Introduction. When molecules scatter off, react or simply vibrate at metal surfaces they can induce electronic excitations in the substrate, in addition to the usual phonon excitations. This energy loss mechanism is a clear violation of the Born-Oppenheimer (BO) approximation and can give rise to intriguing phenomena, including electron transfer processes and generation of chemically-induced currents [1]. Often, though, electronic excitation is of limited extent and reduces to a frictional force of electronic origin that acts on the molecular degrees of freedom, in addition to the usual Born-Oppenheimer forces, a situation where the so-called “BO dynamics with electronic friction” description is appropriate.

Electronic friction has a long history [2]. One early derivation of the frictional forces that electrons exert on a set of (classically) moving nuclei is due to Head-Gordon and Tully [3], who first derived an expression for the relative motion of nuclear and electronic degrees of freedom, in addition to the usual Born-Oppenheimer forces, a situation where the so-called “BO dynamics with electronic friction” description is appropriate.

A theory of electronic friction is developed using the exact factorization of the electron-nuclear wavefunction. No assumption is made regarding the electronic bath, which can be made of independent or interacting electrons, and the nuclei are treated quantally. The ensuing equation of motion for the nuclear wavefunction is a non-linear Schrödinger equation including a friction term. The resulting friction kernel agrees with a previously derived mixed quantum-classical result by Dou, Miao & Subotnik (Phys. Rev. Lett. 119, 046001 (2017)), except for a pseudo-magnetic contribution in the latter that is here removed. More specifically, it is shown that the electron dynamics generally washes out the gauge fields appearing in the adiabatic dynamics. However, at $T=0$ K, the pseudo-magnetic force is fully re-established in the typical situation where the electrons respond rapidly on the slow time-scale of the nuclear dynamics (Markov limit). Hence, we predict Berry’s phase effects to be observable also in the presence of electronic friction, and non-trivial geometric phases should be attainable for molecules on metallic magnetic surfaces.

Quantum Dynamics with Electronic Friction

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A theory of electronic friction is developed using the exact factorization of the electron-nuclear wavefunction. No assumption is made regarding the electronic bath, which can be made of independent or interacting electrons, and the nuclei are treated quantally. The ensuing equation of motion for the nuclear wavefunction is a non-linear Schrödinger equation including a friction term. The resulting friction kernel agrees with a previously derived mixed quantum-classical result by Dou, Miao & Subotnik (Phys. Rev. Lett. 119, 046001 (2017)), except for a pseudo-magnetic contribution in the latter that is here removed. More specifically, it is shown that the electron dynamics generally washes out the gauge fields appearing in the adiabatic dynamics. However, at $T=0$ K, the pseudo-magnetic force is fully re-established in the typical situation where the electrons respond rapidly on the slow time-scale of the nuclear dynamics (Markov limit). Hence, we predict Berry’s phase effects to be observable also in the presence of electronic friction, and non-trivial geometric phases should be attainable for molecules on metallic magnetic surfaces.

\[ \gamma_{kj} = \pi \hbar \sum_{ab} (a|\partial_k \hat{h}|b) \langle b|\partial_j \hat{h}|a \rangle \delta(\epsilon_a - \epsilon_F) \delta(\epsilon_b - \epsilon_F) \tag{1} \]

where $a, b$ label single-particle states, $k, j$ label nuclear degrees of freedom, $\hat{h}$ is the one-particle Hamiltonian and $\epsilon_F$ the Fermi energy, was obtained at zero temperature in the independent electron approximation, and found to be consistent with earlier results on vibrational relaxation at metal surfaces [4-6]. It was later re-derived using different methodologies, including influence functionals [7] and nonequilibrium Green’s functions [8] (see Ref. [2] for a comprehensive account). This form of electronic friction, combined with first principles electronic structure theory [9-11], has been applied to a variety of problems [11-17], and Langevin dynamics with electronic friction and density-functional theory potentials is nowadays a standard tool to investigate the dynamics of molecules at metal surfaces. Other works addressed the issue of non-thermal, yet steady-state, electronic baths (e.g., current-carrying metals) [18-19] and of the electron-electron interactions [20, 21], and showed the importance of going beyond a mean-field treatment of the electronic dynamics [21]. In particular, Dou, Miao & Subotnik (DMS), using a mixed quantum-classical approach, derived a completely general friction kernel that applies to interacting electrons, is valid out of equilibrium, and reduces to previously published expressions for independent electrons [21]. DMS wrote the electronic friction tensor, in the Markov limit, as

\[ \gamma_{kj}^{DMS} = -\int_0^\infty \text{tr}_e \left( (\partial_k H_{el}) e^{-\hat{H}_{el} \tau} (\partial_j \rho) e^{+\hat{H}_{el} \tau} \right) d\tau \tag{2} \]

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

The electronic friction limit can be considered a first order “realization” of the adiabatic approximation in a situation where a continuum of electronic states and the ensuing fast relaxation guarantee that, on the time scale of nuclear motion, the electrons follows adiabatically the nuclei. However, the adiabatic approximation, in addition to the usual BO forces, introduces gauge fields that reflect the geometric properties of the electronic eigenspaces when viewed as functions of the slow parameters (the nuclear degrees of freedom), and it is not clear whether and how these disappear when the electron dynamics is taken into account. The answer to this question lies into the nuclear wavefunction, since the electronic degrees of freedom are traced out in the above electronic-friction description and the phase of the electronic wavefunction cannot be tracked in any realistic experiment. Hence, a full quantum description of the
dynamics is made necessary, and this is the purpose of the present Letter.

The Letter is organized as follows. After summarizing some basic properties of the adiabatic approximation we analyze the $T = 0$ K exact quantum dynamics of the combined electron-nuclear system using a representation that closely resembles the adiabatic one. We shall show that the introduction of the electron dynamics generally washes out the above mentioned gauge fields, and thus removes any Berry’s phase effect from the dynamics. Later, we analyze the case of an electronic bath that relaxes quickly on the time-scale 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, we shall show that the pseudo-magnetic forces are fully restored, thereby making geometric phase effects potentially observable. Importantly, it is further shown how the adiabatic Hamiltonian has to be modified to include friction in the nuclear dynamics, and how the equation of motion for the nuclear wavefunction is turned into a non-linear equation of the Schrödinger-Langevin type.

**Adiabatic approximation.** The adiabatic approximation [22] and the related adiabatic theorem [23, 24] has under-pinned research into quantum systems with slowly evolving parameters, and form the basis of the theory of energy level crossings in molecules, of the Gell-Mann–Low theorem in quantum field theory and of Berry’s geometrical phase. When the slow parameters $x$ (here, the nuclear coordinates) are considered as dynamical variables the approximation can be recast as a variational approximation with the wavefunction ansatz

$$\Psi(t) = \int d^nx \psi_n(x) |u_n(x)\rangle |x\rangle$$

where $|u_n(x)\rangle$ is a chosen time-independent “frame” of the $n^\text{th}$ electronic eigenstate, $|x\rangle$ are position eigenstates of the slow variables, and $\psi(x)$ is the nuclear wavefunction. The latter satisfies the variational equation of motion

$$H^\text{eff}_n \psi = i\hbar \partial_t \psi$$

where the effective Hamiltonian

$$H^\text{eff}_n = \frac{1}{2} \sum_{ij} \xi^{ij} \hat{\pi}_i \hat{\pi}_j + (E_n - \hbar A_0 + \phi)$$

Here, $E_n = \langle u_n | H_\text{el} | u_n \rangle$ is the $n^\text{th}$ potential energy surface, $H_\text{el} \equiv H_\text{el}(x)$ the electronic Hamiltonian, $\xi^{ij}$ is a coordinate-independent inverse-mass tensor of the slow variables and the mechanical momentum for the $j^\text{th}$ degree of freedom $\hat{\pi}_j = \hat{p}_j - \hbar A_j$ is defined in terms of the Berry’s connection $A_j = i \langle u_n | \partial_j u_n \rangle$ and the coordinate representation of the momentum operator $\hat{p}_j$.

The geometric properties of the adiabatic approximation are subsumed in the quantum geometric tensor

$$q_{ij} = \langle \partial_i u_n | Q_n | \partial_j u_n \rangle \quad Q_n \equiv 1 - |u_n(x)\rangle \langle u_n(x)|$$

which determines both the scalar potential $\phi(x)$ and the commutation properties of the $\hat{\pi}_j$’s, through its real (3$q_{ij} = g_{ij}$) and imaginary ($3q_{ij} = -B_{ij}/2$) parts, respectively, i.e.,

$$\phi = \frac{\hbar^2}{2} \sum_{ij} \xi^{ij} g_{ij} \quad [\hat{\pi}_i, \hat{\pi}_j] = i\hbar B_{ij}$$

Here, $g_{ij}$ is a quantum metric and $B_{ij}$ is the $ij^\text{th}$ component of the Berry’s curvature, i.e., the exterior derivative of the linear differential form $\omega = \sum_j A_j dx^j$. Furthermore, for later convenience, we have introduced a term $A_0 = i \langle u_n | \partial_i u_n \rangle$ that allows more general, time-dependent gauge transformations ($A_0 = 0$ is the usual choice) [28].

The ensuing nuclear dynamics is governed by the Born-Oppenheimer force, $F^\text{BO}_k = -\partial_k E_n$, in conjunction with a pseudo-Lorentz force comprising an electric

$$F^\text{el}_k = -\partial_k \phi = -\frac{\hbar^2}{2} \sum_{ij} \xi^{ij} \partial_k g_{ij}$$

and a magnetic contribution

$$F^\text{mag}_k = \frac{\hbar}{2} \sum_j (\hat{\pi}^j B_{kj} + B_{kj} \hat{\pi}^j)$$

($\hat{\pi}^j = \sum_i \xi^{ji} \hat{\pi}_i$ being the velocity operator) that have a purely geometrical origin and represent the legacy of the adiabatic constraint to the wavefunction. The above forces are separately gauge invariant. An additional gauge-invariant component related to the electron dynamics (ED) formally exists

$$F^\text{ED}_k = \hbar (\partial_k A_0 - \partial_i A_k) = -2\hbar \Im \langle \partial_k u | Q_n | \partial_i u \rangle$$

but vanishes identically in the adiabatic approximation.

As shown in the Supplemental Material (SM), the quantum geometric tensor also determines the local-in-time error [29, 30] of the adiabatic approximation. The latter takes approximately the form of an expectation value of the quantized quantum geometric tensor

$$\varepsilon^2 \approx \langle \psi | \sum_{ij} \hat{\pi}^i q_{ij} \hat{\pi}^j | \psi \rangle_X$$

(where $X$ denotes integration w.r.t. the nuclear DOFs only) and measures the tendency of the system to undergo a non-adiabatic transition at short-time. In fact, $P_{\text{nad}} \approx \varepsilon^2(t - t_s)^2$ is the total transition probability, if the adiabatic approximation were suddenly lifted at $t = t_s$. For comparison, we notice that if the slow variables were simply some parameters, and not dynamical variables, we would have exactly

$$\varepsilon^2 = \sum_{ij} V^i q_{ij} V^j \equiv \sum_{ij} V^i g_{ij} V^j$$
where $V^i$ is the classical velocity of the $i$th parameter (see SM for details).

