^{jk}\hat{\pi}_j\hat{\pi}_k + \phi,$$

where $\hat{\pi}_j = \hat{p}_j - \hbar A_j$, $A_j = i\,\langle u|\partial_j u\rangle$, $\phi = \hbar^2/2\sum_{jk}\xi^{jk}g_{jk}$, $g_{jk} = \mathrm{Re}q_{jk}$ and $q_{jk} = \langle\partial_j u|Q|\partial_k u\rangle$, exactly as in Sec. II but now with $|u\rangle$ everywhere meant to be the time-dependent electronic state (correspondingly, $P = |u\rangle\,\langle u|$, $Q = 1 - P$, etc.). Hence, overall, the nuclear wave function is seen to satisfy an effective Schrödinger equation

$$H^{\rm eff}\psi = i\hbar\partial_t\psi \tag{22}$$

with the pseudoelectromagnetic Hamiltonian

$$H^{\rm eff} = \frac{1}{2}\sum_{jk}\xi^{jk}\hat{\pi}_j\hat{\pi}_k + (E_{\rm el} - \hbar A_0 + \phi). \tag{23}$$

Notice that here Berry's connection is dictated by the electron dynamics, and its gauge is inherited from the choice made at $t = 0$.

As for the equation governing the electron dynamics we only need its projection onto the "unoccupied" electronic space, since $P\partial_t\,|u\rangle = |u\rangle\,\langle u|\partial_t u\rangle$ is known once the gauge term A_0 has been fixed. Hence,

$$i\hbar Q\,|\partial_t u\rangle = \frac{1}{\psi}Q\hat{H}(\psi\,|u\rangle),$$

or, if we write the equation for $\partial_t\,|u\rangle$,

$$i\hbar\,|\partial_t u\rangle = +\hbar A_0\,|u\rangle + \frac{1}{\psi}Q\hat{H}(\psi\,|u\rangle).$$

In the case $\psi(\mathbf{x}) = 0$ at a given time (a situation that can be considered incidental) the local electronic state is immaterial, and its short-time evolution can be handled with the spawning approach outlined in the previous section. In the above equation, the effective electronic Hamiltonian operator contains two terms,

$$\frac{1}{\psi}Q\hat{H}(\psi\,|u\rangle) = \frac{1}{\psi}Q\hat{T}(\psi\,|u\rangle) + QH_{\rm el}\,|u\rangle\,,$$

but only the first depends on ψ since $H_{\rm el}$ is local in the nuclear coordinates. The first term, which we denote as $K[\psi]\,|u\rangle$, has been introduced in Sec. II B [see Eq. (15)] and reads as

$$K[\psi]\,|u\rangle = -i\hbar\sum_j V^j Q\,|\partial_j u\rangle - \hbar R\,|u\rangle\,, \tag{24}$$

where $V^j = (\hat{v}^j\psi)/\psi$ is the complex-valued nuclear velocity field of Eq. (17) and $R\,|u\rangle$ is the residue defined in Eq. (16), everywhere with $|u\rangle$ in place of the adiabatic vector $|u_n\rangle$. We recall that the above decomposition has simple gauge transformation properties, since V^j is gauge invariant and both $Q\partial_j$ and R behave tensorially under a gauge transformation. Hence,

$$i\hbar Q\,|\partial_t u\rangle = QH_{\rm el}\,|u\rangle + K[\psi]\,|u\rangle\,, \tag{25}$$

where, on the r.h.s., the first term describes the electron dynamics with the nuclei clamped at $\mathbf{x}$ and the second term describes the drag effect on the electrons due to the motion of the nuclei. Appendix C shows the equivalence of the above equations of motion with those originally derived in Refs. [31,32].

B. Dynamically corrected pseudo-Lorentz force

The striking similarity of Eq. (23) with the effective Hamiltonian H_n governing the adiabatic evolution, allows us to analyze the exact dynamics in parallel to the adiabatic one. The exact forces acting on the nuclear degrees of freedom are very similar to the adiabatic ones, with the usual proviso of replacing the adiabatic electronic states with their time-dependent counterparts. The additional force, due solely to the electronic dynamics, is the (gauge-invariant) force

$$F_k^{\rm ED} = \hbar(\partial_k A_0 - \partial_t A_k) = -2\hbar\mathrm{Im}\,\langle\partial_k u|Q|\partial_t u\rangle \tag{26}$$

that vanishes identically in the adiabatic approximation, where $A_0 \equiv 0$ and A_k are time-independent. That is, the total force reads exactly as $F_k^{\rm tot} = F_k^{\rm BO} + F_k^{\rm el} + F_k^{\rm mag} + F_k^{\rm ED}$, where

$$F_k^{\rm BO} \equiv -\partial_k\,\langle u|H_{\rm el}|u\rangle = -\partial_k E_{\rm el} \tag{27}$$

is a time-dependent Born-Oppenheimer force, the geometric forces $F_k^{\rm el}$ and $F_k^{\rm mag}$ stem from the time-dependent quantum geometric tensor and $F_k^{\rm ED}$ describes the electron dynamics. Plugging the time derivative of the electronic state from Eq. (25) into Eq. (26) one obtains two terms,

$$F_k^{\rm NBO} = 2\mathrm{Re}\,\langle\partial_k u|QH_{\rm el}|u\rangle \tag{28}$$

and

$$F_k^{\rm corr} = 2\mathrm{Re}\,\langle\partial_k u|K[\psi_t]|u\rangle\,, \tag{29}$$

which, by construction, are separately gauge invariant. The first is a genuine non-Born-Oppenheimer term, which vanishes identically when $|u\rangle$ happens to be an eigenstate of $H_{\rm el}$ and, more generally, it is bounded by the size of the (local) energy fluctuations in the electronic subsystem, $|F_k^{\rm NBO}| \leqslant 2\Delta E_{\rm el}\sqrt{g_{kk}}$ where $\Delta E_{\rm el}^2 = \langle(H_{\rm el} - E_{\rm el})^2\rangle$. The second can be considered as a dynamical correction to the pseudo-Lorentz force due to the electron reaction. The interesting result here is that, once the pseudoelectric and the pseudomagnetic forces are corrected for this reaction, they vanish when averaged

over the nuclear state. This can be seen as follows. First, we write explicitly the correction by using Eq. (24) and $\mathrm{Im}q_{kj} = -B_{kj}/2$,

$$F_k^{\mathrm{corr}} = 2\hbar \sum_j g_{kj} \mathrm{Im} V^j - \hbar \sum_j B_{kj} \mathrm{Re} V^j - 2\hbar \mathrm{Re}\, \langle \partial_k u | R u \rangle \,.$$

From this expression the corrected magnetic force is easily identified,

$$F_k^{\mathrm{mag,c}} = \frac{\hbar}{2} \sum_j (\hat{v}^j B_{kj} + B_{kj} \hat{v}^j) - \hbar \sum_j B_{kj} \mathrm{Re} V^j,$$

and found to have a zero average with a simple calculation,

$$\langle \psi | F_k^{\mathrm{mag,c}} | \psi \rangle_X = \frac{\hbar}{2} \sum_j \langle \psi | \hat{v}^j B_{kj} + B_{kj} \hat{v}^j | \psi \rangle_{\mathrm{X}} - \hbar \sum_j \langle \psi | B_{kj} \mathrm{Re} V^j | \psi \rangle_X$$

since

$$\tfrac{1}{2} \langle \psi | \hat{v}^j B_{kj} + B_{kj} \hat{v}^j | \psi \rangle_{\mathrm{X}} = \mathrm{Re} \langle \psi | B_{kj} \hat{v}^j | \psi \rangle_{\mathrm{X}} \,,$$

and, on the other hand,

$$\langle \psi | B_{kj} \mathrm{Re} V^j | \psi \rangle_X \equiv \mathrm{Re} \langle \psi | B_{kj} \hat{v}^j | \psi \rangle_{\mathrm{X}} \,.$$

Hence,

$$\langle \psi | F_k^{\mathrm{mag,c}} | \psi \rangle_X \equiv 0. \tag{30}$$

As for the corrected pseudoelectric force, it takes the form

$$F_k^{\mathrm{el,c}} = 2\hbar \sum_j g_{kj} \mathrm{Im} V^j - \hbar^2 \sum_{ij} \xi^{ij} (\mathrm{Re} \langle \partial_i u | D_{kj} u \rangle + \mathrm{Re} \langle \partial_k u | D_{ij} u \rangle)$$

upon observing the key identity

$$\frac{\partial g_{ij}}{\partial x^k} = \mathrm{Re} \langle \partial_i u | D_{kj} u \rangle + \mathrm{Re} \langle \partial_j u | D_{ki} u \rangle \,. \tag{31}$$

Then, on taking the average

$$\langle \psi | \, 2\hbar \sum_j g_{kj} \mathrm{Im} V^j \, | \psi \rangle_X = 2\hbar \sum_j \langle \psi | \mathrm{Im}(g_{kj} \hat{v}^j) | \psi \rangle = \hbar^2 \sum_i \xi^{ij} \langle \psi | \frac{\partial g_{kj}}{\partial x^i} | \psi \rangle \,,$$

where

$$2\hbar \mathrm{Im}(g_{kj} \hat{v}^j) = -i\hbar [g_{kj}, \hat{v}^j] = \hbar^2 \sum_i \xi^{ij} \frac{\partial g_{kj}}{\partial x^i}$$

has been used. Hence,

$$\langle \psi | F_k^{\mathrm{el,c}} | \psi \rangle = \hbar^2 \sum_{ij} \xi^{ij} \langle \psi | \times \left[\frac{\partial g_{ki}}{\partial x^j} - (\mathrm{Re} \langle \partial_i u | D_{kj} u \rangle + \mathrm{Re} \langle \partial_k u | D_{ij} u \rangle) \right] | \psi \rangle \,,$$

and the operator between square brackets vanishes by virtue of Eq. (31), i.e.,

$$\langle \psi | F_k^{\mathrm{el,c}} | \psi \rangle_X \equiv 0. \tag{32}$$

Importantly, by using Eq. (31) we have in fact exploited

$$\mathrm{Re} \langle \partial_k u | D_{ij} u \rangle = \frac{1}{2} \left(\frac{\partial g_{ik}}{\partial x^j} + \frac{\partial g_{kj}}{\partial x^i} - \frac{\partial g_{ij}}{\partial x^k} \right)$$

that shows how $\mathrm{Re} \langle \partial_k u | D_{ij} u \rangle$ is related to a natural linear connection that is induced on the tangent bundle by the (time-dependent) Fubini-Study metric $g_{ij} = \mathrm{Re} q_{ij}$. Indeed, for any given metric g_{ij} there exists a unique connection ∇^q on the tangent bundle that is both metric and torsion-free. This is the celebrated Levi-Civita connection [40], and it can be defined by setting its Christoffel symbol Γ^l_{ij} according to

$$\sum_l g_{kl} \Gamma^l_{ij} = \frac{1}{2} \left(\frac{\partial g_{ik}}{\partial x^j} + \frac{\partial g_{kj}}{\partial x^i} - \frac{\partial g_{ij}}{\partial x^k} \right).$$