**Exact dynamics.** The exact wavefunction can be yet represented in a form similar to above,

$$|\Psi_t\rangle = \int_X dx \psi_t(x) |u_t(x)\rangle |x\rangle$$

but now with a time-dependent electronic state $|u_t(x)\rangle$ for each nuclear configuration $x$. This is the so-called exact-factorization of the wavefunction [31, 32], which is an “intermediate” representation that can be obtained by introducing a local basis of nuclear states $\{|x\rangle\}$, and imposing a normalization condition on the ensuing local electronic states,

$$\langle x|\Psi_{t}\rangle_{X} = \psi_{t}(x)\langle u_{t}(x)\rangle \langle u_{t}(x)|u_{t}(x)\rangle = 1$$

The corresponding equations of motion [31, 32] are re-derived in SM using a projection-operator technique that emphasizes their gauge transformation properties. They can be summarized as follows. The nuclear wavefunction satisfies $H^{\text{eff}} \psi = i\hbar \partial_t \psi$, where the effective Hamiltonian takes precisely the form of Eq. 5 but now $|u(x,t)\rangle$ replaces $|u_n(x)\rangle$ everywhere and $A_0 = i \langle u|\partial_t u\rangle$ is an arbitrary real gauge constraint that guarantees normalization of the local electronic state. The ensuing equation of motion for the exact nuclear wavefunction are thus formally very similar to the adiabatic ones. The additional force, due solely to the electron dynamics, is the gauge-invariant term of Eq. 4 that, differently from the adiabatic approximation, is generally non zero. That is, the total force reads exactly as $F^{\text{tot}} = F^{\text{BO}} + F^{\text{el}} + F^{\text{mag}} + F^{\text{ED}}$, where $F^{\text{BO}} \equiv -\partial_t \langle u|H_{el}|u\rangle = -\partial_t E_{el}$ is a time-dependent BO force, the geometric forces $F^{\text{el}}$ and $F^{\text{mag}}$ stem from the time-dependent geometric tensor $q_{ij}$ and $F^{\text{ED}}$ describes the electron dynamics.

The electronic equation of motion takes the form

$$i\hbar Q \partial_t |u\rangle = Q H_{el} |u\rangle + K[\psi_t] |u\rangle$$

where the second term on the r.h.s. describes the ‘electron drag’ with the nuclear motion and reads as

$$K[\psi_t] |u(t)\rangle = -i\hbar \sum_j V^{ij} Q \partial_j u(t) - \hbar R |u(t)\rangle$$

Here $V^{ij}(x) = \langle \psi_t | \partial_j u(t) | u(t) \rangle / \langle \psi_t | u(t) \rangle$ is the (gauge-invariant) time-dependent, complex-valued nuclear velocity field, $Q = 1 - |u\rangle \langle u|$, $R |u\rangle = \frac{1}{2} \sum_{ij} \xi^{ij} D_{ij} |u\rangle$, and

$$D_{ij} |u\rangle = i A_i Q \partial_j u + i A_j Q \partial_i u + Q |\partial_i \partial_j u\rangle$$

is a second derivative of the electronic states. In this form the effective electronic Hamiltonian is the sum of gauge tensorial terms $G$, i.e., of terms that behave simply as $G |u\rangle \rightarrow e^{-iQ} G |u\rangle$ under the gauge transformation $|u\rangle \rightarrow e^{-i\xi} |u\rangle$. This Hamiltonian can be used to include explicitly the electron reaction into the nuclear equation of motion. Specifically, plugging $Q \partial_t |u\rangle$ into $F^{\text{ED}}$ above one obtains a correction to the previous pseudo-electric and pseudo-magnetic forces, that are turned into

$$F_{k}^{\text{el}} = 2\hbar \sum_j g_{kj} \Im V^j$$

$$- \hbar^2 \sum_{ij} \xi^{ij} (\Re \langle \partial_t u|D_{kj} u\rangle + \Re \langle \partial_t u|D_{ij} u\rangle)$$

$$F_{k}^{\text{mag}} = \frac{\hbar}{2} \sum_j (\partial^j B_{kj} + B_{kj} \partial^j) - \hbar \sum_j B_{kj} \Im V^j$$

plus a genuine non-Born-Oppenheimer term

$$F_{k}^{\text{NBO}} = 2\hbar \langle \partial_t u|Q H'_{el}\rangle |u\rangle$$

where $H'_{el} = H_{el} - E_{el}$ for later convenience. The latter force vanishes identically when $|u\rangle$ is an eigenstate of $H_{el}$ and, more generally, is bound by the size of the (local) energy fluctuations in the electronic subsystem, $\Delta E_{el}^2 = \langle (H_{el} - E_{el})^2 \rangle$, through the $k$th diagonal component of the quantum geometric tensor, namely $|F_{k}^{\text{NBO}}| \leq 2\Delta E_{el} \sqrt{g_{kk}}$. Thus, the total force acting on the $k$th nuclear degree of freedom can be written as

$$F_{k}^{\text{tot}} = F_{k}^{\text{BO}} + F_{k}^{\text{el}} + F_{k}^{\text{mag}} + F_{k}^{\text{NBO}}$$

and represents the same total force given above but now explicitly including the electron reaction. The key point about this expression is that, as shown in SM, the dynamically corrected pseudo-Lorentz force vanishes identically when averaged over an arbitrary nuclear state since

$$\langle \psi|F_{k}^{\text{el}}|\psi\rangle_X = \langle \psi|F_{k}^{\text{mag}}|\psi\rangle_X = 0$$

and thus it disappears in the quantum-classical limit where the electronic friction approximation is often invoked. Hence, electronic friction must come from the term $F_{k}^{\text{NBO}}$.

We stress that the above results are exact and tell us that, in general, the effect of the electron dynamics is to wash out the pseudo-Lorentz force appearing in the adiabatic limit. As shown in SM, the vanishing of the average pseudo-electric force expresses conservation of the quantum metric, since such force takes the form of a(n expectation value of the) Ricci-Levi Civita covariant derivative of the metric tensor. This appears reasonable since the quantum metric and the related pseudo-electric force measure the error in the adiabatic approximation while the dynamics considered here is exact. Likewise, the vanishing of the pseudo-magnetic force signals the quenching of geometric phase effects that, in fact, should disappear when the dynamics is far from the adiabatic regime [33].

**Electronic friction.** Let us now focus on the electronic equation Eq. 5 in the situation where the electronic system relaxes quickly to the ground-state $|u_0\rangle$.
and the deviation $|\Delta u| = |u(t)| - |u(0)|$ remains small throughout the nuclear dynamical evolution (here, $|u(0)|$ 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 (see SM for details). Under these circumstances, $\langle \Delta u | u \rangle \equiv 0$, the BO forces $F^B_k$ acting on the molecular degrees of freedom are the same as the ground-state ones, $E_k = E_k + 2 \hbar \omega \Re \langle \Delta u | u \rangle \equiv E_k$, and $F^{\text{NPO}}_k \equiv 2 \hbar \gamma_k |H^{el}_0|\Delta u$ represents the main effect of the electronic reaction. Hence, upon plugging the LRT result for $|\Delta u|$ into the above expression for $F^{\text{NPO}}_k$ one obtains a friction-like term $F_k^\gamma = -2 \sum_j \Re \int_0^\infty \Gamma_{kj}(\tau) V^j(t-\tau) d\tau$, where $V^j$ becomes the real particle velocity in the classical limit, and $\Gamma$ is the kernel

$$
\Gamma_{kj}(\tau) = \langle \partial_k u | Q_0 H^{el}_0 e^{-iH^{el}_0 \tau} | \partial_j u \rangle
$$

In the Markov limit we can set $V^j(t-\tau) \approx V^j(t)$ and the frictional force takes the form $F_k^\gamma = -\sum_j \gamma_{kj} V^j$ is the zero-frequency limit of the frequency-dependent kernel $\gamma_{kj}(\omega) = 2\hbar \sum_{\tau} e^{-i\omega \tau} \Gamma_{kj}(\tau) d\tau$. As shown in SM, the real part of the tensor $\gamma_{kj}$ is precisely the $T \rightarrow 0$ limit of the mixed quantum-classical DMS expression [21], Eq. 2, and contains a pseudo-magnetic contribution $2\hbar \Im \langle \partial_k u | Q_0 | \partial_j u \rangle = 2\hbar \Im \gamma_{kj}$. The latter, when used to evaluate the forces acting on the nuclei, is seen to give a term $+h \sum_j B_{kj} jV^j$ that precisely cancels the magnetic dynamical correction introduced above (see Eq. 5). This corrective effect is physically sound: electronic friction cools the nuclear motion and enforces the adiabatic limit, with its gauge fields. Upon removing the spurious pseudo-magnetic contribution, the ordinary electronic friction tensor is the real part of the expression

$$
\gamma_{kj} = 2\hbar \langle \partial_k u | Q_0 (H_0 - E_0) \delta(E^+_0 - H_0) \partial_j u \rangle
$$

where $E^+_0 = E_0 + \hbar \omega$ in the limit $\omega \rightarrow 0^+$. Notice the symmetries $\gamma_{kj} = \gamma_{jk}$ and $\gamma_{kj}^{(0)} = -\gamma_{kj}^{(0)}$ for the real and imaginary parts of $\gamma_{kj}$, respectively, and the fact that $\gamma_{kj}$ satisfies the second fluctuation-dissipation relation as described in Ref. [21] (in the $T \rightarrow 0$ K limit considered here), since the argument used by Dou et al. remain valid in this context. Furthermore, upon using $\langle \partial_k u | Q_0 H^{el}_0 \rangle = -\langle u_0 \partial_k H_0 \rangle Q_0$ we can equivalently rewrite $\gamma_{kj}$ as

$$
\gamma_{kj} = -2\pi \hbar \Re \langle u_0 | (\partial_k H_0) \delta(E^+_0 - H_0) | \partial_j u_0 \rangle
$$

It is this expression that reduces to Eq. 1 in the independent electron approximation (see SM), and that shows more explicitly why $\gamma_{kj}$ needs a manifold of states lying infinitesimally close to the ground state to be non-vanishing. [The required excitation energy $\hbar \omega \rightarrow 0$ can also be viewed as the “running” correction to $E_0$ in the dynamical phase factor of the evolving electronic state.]

In the context of the exact factorization of the wave-function, the electronic-friction regime considered here is best handled by using local electronic states in the “standard” gauge, i.e., $\langle u^+ | \partial u^+ \rangle = 0$ where $+$ denotes this gauge. In the LRT limit this amounts to setting $E_k = E_k = 0$ in the electronic problem and writing $|u^+ \rangle = |u_0 \rangle + |\Delta u \rangle$, where now only the second term is time-dependent. This implies that the nuclear Hamiltonian in the chosen gauge, $H^+$, very closely resembles the n = 0 adiabatic Hamiltonian of Eq. 3. In fact, as shown in SM, the main difference is a modified vector potential $A_k \rightarrow A_k + \delta A_k$ where

$$
\delta A_k = 2\hbar \Im \langle \partial_k u_0 | Q_0 \rangle
$$

This term is of second order in the spatial derivatives of the electronic states and generates a correction of the same order to the adiabatic forces through its time dependence, $F_k \rightarrow F_k - \hbar \partial_t (\delta A_k)$. An integration by parts transforms $\delta A_k$ into

$$
\delta A_k = -2 \sum_j \Im \int_0^\infty \langle \partial_k u_0 | e^{-iH^{el}_0 t} Q_0 | \partial_j u_0 \rangle V^j_{t-0} dt'
$$

where $V^j$’s are the integrated velocity fields, $V^j(x, t) = \int_{-\infty}^t V^j(x, t') dt'$ and the first term is seen to be the source of the dynamical correction to the pseudo-Lorentz force (Eqs. 78). In the Markov limit, as seen above, only the integrated kernel $\gamma_{kj} = 2\hbar \Im \gamma_{kj}$ matters, for which we have $\gamma_{kj} = -2\hbar \delta A_k$. Hence, in this limit Eq. 11 reduces to

$$
\delta A_k = -\hbar^{-1} \sum_j \Re (\gamma_{kj} X^j_k)
$$

where the same cancellation effect occurs as discussed above.

Eq. 12 is a key result of this Letter. It represents the simple amendment to the adiabatic Hamiltonian that is necessary in order to include the effect of electronic friction into the quantum dynamics of the nuclei, in the most relevant case where the Markov limit applies. This term turns the Schrödinger equation into a non-linear equation of motion, which conserves the wavefunction norm and describes energy dissipation. In the simplest case where $\xi^{ij} = \delta^{ij} M^{-1}$, if $\gamma_{kj}$ can be taken diagonal and uniform in the configuration space of the system where the dynamics occurs, one finds

$$
\delta A_k = \Re (\gamma X^k_k) \approx \partial_k \Re \left(-i\hbar M^{-1} \gamma \int_{-\infty}^t \ln \psi_V(x) dt'\right)
$$

upon neglecting the contribution of the vector potential to the velocity field. Hence, $\delta A_k$ becomes longitudinal and can be replaced by an appropriate scalar field
δφ ≈ ℏM⁻¹γ₃(ln ψᵣ(x)) for negligible γ'''. This scalar potential is precisely the “phase potential” appearing in the effective Hamiltonian of the (non-linear) Kostin equation [34], and represents a very simple way to introduce dissipation into a Schrödinger-like equation.