Hence,

$$\mathrm{Re} \langle \partial_k u | D_{ij} u \rangle \equiv \sum_l g_{kl} \Gamma^l_{ij} \tag{33}$$

holds for the above connection, and the zeroing of the average pseudoelectric force merely expresses the conservation of the metric, that is the condition

$$\left(\nabla^q_j g \right)_{ik} = \frac{\partial g_{ik}}{\partial x^j} - \sum_l g_{il} \Gamma^l_{jk} - \sum_l g_{lk} \Gamma^l_{ji} = 0$$

for the ikth component of the covariant derivative of g taken with the connection ∇^q along the direction j. In other words, the result of Eq. (32) amounts to

$$\langle \psi | F_k^{\mathrm{el,c}} | \psi \rangle = \hbar^2 \sum_{ij} \xi^{ij} \langle \psi | \left(\nabla^q_j g \right)_{ik} | \psi \rangle = 0. \tag{34}$$

C. Statistical properties

We emphasize here that, despite its role of a marginal probability amplitude, $\psi(\mathbf{x})$ alone cannot determine the full statistical properties of the nuclear subset of particles, not even instantaneously. This is evident from the fact that the (equal-time) statistical properties require the reduced density operator $\rho_X = \mathrm{tr}_e \rho$ which, for pure states and the factorization introduced above, reads as

$$\langle \mathbf{x} | \rho_X | \mathbf{x}' \rangle = \mathrm{tr}_e [\psi(\mathbf{x}) \, |u(\mathbf{x})\rangle \, \langle u(\mathbf{x}')| \, \psi^*(\mathbf{x}')] = \sigma(\mathbf{x}, \mathbf{x}') \, \langle u(\mathbf{x}') | u(\mathbf{x}) \rangle \,,$$

where $\sigma(\mathbf{x}, \mathbf{x}') = \psi(\mathbf{x}) \psi^*(\mathbf{x}')$ is the "apparent" nuclear density matrix. In view of this, we have two different strategies (and interpretative tools) to investigate the statistical properties of nuclear observables. Either we use the true density matrix $\rho_X(\mathbf{x}, \mathbf{x}')$ and bare nuclear observables N

$$\langle N \rangle = \int d\mathbf{x} \int d\mathbf{x}' \rho_X(\mathbf{x}, \mathbf{x}') N(\mathbf{x}', \mathbf{x}),$$

or we use the apparent density matrix $\sigma(\mathbf{x}, \mathbf{x}')$ and dressed nuclear observables $\tilde{N}$,

$$\langle N \rangle = \int d\mathbf{x} \int d\mathbf{x}' \sigma(\mathbf{x}, \mathbf{x}') \tilde{N}(\mathbf{x}', \mathbf{x}),$$

where

$$\tilde{N}(\mathbf{x},\mathbf{x}') = N(\mathbf{x},\mathbf{x}')\,\langle u(\mathbf{x})|u(\mathbf{x}')\rangle$$

or, equivalently,

$$\tilde{N}(\mathbf{x},\mathbf{x}') = \langle u(\mathbf{x})|N(\mathbf{x},\mathbf{x}')|u(\mathbf{x}')\rangle_{\rm el}\,,$$

which shows that the dressed observables are "averaged" over the electronic states.

As for the electronic density operator $\rho_{\rm el}$, it takes the form of a convex combination of electronic density operators $\rho_{\rm el}(\mathbf{x})$,

$$\rho_{\rm el} = \int_X d\mathbf{x} P(\mathbf{x})\rho_{\rm el}(\mathbf{x}),$$

where $P(\mathbf{x}) = |\psi(\mathbf{x})|^2$ is the probability density of finding the nuclei at $\mathbf{x}$ and $\rho_{\rm el}(\mathbf{x})$ is the conditional density operator

$$\rho_{\rm el}(\mathbf{x}) = \frac{\langle\mathbf{x}|\rho|\mathbf{x}\rangle}{P(\mathbf{x})} \equiv |u(\mathbf{x})\rangle\,\langle u(\mathbf{x})|\,,$$

which describes a pure local state, the one defined locally by the exact factorization representation. The results in the adiabatic approximation are very similar to the ones given here, the only difference being that $|u\rangle$ is in that case a stationary state. Therefore, the concept that the adiabatic approximation "artificially" forces the local electronic state to be a pure state is misleading, because this is true for an arbitrary wave function.

In order to clarify the meaning of observables dressed by the electronic state let us consider in detail the nuclear momentum for the kth degree of freedom, $\hat{p}_k$ (in the coordinate representation appropriate for the exact factorization). This is first "extended" to an operator $\hat{P}_k = \hat{p}_k \otimes \mathbb{I}_{\rm el}$ acting on the Hilbert space of the electronic-nuclear system, and then "reduced" to an operator $\tilde{p}_k$ on the nuclear space by averaging over the electronic state

$$\tilde{p}_k = \langle u|\hat{P}_k|u\rangle = \hat{p}_k - i\hbar\,\langle u|\partial_k u\rangle \equiv \hat{\pi}_k.$$

The result is the operator for the mechanical momentum $\hat{\pi}_k$, which can thus be considered the canonical momentum dressed by the electronic state. In general, for notational convenience, one does not distinguish $\hat{P}_k$ from $\hat{p}_k$, and then care is needed in interpreting $\hat{p}_k$ as the "microscopic" operator acting on the electronic-nuclear space or the one acting on the nuclear space only. As for the dressed operators, they are always averaged over the electronic state, and thus meant to be operators on the Hilbert space of the nuclei.

It is instructive at this point to reconsider the total force F_k acting on the kth nuclear degree of freedom in light of the above difference between "microscopic" and "electronically averaged" quantities. On the one hand we have

$$\frac{d\,\langle\hat{p}_k\rangle}{dt} = \langle\Psi|\frac{i}{\hbar}[H,\hat{p}_k]|\Psi\rangle = \int d\mathbf{x}\psi^*(\mathbf{x})\,\langle-\partial_k H_{\rm el}\rangle_{\rm el}\,\psi(\mathbf{x}),$$

where, to avoid confusion, we used the subscript "el" on the angular bracket to denote the electronic average. This shows that the average total force is the expectation value of the dressed microscopic force $-\partial_k H_{\rm el}$ acting on the given nuclear degree of freedom. This term can be further manipulated to make evident the Born-Oppenheimer-like contribution [Eq. (27)]

$$\langle-\partial_k H_{\rm el}\rangle_{\rm el} = F_k^{\rm BO} + F_k^{\rm NBO} \tag{35}$$

upon noticing that $\mathrm{Re}(\langle\partial_k u|u\rangle\,\langle u|H_{\rm el}|u\rangle) = 0$. On the other hand, we also have

$$\frac{d\,\langle\hat{p}_k\rangle}{dt} = 2\mathrm{Re}\,\langle\Psi|\hat{p}_k|\partial_t\Psi\rangle\,,$$

where the time derivative of the total wave function in the exact factorization form can be written as

$$\begin{aligned}\partial_t(\psi\,|u\rangle) &= [(\partial_t\psi) + \psi\,\langle u|\partial_t u\rangle]\,|u\rangle + \psi Q\,|\partial_t u\rangle \\ &= -\frac{i}{\hbar}\,(\langle H\rangle_{\rm el}\psi)\,|u\rangle + \psi Q\,|\partial_t u\rangle\,,\end{aligned}$$

hence

$$\begin{aligned}\frac{d\,\langle\hat{p}_k\rangle}{dt} &= 2\mathrm{Re}\int d\mathbf{x}\psi^*(\mathbf{x})\Big(-\frac{i}{\hbar}\Big)(\hat{\pi}_k\,\langle H\rangle_{\rm el})\psi(\mathbf{x}) \\ &\quad + 2\mathrm{Re}\int d\mathbf{x}\psi^*(\mathbf{x})[+i\hbar\,\langle\partial_k u|Q\partial_t u\rangle]\psi(\mathbf{x}).\end{aligned} \tag{36}$$

Here for the first line we have used $\langle\hat{p}_k\rangle_{\rm el} = \hat{\pi}_k$, whereas for the second one we have exploited

$$\begin{aligned}\langle u|\hat{p}_k Q\partial_t u\rangle &= \langle u|Q\partial_t u\rangle\,\hat{p}_k - i\hbar\partial_k\,\langle u|Q\partial_t u\rangle + i\hbar\,\langle\partial_k u|Q\partial_t u\rangle \\ &\equiv i\hbar\,\langle\partial_k u|Q\partial_t u\rangle\end{aligned}$$

(notice that the in the adopted representation the angular brackets denote scalar products in the electronic space only). Furthermore, since

$$\begin{aligned}&2\mathrm{Re}\int d\mathbf{x}\psi^*(\mathbf{x})\Big(-\frac{i}{\hbar}\Big)(\hat{\pi}_k\,\langle H\rangle_{\rm el})\psi(\mathbf{x}) \\ &\quad = \int d\mathbf{x}\psi^*(\mathbf{x})\frac{i}{\hbar}[\langle H\rangle_{\rm el}\,,\hat{\pi}_k]\psi(\mathbf{x})\end{aligned}$$

and the second term on the r.h.s. of Eq. (36) is the expectation value of $F_k^{\rm ED}$ of Eq. (26), we finally arrive at

$$\frac{d\,\langle\hat{p}_k\rangle}{dt} = \int d\mathbf{x}\psi^*(\mathbf{x})\big(F_k^{\rm BO} + F_{\rm k}^{\rm mag} + F_k^{\rm el} + F_k^{\rm ED}\big)\psi(\mathbf{x}).$$

On comparing with Eq. (35) and remembering that $F_{\rm k}^{\rm mag} + F_k^{\rm el} + F_k^{ED} = F_{\rm k}^{\rm mag,c} + F_k^{\rm el,c} + F_k^{\rm NBO}$ we find

$$\int d\mathbf{x}\psi^*(\mathbf{x})\big(F_{\rm k}^{\rm mag,c} + F_k^{\rm el,c}\big)\psi(\mathbf{x}) = 0.$$

This is consistent with Eqs. (30) and (32); however, the proof given in the previous section makes clear that the dynamically corrected pseudoelectric and pseudomagnetic forces vanish separately when averaged.

IV. ELECTRONIC FRICTION

The analysis of Secs. II and III has singled out in the force of Eq. (26) [and its components, Eq. (28) and Eq. (29)] the key effect of introducing the electron dynamics in the description of the dynamical behavior of the nuclei. Of particular importance for our purposes is the vanishing of the (average) pseudo-Lorentz force, since this leads us to identify the genuine non-Born-Oppenheimer force, $F_k^{\rm NBO}$ of Eq. (28), as the potential source of electronic friction. We address

here the relevant dynamical regime, derive the appropriate electronic-friction kernel and the Schrödinger-Langevin-like equation of motion of the nuclear wave function, obtaining the corresponding effective Hamiltonian.

A. Linear response

Let us now focus on the electronic equation Eq. (25) in the situation where the electronic system relaxes quickly to the ground state $|u_0\rangle$ and the deviation $|\Delta u\rangle = |u(t)\rangle - |u_0(t)\rangle$ remains small throughout the nuclear dynamical evolution [here $|u_0(t)\rangle$ is the time-evolving ground electronic state]. This is the condition where linear response theory (LRT) applies and also the situation where the electronic-friction picture is appropriate. Let us then consider the integral form of the electronic equation and handle the drag term of Eq. (25) in the spirit of linear response theory. We set $\hbar A_0 \equiv E_{\rm el} = \langle u|H_{\rm el}|u\rangle$ and assume that $|u(t_0)\rangle = e^{-\frac{i}{\hbar}E_0 t_0}|u_0\rangle$ holds for some initial time t_0 in the infinite past. Following a common strategy, we start by considering a simple impulsive "kick" $\delta(t-\tau)\tilde{K}[\psi_\tau]\,|u(\tau)\rangle$ acting at time τ only, for which we find

$$|u(t)\rangle \approx e^{-\frac{i}{\hbar}E_0 t}|u_0\rangle - \frac{i}{\hbar}e^{-\frac{i}{\hbar}H_{\rm el}(t-\tau)}K_0[\psi_\tau]\,|u_0\rangle\, e^{-\frac{i}{\hbar}E_0\tau}\Theta(t-\tau),$$

where $\Theta(t) = 1$ for $t > 0$ and zero otherwise. This can be readily obtained from the integral version of the equation of motion by shrinking the time interval around the kick time τ to find the electronic state soon after the kick,

$$|u(\tau^+)\rangle \approx |u(\tau^-)\rangle - \frac{i}{\hbar}K_0[\psi_\tau]\,|u(\tau^-)\rangle\,,$$

where $|u(\tau^-)\rangle = e^{-\frac{i}{\hbar}E_0\tau}|u_0\rangle$ is the freely propagating state and $Q \to Q_0 = 1 - |u_0\rangle\langle u_0|$ has been used for $t = \tau - \eta$, $\eta > 0$. Note that, correspondingly, the operator K of Eq. (24) has been replaced by K_0 to remind us of the use of Q_0 rather than Q and of the ground-state connection in the velocity operators. Next, for the full driving term

$$K[\psi_t]\,|u(t)\rangle = \int_{-\infty}^{+\infty} dt'\delta(t-t')K[\psi_{t'}]\,|u(t')\rangle\,,$$

we assume linear response to write

$$|u(t)\rangle \approx e^{-\frac{i}{\hbar}E_0 t}|u_0\rangle - \frac{i}{\hbar}\int_{-\infty}^{t} e^{-\frac{i}{\hbar}H_{\rm el}(t-t')}K_0[\psi_{t'}]\,|u_0\rangle\, e^{-\frac{i}{\hbar}E_0 t'}dt'. \quad (37)$$

We thus see that $|\Delta u\rangle$ takes the form

$$|\Delta u\rangle \approx -\frac{i}{\hbar}e^{-\frac{i}{\hbar}E_0 t}\int_0^\infty e^{-\frac{i}{\hbar}(H_{\rm el}-E_0)\tau}K_0[\psi_{t-\tau}]\,|u_0\rangle\,d\tau, \quad (38)$$

and it is such that $\langle\Delta u|u_0\rangle = 0$ since $K_0 = Q_0 K_0$. Plugging Eq. (37) in the genuine non-Born-Oppenheimer force [Eq. (28)], and using Eq. (24), we find, to first order in $|\Delta u\rangle$, two contributions

$$F_k^{\rm NBO,I} = -2\sum_j {\rm Re}\int_0^\infty \Gamma_{kj}(\tau)V^j(t-\tau)\,d\tau \quad (39)$$

and

$$F_k^{\rm NBO,II} = -2{\rm Im}\int_0^\infty \langle\partial_k u_0|Q_0 H'_{\rm el}e^{-\frac{i}{\hbar}H'_{\rm el}\tau}R|u_0\rangle\,d\tau. \quad (40)$$

We are mostly interested in the first one, since it represents a friction-like force with kernel

$$\Gamma_{kj}(t) = \langle\partial_k u_0|Q_0 H'_{\rm el}e^{-\frac{i}{\hbar}H'_{\rm el}t}|\partial_j u_0\rangle\,, \quad (41)$$

where $H'_{\rm el} = H_{\rm el} - E_0$. Here $2{\rm Re}\Gamma_{kj}(t)$ is suggestive of a frictional memory kernel, as becomes evident upon taking the classical limit of Eq. (39) and letting V^j be real. However, some care is needed in this interpretation since velocity-dependent terms may also arise from pseudomagnetic contributions. We shall see below that this is indeed the case in the physically most relevant situation of an electronic bath that responds rapidly on the timescale set by the nuclear motion. In this Markov limit $\Gamma_{kj}(t)$ decays rapidly on the relevant timescale and we can replace $V^j(t-\tau) \approx V^j(t)$ in Eq. (39) to write

$$F_k^{\rm NBO,I} = -{\rm Re}\left(\sum_j \bar{\gamma}_{kj}V^j(t)\right), \quad (42)$$

where the kernel is

$$\bar{\gamma}_{kj} = 2\lim_{\epsilon\to 0^+}\int_0^\infty e^{-\epsilon\tau}\Gamma_{kj}(\tau)\,d\tau \quad (43)$$

and the usual ϵ converging factor has been introduced. As shown in Appendix D this is equivalent to the $T = 0\,$K limiting expression derived by DMS in Ref. [26] [Eq. (2) of the present article]. Later we shall find that $\bar{\gamma}_{kj}$ is better defined as the zero-frequency limit (from above) of a frequency-dependent kernel $\bar{\gamma}_{kj}(\omega)$ in which the excitation energy $\hbar\omega$ can be viewed as a "running" correction to E_0 in the dynamical phase factor $e^{\frac{i}{\hbar}E_0 t}$ appearing in $\Gamma_{kj}(t)$.

Notice that the friction-like kernels of Eq. (41) and Eq. (43)—and similar expressions introduced below—are all position dependent, e.g., $\bar{\gamma}_{kj} \equiv \bar{\gamma}_{kj}(\mathbf{x})$, but we shall omit this dependence in the following.

B. Pseudomagnetic contribution

We show here that the memoryless friction of Eq. (43) contains in fact a pseudomagnetic contribution. To this end we need

$$H'_{\rm el}e^{-\epsilon t}e^{-\frac{i}{\hbar}H'_{\rm el}t} = i\hbar\frac{d}{dt}(e^{-\epsilon t}e^{-\frac{i}{\hbar}H'_{\rm el}t}) + i\hbar\epsilon(e^{-\epsilon t}e^{-\frac{i}{\hbar}H'_{\rm el}t})$$

and

$$H'_{\rm el}\int_0^\infty e^{-\epsilon t}e^{-\frac{i}{\hbar}H'_{\rm el}t}dt = -i\hbar\left(1 + \frac{i\epsilon\hbar}{H'_{\rm el} - i\epsilon\hbar}\right) = -i\hbar\left[1 + i\epsilon\hbar\frac{H'_{\rm el} + i\epsilon\hbar}{(H'_{el})^2 + \epsilon^2\hbar^2}\right] \to -i\hbar[1 + i\pi H'_{\rm el}\delta(H'_{\rm el})],$$

where we have used the common notation $\frac{1}{A}$ for A^{-1}. Notice that in this expression the second term on the r.h.s. $\propto H'_{\rm el}\delta(H'_{\rm el})$ would vanish if it were applied to a regular electronic state, but this is not the case here because of the

presence of the derivative couplings. Inserting this identity in Eq. (43) we find

$$\bar{\gamma}_{kj} = -2i\hbar q_{kj} + \gamma_{kj}, \tag{44}$$

where the "corrected" Markovian friction kernel γ_{kj} takes the form

$$\gamma_{kj} = 2\pi\hbar \langle \partial_k u_0 | Q_0 H'_{\rm el} \delta(H'_{\rm el}) | \partial_j u_0 \rangle . \tag{45}$$

We are interested in the real part of Eq. (44), in particular in the contribution $2\hbar \mathrm{Im} q_{kj} = -\hbar B_{kj}$. Plugging this term into Eq. (42) it is seen to give rise to a magnetic component $+\hbar \sum_j B_{kj} \mathrm{Re} V^j$ that precisely cancels the magnetic correction introduced in Eq. (29). This term does not appear in the common case when the electronic states can be taken as real functions of the electron coordinates (as DMS [26] assumed), which is possible in the absence of magnetic fields and for a trivial topology of the ground adiabatic state. It is however necessary when the magnetic field is turned on or if conical intersections exist that can be encircled by the evolving nuclear wave packet.

More generally, in the Markov limit we have

$$F_k^{\rm NBO,I} = \hbar \sum_j B_{kj} \mathrm{Re} V^j - 2\hbar \sum_j g_{kj} \mathrm{Im} V^j + F_k^{\rm friction}.$$

where

$$F_k^{\rm friction} = -\mathrm{Re}\left(\sum_j \gamma_{kj} V^j \right) \tag{46}$$

is the same as Eq. (42) with γ_{kj} in place of $\bar{\gamma}_{kj}$, and

$$\begin{aligned} F_k^{\rm NBO,II} = {} & 2\hbar \mathrm{Re} \langle \partial_k u_0 | R u_0 \rangle \\ & - 2\pi\hbar \mathrm{Im} \langle \partial_k u_0 | Q_0 H'_{\rm el} \delta(H'_{\rm el}) | R u_0 \rangle \end{aligned}$$

for reasons similar to those given above. Hence, summing up these contributions, we see that in the Markov limit the electron dynamical force of Eq. (25) reduces to a frictional force and a secondary correction

$$F_k^{\rm ED} = F_k^{\rm friction} - 2\pi\hbar \mathrm{Im} \langle \partial_k u_0 | Q_0 H'_{\rm el} \delta(H'_{\rm el}) | R u_0 \rangle , \tag{47}$$

and, upon neglecting the latter, the total force reads approximately as

$$F_k \approx F_k^{\rm BO} + F_k^{\rm el} + F_k^{\rm mag} + F_k^{\rm friction}$$

without any dynamic correction to the pseudo-Lorentz force. This may be physically viewed as restoration of the full adiabatic dynamics: electronic friction cools the nuclear motion and enforces the adiabatic limit, with its gauge fields.