We remark that the resulting equation for the nuclear wavefunction has no fluctuating term since it describes the evolution of electronically averaged quantities, i.e., the nuclear observables dressed by the electronic state.

**Conclusions.** We have developed a 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 wavefunction into a non-linear equation, where the vector potential depends on the past wavefunction behaviour. This low-temperature, frictional limit seems to be ideal to explore the nuclear dynamics in a situation where energy dissipation through excitation of electron-hole pairs of a metallic substrate enforces the adiabatic dynamics. We have shown that in this limit the gauge fields appropriate for an adiabatic dynamics are fully restored, hence we expect Berry’s phase effects to be operative. In molecular problems, the latter typically reduce to a sign change, since the Berry’s connection is flat in the presence of time-reversal symmetry. However, in the presence of a magnetic field (that here can come from the metallic surface itself) a non-zero curvature is present, thereby allowing the geometric phase to attain arbitrary values. A magnetic field also modifies the effective Hamiltonian of the (non-linear) Kostin equation [34], and represents a very simple way to introduce corrections to the forces – rather to F_{kin} – that would leave the electron – G, etc. and of the quantum geometric tensor q₀ introduced below.

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[33] We remark that the adiabatic approximation does not correspond to F^{BO}_{kin} = 0 – that would leave the electron corrections to the forces – rather to F^{AD}_{kin} = 0. In a sense, the Born-Oppenheimer approximation incorporates these corrections and thus accounts partially for the electron reaction, thereby removing geometric phase effects and the repulsive pseudo-electric forces that become impor-
SUPPLEMENTAL MATERIAL

A. Adiabatic approximation

I. Slow variables as external parameters

When the slow variables $x$ are regarded as parameters that are under the control of the experimenter, the Hamiltonian governing the evolution of the system has a pre-defined time-dependence $H = H(x(t))$ for any given path $x(t)$ of the parameters. The adiabatic approximation can be recast as a variational approximation

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

which uses a time-dependent variational manifold $V(t)$ (the $n$th eigenspace of $H(t)$, here assumed to be non-degenerate) and a complex-analytic representation of the wavefunction. In other words, one describes the wavefunction at any time in the form $|\Psi\rangle = C |u_n(s)\rangle$ where $C$ is the only (complex) variational parameter of the problem. The Dirac-Frenkel condition amounts to

$$P_n (i\hbar \partial_t - H(t)) |\Psi_t\rangle = 0$$

where $P_n = P_n(t)$ is the instantaneous eigenprojector on the target manifold and $Q_n = 1 - P_n$ its orthogonal complement. Hence

$$i\hbar |\dot{\Psi}_t\rangle = H_{PP}(t) |\Psi_t\rangle + i\hbar \dot{P}_n |\Psi_t\rangle$$

where $Q_n |\dot{\Psi}_t\rangle \equiv \dot{P}_n |\Psi_t\rangle$ has been used to re-write the time-derivative in terms of the manifold dynamics (contained in $\dot{P}_n$) and of $H_{PP} \equiv P_n HP_n$. Furthermore, since $P_n \dot{P}_n |\Psi_t\rangle = 0$ the equation of motion can be recast as an effective Schrödinger equation

$$i\hbar \frac{d}{dt} |\Psi_t\rangle = H_n(t) |\Psi_t\rangle$$

involving the self-adjoint effective Hamiltonian

$$H_n(t) = H_{PP}(t) + i\hbar |\dot{P}_n, P_n\rangle$$

Local-in-time-error in case I (Slow variables as parameters)

The local-in-time error (LITE) accompanying a variational solution [29] takes the general form

$$\epsilon[\Psi] = \hbar^{-1} \| (i\hbar \partial_t - H) \Psi \|$$

and, in the case of a time-dependent, complex-analytic manifold, can be given in terms of the above introduced variational Hamiltonian as

$$\hbar^2 \epsilon^2[\Psi] = \| (H_n - H) \Psi \|^2$$

$$\equiv \left\| \left( H - i\hbar \dot{P}_n \right) \Psi \right\|^2 - \left\| \left( H_n - i\hbar \dot{P}_n \right) \Psi \right\|^2$$
This result follows upon noticing that, for \( |Ψ⟩ = P_n |Ψ⟩ \), we have \( (H - H_n) |Ψ⟩ = Q_n (H - i\hbar \dot{P}_n) |Ψ⟩ \) hence
\[
\hbar^2 \varepsilon^2 |Ψ⟩ = (|Ψ⟩(H + i\hbar \dot{P}_n) Q_n (H - i\hbar \dot{P}_n) |Ψ⟩)
\]
\[
= (|Ψ⟩(H + i\hbar \dot{P}_n) (H - i\hbar \dot{P}_n) |Ψ⟩) +
\]
\[
- ⟨|Ψ⟩(H + i\hbar \dot{P}_n) P_n (H - i\hbar \dot{P}_n) |Ψ⟩
\]
\[
= ||(H - i\hbar \dot{P}_n) |Ψ⟩||^2 - ||H_{P_P} |Ψ⟩||^2
\]
which is the same as the above result since in the last expression \( H_{P_P} \) can be replaced with \( H_n - i\hbar \dot{P}_n \).

Now, upon noticing that in the adiabatic problem \( H_{P_P} = E_n P_n \),
\[
\hbar^2 \varepsilon^2 |Ψ⟩ = \left\| E_n |Ψ⟩ - i\hbar \dot{P}_n |Ψ⟩ \right\|^2 - \left\| E_n |Ψ⟩ \right\|^2
\]
we find
\[
ε = \| \dot{P}_n |Ψ⟩ \|
\]
where \( \langle |Ψ⟩ \dot{P}_n |Ψ⟩ = 0 \) has been used. This error is a purely geometrical property, i.e., for a given infinitesimal displacement in parameter space it does not depend on the evolution time. In fact, using \( || \dot{P}_n |Ψ⟩ || = || \dot{P}_n u_n || = ||Q_n \dot{u}_n || \), the LITE is seen to be a property of the moving manifold only and takes the form \( ε^2 = \langle \dot{u}_n |Q_n | \dot{u}_n \rangle \) or, equivalently, introducing the parameter derivative,
\[
ε^2 = \sum_{i,j} \langle \partial_i u_n |Q_n | \partial_j u_n \rangle \dot{x}^i \dot{x}^j = \sum_{i,j} g_{ij} \dot{x}^i \dot{x}^j
\]
where \( \partial_i \equiv \partial/\partial x^i \) and \( g_{ij} \) is the symmetric part of the covariant tensor on the parameter space
\[
q = \sum_{i,j} \langle \partial_i u_n |Q_n | \partial_j u_n \rangle dx^i dx^j
\]
known as quantum geometric tensor. Such symmetric (real) part \( g \) is a quantum metric (a Fubini-Study metric on the tangent bundle), while the antisymmetric (imaginary) part is related to the Berry’s curvature. In a single equation,
\[
q = g - \frac{i}{2} d\omega
\]
where \( d \) denotes the exterior derivative and \( ω \) is the differential form \( ω = \sum A_j dx^j \), i.e.,
\[
dω = \sum B_{ij} dx^i dx^j
\]
Here, \( A_j = i \langle u_n | \partial_j u_n \rangle \) subsumes the Berry’s connection on the vector bundle \( π : E → M \) defined by the parametric dependence of the given eigenspace and \( B_{ij} \equiv \partial_i A_j - \partial_j A_i \) (here \( M \) is the nuclear configuration space and \( π^{-1}(x) \) is the \( n \)th eigenspace of the electronic Hamiltonian \( H_{el} \)).

II. Slow variables as dynamical variables

If the slow variables are considered as dynamical variables the electron-nuclear wavefunction is written as
\[
|Ψ⟩ = \int dx \psi(x) |u_n(x)⟩ x
\]
The variational manifold is complex and application of the variational principle reduces to the Dirac-Frenkel condition,
\[
\int dx' dx δ ψ^*(x') ⟨u_n(x'), x' | [i\hbar \partial_t - H] |u_n(x), x⟩ ψ(x) = 0
\]
Here
\[
⟨u_n(x'), x' | H_n |u_n(x), x⟩ = δ(x - x') \langle \hat{T}_n | E_n \langle x \rangle
\]
where \( E_n(x) \) is the Born-Oppenheimer potential energy surface and \( \langle \hat{T}_n \rangle \) is the coordinate-representation of the nuclear kinetic energy operator averaged over the electronic state,
\[
\langle \hat{T}_n \rangle = \langle u_n(x) | \hat{T} | u_n(x) \rangle
\]
Setting \( H_n = \langle \hat{T} \rangle + E_n(x) \), the variational equation of motion takes the form of a Schrödinger equation for the nuclear wavefunction
\[
H_n ψ = i\hbar \frac{∂ψ}{∂t}
\]
with an effective Hamiltonian specific of the electronic state under consideration. The main difference with respect to the common Born-Oppenheimer Hamiltonian lies in the nuclear kinetic 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 derived equation of motion, differently from the BO Hamiltonian, correctly conserves energy since it is variational, and this occurs upon including the above mentioned gauge fields.

Let us now examine the dressed kinetic energy operator. Let \( T \) be of the form
\[
\hat{T} = \frac{1}{2} \sum_{ij} \xi_{ij} \hat{p}_i \hat{p}_j
\]
and notice that
\[
\langle \hat{p}_i \hat{p}_j \rangle_n = \hat{p}_i \hat{p}_j - i\hbar \langle u_n | \partial_j u_n \rangle \hat{p}_i - i\hbar \langle u_n | \partial_i u_n \rangle \hat{p}_j - \hbar^2 \langle u_n | \partial_i \partial_j u_n \rangle
\]
where, as above, \( A_j = i \langle u_n | \partial_j u_n \rangle \in \mathbb{R} \) and
\[
\langle u_n | \partial_i \partial_j u_n \rangle = \partial_i \langle u_n | \partial_j u_n \rangle - \partial_j \langle u_n | \partial_i u_n \rangle
\]
\[
= -i\partial_i A_j - (\partial_i u_n | Q \partial_j u_n \rangle - \partial_j u_n | P | \partial_j u_n \rangle
\]
\[
= -i\partial_i A_j - q_{ij} - A_i A_j
\]
where \( q_{ij} \) is the \( ij \)th component of the quantum geometric tensor (we omit the index \( n \) from these quantities).

Hence,

\[
\langle \hat{p}_i \hat{p}_j \rangle_n = (\hat{p}_i - \hbar A_i) (\hat{p}_j - \hbar A_j) + \hbar^2 q_{ij}
\]

and, since \( \xi^{ij} \) is symmetric,

\[
\langle T \rangle_n = \frac{1}{2} \sum_{ij} \xi^{ij} (\hat{p}_i - \hbar A_i) (\hat{p}_j - \hbar A_j) + \frac{\hbar^2}{2} \sum_{ij} \xi^{ij} g_{ij}
\]

Clearly, the \textit{dressed} operator contains terms analogous to a vector \( (A_i) \) and scalar \( (g_{ij}) \) electromagnetic potential and the latter modify the nuclear dynamics, when a comparison is made with the simpler Born-Oppenheimer one. To see the effect of the \textit{gauge} fields on the nuclear dynamics it is enough to consider the nuclear's velocity

\[
\dot{\vec{v}}^k = \frac{i}{\hbar} \left[ \langle H \rangle_n, \vec{x}^k \right] = \sum_j \xi^{kj} \hat{\pi}_j
\]

where \( \hat{\pi}_k = \hat{p}_k - \hbar A_k \) is thus the mechanical momentum for the \( k \)th degree of freedom. The latter satisfies the commutation relation

\[
[\hat{\pi}_i, \hat{\pi}_j] = i\hbar B_{ij}
\]

where \( B_{ij} = \partial_i A_j - \partial_j A_i \) is the \( ij \)th component of the Berry’s curvature, \textit{i.e.}, \( d\omega = \sum_{ij} B_{ij} dx^i dx^j \) (with \( B_{ij} = -B_{ji} \)). Notice that the commutator is \textit{gauge} independent \( \{ \text{The gauge freedom mentioned here is the arbitrariness in the choice of the electronic frame. A \textit{gauge} transformation } |u_n\rangle \rightarrow e^{-i\varphi} |u_n\rangle \text{ amounts to adding an exact 1-form to } \omega \text{ without altering the scalar potential } (\omega \rightarrow \omega + d\varphi) \text{ and, at the same time, to adding a phase factor to the nuclear wavefunction, } \psi \rightarrow e^{i\varphi}\psi. \text{ In this respect, the \textit{gauge} transformations involved here are more limited than those allowed for a true electromagnetic potential, since they are always stationary w.r.t. } t \}. \) The force is then obtained by the rate of variation of particles’ mechanical momentum,

\[
\hat{\dot{\hat{\pi}}}^k = \frac{i}{\hbar} \left[ \langle H \rangle_n, \hat{\pi}^k \right] = \frac{i}{\hbar} \left[ \sum_{ij} \xi^{ij} [\hat{\pi}_i, \hat{\pi}_j] + E'_n, \hat{\pi}^k \right]
\]

where \( E'_n = E_n + \frac{\hbar^2}{2} \sum_{ij} \xi^{ij} g_{ij} \). It is convenient to separate two contributions. The first does \textit{not} involve derivatives of the inverse mass tensor and reads as

\[
\hat{\dot{\hat{\mathbf{F}}}}^k = \frac{i}{\hbar} \left\{ \frac{1}{2} \sum_{ij} \xi^{ij} [\hat{\pi}_i, \hat{\pi}_j] + [E_n', \hat{\pi}^k] \right\}
\]

whereas the second only appears when the mass tensor is coordinate-dependent,

\[
\hat{\dot{\hat{U}}}^k = \frac{i}{2\hbar} \sum_{ij} [\xi^{ij}, \hat{\pi}_k] \hat{\pi}_i \hat{\pi}_j = \frac{i}{2\hbar} \sum_{ij} [\xi^{ij}, \hat{p}_k] \hat{\pi}_i \hat{\pi}_j
\]

\[
= -\frac{1}{2} \sum_{ij} \left( \partial_k \xi^{ij} \right) \hat{\pi}_i \hat{\pi}_j
\]

Henceforth we consider only the first term and write the \( k \)th component of the force as

\[
F_k = -\partial_k E'_n + \frac{\hbar}{2} \sum_{ij} \left( \hat{\pi}_i B_{kj} + B_{kj} \hat{\pi}_i \right)
\]

that is, \( F_k = F_{kBO}^BO + F_{k}^{el} + F_{k}^{mag} \), where the first term represents the Born-Oppenheimer force

\[
F_{kBO}^BO = -\frac{\partial E_n(x)}{\partial x_k}
\]

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

\[
F_{k}^{el} = -\frac{\hbar^2}{2} \sum_{ij} \xi^{ij} \frac{\partial q_{ij}}{\partial x_k}
\]

arising from the Fubini-Study metric tensor, and a magnetic component

\[
F_{k}^{mag} = \frac{\hbar}{2} \sum_{ij} \left( \hat{\pi}_i B_{kj} + B_{kj} \hat{\pi}_i \right)
\]

due to the Berry’s curvature. (To check that this indeed represents a \textit{pseudo}-magnetic force one can consider the three-dimensional case and observe that \( B_{xy} = H_z \) \( B_{xz} = -H_y \) \( B_{yx} = H_x \), where \( H \) is the \textit{pseudo}-magnetic field. Hence \( F_{k}^{mag} = \frac{\hbar}{2} \left[ v \wedge H - H \wedge v \right] \), which is the correct quantum expression of the magnetic component of the Lorentz force). The two components behave very differently from each other: the \textit{pseudo}-magnetic field may vanish almost everywhere (see below) yet give rise to observable effects, similarly to what happens with the Aharonov-Bohm effect, while the \textit{pseudo}-electric field is ubiquitous (\textit{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. Amazingly, though, they both arise from one and the same object, namely the quantum geometric tensor, here re-written in a form that makes explicit its connections with the omitted adiabatic states

\[
q = \sum_{ij} \sum_{m} \langle \partial u_n | u_m \rangle \langle u_m | \partial_j | u_n \rangle dx^i dx^j
\]

\[
\sum_{ij} \sum_{m} \langle u_m | \partial_j | u_n \rangle \langle u_n | \partial_i | u_m \rangle dx^i dx^j
\]
Local-in-time error in case II
[Slow variables as dynamical variables]

Next we consider the LITE in the “dynamic” adiabatic approximation [29]. To this end, we need the time-derivative of the whole wavefunction in the “standard” gauge \( \langle \Psi | \Psi^+ \rangle = 0 \) (where the superscript + is used for the trajectory \( |\Psi\rangle = \Psi(t) \) to denote this gauge) and in particular its squared norm. By this we mean
\[
h^2||\Psi^+||^2 = \int dx \psi^*(x) \left[ (\hat{T})_n + (E_n(x) - \bar{E}) \right]^2 \psi(x)
\]
where \((\hat{T})_n\) is the dressed kinetic energy operator introduced above
\[
(\hat{T})_n = \frac{1}{2} \sum_{ij} \xi^{ij} \hat{\pi}_i \hat{\pi}_j + \phi
\]
with
\[
\hat{\pi}_i = \hat{p}_i - hA_i \quad \phi = \frac{h^2}{2} \sum_{ij} \xi^{ij} g_{ij}
\]
and \(\bar{E} = \langle \Psi | H | \Psi \rangle\) is the average total energy. We also need the energy variance
\[
\Delta E^2 = \int dx \psi^*(x) \left[ \langle \hat{T} + (H_{el}(x) - \bar{E}) \rangle^2 \right]_n \psi(x)
\]
and the result
\[
\left( \langle \hat{T} + (H_{el}(x) - \bar{E}) \rangle^2 \right)_n = \langle \hat{T}^2 \rangle_n + \langle (E_n(x) - \bar{E})^2 \rangle + 2 \Re \langle \hat{T}(E_n(x) - \bar{E}) \rangle
\]
\[
= \langle \hat{T}^2 \rangle_n + (E_n(x) - \bar{E})^2 + 2 \Re \langle \hat{T} \rangle_n (E_n(x) - \bar{E})
\]
Hence, upon taking the difference of the two, we find for the local-in-time error the expression
\[
\varepsilon^2[\Psi] = \frac{1}{h^2} \int dx \psi^*(x) \left[ \langle \hat{T}^2 \rangle_n - \langle \hat{T}^2 \rangle_n \right] \psi(x)
\]
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 \(\langle \hat{T} \rangle_n\)). 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
\[
\langle \hat{T}^2 \rangle_{nm} - \langle \hat{T} \rangle^2 = \sum_{m \neq n} \langle \hat{T} \rangle_{nm} \langle \hat{T} \rangle_{mn} \equiv \sum_{m \neq n} \langle T \rangle_{mn}^\dagger \langle T \rangle_{mn}
\]
In turn, upon defining
\[
\varphi_{m \rightarrow n}(x) = \langle \hat{T} \rangle_{mn} \psi(x) \equiv \langle u_n | \hat{T} | u_m \rangle \psi(x)
\]
we have the error in terms of contributing electronic transitions,
\[
\varepsilon^2[\Psi] = \frac{1}{h^2} \int dx |\varphi_{m \rightarrow n}(x)|^2
\]
where
\[
\nu_{m \rightarrow n}(x) = \frac{1}{h^2} |\varphi_{m \rightarrow n}(x)|^2
\]
is a “transition probability density” which, in this form, is manifestly gauge-invariant since \(\psi(x) |u_n\rangle = \langle x|\Psi\rangle\).

In order to make a closer comparison with the error obtained in the previous section for the “static” adiabatic approximation, we introduce \(\nu(x) = \sum_{m \neq n} \nu_{m \rightarrow n}(x)\) and the total conditional transition probability density \(\vartheta(x) = \nu(x)/|\psi(x)|^2\) such that
\[
\varepsilon^2[\Psi] = \int dx |\vartheta(x)|^2 \vartheta(x)
\]
which is well defined provided \(\psi(x) \neq 0\). Clearly, \(\vartheta(x)\) measures the error locally in configuration space (as well as in time), and thus describes the tendency of the system in configuration space to jump to an electronic state other than \(n\). For a nuclear wavefunction \(\psi(x)\) and a frame \(|u_n(x)\rangle\) in the vector bundle \(\pi : E \rightarrow \mathcal{M}\) we consider \(|\psi_n(x)\rangle = \psi(x) |u_n(x)\rangle\) as a smooth section of \(E\), and the map to the normal bundle \(|\psi_n(x)\rangle \rightarrow \varphi(x) = QT |\psi_n(x)\rangle\) which gives \(\nu(x) = h^{-2} \langle \varphi(x)|\varphi(x)\rangle\). We find
\[
Q \hat{T} |\psi_n(x)\rangle = -i \hbar \sum_{ij} \xi^{ij} \langle \partial_j \psi | Q \partial_i u_n \rangle
\]
Then, upon introducing \(\hat{\pi}_i = -i \hbar \partial_i - hA_i\),
\[
Q \hat{T} |\psi_n(x)\rangle = -i \hbar \sum_{ij} \xi^{ij} \langle \hat{\pi}_i \psi | Q \partial_j u_n \rangle
\]
\[
- \frac{h^2}{2} \sum_{ij} \xi^{ij} \psi D_{ij} |u_n\rangle
\]
\[
- i \hbar \sum_{ij} \langle \hat{\psi} | Q \partial_j u_n \rangle
\]
\[
- \frac{h^2}{2} \psi \sum_{ij} \xi^{ij} \psi D_{ij} |u_n\rangle
\]
where \(\hat{\psi}\) is the \(j^{th}\) component of the velocity operator and
\[
D_{ij} |u_n\rangle = i A_j Q | \partial_j u_n \rangle + i A_j Q | \partial_i u_n \rangle + Q | \partial_i \partial_j u_n \rangle
\]
The reason why we introduce these two components is that they are separately gauge-invariant: under the gauge transformation \( |u_n\rangle \rightarrow |u_n\rangle e^{-i\varphi} \), \( \psi \rightarrow \psi e^{+i\varphi} \) we have \( A_i \rightarrow A_i + \partial_i \varphi \) and

\[
Q |\partial_j u_n\rangle \rightarrow e^{-i\varphi} Q |\partial_j u_n\rangle \\
\bar{\pi}_i \psi \rightarrow e^{i\varphi} \bar{\pi}_i \psi \\
D_{ij} |u_n\rangle = e^{-i\varphi} D_{ij} |u_n\rangle
\]

since (there is no need to verify it with an explicit calculation, since both \( |\psi_n(x)\rangle \) and the velocity term are gauge invariant)

\[
Q |\partial_i \partial_j u_n\rangle \rightarrow e^{-i\varphi} [Q |\partial_i \partial_j u_n\rangle - i(\partial_i \varphi)Q |\partial_j u_n\rangle - i(\partial_j \varphi)Q |\partial_i u_n\rangle]
\]