Notice that the residual correction [second term on the r.h.s. of Eq. (47)], as well as the "nonclassical" frictional term $\sum_j \mathrm{Im}\gamma_{kj} \mathrm{Im} V^j$, appears only when time-reversal symmetry is broken.

C. A posteriori correction to LRT

The friction kernel γ_{kj} defined in Eq. (45) is, strictly speaking, ill-defined, as is apparent from the presence of both Q_0 and $\delta(H'_{\rm el})$. A more appropriate definition is obtained by identifying the genuine friction term from the zero-frequency limit (from above) of the frequency-dependent kernel

$$\bar{\gamma}_{kj}(\omega) = 2 \lim_{\epsilon \to 0^+} \int_0^\infty e^{-\epsilon t} e^{i\omega t} \Gamma_{kj}(t)\, dt \tag{48}$$

that is most appropriate for the force of Eq. (39) when taking the Markov limit [41] that leads to Eq. (42). The physical motivation for introducing here a small (eventually vanishing) positive frequency ω is that the evolving ground-electronic state has an energy slightly above E_0, i.e., $E_0 + \hbar\omega$ for $\hbar\omega \to 0^+$, right because of excitations of $e-h$ pairs into the substrate. Thus the replacement

$$\exp\left(\frac{i}{\hbar} E_0 \tau\right) \to \exp(i\omega\tau) \exp\left(\frac{i}{\hbar} E_0 \tau\right)$$

is needed to correct the LRT result [the integrand of Eq. (38)] for this effect.

Before addressing this issue in detail, let us first derive some relationships needed to handle the derivative couplings, and useful to derive different equivalent expressions for the friction kernel. Let first E_0 be a discrete, nondegenerate energy eigenvalue of the electronic Hamiltonian $H_{\rm el}$ for some value of the nuclear coordinates $\mathbf{x}$. Upon taking the derivative of the electronic Schrödinger equation with respect to (w.r.t.) x^k, $(\partial_k H_{\rm el}) |u_0\rangle = (\partial_k E_0) |u_0\rangle + (E_0 - H_{\rm el}) |\partial_k u_0\rangle$, and projecting with Q_0 one easily finds

$$Q_0 |\partial_k u_0\rangle = G_0(E_0) Q_0 (\partial_k H_{\rm el}) |u_0\rangle ,$$

where $G_0(\lambda) = (\lambda - H_{\rm el}^0)^{-1}$ is the resolvent of the restriction of $H_{\rm el}$ to $Q_0 \mathcal{H}_{\rm el}$, i.e., the operator $H_{\rm el}^0 = Q_0 H_{\rm el} = H_{\rm el} Q_0$ defined in the subspace $Q_0 \mathcal{H}_{\rm el}$ (here $\mathcal{H}_{\rm el}$ represents the Hilbert space of the electronic system). More generally, for $\lambda \in \mathbb{C}$

$$Q_0 |\partial_k u_0\rangle = [1 + (E_0 - \lambda) G(\lambda)]^{-1} G(\lambda) Q_0 (\partial_k H_{\rm el}) |u_0\rangle$$

and thus

$$\begin{aligned} Q_0 |\partial_k u_0\rangle = {} & [1 + (\lambda - E_0) G(\lambda) + (\lambda - E_0)^2 G(\lambda)^2 + \cdots] \\ & \times G(\lambda) Q_0 (\partial_k H_{\rm el}) |u_0\rangle \end{aligned}$$

provided λ is closer to E_0 than to any other eigenvalue [here the projector Q_0 effectively removes the pole at E_0 in the spectral representation of $G(\lambda)$]. If E_0 is part of the continuous spectrum we shall use

$$Q_0 |\partial_k u_0\rangle = G^+(E_0) Q_0 (\partial_k H_{\rm el}) |u_0\rangle , \tag{49}$$

which amounts to defining the eigenvectors $|u_0\rangle$ through a limiting procedure. Specifically, given $H_{\rm el}$, E_0 and $|u_0\rangle$ at some point $\mathbf{x}$, in order to fix $|u_0\rangle$ at a neighboring geometry $\mathbf{x}' = \mathbf{x} + d\mathbf{x}$ one first defines the family of vectors $|u_0^\lambda\rangle$ through the (well-defined and unique) solutions of

$$[\lambda - (H_{\rm el} + \Delta H)] \left|u_0^\lambda\right\rangle = (\lambda - H_{\rm el}) |u_0\rangle$$

for $\Delta H = \sum_k (\partial_k H_{\rm el} - \partial_k E_0) dx^k$. This gives

$$\left|u_0^\lambda\right\rangle - |u_0\rangle = G(\lambda) \Delta H \left|u_0^\lambda\right\rangle ,$$

i.e., for infinitesimal displacements of the nuclear coordinates,

$$Q_0 |\partial_k u_0^\lambda\rangle \approx G(\lambda) Q_0 (\partial_k H_{\rm el}) |u_0\rangle ,$$

from which the above result follows upon taking the limit $\lambda \to E_0$ for $\mathrm{Im}\lambda > 0$.

Consider now the frequency-dependent friction kernel of Eq. (48). Upon noticing that

$$\begin{aligned}\Gamma_{kj}(t) &= \langle \partial_k u_0 | Q_0 H'_{\rm el} e^{-\frac{i}{\hbar}H'_{\rm el}t} | \partial_j u_0 \rangle \\ &= -\langle u_0 | (\partial_k H_{\rm el}) Q_0 e^{-\frac{i}{\hbar}H'_{\rm el}t} | \partial_j u_0 \rangle ,\end{aligned}$$

it can be manipulated to give

$$\begin{aligned}\bar{\gamma}_{kj}(\omega) &= -2i\hbar \langle u_0 | (\partial_k H_{\rm el}) Q_0 G^+(E_0+\hbar\omega) | \partial_j u_0 \rangle \\ &= -2i\hbar q_{kj}(\omega) + 2\gamma_{kj}(\omega)\end{aligned} \tag{50}$$

[cf. Eq. (44)] where

$$\gamma_{kj}(\omega) = -\pi\hbar \langle u_0 | (\partial_k H_{\rm el}) Q_0 \delta(E_0+\hbar\omega - H_{\rm el}) | \partial_j u_0 \rangle \tag{51}$$

comes from the imaginary part of the resolvent, and

$$q_{kj}(\omega) = \langle u_0 | (\partial_k H_{\rm el}) Q_0 G_P(E_0+\hbar\omega) | \partial_j u_0 \rangle \tag{52}$$

from its real (or principal) part $G_P(E)$.

Equation (52) defines a frequency-dependent generalization of the quantum geometric tensor. It indeed gives q_{kj} in the limit $\omega \to 0$, since $Q_0 G_P(E_0) = Q_0 G^+(E_0) = Q_0 G^-(E_0)$ holds due to $\delta(E_0 - H_{\rm el})Q_0 = 0$, and this allows one to exploit Eq. (49) and recover the usual definition of the quantum geometric tensor [Eq. (7)].

Equation (51), on the other hand, is the sought-for frequency-dependent version of Eq. (45), as can be seen by recasting it in the form

$$\gamma_{kj}(\omega) = \pi\hbar \langle \partial_k u_0 | Q_0 (H_{\rm el} - E_0) \delta(E_0+\hbar\omega - H_{\rm el}) | \partial_j u_0 \rangle , \tag{53}$$

which shows the key role played by the excitation energy $\hbar\omega$. The reason for singling out a factor of 2 in the second term of Eq. (50) is that, in this way, the Markovian friction kernel—that is, γ_{kj} in Eq. (44)—takes the form of the $\omega \to 0^+$ limit of Eq. (51),

$$\gamma_{kj} = \lim_{\omega\to 0} \frac{2\gamma_{kj}(\omega) + 2\gamma_{kj}(-\omega)}{2} \equiv \lim_{\omega\to 0} \gamma_{kj}(|\omega|), \tag{54}$$

since $\gamma_{kj}(\omega) = 0$ for $\omega < 0$. In other words, Eq. (45) needs to be interpreted as the following limiting procedure:

$$\begin{aligned}&\langle \partial_k u_0 | Q_0 H'_{\rm el} \delta(E_0 - H_{\rm el}) | \partial_j u_0 \rangle \\ &= \frac{1}{2} \lim_{\omega\to 0^+} \langle \partial_k u_0 | Q_0 H'_{\rm el} \delta(E_0+\hbar\omega - H_{\rm el}) | \partial_j u_0 \rangle\end{aligned}$$

(see Appendix E for a discussion of the subtleties associated with the Markov limit).

Equation (51) can be further rearranged to make explicit the role of $\partial_j H_{\rm el}$. Specifically, upon replacing $|\partial_j u_0\rangle$ with $-(\hbar\omega)^{-1}\partial_j H_{\rm el}|u_0\rangle$, the kernel can be written as $\gamma_{kj}(\omega) = \Lambda_{kj}(\omega)/\omega$ where

$$\begin{aligned}\Lambda_{kj}(\omega) = \pi \langle u_0 | &(\partial_k H_{\rm el}) Q_0 \delta(E_0+\hbar\omega - H_{\rm el}) \\ &\times Q_0 (\partial_j H_{\rm el}) | u_0 \rangle\end{aligned} \tag{55}$$

is a sound spectral density of the coupling. This can be seen by casting it in the form

$$\Lambda_{kj}(\omega) = \pi \rho(\omega) \langle F_k^* F_j \rangle_\omega , \tag{56}$$

where $\rho(\omega)$ is the many-body density of states at energy $\hbar\omega$ and $\langle F_k^* F_j \rangle_\omega$ is a force-force correlator

$$\langle F_k^* F_j \rangle_\omega = \frac{1}{\rho(\omega)} \sum_f^{[\omega]} \left(F_k^{f\leftarrow 0}\right)^* F_j^{f\leftarrow 0}. \tag{57}$$

Here $F_k^{f\leftarrow 0} = \langle u_f | \partial_k H_{\rm el} | u_0 \rangle$ and the sum runs over the energy shell $\hbar\omega$ above the ground-state. Notice that $\Lambda_{kj}(\omega)$ defined in Eq. (55) correctly vanishes in the $\omega \to 0$ limit and it is positive semidefined, since

$$\sum_{kj} X^k X^j \Lambda_{kj} = \pi \langle u_0 | W \delta(E_0+\hbar\omega - H_{\rm el}) W | u_0 \rangle \geqslant 0$$

holds for an arbitrary nuclear displacement $X = (X^1, \ldots, X^k, \ldots)$, with $W = Q_0 \sum_k X^k \partial_k H_{\rm el}$. Hence, overall, Eq. (55) clearly displays the symmetry properties of the kernel $\gamma_{kj}(\omega)$

$$\mathrm{Re}\gamma_{kj}(\omega) = \mathrm{Re}\gamma_{jk}(\omega), \quad \mathrm{Im}\gamma_{kj}(\omega) = -\mathrm{Im}\gamma_{jk}(\omega) \tag{58}$$

and the positive semidefinitness of $\mathrm{Re}\gamma_{kj}(\omega)$ for $\omega \geqslant 0$, as is required for a friction kernel. Appendix E details the relationship between $\mathrm{Re}\gamma_{kj}(\omega)$ and the spectral function of the "ordinary" friction kernel—i.e., of the real part of the Fourier transform of $2\gamma_{kj}(\omega)$—and justifies the factor of 2 in Eq. (50) beyond the Markov limit.