Stated differently, the operators \( Q \partial_j, \bar{\pi}_i, \bar{v}^i, D_{ij}, \) etc. are tensorial under gauge transformations. Hence, upon introducing the (gauge-tensorial) residue

\[
R |u_n\rangle = \frac{\hbar}{2} \sum_{ij} \epsilon^{ij} D_{ij} |u_n\rangle
\]

and the (complex-valued) quantum velocity fields \( V^j \)

\[
V^j = \bar{v}^j \psi = \frac{\psi^* \bar{v}^j \psi}{|\psi|^2} \equiv V^j(x)
\]

we find

\[
\rho(x) = \sum_{ij} (V^i)^* V^j g_{ij} - i \sum_j (V^j)^* \langle \partial_j u_n | Ru_n \rangle + i \sum_j V^j \langle Ru_n | \partial_j u_n \rangle + \langle Ru_n | Ru_n \rangle
\]

where \( g_{ij} = \langle \partial_i u_n | Q | \partial_j u_n \rangle \) is the quantum geometric tensor and the remaining scalar products contain higher derivatives of the electronic state in a gauge invariant form. The first term closely resembles the local-in-time error in the standard adiabatic approximation analyzed in the previous section

\[
\varepsilon^2 = \sum_{ij} V^i V^j q_{ij}
\]

where \( V^i \equiv \frac{\partial}{\partial x^i} \) is now the classical velocity of the \( i \)th parameter. There are though notable differences: when turning the slow variables into quantum variables \( \text{both} \) the real (symmetric) and the imaginary (antisymmetric) parts of \( q_{ij} \) matter for the error, since

\[
\sum_{ij} (V^i)^* V^j q_{ij} = \sum_{ij} K^{ij} g_{ij} + \frac{1}{2} \sum_{ij} Y^{ij} B_{ij}
\]

where

\[
K^{ij} = \Re \left( (V^i)^* (V^j) \right) \quad Y^{ij} = \Im \left( (V^i)^* (V^j) \right)
\]

and \( g_{ij} \) and \( B_{ij} \) have been introduced above. It is instructive then to consider their total contribution upon integrating over configuration space. For the first we find

\[
\int d\mathbf{x} |\psi(x)|^2 \sum_{ij} K^{ij} g_{ij} = \sum_{ij} \int d\mathbf{x} \Re \left( (\bar{v}^i \psi)^* g_{ij} (\bar{v}^j \psi) \right)
= \Re \left( \langle \psi \sum_{ij} \bar{v}^i g_{ij} \bar{v}^j | \psi \rangle \right)
= \langle \psi \sum_{ij} \bar{v}^i g_{ij} \bar{v}^j | \psi \rangle
\]

where the scalar product \( \langle ., . \rangle_X \) is that of the Hilbert space \( L^2(M) \) describing the nuclear degrees of freedom and where the last equality follows from the fact that the operator \( \sum_{ij} \bar{v}^i g_{ij} \bar{v}^j \) is self-adjoint on that space. As for the second we have similarly

\[
\int d\mathbf{x} |\psi(x)|^2 \sum_{ij} Y^{ij} B_{ij} = \sum_{ij} \int d\mathbf{x} \Im \left( (\bar{v}^i \psi)^* B_{ij} (\bar{v}^j \psi) \right)
= \Im \left( \langle \psi \sum_{ij} \bar{v}^i B_{ij} \bar{v}^j | \psi \rangle \right)
= -i \langle \psi \sum_{ij} \bar{v}^i B_{ij} \bar{v}^j | \psi \rangle
\]

since the operator \( \sum_{ij} \bar{v}^i B_{ij} \bar{v}^j \) is anti-hermitian

\[
\left( \sum_{ij} \bar{v}^i B_{ij} \bar{v}^j \right)^\dagger = \sum_{ij} \bar{v}^j B_{ij} \bar{v}^i = -\sum_{ij} \bar{v}^i B_{ij} \bar{v}^j
\]

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

\[
\hat{q} = \sum_{ij} \bar{v}^i \left( g_{ij} - \frac{i}{2} B_{ij} \right) \bar{v}^j = \sum_{ij} \bar{v}^i q_{ij} \bar{v}^j
\]

which is nothing but the quantum version of the quantum geometric tensor. That is, to leading order, we have

\[
\varepsilon^2 \approx \langle \psi | \sum_{ij} \bar{v}^i q_{ij} \bar{v}^j | \psi \rangle_X
\]

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

To understand better the meaning of $g(x)$ and its components $g_{m \rightarrow n}$ we consider the situation in which, during the time evolution, the local-in-time error exceeds a given threshold, thereby suggesting the need of going beyond the adiabatic approximation. This can be accomplished dynamically by “spawning” the electronic basis that forms the variational manifold, e.g., by expanding the wavefunction ansatz to

$$|\Psi_t\rangle = \int dx \psi_t(x) |u_n(x), x\rangle + \int dx \phi_t(x) |u_s(x), x\rangle$$

where $s = n \pm 1$ depending on which gap $|E_n - E_{n \pm 1}|$ 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 $\phi_t(x)$ must vanish and its time derivative is determined by the variational equations of motion

$$\begin{cases} i\hbar \frac{d\phi}{dt} = (\langle T \rangle_{nn} + E_n) \psi + \langle T \rangle_{ns} \phi \\ i\hbar \frac{d\phi}{dt} = \langle T \rangle_{sn} \psi + \langle T \rangle_{ss} + E_s \rangle \phi \end{cases}$$

which give, for $t = t_s$,

$$i\hbar \frac{d\phi}{dt} \bigg|_{t_s} = \langle T \rangle_{sn} \psi \equiv \varphi_{s \rightarrow n}$$

(notice that the gauge does not affect this off-diagonal term). Thus, we see that the probability

$$\nu_{s \rightarrow n} = \hbar^{-2} \int dx |\varphi_{s \rightarrow n}|^2$$

represents precisely the error reduction due to electronic spawning,

$$\varepsilon_{\nu}^2 \rightarrow \varepsilon_{\nu}^2, \quad \varepsilon_{\nu}^2 = \varepsilon_{\nu}^2 - \nu_{s \rightarrow n} \quad \text{at} \quad t = t_s$$

i.e., the error reduction arising from lifting the adiabatic approximation by allowing non-adiabatic transitions to the state $s$. On the other hand, the above equation also determines the short-time behaviour of the non-adiabatic transition probability $P_s$ to the state $s$ as

$$P_s \approx \nu_{s \rightarrow n} (t - t_s)^2 \quad t \geq t_s$$

since

$$\left. \frac{d|\phi|^2}{dt} \right|_{t_s} = \phi^* \left. \frac{d\phi}{dt} \right|_{t_s} + \left. \frac{d\phi^*}{dt} \right|_{t_s} = 0$$

and

$$\left. \frac{d^2|\phi|^2}{dt^2} \right|_{t_s} = 2 \left. \frac{d\phi^*}{dt} \right|_{t_s} = \frac{2}{\hbar^2} |\langle T \rangle_{sn} \psi|^2$$

[Notice that $\nu_{s \rightarrow n}$ is half the second derivative of the transition probability at $t = t_s$, a result which follows in general from the definition of local-in-time error.] This finding leads to an interesting conclusion: when a single term $s$ dominates the sum, $\nu_{s \rightarrow n}$ is approximately the total squared error in the dynamic adiabatic approximation and we have seen above that 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 $\delta t = t - t_s$,

$$P_s \approx \int dx \sum_{ij} (\delta \hat{x}^i \psi_{s,i})^* (\delta \hat{x}^j \psi_{s,j}) (x) q_{ij} (x)$$

with $\delta \hat{x}^i := \hat{v}^i \delta t$

if the most important non-adiabatic 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 wavefunction is allowed to expand into the whole Hilbert space

$$|\Psi_t\rangle = \int dx \psi_t(x) |u_n(x), x\rangle \rightarrow$$

$$|\Psi_t\rangle = \int dx \psi_t(x) |u_n(x), x\rangle + \sum_{m \neq n} \int dx \phi^{(m)}(x) |u_m(x), x\rangle$$

Again, we have $\phi^{(m)} = 0$ at the time of spawning,

$$i\hbar \frac{d\phi^{(m)}}{dt} \bigg|_{t_s} = \langle T \rangle_{mn} \psi \equiv \varphi_{m \rightarrow n}$$

holds for any $m \neq n$ and now the local-in-time error is reduced exactly to zero upon spawning. Thus, the total non-adiabatic transition probability $P$ can be given, up to second order in $\delta t$, as

$$P \approx \int dx \sum_{ij} (\delta \hat{x}^i \psi_{s,i})^* (\delta \hat{x}^j \psi_{s,j}) (x) q_{ij} (x)$$

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 non-adiabatic transitions. In a sense, this is an obvious result since the latter transitions represent precisely the failure of the adiabatic approximation. At a closer look, though, it is rather surprising that the exact dynamics of the system beyond the adiabatic paradigm is determined solely by the geometric properties of the approximation.
B. Exact factorization of the wavefunction

As mentioned in the main text, the exact factorization \[31, 32\] is an “intermediate” representation which is obtained by introducing a local basis of nuclear states \( \{ |x_i \rangle \} \) to represent the exact wavefunction describing the combined electron-nuclear states, i.e.,

\[
|\Psi_t\rangle = \int dx |x\rangle \langle x|\Psi_t\rangle
\]

where \( \langle x|\Psi_t\rangle \) is yet another vector in the electronic Hilbert space \( \mathcal{H}_{el} \) that we write as

\[
\langle x|\Psi_t\rangle = \psi_t(x) |u_t(x)\rangle
\]

upon imposing a normalization condition and choosing a smoothly varying phase for the local electronic states \( |u_t(x)\rangle \). This gives the wavefunction in the (local) exactly-factorized representation

\[
|\Psi_t\rangle = \int dx \psi_t(x) |x\rangle |u_t(x)\rangle
\]

Clearly, there is some freedom in choosing \( |u_t\rangle \) (and correspondingly in defining the nuclear wavefunction \( \psi_t \)) that we may fix by imposing the arbitrary (but real) gauge term

\[
A_0 = i \langle u|\partial_t u \rangle
\]

in the equation of motion, besides the usual Berry’s connection terms \( A_k = i \langle u|\partial_k u \rangle \).

Equations of motion

To obtain the equations of motion for the above nuclear wavefunction and the electronic state we write the total Hamiltonian using the coordinate representation for the nuclear variables, i.e. in the form

\[
\hat{H} = \hat{T} + H_{el}(x)
\]

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

\[
\hat{T} = \frac{1}{2} \sum_{ij} \xi_{ij} \hat{p}_i \hat{p}_j \text{ with } \hat{p}_j = -i\hbar \partial_j
\]

and \( H_{el}(x) \) is the electronic operator with the nuclei clamped at a configuration \( x \).

From the Schrödinger equation

\[
\hat{H} \langle \psi|u\rangle = i\hbar \langle \partial_t \psi|u\rangle + i\hbar \psi \langle \partial_t u \rangle
\]

we immediately obtain the equation of motion for the nuclear wavefunction by projecting the above equation onto \( |u\rangle \)

\[
\left( (\hat{H}_{el} - \hbar A_0) \psi = i\hbar (\partial_t \psi) \right)
\]

where \( \langle \hat{H}_{el} \rangle = \langle \hat{T}_{el} \rangle + \langle u|H_{el}|u \rangle \) contains the dressed kinetic energy operator and the “Born-Oppenheimer” average energy \( E_{el} = \langle u|H_{el}|u \rangle \), and \( A_0 \) is the gauge potential introduced above. We remark that \( \langle \hat{T}_{el} \rangle \) appearing here is the nuclear kinetic energy operator averaged over the time-dependent electronic state and reads explicitly

\[
\langle \hat{T}_{el} \rangle = \frac{1}{2} \sum_{ij} \xi_{ij} \hat{p}_i \hat{p}_j + \sum_{ij} \xi_{ij} q_{ij}
\]

where \( \hat{p}_j = \hat{p}_j - \hbar A_j \) and \( q_{ij} = \langle \partial_t u|Q|\partial_j u \rangle \). We use the hat symbol to remind us the coordinate representation adopted, but notice that \( |u\rangle \) is everywhere meant to be the time-dependent electronic state (correspondingly, \( P = |u\rangle \langle u|, Q = 1 - P \), etc.).