Below we expand on an important limiting case, namely, that provided by independent electrons. A further interesting limiting case is considered in Appendix F where we apply Eq. (55) to the widely used model of dissipation defined by the independent oscillator (also known as Caldeira-Leggett) Hamiltonian [42,43].

D. Independent electrons

Equations (51) and (55) provide general expressions for the electronic friction kernel, which apply equally well to independent or interacting electrons. Here we show that for independent electrons, in the Markov limit, they lead to the result first obtained by Head-Gordon and Tully [17], i.e., to Eq. (1) of the present manuscript. We shall use Eq. (51), but the same result follows of course from Eq. (55).

For independent electrons, $\partial_k H_{\rm el}$ is a monoelectronic operator that we write as

$$\partial_k H_{\rm el} = \sum_{\mu,\nu} D^k_{\mu\nu} c^\dagger_\mu c_\nu$$

using the second-quantization annihilation (c_μ) and creation ($c^\dagger_\mu$) operators for the single-particle state $|\phi_\mu\rangle$, and denoting with $D^k_{\mu\nu}$ the single-particle matrix element $D^k_{\mu\nu} = \langle \phi_\mu | \partial_k h | \phi_\nu \rangle$. As a consequence, the on-shell projector

$$\delta(E_0+\hbar\omega - H_{\rm el}) = \sum_K^{[\omega]} |\Psi_K\rangle \langle \Psi_K|$$

(where the sum runs over all the many-body states with energy $\hbar\omega$ above the Hartree-Fock ground state $|\Phi_0\rangle$) can be restricted to singly excited Slater determinants, i.e., to states of the form $|\Psi^b_a\rangle = c^\dagger_b c_a |\Phi_0\rangle$ where now a (b) labels occupied (empty) states in $|\Phi_0\rangle$. Here $\hbar\omega = \epsilon_b - \epsilon_a = \Delta\epsilon_{ba}$, and the single-particle energies are such that $\epsilon_a < \epsilon_F < \epsilon_b$, where ϵ_F

is the Fermi level. Notice that the restriction to singly excited determinants automatically accounts for the projector Q_0 appearing in Eq. (51) (all the way down to $\omega = 0$).

Equation (51) then reads as

$$\begin{aligned}\gamma_{kj}(\omega) &= -\pi\hbar \sum_{a}^{\text{occ}} \sum_{b}^{\text{nocc}} D^k_{ab} \langle \phi_b | \partial_j \phi_a \rangle \, \delta(\hbar\omega - \Delta\epsilon_{ba}) \\ &= -\pi\hbar \sum_{a}^{\text{occ}} \sum_{b}^{\text{nocc}} D^k_{ab} D^j_{ba} \frac{f(\epsilon_b) - f(\epsilon_a)}{\epsilon_b - \epsilon_a} \delta(\hbar\omega - \Delta\epsilon_{ba}) \\ &= -\pi\hbar \sum_{a,b} D^k_{ab} D^j_{ba} \frac{f(\epsilon_b) - f(\epsilon_a)}{\epsilon_b - \epsilon_a} \delta(\hbar\omega - \Delta\epsilon_{ba}),\end{aligned} \tag{59}$$

where we have introduced the $T = 0\,\text{K}$ electron occupation function, $f(\epsilon) = \Theta(\epsilon_F - \epsilon)$, and, in the last step, we have used the condition $\omega > 0$ to free the sums over the orbitals from any constraint. The rightmost side of Eq. (59) is now a well-defined function of $\omega \in \mathbb{R}$, and its real part (the "physical" component of the friction kernel) takes a unambiguous zero-frequency limit since it is an even function of ω. Hence, upon setting $\epsilon_b = \epsilon_a + \hbar\omega$ in the incremental ratio of f, in the limit $\omega \to 0$ we find

$$\text{Re}\gamma_{kj} = \pi\hbar \sum_{a,b} D^k_{ab} D^j_{ba} \delta(\epsilon_b - \epsilon_F)\delta(\epsilon_a - \epsilon_F)$$

after using $f'(\epsilon_a) = -\delta(\epsilon_a - \epsilon_F)$. This is the HGT expression, Eq. (1), as we set out to show.

E. Frictional vector potential

We show here how the above results follow, in linear response, by an appropriate modification of the Hamiltonian governing the adiabatic dynamics, in particular of the vector potential entering the Hamiltonian. This is important for introducing friction (i.e., dissipation) into an effective Hamiltonian for the nuclei. As shown below, this turns the corresponding Schrödinger equation into a nonlinear equation, but this is the price to pay if the energy transfer mechanism has to depend on the system dynamics and it is not due simply to an "external" field.

To this end, we work in the standard gauge for the electron dynamics where $\langle u^+ | \partial_t u^+ \rangle = 0$, using the superscript "$^+$" to denote the chosen gauge. In linear response this amounts to reference the electronic Hamiltonian to the ground-state energy, E_0, and to write $|u^+\rangle = |u_0\rangle + |\Delta u^+\rangle$ where

$$|\Delta u^+\rangle := -\frac{i}{\hbar} \int_0^{+\infty} e^{-\frac{i}{\hbar} H'_{\text{el}} \tau} K_0[\psi_{t-\tau}] \, |u_0\rangle \, d\tau$$

since $\langle u | H_{\text{el}} | u \rangle \approx E_0 + 2\text{Re}\,\langle u_0 | \Delta u^+ \rangle \equiv E_0$ holds thanks to $\langle \Delta u^+ | u_0 \rangle = 0$. This also implies that the nuclear Hamiltonian in this gauge

$$H^+ \approx \frac{1}{2} \sum_{ij} \xi^{ij} \hat{\pi}^+_i \hat{\pi}^+_j + [E_0(\mathbf{x}) + \phi^+]$$

resembles closely the $n = 0$ adiabatic Hamiltonian of Eq. (11), that we denote here as H^0 for notational convenience: the only difference is the presence of $|u^+\rangle = |u_0\rangle + |\Delta u^+\rangle$ in place of $|u_0\rangle$ in the vector and scalar potentials, e.g.,

$$A^0_k \to A^0_k + 2\text{Im}\,\langle \partial_k u_0 | \Delta u^+ \rangle$$

to first order in $|\Delta u^+\rangle$. In fact, it turns out that the main modification is precisely the time-dependent term

$$\begin{aligned}\delta A_k &= A_k - A^0_k \\ &= 2\text{Im}\left(-\frac{i}{\hbar} \int_0^{\infty} \langle \partial_k u_0 | e^{-\frac{i}{\hbar} H'_{\text{el}} \tau} K_0[\psi_{t-\tau}] | u_0 \rangle \, d\tau \right)\end{aligned}$$

since this is of second order in the spatial derivative of the electronic states and generates a force term of the same order through its time derivative,

$$\begin{aligned}F_k &= \frac{\partial \hat{\pi}^+_k}{\partial t} + \frac{i}{\hbar}[H^+, \hat{\pi}_k] = -\hbar \frac{\partial(\delta A_k)}{\partial t} + \frac{i}{\hbar}[H^+, \hat{\pi}^+_k] \\ &\approx -\hbar \frac{\partial(\delta A_k)}{\partial t} + \frac{i}{\hbar}\big[H^0, \hat{\pi}^0_k\big],\end{aligned}$$

where $\hat{\pi}^0_k = \hat{p}_k - \hbar A^0_k$ is the adiabatic momentum. Here, the last line holds if we retain only terms that contain up to three derivatives in nuclear coordinates at a time, e.g., of the form

$$-\partial_k \phi_0 = -\frac{\hbar^2}{2} \sum_{ij} \xi^{ij} \partial_k \text{Re}\,\langle \partial_i u_0 | Q_0 | \partial_j u_0 \rangle \, .$$

In other words, to this "order" in the spatial derivatives, we have

$$[\hat{\pi}^+_i, \hat{\pi}^+_j] \approx \big[\hat{\pi}^0_i, \hat{\pi}^0_j\big], \quad \phi^+ \approx \phi^0,$$

and the geometric properties are the same as in the adiabatic limit, $q^+_{ij} \approx q^0_{ij}$.

Let us then take a closer look at the correction δA_k to the vector potential. From the definition of K_0, Eq. (24) with $|u\rangle \equiv |u_0\rangle$, we have

$$\begin{aligned}\delta A_k = &-2 \sum_j \text{Im} \int_0^{\infty} \langle \partial_k u_0 | e^{-\frac{i}{\hbar} H'_{\text{el}} \tau} Q_0 | \partial_j u_0 \rangle \, V^j(t - \tau) \, d\tau \\ &+ 2\text{Re} \int_0^{\infty} \langle \partial_k u_0 | e^{-\frac{i}{\hbar} H'_{\text{el}} \tau} R | u_0 \rangle \, d\tau,\end{aligned}$$

where the second term can be neglected in the approximation above since it is time independent and it is of third order in the sense specified above, hence it contributes to the force only with a fourth-order term. Upon introducing the complex-valued "position" fields

$$X^j(\mathbf{x}, t) = \int_{-\infty}^{t} V^j(\mathbf{x}, t') \, dt', \tag{60}$$

and integrating by parts we find

$$\begin{aligned}\delta A_k = &-2 \sum_j \text{Im}\big(q^0_{kj} X^j\big) \\ &+ \frac{2}{\hbar} \sum_j \text{Re}\left[\int_0^{\infty} \Gamma_{kj}(\tau) X^j(t - \tau) \, d\tau \right],\end{aligned} \tag{61}$$

where $\Gamma_{kj}(\tau)$ was defined in Eq. (41). In the Markov limit we have

$$\int_0^{\infty} \Gamma_{kj}(\tau) X^j(t - \tau) \, d\tau \approx X^j(t) \lim_{\epsilon \to 0^+} \int_0^{\infty} e^{-\epsilon t} \Gamma_{kj}(\tau) \, d\tau,$$

where [see Eqs. (43) and (44) and Sec. IV C]

$$2\lim_{\epsilon\to 0^+}\int_0^\infty e^{-\epsilon\tau}\Gamma_{kj}(\tau)\,d\tau=\bar{\gamma}_{kj}=-2i\hbar q^0_{kj}+\gamma_{kj}.$$

Hence, in this limit, we find the following simple "frictional correction" to the adiabatic dynamics:

$$\delta A_k=\frac{1}{\hbar}\sum_j \mathrm{Re}(\gamma_{kj}X^j). \tag{62}$$

Here the disappearance of the quantum geometric contribution [first term on the r.h.s. of Eq. (61)] signals the full restoration of the pseudo-Lorentz force discussed above, i.e., the fact that in this limit the force takes the same form as in the adiabatic approximation.