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,

\[
Q \hat{H} \langle \psi|u\rangle = + i\hbar \psi Q \langle \partial_t u \rangle
\]

which gives

\[
i\hbar Q \langle \partial_t u \rangle = \frac{1}{\psi} Q \hat{H} \langle \psi|u\rangle
\]

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

\[
i\hbar \langle \partial_t u \rangle = + \hbar A_0 \langle u| + \frac{1}{\psi} Q \hat{H} \langle \psi|u\rangle
\]

Here, the effective electronic Hamiltonian operator contains two terms

\[
\frac{1}{\psi} Q \hat{H} \langle \psi|u\rangle = \frac{1}{\psi} Q \hat{T} \langle \psi|u\rangle + Q H_{el} \langle u\rangle
\]

but only the first depends on \( \psi \) since \( H_{el} \) is local in nuclear coordinates. The first term, which we denote as \( K[\psi]|u\rangle \), is found to be

\[
K[\psi]|u\rangle = - i\hbar \sum_j V^j Q \langle \partial_j u \rangle - \hbar R \langle u\rangle
\]

where \( V^j = (\bar{v}^j \psi)/\psi \) is the complex-valued nuclear velocity field, \( R \langle u\rangle = \frac{\hbar}{2} \sum_{ij} \xi_{ij} D_{ij} \langle u \rangle \), and

\[
D_{ij} \langle u\rangle = i A_i Q \langle \partial_j u \rangle + i A_j Q \langle \partial_i u \rangle + Q \langle \partial_i \partial_j u \rangle
\]

We stress that the above decomposition has simple gauge transformation properties, since \( V^j \) is gauge invariant and both \( Q \partial_j \) and \( D_{ij} \) (hence \( R \)) behave tensorially under a gauge transformation. Hence,

\[
i\hbar Q \langle \partial_t u \rangle = Q H_{el} + K[\psi]|u\rangle
\]

where, on the r.h.s., the first term describes the electron dynamics with the nuclei clamped at \( x \) and the second term describes the drag effect on the electrons due to the motion of the nuclei.
The above equations for the nuclear and electronic “wavefunctions” are identical to those given in Ref. [31, 32]. This is evident for the nuclear equation but not for the electronic equation since the authors of Ref. [31, 32] wrote it in a rather different form which, in our notation, would read

\[
\begin{align*}
\langle \hat{p}_i | \langle p_i \phi + hA_i \rangle | u \rangle = \\
\sum_{ij} \frac{\xi_{ij}}{2} (\hat{p}_j + hA_j)
\end{align*}
\]

Hence,

\[
F | u \rangle = -i \hbar \sum_{j} \frac{\partial \psi}{\partial \psi} Q \partial_{j} | u \rangle
\]

Finally, upon observing that

\[A_i A_j + q_{ij} = \langle \partial_i u | u \rangle \langle u | \partial_j u \rangle + \langle u | q_{ij} Q \partial_j u \rangle \equiv \langle \partial_i u | \partial_j u \rangle - \langle u | \partial_i \partial_j u \rangle\]

we write

\[\sum_{ij} \xi_{ij} I A_i A_j | u \rangle - i \hbar^2 \sum_{ij} \frac{\xi_{ij}}{2} (\partial_i A_j) | u \rangle = \frac{\hbar^2}{2} \sum_{ij} \xi_{ij} P | \partial_i \partial_j u \rangle + \frac{\hbar^2}{2} \sum_{ij} \xi_{ij} q_{ij} | u \rangle\]

and obtain

\[
F | u \rangle = -i \hbar \sum_{j} \frac{\partial \psi}{\partial \psi} Q \partial_{j} | u \rangle - \hbar^2 \sum_{ij} \xi_{ij} (A_i Q | \partial_j u \rangle + iA_j Q | \partial_i u \rangle + Q | \partial_i \partial_j u \rangle) + \frac{\hbar^2}{2} \sum_{ij} \xi_{ij} q_{ij} | u \rangle
\]

where

\[iA_i Q | \partial_j u \rangle + iA_j Q | \partial_i u \rangle + Q | \partial_i \partial_j u \rangle \equiv D_{ij} | u \rangle\]

i.e.,

\[
F | u \rangle = -i \hbar \sum_{j} \frac{\partial \psi}{\partial \psi} Q \partial_{j} | u \rangle - \hbar R | u \rangle + \frac{\hbar^2}{2} \sum_{ij} \xi_{ij} q_{ij} | u \rangle
\]

as we intended to show.
Dynamically corrected pseudo-Lorentz force: proof of the vanishing of its average

In the main text, we have mentioned that introducing the time derivative of the electronic state

\[ \hbar Q \partial_t |u\rangle = -iQH_{el} |u\rangle - iK[\psi_1 |u\rangle \]

in the electron dynamical force

\[ F_{k}^{ED} = -2 \mathcal{H} \langle \partial_k u |Q| \hbar \partial_t u \rangle \]

one obtains a genuine non-adiabatic term

\[ F_{k}^{nad} = 2R \langle \partial_k u |QH_{el} |u\rangle \]

and a correction

\[ F_{k}^{corr} = 2R \langle \partial_k u |K[\psi_1 |u\rangle \]

to the pseudo-Lorentz force that makes the latter vanish on average. We give here the details of the calculation, and, on the other hand, in the electron dynamical force

\[ F_{k}^{mag,c} \equiv \frac{2}{\hbar} \sum_j \mathcal{H} \langle \partial_k u |Q \partial_j u \rangle V_j - 2hR \langle \partial_k u |Ru \rangle \]

where \(3g_{kj} = -B_{kj}/2\) has been used. The corrected magnetic force is easily identified

\[ F_{k}^{mag,c} = \frac{\hbar}{2} \sum_j (\hat{v}^j B_{kj} + B_{kj} \hat{v}^j) - \hbar \sum_j B_{kj} \mathcal{R}V_j \]

and found to have zero average with a simple calculation,

\[ \langle \psi | F_{k}^{mag,c} |\psi \rangle_X = \frac{\hbar}{2} \sum_j \langle \psi | \hat{v}^j B_{kj} + B_{kj} \hat{v}^j | \psi \rangle_X \]

Hence,

\[ \langle \psi | F_{k}^{mag,c} |\psi \rangle_X = 0 \]

for any state of the nuclei. The corrected pseudo-electric force reads as

\[ F_{k}^{el,c} = 2h \sum_j g_{kj} 3V_j \]

\[ - \frac{h^2}{2} \sum_i \xi_{ij} \mathcal{R} \langle \partial_i u |D_{ij} u \rangle - \frac{h^2}{2} \sum_i \xi_{ij} \mathcal{R} \langle \partial_i u |D_{ij} u \rangle \]

and can be re-written in a more symmetric form

\[ F_{k}^{el,c} = 2h \sum_j g_{kj} 3V_j \]

\[ - \frac{h^2}{2} \sum_i \xi_{ij} \mathcal{R} \langle \partial_i u |D_{ij} u \rangle + \mathcal{R} \langle \partial_j u |D_{ij} u \rangle \]

This can be seen by observing that

\[ \frac{\partial g_{ij}}{\partial x^k} = \mathcal{R} \langle \partial_i u |Q \partial_j u \rangle \]

\[ = \mathcal{R} \langle \partial_i u |Q \partial_j u \rangle + \mathcal{R} \langle \partial_j u |Q \partial_i u \rangle \]

where the (gauge-invariant) derivatives

\[ Q \frac{\partial}{\partial x^k} |\partial_j u \rangle = -Q |\partial_k P |\partial_j u \rangle + Q |\partial_k P |\partial_j u \rangle \]

\[ \equiv +iA_k Q |\partial_j u \rangle + Q |\partial_j u \rangle \]

\[ \equiv D_{kj} |u\rangle - iA_k Q |\partial_j u \rangle \]

can be used to write

\[ \frac{\partial g_{ij}}{\partial x^k} = \mathcal{R} \langle \partial_i u |D_{kj} u \rangle + A_k \mathcal{R}g_{ij} + A_k \mathcal{R}g_{ji} \]

\[ \equiv \mathcal{R} \langle \partial_i u |D_{kj} u \rangle + \mathcal{R} \langle \partial_j u |D_{ki} u \rangle \]

(this is of course symmetric w.r.t. exchange of \(i\) and \(j\)). Now, on taking the average

\[ \langle \psi | 2h \sum_j g_{kj} 3V_j |\psi \rangle_X = 2h \sum_j \mathcal{H} \int dx \mathcal{R} \langle \psi | g_{kj} \hat{v}^j \psi(x) \]

\[ \equiv 2h \sum_j \langle \psi | \mathcal{R} \langle g_{kj} \hat{v}^j |\psi \rangle \]

and, on the other hand,

\[ \langle \psi | B_{kj} \mathcal{R}V_j |\psi \rangle_X = \mathcal{R} \langle \psi | B_{kj} \hat{v}^j |\psi \rangle_X \]

and

\[ \frac{1}{2} \langle \psi | B_{kj} \hat{v}^j + B_{kj} \hat{v}^j |\psi \rangle_X = \mathcal{R} \langle \psi | B_{kj} \hat{v}^j |\psi \rangle_X \]
where the operator to be averaged reads as
\[
\Re \langle \partial_k u | D_{ij} u \rangle + \Re \langle \partial_i u | D_{kj} u \rangle + \nonumber
-\Re \langle \partial_j u | D_{ki} u \rangle - \Re \langle \partial_k u | D_{ij} u \rangle \equiv 0
\]
since \( \Re \langle \partial_i u | D_{kj} u \rangle = \Re \langle \partial_i u | D_{kj} u \rangle \). In fact, importantly, we have exploited
\[
\Re \langle \partial_i u | D_{kj} u \rangle = \Re \langle \partial_i u | D_{kj} u \rangle
\]
that shows how \( \Re \langle \partial_i u | D_{kj} u \rangle \) is related to the connection \( \nabla^g \) on the tangent bundle induced by the Fubini-Study metric,
\[
\Re \langle \partial_i u | D_{kj} u \rangle = g_{kl} \Gamma^l_{ij}
\]
where \( \Gamma^l_{ij} \) is the Christoffel symbol of the connection. Indeed, the zeroing of the average pseudo-electric force merely expresses the conservation of the metric by the corresponding Ricci- Levi Civita connection
\[
\langle \psi | F^{el,c}_{k} | \psi \rangle = \hbar^2 \sum_{ij} \epsilon^{ij} \langle \psi | \frac{\partial g_{ki}}{\partial x^j} - g_{ij} \Gamma^l_{kj} - g_{kl} \Gamma^l_{ij} | \psi \rangle
\]
\[
= \hbar^2 \sum_{ij} \epsilon^{ij} \langle \psi | (\nabla^g j_{ik})_{ik} | \psi \rangle
\]
where \( (\nabla^g j_{ik})_{ik} \) is the \( ik \)th component of the covariant derivative of \( g \) taken with the connection \( \nabla^g \) along the direction \( j \).

**Statistical properties**

We emphasize here that, despite its role of a marginal probability amplitude, \( \psi(x) \) alone cannot determine the full statistical properties of the nuclear subset of particles, not even instantaneously, i.e., at a given instant of time. This is evident from the fact that the (instantaneous) statistical properties require the reduced density operator \( \rho_X = \text{tr}_P \rho \) which for pure states and the factorization introduced above reads
\[
\langle x | \rho_X | x' \rangle = \text{tr}_P (\psi(x) | u(x) \rangle \langle u(x') | \psi^*(x') \rangle)
\]
where \( \sigma(x, x') = \psi(x) \psi^*(x') \) 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 \( \rho_X(x, x') \) and bare nuclear observables \( N \)
\[
\langle N \rangle = \int dx \int dx' \rho_X(x, x') N(x', x)
\]
or we use the apparent density matrix \( \sigma(x, x') \) and dressed nuclear observables \( \tilde{N} \),
\[
\langle \tilde{N} \rangle = \int dx \int dx' \sigma(x, x') \tilde{N}(x', x)
\]
where
\[
\tilde{N}(x, x') = N(x, x') \langle u(x) | u(x') \rangle
\]
or, equivalently,
\[
\tilde{N}(x, x') = \langle u(x') | N(x, x') | u(x) \rangle_{el}
\]
which shows that the dressed observables are “averaged” over the electronic states.