Equation (61), and Eq. (62) for the Markov limit, is the key result of this article. It represents the crucial amendment to the adiabatic Hamiltonian that is necessary in order to include the effect of electronic friction into the quantum dynamics of the nuclei. It is not hard to show that it gives precisely the same contribution to the force as found in Sec. IV A. For instance, in the Markov limit, upon taking the time derivative of Eq. (62) one immediately finds that

$$F_k=F^0_k+F^{\mathrm{friction}}_k,$$

where F^0_k is the force computed in the adiabatic approximation and the second term on the r.h.s. is the frictional force of Eq. (46). Furthermore, the above corrections to the vector potential and the ensuing effective Hamiltonian

$$H^+\approx\frac{1}{2}\sum_{ij}\xi^{ij}\big(\hat{\pi}^0_i-\hbar\delta A_i\big)\big(\hat{\pi}^0_j-\hbar\delta A_j\big)+[E_0(\mathbf{x})+\phi^0] \tag{63}$$

give simple expressions for the average rate of change of the energy of the nuclear degrees of freedom. For instance, in the Markov limit we find

$$\begin{aligned}\frac{d\bar{E}}{dt}&=\left\langle\frac{\partial H^+}{\partial t}\right\rangle_X\approx-\hbar\mathrm{Re}\sum_k\left\langle\frac{\partial(\delta A_k)}{\partial t}\hat{v}^k\right\rangle_X\\&=-\int d\mathbf{x}|\psi(\mathbf{x})|^2\sum_{jk}\mathrm{Re}(\gamma_{kj}V^j)\mathrm{Re}V^k\\&=+\int d\mathbf{x}|\psi(\mathbf{x})|^2\sum_k F^{\mathrm{friction}}_k\,\mathrm{Re}V^k\end{aligned} \tag{64}$$

consistent with the frictional picture (here $\hat{v}^k=\sum_j\xi^{kj}\hat{\pi}^0_j$ is the velocity operator in the adiabatic approximation and V^k is the corresponding velocity field).

Before closing this section it is worth considering the simplified situation where the Markov limit applies, $\xi^{ij}=\delta^{ij}M^{-1}$ and $\gamma_{kj}=\delta_{kj}\gamma\in\mathbb{R}$, uniformly in system configuration space, at least where the dynamics occurs. Under such circumstances we find [44]

$$\delta A_k=\frac{1}{\hbar}\mathrm{Re}(\gamma X^k)=\frac{\gamma}{M}\partial_k\int_{-\infty}^t\mathrm{Im}\ln\psi_{t'}(\mathbf{x})\,dt',$$

which shows that δA_k becomes longitudinal and can be replaced by an appropriate scalar field

$$\delta\phi(\mathbf{x})=\frac{\hbar\gamma}{M}\mathrm{Im}\ln\psi_t(\mathbf{x})$$

upon applying a pseudoelectromagnetic gauge transformation. The resulting Hamiltonian $H=H^0+\delta\phi$ is the Hamiltonian proposed long ago by Kostin [33], who introduced dissipation in the Schrödinger picture with the help of a "phase potential," depending on the phase of the system wave function in the position representation. Here this type of equation has been rederived from a microscopic model, using a fully quantum approach. Furthermore, we generalized the friction force to the case where friction is position-dependent and tensorial and, potentially, has a nonvanishing memory [Eq. (63) with δA_k given by Eq. (61) or its Markovian limit Eq. (62)]. As mentioned in the Introduction, traditional arguments against this kind of models (e.g., the incompatibility with the superposition principle arising from nonlinearity) are here settled from the outset: it is clear from the derivation given above that the wave function of the dissipative system does not represent the wave function of a closed system, rather it is a marginal probability amplitude of a *sub*system, in contact with a reservoir. Finally, we notice that the equation describes the evolution of averaged quantities, here the nuclear observables dressed by the electronic state, and thus it lacks any fluctuating term, similarly to what happens when averaging the Langevin equation to obtain an equation for the average velocity.

V. CONCLUSIONS

We have developed a fully quantum theory of electronic friction that describes the nuclear dynamics in a quantum setting at $T=0$ K. Friction is seen to turn the equation of motion for the nuclear wave function into a nonlinear equation, where the vector potential depends on the past wave function behavior. The latter takes the simple form of Eq. (62) in the commonly relevant Markovian limit where energy dissipation through excitation of electron-hole pairs of a metallic substrate may enforce a true quasiadiabatic dynamics. The theory, though, has been formulated for general memory kernels [Eq. (61)] and it is entirely suitable to address issues like the importance of a nonvanishing memory in the friction kernel [12]. Furthermore, it is not limited to independent electrons and applies equally well to interacting electrons, potentially in a strongly correlated state. The impact of the electronic state on the dynamical behavior of the nuclei has just begun to be explored [26], and the present theory sets a framework to extend these investigations to a regime where the nuclei need to be treated as quantum objects. In fact, the interplay between nuclear quantum effects and electronic friction (with a potentially nonvanishing memory), and its impact on elementary gas-surface processes remain yet to be explored.

Note added in proof. A recent work by Li *et al.*, [45] derives Ehrenfest identities in the context of the exact factorization and shows certain analogies to the formal framework developed in our work.

APPENDIX A: VARIATIONAL EQUATION OF MOTION AS PARALLEL TRANSPORT CONDITION

The Berry connection of Eq. (9) allows one to reinterpret the variational condition of Eq. (3), here written in reduced time units $s=t/T$,

$$P(s)[i\hbar\partial_s-TH(s)]\,|\Psi_s\rangle=0,$$

as a differential equation defining a section of E along a curve $\kappa\colon[0,1]\to\mathcal{M}$. Since $P(s)\partial_s|\Psi(\kappa(s))\rangle=\sum_j\dot\kappa^j P\partial_j|\Psi\rangle\equiv\nabla_{\dot\kappa}|\Psi\rangle$ the equation can be recast in the form

$$i\hbar\frac{\nabla}{ds}|\Psi\rangle=TH_{PP}|\Psi\rangle,$$

where $\frac{\nabla}{ds}$ is the covariant derivative along the curve $\kappa(s)$. Then, if $H_{PP}=E_nP$ (irrespective of the dimension of the eigenspace), the variational equation of motion is equivalent to the parallel transport condition

$$\frac{\nabla}{ds}|\Phi\rangle=0$$

for the vector $|\Phi\rangle=\exp[+\frac{i}{\hbar}T\int_0^s E_n(s')\,ds']|\Psi\rangle$. This equation uniquely defines a unitary map $U_x(s;\kappa)$, the parallel transport map, between the space $\mathcal{V}_x$ above $\mathbf{x}=\kappa(0)$ and the space $\mathcal{V}_y$ above $\mathbf{y}=\kappa(s)$, for any $s\in[0,1]$. The latter solves the equation

$$i\hbar\frac{\partial U_x}{\partial s}=K_\kappa U_x,\ U_x(0;\kappa)=1,$$

where K_κ is the self-adjoint operator defined by

$$K_\kappa=i\hbar\sum_j\dot\kappa^j[\partial_jP,P]$$

(similarly to the case of the variational equation of motion discussed in Sec. II).

Finally, to further emphasize the role played by the manifold dynamics we notice that $\dot P$ determines the adiabatic currents associated to time-independent observables O,

$$\begin{aligned}\frac{d\langle O\rangle}{dt}&=2\mathrm{Re}\langle\Psi|O|\dot\Psi\rangle\\&\equiv2\mathrm{Re}\langle\Psi|O|\dot P\Psi\rangle=2\sum_j\mathrm{Re}\langle\Psi|O|\partial_j\Psi\rangle\dot x^j,\end{aligned}$$

where we have used Eq. (4) and in the last step we have assumed a nondegenerate eigenspace. Here on the rightmost side only the change of $|\Psi\rangle$ in the complementary space matters, since $\mathrm{Re}\langle\Psi|OP|\partial_j\Psi\rangle=0$.

APPENDIX B: FUBINI-STUDY METRIC AND GEOMETRY OF THE LITE

In the projective Hilbert space $\mathrm{P}(\mathcal{H})$ whose elements $\hat\psi$ are rays associated to quantum vectors $|\psi\rangle\in\mathcal{H}$, a distance D_{FS} can be introduced by referencing to the unit sphere in $\mathcal{H}$. This is the Fubini-Study metric and can be defined for any pair of states $\hat\psi$ and $\hat\phi$ as

$$D^2_{\mathrm{FS}}(\hat\psi,\hat\phi)=\min||\psi-\phi||^2=2(1-|\langle\psi|\phi\rangle|),\tag{B1}$$

where $|\psi\rangle$ and $|\phi\rangle$ are normalized representatives of the rays $\hat\psi$ and $\hat\phi$, respectively, and the minimum is taken over their phase difference. When the rays are the one-dimensional fibers of a vector bundle $\pi\colon E\to\mathcal{M}$, as is the case in the adiabatic approximation with nondegenerate states discussed in the main text, the above distance turns the base manifold $\mathcal{M}$ Riemannian. This can be seen by introducing a smooth parametrization of the manifold, considering two nearby points $\mathbf{x}$ and $\mathbf{x}+d\mathbf{x}$ in $\mathcal{M}$ and the distance between the rays above them, i.e.,

$$\begin{aligned}&D^2_{\mathrm{FS}}(\hat\psi(\mathbf{x}),\hat\psi(\mathbf{x}+d\mathbf{x}))\\&\quad=\sum_{ij}\mathrm{Re}\,\langle\partial_i\psi|(1-|\psi\rangle\langle\psi|)|\partial_j\psi\rangle\,dx^idx^j\\&\quad=\sum_{ij}g_{ij}dx^idx^j.\end{aligned}\tag{B2}$$

This follows from Eq. (B1) for a normalized representative $|\psi\rangle$ of $\hat\psi$ upon exploiting $\partial_i\langle\psi|\psi\rangle=0$ and $\partial_j\partial_i\langle\psi|\psi\rangle=0$, and keeping terms up to second order in dx^i. The tensor appearing on the r.h.s. of Eq. (B2) defines, under mild conditions, the Fubini-Study metric on $T\mathcal{M}$, as first observed by Provost and Vallee [36], and it is precisely the real part of the (gauge-invariant) quantum geometric tensor of Eq. (7) based on the section $|\psi(\mathbf{x})\rangle$ of normalized vectors. Notice that the construction just outlined is entirely general and holds also when the Hilbert space itself is viewed as a vector bundle with base $\mathcal{M}=\mathrm{P}(\mathcal{H})$ and its fibers are all the possible rays.

In the main text, we have shown that in the adiabatic approximation the LITE is closely related to the above metric [Eq. (6)]. The connection is entirely general and not tied to the validity of the adiabatic approximation. Specifically, as shown in Refs. [29,30] the FS distance between the variational ($\hat\psi_{dt}$) and the exact ($\hat\psi^{\mathrm{exact}}_{dt}$) states evolved in the infinitesimal time dt from the same state $\hat\psi_t$ reads as (up to second order in dt)

$$\begin{aligned}D^2_{\mathrm{FS}}\big(\hat\psi_{t+dt},\hat\psi^{\mathrm{exact}}_{t+dt}\big)&=\varepsilon^2dt^2\\&=\frac{1}{\hbar^2}\big(\Delta E_t^2-\hbar^2||\dot\psi_t^+||^2\big)dt^2,\end{aligned}\tag{B3}$$

where ΔE_t^2 is the energy variance associated with $\hat\psi_t$ and $|\dot\psi_t^+\rangle$ is the time derivative of the representative defined by the standard (dynamical) gauge along the variational trajectory (i.e., by the condition $\langle\psi_t|\dot\psi_t^+\rangle=0$). This result follows from the McLachlan variational principle, upon exploiting Eqs. (4) and (6) of Ref. [29]. In Eq. (B3) the first term on the r.h.s. is related to the squared velocity of the exact system evolution [46],

$$D^2_{\mathrm{FS}}\big(\hat\psi^{\mathrm{exact}}_t,\hat\psi^{\mathrm{exact}}_{t+dt}\big)=\frac{\Delta E_t^2}{\hbar^2}dt^2+O(dt^3),\tag{B4}$$

and the second term connects similarly to the squared velocity of the variationally evolved state $\hat\psi_t$, as becomes apparent for complex-analytic manifolds which admit a variational effective Hamiltonian as generator of the time evolution. In other words, we have that Pythagoras' identity

$$\begin{aligned}D^2_{\mathrm{FS}}\big(\hat\psi_t,\hat\psi^{\mathrm{exact}}_{t+dt}\big)&=D^2_{\mathrm{FS}}(\hat\psi_t,\hat\psi_{t+dt})\\&\quad+D^2_{\mathrm{FS}}\big(\hat\psi_{t+dt},\hat\psi^{\mathrm{exact}}_{t+dt}\big)\end{aligned}\tag{B5}$$

holds locally, up to second order in dt, for the elementary basic triangles formed by the points $\hat\psi_t$, $\hat\psi_{t+dt}$, and $\hat\psi^{\mathrm{exact}}_{t+dt}$ in the projective Hilbert space of the system.

APPENDIX C: EXACT FACTORIZATION AND FORMULATION BY ABEDI *ET AL.* [31]

The exact-factorization equations for the nuclear and electronic "wave functions" given in Sec. III are identical to those given in Refs. [31,32]. This is evident for the nuclear equation but not for the electronic equation since the authors of Refs. [31,32] wrote the latter in a rather different form which, in our notation, would read

$$\begin{aligned} i\hbar\,|\partial_t u\rangle = &\left[H_{\rm el} - \left(\bar{E} - \hbar A_0 + \frac{\hbar^2}{2}\sum_{ij}\xi^{ij}q_{ij}\right)\right]|u\rangle \\ &+\left[\sum_{ij}\frac{\xi^{ij}}{2}(\hat{p}_i - \hbar A_i)(\hat{p}_j + \hbar A_j)\right. \\ &\left.+\sum_{ij}\xi^{ij}\left(\frac{\hat{p}_i\psi}{\psi}\right)(\hat{p}_j + \hbar A_j)\right]|u\rangle\,. \end{aligned}$$

Here $(\bar{E} - \hbar A_0 + \frac{\hbar^2}{2}\sum_{ij}\xi^{ij}q_{ij}) = \varepsilon$ is the effective energy introduced by the authors of Ref. [31,32], and the second bracket, denoted F in the following, contains Hamiltonian momentum terms $\hat{p}_i$'s rather than $\hat{\pi}_i$'s or $\hat{v}^i$'s (which are gauge tensorial). However, it is only a matter of simple algebra to show that indeed

$$F - \varepsilon = K[\psi] + \hbar A_0 - \bar{E}$$

as required by the equation above or, equivalently,

$$F = K[\psi] + \frac{\hbar^2}{2}\sum_{ij}\xi^{ij}q_{ij}.$$

To see this notice that

$$\begin{aligned} F &\equiv \sum_{ij}\xi^{ij}\left(\frac{\hat{\pi}_i}{2} + \frac{\hat{\pi}_i\psi}{\psi} + \hbar A_i\right)(\hat{p}_j + \hbar A_j) \\ &= \sum_{ij}\xi^{ij}\left(\frac{\hat{p}_i + \hbar A_i}{2} + \frac{\hat{\pi}_i\psi}{\psi}\right)(\hat{p}_j + \hbar A_j) \\ &= \sum_{ij}\frac{\xi^{ij}}{2}\hat{p}_i\hat{p}_j + \sum_{ij}\frac{\xi^{ij}}{2}\hbar\hat{p}_i A_j + \sum_{ij}\frac{\xi^{ij}}{2}\hbar A_i\hat{p}_j \\ &\quad + \frac{\hbar^2}{2}\sum_{ij}\xi^{ij}A_iA_j + \sum_{ij}\frac{\hat{v}^j\psi}{\psi}(\hat{p}_j + \hbar A_j), \end{aligned}$$

where

$$(\hat{p}_j + \hbar A_j)\,|u\rangle = -i\hbar(\partial_j - \langle u|\partial_j u\rangle)\,|u\rangle \equiv -i\hbar Q\partial_j\,|u\rangle$$

gives

$$\sum_j\frac{\hat{v}^j\psi}{\psi}(\hat{p}_j + \hbar A_j)\,|u\rangle = -i\hbar\sum_j\frac{\hat{v}^j\psi}{\psi}Q\partial_j\,|u\rangle$$

and, on the other hand,

$$\begin{aligned} &\sum_{ij}\frac{\xi^{ij}}{2}\hbar(\hat{p}_i A_j + A_i\hat{p}_j)\,|u\rangle \\ &\quad = -i\hbar^2\sum_{ij}\frac{\xi^{ij}}{2}(\partial_i A_j)\,|u\rangle \\ &\qquad - i\hbar^2\sum_{ij}\frac{\xi^{ij}}{2}(A_i\,|\partial_j u\rangle + A_j\,|\partial_i u\rangle) \\ &\quad = -i\hbar^2\sum_{ij}\frac{\xi^{ij}}{2}(A_iQ\,|\partial_j u\rangle + A_jQ\,|\partial_i u\rangle) \\ &\qquad - i\hbar^2\sum_{ij}\frac{\xi^{ij}}{2}(\partial_i A_j)\,|u\rangle - \hbar^2\sum_{ij}\xi^{ij}A_iA_j\,|u\rangle\,. \end{aligned}$$

Hence,

$$\begin{aligned} F\,|u\rangle = &-i\hbar\sum_j\frac{\hat{v}^j\psi}{\psi}Q\partial_j\,|u\rangle \\ &- i\hbar^2\sum_{ij}\frac{\xi^{ij}}{2}(A_iQ\,|\partial_j u\rangle + A_jQ\,|\partial_i u\rangle) \\ &+\sum_{ij}\frac{\xi^{ij}}{2}\hat{p}_i\hat{p}_j - i\hbar^2\sum_{ij}\frac{\xi^{ij}}{2}(\partial_i A_j)\,|u\rangle \\ &- \frac{\hbar^2}{2}\sum_{ij}\xi^{ij}A_iA_j\,|u\rangle\,. \end{aligned}$$

Finally, upon observing that

$$\begin{aligned} A_iA_j + q_{ij} &= \langle\partial_i u|u\rangle\,\langle u|\partial_j u\rangle + \langle\partial_i u|Q\partial_j u\rangle \\ &\equiv \langle\partial_i u|\partial_j u\rangle \equiv \partial_i(\langle u|\partial_j u\rangle) - \langle u|\partial_i\partial_j u\rangle\,, \end{aligned}$$

we write

$$\begin{aligned} &-\frac{\hbar^2}{2}\sum_{ij}\xi^{ij}A_iA_j\,|u\rangle - i\hbar^2\sum_{ij}\frac{\xi^{ij}}{2}(\partial_i A_j)\,|u\rangle \\ &\quad = \frac{\hbar^2}{2}\sum_{ij}\xi^{ij}P\,|\partial_i\partial_j u\rangle + \frac{\hbar^2}{2}\sum_{ij}\xi^{ij}q_{ij}\,|u\rangle \end{aligned}$$

and obtain

$$\begin{aligned} F\,|u\rangle = &-i\hbar\sum_j\frac{\hat{v}^j\psi}{\psi}Q\partial_j\,|u\rangle \\ &-\frac{\hbar^2}{2}\sum_{ij}\xi^{ij}(iA_iQ\,|\partial_j u\rangle + iA_jQ\,|\partial_i u\rangle + Q\,|\partial_i\partial_j u\rangle) \\ &+\frac{\hbar^2}{2}\sum_{ij}\xi^{ij}q_{ij}\,|u\rangle\,, \end{aligned}$$

where

$$iA_iQ\,|\partial_j u\rangle + iA_jQ\,|\partial_i u\rangle + Q\,|\partial_i\partial_j u\rangle \equiv D_{ij}\,|u\rangle$$

i.e.,

$$F\,|u\rangle = -i\hbar\sum_j\frac{\hat{v}^j\psi}{\psi}Q\partial_j\,|u\rangle - \hbar R\,|u\rangle + \frac{\hbar^2}{2}\sum_{ij}\xi^{ij}q_{ij}\,|u\rangle$$

as we intended to show.