As for the electronic density operator \( \rho_{el} \), it takes the form of a convex combination of electronic density operators \( \rho_{el}(x) \)
\[
\rho_{el} = \int_x d\mathbf{x} P(x) \rho_{el}(x)
\]
where \( P(x) = |\psi(x)|^2 \) is the probability density of finding the nuclei at \( x \) and \( \rho_{el}(x) \) is the conditional density operator
\[
\rho_{el}(x) = \frac{\langle \mathbf{x} | \rho | \mathbf{x} \rangle}{P(X)} \equiv |u(x)\rangle \langle u(x)|
\]
which describes a pure local state, the one defined locally by the exact factorization representation.

For comparison, notice that the results in the adiabatic approximation are very similar to the one given here, the only difference being that \( |u\rangle \) is replaced by 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 wavefunction.

In order to clarify the meaning of observables dressed by the electronic state let us consider in detail the nuclear momentum for the \( k \)th nuclear degree of freedom, \( \hat{p}_k \) (in the coordinate representation appropriate for the exact factorization). This is first “extended” to an operator \( \hat{P}_k = \hat{p}_k \otimes I_{el} \) acting on the Hilbert space of the electronic-nuclear system, and then “reduced” to an operator \( \hat{\rho}_k \) on the nuclear space by averaging over the electronic state
\[
\hat{\rho}_k = \langle u | \hat{P}_k | u \rangle = \hat{p}_k - i\hbar \langle u | \partial_k u \rangle \equiv \hat{\pi}_k
\]
The result is the operator for the mechanical momentum \( \hat{\pi}_k \) introduced in the main text, 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 \( \hat{\rho}_k \), and then care is needed in interpreting \( \hat{p}_k \) as the “microscopic” operator acting on the electronic-nuclear space or the “averaged” 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 re-consider the total force \( F_k \) acting on the \( k \)th nuclear degree of freedom in light of the above difference between “microscopic” and
“electronically averaged” quantities. On the one hand we have
\[ \frac{d}{dt} \langle \hat{p}_k \rangle = \langle \Psi | i \frac{\hbar}{i} [H, \hat{p}_k] | \Psi \rangle = \langle \Psi | -\partial_k H_{el} | \Psi \rangle \]
\[ = \int d\mathbf{x} \psi^*(\mathbf{x}) (-\partial_k H_{el})_{el} \psi(\mathbf{x}) \]
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 $-\partial_k H_{el}$ acting on the given nuclear degree of freedom. The latter can be equivalently re-written as
\[ \langle -\partial_k H_{el} \rangle_{el} = F_k^{BO} + 2\Re \langle \partial_k u | H_{el} | u \rangle \equiv F_k^{BO} + F_k^{NBO} \]
since $\Re \langle (\partial_k u | u \rangle | H_{el} | u \rangle) = 0$, in order to make evident the Born-Oppenheimer-like contribution. On the other hand, we also have
\[ \frac{d}{dt} \langle \hat{p}_k \rangle = 2\Re \langle \hat{p}_k | \partial_k \Psi \rangle \]
where the time-derivative of the total wavefunction in the exact factorized form can be written as
\[ \partial_t (\psi | u \rangle) = \left[ (\partial_t \psi) + \psi (u | \partial_k u \rangle) \right] u + \psi Q | \partial_k u \rangle \]
Here, the term between square brackets amounts to
\[ [(\partial_t \psi) + \psi (u | \partial_k u \rangle) = -\frac{i}{\hbar} \langle H \rangle_{el} \psi \]
and thus
\[ \frac{d}{dt} \langle \hat{p}_k \rangle = 2\Re \int d\mathbf{x} \psi^*(\mathbf{x}) \left( -\frac{i}{\hbar} \right) (\pi_k \langle H \rangle_{el} \psi(\mathbf{x}) + \int d\mathbf{x} \psi^*(\mathbf{x}) [+i \partial_k u | Q \partial_k u \rangle \psi(\mathbf{x}) \]
Here, for the first line we have used $\langle \hat{p}_k \rangle_{el} = \pi_k$, whereas for the second one we have exploited
\[ \langle u | \pi_k Q \partial_k u \rangle = -i \hbar \langle u | (\partial_k Q | \partial_k u \rangle + \langle u | Q \partial_k u \rangle \rangle \]
\[ = -i \hbar \partial_t \langle u | Q \partial_k u \rangle + i \hbar \langle \partial_k u | Q \partial_k u \rangle \]
\[ = i \hbar \langle \partial_k u | Q \partial_k u \rangle \]
since $\langle u | Q \partial_k u \rangle \equiv 0$ (here the scalar products are all meant to be on the electronic space only). Furthermore, since
\[ 2\Re \int d\mathbf{x} \psi^*(\mathbf{x}) \left( -\frac{i}{\hbar} \right) (\pi_k \langle H \rangle_{el} \psi(\mathbf{x}) \]
\[ = \int d\mathbf{x} \psi^*(\mathbf{x}) \left( \frac{i}{\hbar} \right) [\langle H \rangle_{el}, \pi_k] \psi(\mathbf{x}) \]
and the second term is the expectation value of $F_k^{ED}$ introduced in the main text, we finally arrive at
\[ \frac{d}{dt} \langle \hat{p}_k \rangle = \int d\mathbf{x} \psi^*(\mathbf{x}) \left[ F_k^{BO} + F_k^{mag} + F_k^{el} + F_k^{ED} \right] \psi(\mathbf{x}) \]
On comparing with the previous expression and remembering that $F_k^{mag} + F_k^{el} + F_k^{ED} = F_k^{mag,c} + F_k^{el,c} + F_k^{ED}$ we find,
\[ \int d\mathbf{x} \psi^*(\mathbf{x}) \left[ F_k^{mag,c} + F_k^{el,c} \right] \psi(\mathbf{x}) = 0 \]
This is consistent with the result given in the previous section, however the proof given there makes clear that the dynamically corrected pseudo-electric and pseudo-magnetic forces vanish separately when averaged.

C. Electronic friction

Linear response

Let us consider the integral form of the electronic equation in the spirit of linear response theory, set $\hbar A_0 = E_{el} = \langle u | H_{el} | u \rangle$ and assume that $|u(t_0)\rangle = e^{-i\frac{\hbar}{i}E_{el,t}t_0} |u_0\rangle$ holds for some initial time $t_0$ in the infinite past. Let us first take the simpler non-adiabatic term represented by the following impulsive ‘kick’
\[ \delta(t - \tau) \tilde{K} [\psi_{\tau}] | u(\tau) \rangle \]
that acts instantaneously, i.e., only at time $t = \tau$. The electronic state soon after the kick reads
\[ |u(\tau^+)\rangle \approx |u(\tau^-)\rangle - \frac{i}{\hbar} K_0 |\psi_\tau\rangle \approx |u(\tau^-)\rangle \]
where $|u(\tau^-)\rangle = e^{-i\frac{\hbar}{i} E_{el} t} |u_0\rangle$ is the freely propagating state and $Q \rightarrow Q_0 = 1 |u_0\rangle \langle u_0| |u_0\rangle$ has been used for $t = \tau - \epsilon, \epsilon > 0$. This follows from the integral version of the equation of motion by shrinking the time interval around the kick time $\tau$. Note that, correspondingly, $K$ has been replaced by $K_0$ to remind us the use of $Q_0$ rather than $Q$, and of the ground-state connection in the velocity operators. Hence, for any time $t$, we have
\[ |u(t)\rangle \approx e^{-i\frac{\hbar}{i} E_{el} t} |u_0\rangle \]
\[ - \frac{i}{\hbar} e^{-i\frac{\hbar}{i} E_{el,t}(t-\tau)} K_0 |\psi_{\tau}\rangle |u_0\rangle e^{-i\frac{\hbar}{i} E_{el,t} t} \Theta(t - \tau) \]
where $\Theta(t) = 1$ for $t > 0$ and zero otherwise. Now, when considering the full driving term
\[ K[\psi_{\tau}] |u(t)\rangle = \int_{-\infty}^{+\infty} d\tau \delta(t - \tau) K[\psi_{\tau}] |u(\tau)\rangle \]
we have, assuming linear response,
\[ |u(t)\rangle \approx e^{-i\frac{\hbar}{i} E_{el} t} |u_0\rangle \]
\[ - \frac{i}{\hbar} \int_{-\infty}^{+\infty} e^{-i\frac{\hbar}{i} E_{el,t}(t-\tau)} K_0 |\psi_{\tau}\rangle |u_0\rangle e^{-i\frac{\hbar}{i} E_{el,t} t} \Theta(t - \tau) d\tau \]
hence
\[ |\Delta u| \approx -\frac{i}{\hbar} e^{-\frac{1}{2}(H_{el} - E_0) t} \int_0^\infty e^{-\frac{1}{2}(H_{el} - E_0) t} K_0 [\psi_t - \psi] |u_0\rangle dt \]
is such that \( \langle \Delta u | u_0\rangle = 0 \) since \( K_0 = Q_0 K_0 \).

Plugging this expression in the genuine non-Born-Oppenheimer force given above we obtain two terms,
\[ F_{k_{NBO,1}} = -2 \sum_k \Re \left[ \int_0^\infty \Gamma_{kj}(\tau) V^j(t - \tau) d\tau \right] \]
with the kernel
\[ \Gamma_{kj}(t) = \langle \partial_k u_0 | Q_0 H'_{el} e^{-\frac{1}{2}H'_{el} t} | \partial_j u_0 \rangle \]
and
\[ F_{k_{NBO,II}} = -2 \Im \left[ \int_0^\infty \langle \partial_k u_0 | Q_0 H'_{el} e^{-\frac{1}{2}H'_{el} t} R | u_0 \rangle d\tau \right] \]
where we have set \( H'_{el} = H_{el} - E_0 \). The first is a friction-like term, with \( 2 \Re \Gamma_{kj}(t) \) playing the role of memory kernel in the classical limit where \( V^j \) is real. In the Markov limit
\[ F_{k_{NBO,1}} = -\sum_j \tilde{\gamma}_{kj} V^j(t) \]
where
\[ \tilde{\gamma}_{kj} = 2 \lim_{\epsilon \to 0^+} \int_0^\infty e^{-\epsilon t} \Gamma_{kj}(t) dt \]
with the usual \( \epsilon \) converging factor included. Later we shall find that \( \tilde{\gamma}_{kj} \) is better defined as the zero-frequency limit (from above) of the frequency-dependent kernel
\[ \gamma_{kj}(\omega) = 2 \lim_{\epsilon \to 0^+} \int_0^\infty e^{-\epsilon t} e^{i\omega t} \Gamma_{kj}(t) dt \]
where the excitation energy \( \hbar \omega \) can be viewed as a “running” correction to \( E_0 \) in the dynamical phase factor \( e^{i\hbar E_0 t} \) appearing in \( \Gamma_{kj}(t) \).

**Equivalence with DMS friction at \( T=0 \) K**

Let us first prove the equivalence of the DMS expression for the friction (Eq. 2 of the main text) with the one obtained above. 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
\[ \gamma_{kj}^{DMS} = -\int_0^\infty \text{tr}_e \left( (\partial_k H_{el}) e^{-\frac{1}{2}H'_{el} t} |\partial_j u_0\rangle \langle u_0| \right) d\tau \]
\[ -\int_0^\infty \text{tr}_e \left( (\partial_k H_{el}) |u_0\rangle \langle \partial_j u_0| e^{+\frac{1}{2}H'_{el} t} \right) d\tau \]
which are the complex conjugate of each other, i.e.,
\[ \gamma_{kj}^{DMS} = -2 \Re \left[ \int_0^\infty \langle u_0| (\partial_k H_{el}) e^{-\frac{1}{2}H'_{el} t} |\partial_j u_0\rangle d\tau \right] \]
Then, upon noticing that
\[ (\partial_k H) |u_0\rangle = (E_0 - H_{el}) |\partial_k u_0\rangle + (\partial_k E_0) |u_0\rangle \]
and introducing the projector \( Q_0 = 1 - P_0 \) we find
\[ \gamma_{kj}^{DMS} = 2 \Re \left[ \int_0^\infty \langle \partial_k u_0 | Q_0 H'_{el} e^{-\frac{1}{2}H'_{el} t} |\partial_j u_0\rangle d\tau \right] \]
\[ - 2 \langle \partial_k E_0 | \int_0^\infty \Re \langle u_0 | \partial_j u_0 \rangle d\tau \]
where the first term is precisely the real part of \( \tilde{\gamma}_{kj} \) 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 here tacitly assumed.