APPENDIX D: EQUIVALENCE OF THE BARE FRICTION KERNEL [Eq. (43)] WITH DMS FRICTION [26] at $T = 0$ K

Here, we prove the equivalence of the $T = 0$ K limit of the DMS expression for the friction [Eq. (2)] with the one

obtained in Eq. (43). When the electronic bath is not carrying any current the steady-state density operator is the canonical one, and in the limit $T \to 0$ we have $\rho \to |u_0\rangle\langle u_0| = P_0$ and $\partial_j \rho = |\partial_j u_0\rangle\langle u_0| + |u_0\rangle\langle \partial_j u_0|$. This gives two terms,

$$\gamma_{kj}^{\mathrm{DMS}} = -\int_0^\infty \mathrm{tr}_e[(\partial_k H_{\mathrm{el}}) e^{-\frac{i}{\hbar}H'_{\mathrm{el}}\tau} |\partial_j u_0\rangle\langle u_0|] d\tau - \int_0^\infty \mathrm{tr}_e[(\partial_k H_{\mathrm{el}}) |u_0\rangle\langle \partial_j u_0| e^{+\frac{i}{\hbar}H'_{\mathrm{el}}\tau}] d\tau,$$

which are the complex conjugate of each other, i.e.,

$$\gamma_{kj}^{\mathrm{DMS}} = -2\mathrm{Re}\int_0^\infty \langle u_0|(\partial_k H_{\mathrm{el}}) e^{-\frac{i}{\hbar}H'_{\mathrm{el}}\tau} |\partial_j u_0\rangle\, d\tau.$$

Then, upon noticing that

$$(\partial_k H)|u_0\rangle = (E_0 - H_{\mathrm{el}})|\partial_k u_0\rangle + (\partial_k E_0)|u_0\rangle$$

and introducing the projector $Q_0 = 1 - P_0$, we find

$$\gamma_{kj}^{\mathrm{DMS}} = 2\mathrm{Re}\int_0^\infty \langle \partial_k u_0| Q_0 H'_{\mathrm{el}} e^{-\frac{i}{\hbar}H'_{\mathrm{el}}\tau} |\partial_j u_0\rangle\, d\tau - 2(\partial_k E_0)\int_0^\infty \mathrm{Re}\,\langle u_0|\partial_j u_0\rangle\, d\tau,$$

where the first term is precisely the real part of $\bar{\gamma}_{kj}$ introduced above, and the second term vanishes identically since $\langle u_0|\partial_j u_0\rangle$ is pure imaginary. Note that the usual converging factor has been tacitly assumed.

APPENDIX E: MARKOV LIMIT

We detail here how to correctly interpret the zero-frequency limit that appears in the Markovian regime. We are interested in expressions of the kind

$$I(t) = \mathrm{Re}\int_{-\infty}^{+\infty} h(\tau) V(t-\tau)\, d\tau, \tag{E1}$$

where $V(t)$ is a complex-valued velocity field and $h(t)$ is a causal memory kernel. The Fourier transform of the latter, $\tilde{h}(\omega)$, is taken to be nonzero only for $\omega > 0$, a feature that makes the $\omega \to 0$ limit ambiguous and $h(t)$ necessarily complex [otherwise $\mathrm{Re}\hat{h}(\omega) = \mathrm{Re}\tilde{h}(-\omega)$ would hold]. Let us then rewrite I in the form

$$I(t) = \int_{-\infty}^{+\infty} h_r(\tau) V_r(t-\tau)\, d\tau - \int_{-\infty}^{+\infty} h_i(\tau) V_i(t-\tau)\, d\tau, \tag{E2}$$

where the subscripts r and i denote the real and imaginary parts, respectively, and assume that V is Fourier-transformable, in such a way that

$$\int_{-\infty}^{+\infty} h_a(\tau) V_a(t-\tau)\, d\tau = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \tilde{V}_a(\omega)\tilde{h}_a(\omega) e^{-i\omega t}\, d\omega$$

holds for $a = r, i$. In the Markov limit, the $\tilde{V}_a(\omega)$'s can be taken sharply and symmetrically peaked around $\omega = 0$, so that

$$\frac{1}{2\pi}\int_{-\infty}^{+\infty} \tilde{V}_a(\omega)\tilde{h}_a(\omega) e^{-i\omega t}\, d\omega \approx \mathrm{Re}\tilde{h}_a(0)\,\frac{1}{2\pi}\int_{-\infty}^{+\infty} \tilde{V}_a(\omega) e^{-i\omega t}\, d\omega = \mathrm{Re}\tilde{h}_a(0)\, V_a(t)$$

irrespective of whether the $\mathrm{Im}\tilde{h}_a(\omega)$'s (which are odd functions of ω) are continuous or not at $\omega = 0$. The limit $\omega \to 0$ is now unambiguous,

$$\mathrm{Re}\tilde{h}_r(\omega) = \tfrac{1}{2}\mathrm{Re}[\tilde{h}(\omega) + \tilde{h}^*(-\omega)],$$
$$\mathrm{Re}\tilde{h}_i(\omega) = \tfrac{1}{2}\mathrm{Im}[\tilde{h}(\omega) - \tilde{h}^*(-\omega)],$$

and, upon recalling that $\tilde{h}(\omega) = 0$ for $\omega < 0$, takes the form

$$\lim_{\omega\to 0}\mathrm{Re}\tilde{h}_r(\omega) = \tfrac{1}{2}\lim_{\omega\to 0}\mathrm{Re}\tilde{h}(|\omega|),$$
$$\lim_{\omega\to 0}\mathrm{Re}\tilde{h}_i(\omega) = \tfrac{1}{2}\lim_{\omega\to 0}\mathrm{Im}\tilde{h}(|\omega|).$$

In other words, in the Markov limit one can write $I(t) \approx \mathrm{Re}(\gamma V(t))$ with

$$\gamma = \tfrac{1}{2}\lim_{\omega\to 0^+}\tilde{h}(\omega),$$

thereby justifying the factor of 2 in Eq. (50).

The definition of the friction kernel $\gamma_{kj}(\omega)$ as given by Eqs. (50) and (51) is further consistent with the usual description of the non-Markovian dynamics given by the real (i.e., "truly frictional") part of $h(t)$. To show this, let us consider the spectral representation of the causal kernel $h(t)$ in terms of $\mathrm{Re}\tilde{h}(\omega)$

$$h(t) = \Theta(t)\left[\frac{1}{\pi}\int_{\mathbb{R}} e^{-i\omega t}\mathrm{Re}\tilde{h}(\omega)\, d\omega\right],$$

and let us focus on the "ordinary" memory kernel $g(t) = \mathrm{Re}h(t)$. From

$$g(t) = \frac{h(t) + h^*(t)}{2} \equiv \frac{\Theta(t)}{\pi}\int_{\mathbb{R}} e^{-i\omega t}\frac{\mathrm{Re}\tilde{h}(\omega) + \mathrm{Re}\tilde{h}(-\omega)}{2}\, d\omega$$

the spectral function $\mathrm{Re}\tilde{g}(\omega)$ follows as

$$\mathrm{Re}\tilde{g}(\omega) = \frac{\mathrm{Re}\tilde{h}(\omega) + \mathrm{Re}\tilde{h}(-\omega)}{2} \equiv \frac{\mathrm{Re}\tilde{h}(|\omega|)}{2},$$

where in the last step we have made use of the fact that $\mathrm{Re}\tilde{h}(-|\omega|) = 0$. In other words, the spectral function $\mathrm{Re}\tilde{h}(\omega)$ of an "excitation" kernel (i.e., a kernel that is nonzero only for positive ω) can be converted into an ordinary spectral function by *halving* the value it attains at the magnitude of the given frequency. The ordinary spectral density then reads for any $\omega \in \mathbb{R}$:

$$J(\omega) = \omega\mathrm{Re}\tilde{g}(\omega) = \frac{\omega\mathrm{Re}\tilde{h}(|\omega|)}{2}.$$

For comparison, notice that in the main text, it is the second term of Eq. (50), i.e., $2\gamma_{kj}(\omega)$, that plays the role of $\tilde{h}(\omega)$.

APPENDIX F: INDEPENDENT OSCILLATOR MODEL

We show in this Appendix that the real part of Eq. (55) reduces to a familiar expression when the bath is a collection of independent oscillators coupled linearly to a "system" coordinate s. This common model of dissipation [42,43] fits well within the setup described in the main text, provided the electronic bath is replaced by a phononic one. The coupling is linear in the oscillator coordinates q_k, and takes the form $H_{\mathrm{int}} = \sum_k c_k s q_k$ in the simplest coupling model that gives rise to classical and quantum generalized Langevin equations for

s. Hence, the on-shell projector appearing in Eq. (55) can be restricted to one-phonon states,

$$\delta(E_0 + \hbar\omega - H_{\text{bath}}) = \frac{1}{\hbar}\sum_b \delta(\omega - \omega_b) a_b^\dagger |\mathbf{0}\rangle \langle \mathbf{0}| a_b,$$

where the sum runs over the oscillator modes, $|\mathbf{0}\rangle$ is the vacuum state of the (local) bath Hamiltonian and $a_b^\dagger$ is the phonon-creation operator. There is only one degree of freedom for the system, whose interaction with the environment is described by the spectral density $J(\omega) = \text{Re}\Lambda_{ss}(\omega)$. Using Eq. (55) the latter reads as

$$\begin{aligned} J(\omega) &= \frac{\pi}{\hbar}\sum_{b,k} \delta(\omega - \omega_b) c_k \langle \Psi_0 | (\partial_s H) a_b^\dagger | \Psi_0 \rangle \langle \Psi_0 | a_b q_k | \Psi_0 \rangle \\ &\equiv \frac{\pi}{\hbar}\sum_b \Delta q_b c_b \delta(\omega - \omega_b) \langle \Psi_0 | (\partial_s H) a_b^\dagger | \Psi_0 \rangle , \end{aligned}$$

where ∂_s denotes differentiation w.r.t. s and $q_k = \Delta q_k (a_k + a_k^\dagger)$ has been used. Here Δq_k is the "width" of the ground-state harmonic oscillator wave function for the kth mode, namely, $(\Delta q_k)^2 = \hbar/(2m_k\omega_k)$. Hence, upon making explicit the remaining coupling, we obtain

$$\begin{aligned} J(\omega) &= \frac{\pi}{\hbar}\sum_b \delta(\omega - \omega_b) \sum_k c_k^2 \frac{\hbar}{2m_k\omega_k}\delta_{kb} \\ &\equiv \frac{\pi}{2}\sum_k \frac{c_k^2}{m_k\omega_k}\delta(\omega - \omega_k), \end{aligned}$$

which is the known expression of the spectral density for this kind of model [42] (for $\omega \in \mathbb{R}^+$).

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