**Pseudo-magnetic contribution**

Secondly, we show that the memoryless friction
\[ \tilde{\gamma}_{kj} = 2 \lim_{\epsilon \to 0^+} \int_0^\infty e^{-\epsilon t} \Gamma_{kj}(t) dt \]
contains in fact a pseudo-magnetic contribution. To this end we need
\[ H'_{el} e^{-\epsilon t} e^{-\frac{1}{2}H'_{el} t} dt = i\hbar \frac{d}{dt} \left( e^{-\epsilon t} e^{-\frac{1}{2}H'_{el} t} \right) + i\hbar e \left( e^{-\epsilon t} e^{-\frac{1}{2}H'_{el} t} \right) \]
and
\[ H'_{el} \int_0^\infty e^{-\epsilon t} e^{-\frac{1}{2}H'_{el} t} dt = -i\hbar \left( 1 + \frac{i\epsilon \hbar}{H'_{el} - i\hbar} \right) \]
\[ = -i\hbar \left( 1 + i\hbar \frac{H'_{el} + i\hbar}{(H'_{el})^2 + \epsilon^2 \hbar^2} \right) \]
\[ \to -i\hbar \left( 1 + i\pi H'_{el} \delta(H'_{el}) \right) \]
where we have used the common notation \( \frac{1}{\hbar} \) for \( A^{-1} \).
Notice that in this expression the second term on the r.h.s. \( \propto H'_{el} \delta(H'_{el}) \) 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.

Plugging this identity in the friction expression we find
\[ \Re \tilde{\gamma}_{kj} = \gamma_{kj}^{DMS} = 2 \hbar \Im \left( \partial_k u_0 \langle Q_0 | \partial_j u_0 \right) \]
\[ + 2 \pi \hbar \Re \langle \partial_k u_0 | Q_0 H'_{el} \delta(H'_{el}) | \partial_j u_0 \rangle \]
where the first term
\[ 2 \hbar \Im \langle \partial_k u_0 | Q_0 | \partial_j u_0 \rangle = 2 \hbar \Im q_{kj} = -\hbar B_{kj} \]
gives a magnetic component \( +\hbar \sum_j B_{kj} V^j \) that, when evaluating the force, precisely cancels the magnetic correction introduced in the main text. 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 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 wavepacket. This corrective effect may thus be viewed physically as restoration of the full adiabatic dynamics in this friction limit: electronic friction cools the nuclear motion and enforces the adiabatic limit (with its gauge fields).

To summarize

$$\gamma_{kj} = -2i\hbar q_{kj} + \gamma_{kj}$$

where the “corrected” friction kernel $\gamma_{kj}$ takes the form of the real part of the expression

$$\gamma_{kj} = 2\pi \hbar \lim_{\epsilon \to +0} \epsilon \int_0^{\infty} e^{-\epsilon t} \langle \partial_k u_0 | Q_0 e^{-iH'_{el} t} | \partial_j u_0 \rangle$$

or, equivalently,

$$\gamma_{kj} = 2i\hbar \lim_{\epsilon \to 0^+} \epsilon \int_0^{\infty} e^{-\epsilon t} e^{i\omega t} \langle \partial_k u_0 | Q_0 e^{-\hbar \hat{H}'_{el} t} | \partial_j u_0 \rangle$$

Running correction to $E_0$

The friction kernel $\gamma_{kj}$ defined above is, strictly speaking, ill-defined, as it is apparent from the presence of both $Q_0$ and $\delta(H'_{el})$. A more appropriate definition is obtained by taking the zero-frequency limit (from above) of the frequency-dependent kernel

$$\gamma_{kj}(\omega) = 2i\hbar \lim_{\epsilon \to 0^+} \epsilon \int_0^{\infty} e^{-\epsilon t} e^{i\omega t} \langle \partial_k u_0 | Q_0 e^{-\hbar \hat{H}'_{el} t} | \partial_j u_0 \rangle$$

The physical motivation for introducing a small (eventually vanishing in the end) positive frequency $\omega$ 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 $\epsilon - \hbar$ pairs into the substrate. Thus the replacement

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

is needed to correct the LRT result 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, non-degenerate energy eigenvalue of the electronic Hamiltonian $H_{el}$ for some value of the nuclear coordinates $x = (x^1, x^2, ... x^k, ...)$. Upon taking the derivative of the electronic Schrödinger equation w.r.t. $x^k$, $(\partial_k H_{el}) | u_0 \rangle = (\partial_k E_0) | u_0 \rangle + (E_0 - H_{el}) | \partial_k u_0 \rangle$, and projecting with $Q_0$, one easily finds

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

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

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

and thus

$$Q_0 | \partial_k u_0 \rangle = (1 + (\lambda - E_0)G(\lambda) + (\lambda - E_0)^2G(\lambda)^2 + ... \times G(\lambda))Q_0 (\partial_k H_{el}) | u_0 \rangle$$

provided $\lambda$ 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

$$Q_0 | \partial_k u_m \rangle = G^+(E_0)Q_0 (\partial_k H_{el}) | u_0 \rangle$$

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

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

for $\Delta H = (\partial_k H_{el} - \partial_k E_0) dx^k$. This gives, for infinitesimal displacements of the nuclear coordinates,

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

from which the above result follows upon taking the limit $\lambda \to E_0$ for $\lambda \in \mathbb{C}$.

Consider now the frequency-dependent friction kernel. In the limit $\omega \to 0$ we can use the above expression for $\lambda = E_0 + \hbar (\omega + i\epsilon)$ to write

$$\gamma_{kj}(\omega) = 2i\hbar \lim_{\epsilon \to 0^+} \epsilon \int_0^{\infty} dt e^{-\epsilon t} e^{i\omega t} \times \langle u_0 | (\partial_k H_{el}) Q_0 G(\lambda^*) e^{-\hbar \hat{H}'_{el} t} (\partial_j u_0)$$

$$= -2\hbar^2 \lim_{\epsilon \to 0^+} \epsilon (u_0 | (\partial_k H_{el}) Q_0 G(\lambda) (\partial_j u_0)$$

and thus, to leading order in $\omega$,

$$\gamma_{kj}(\omega) = -2\pi \hbar \langle u_0 | (\partial_k H_{el}) \delta(E_0 + \hbar \omega - H_{el}) | \partial_j u_0 \rangle$$

where $\lim_{\omega \to 0} \hbar \epsilon G(E-i\hbar \epsilon)G(E+i\hbar \epsilon) = \pi \delta(E - H_{el})$ has been used (here $Q_0$ could be removed since the $\delta$ term projects onto states with energy above $E_0$). This is precisely $\textbf{Eq. (11)}$ appearing in the main text.
Equivalently, in the same limit as above, we can also make explicit the role of $\partial_j H_{el}$

$$
\gamma_{kj}(\omega) = -2\pi\hbar \langle u_0 | (\partial_k H_{el}) \delta(E_0 + \hbar \omega - H_{el}) \rangle
$$

$G_p(E_0) \partial_j H_{el} | u_0 \rangle$

where $G_p(E_0)$ is the principal part of $G^+(E_0)$, that is, $G_p(E_0) = \lim_{\epsilon \to 0} \Re G(E_0 + i \eta)$, and $\Im G^+(E_0) = -\pi \delta(E_0 - H_{el})$ has been neglected since it gives a vanishing contribution. [Here and in the following $\Re A = (A + A^\dagger)/2$ and $\Im A = (A - A^\dagger)/2i$.] In the limit $\omega \to 0$ in which we are interested we can replace the above expression with

$$
\gamma_{kj}(\omega) = -2\pi\hbar \langle u_0 | (\partial_k H_{el}) \delta(E_0 + \hbar \omega - H_{el}) \rangle
$$

and thus write the friction kernel as the zero-frequency limit of

$$
\gamma_{kj}(\omega) = \frac{\partial}{\partial \omega} \langle u_0 | (\partial_k H_{el}) \delta(E_0 + \hbar \omega - H_{el}) (\partial_j H_{el}) | u_0 \rangle
$$

where use has been made of

$$
\delta(E - H_{el}) G_p(E) = \frac{1}{2} \lim_{\epsilon \to 0} \epsilon \left[ G(\lambda^*) G(\lambda)^2 + G(\lambda^q)^2 G(\lambda) \right]
$$

$$
= -\frac{1}{2} \frac{\partial}{\partial \omega} \lim_{\epsilon \to 0} \epsilon G(\lambda^*) G(\lambda)
$$

$$
= -\frac{1}{2h} \frac{\partial}{\partial \omega} \delta(E_0 + \hbar \omega - H_{el})
$$

for $\lambda = E + i \epsilon$, with $E = E_0 + \hbar \omega$. For comparison notice that

$$
q_{kj}(\omega) = -\frac{1}{\hbar} \frac{\partial}{\partial \omega} \langle u_0 | (\partial_k H_{el}) G_p(E_0 + \hbar \omega) (\partial_j H_{el}) | u_0 \rangle
$$

gives, in the limit $\omega \to 0$, the quantum geometric tensor.

Notice further that if the excitation energy $\hbar \omega$ is introduced at the level of the “bare” kernel $\gamma_{kj}$, the above conclusions about the pseudo-magnetic contribution and the residual friction kernel $\gamma_{kj}$ remain unaltered. In fact, one finds

$$
\tilde{\gamma}_{kj}(\omega) = -2i\hbar q_{kj} + \gamma_{kj}(\omega)
$$

$$
+ 2\hbar \omega (\partial_k u_0) Q_{0} G^+(E_0 + \hbar \omega) (\partial_j u_0)
$$

where the last term vanishes in the limit we are interested in.

Independent electrons

For independent electrons $\partial_k H_{el}$ is a mono-electronic operator that we write as $\partial_k h$ and the projector $\delta(E_0 + \hbar \omega - H_{el})$ can thus be restricted to singly-excited Slater determinants, i.e., $\langle \Psi^b_i | c_i^\dagger c_a | \Phi_0 \rangle$ where $| \Phi_0 \rangle$ is the Hartree-Fock ground-state and $c_a$ ($c_i^\dagger$) is an annihilation (creation) operator for the single-particle state $| \phi_a \rangle$ ($| \phi_i \rangle$). Here, the single-particle energies are such that $\epsilon_a < \epsilon_F < \epsilon_b$, where $\epsilon_F$ is the Fermi level, and $\hbar \omega = \epsilon_b - \epsilon_a = \Delta \epsilon_{ba}$. As a result, Eq. 10 of the main text becomes

$$
\gamma_{kj}(\omega) = -2\pi\hbar \sum_a \sum_b \langle \phi_b | (\partial_j \phi_a) \delta(\hbar \omega - \Delta \epsilon_{ba})
$$

$$
= -2\pi\hbar \sum_a \sum_b D_{ab}^k \frac{f(\epsilon_b - f(\epsilon_a)) \delta(\hbar \omega - \Delta \epsilon_{ba})}{\epsilon_b - \epsilon_a}
$$

where we have defined $D_{ab}^k = \langle \phi_b | (\partial_j \phi_a) | \hbar \omega = \epsilon_b - \epsilon_a = \Delta \epsilon_{ba} \rangle$

which is the HGT expression, Eq. 1 of the main text. Notice that $\gamma_{kj}(\omega)$ above becomes real in the limit $\omega \to 0$.

Frictional vector potential

Let us 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 such 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 non-linear 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 a gauge where the electronic states evolve according to a zero-averaged Hamiltonian (the “standard” gauge), i.e., $\langle u^+ | (\partial_t u^+) = 0$ where $+$ denotes the chosen gauge. Clearly, in linear-response this amounts to reference the electronic Hamiltonian to the ground-state energy, $E_0$, and to write $| u^+ \rangle = | u_0 \rangle + | \Delta u^\dagger \rangle$

where

$$
| \Delta u^\dagger \rangle := -\frac{i}{\hbar} \int_0^{+\infty} e^{-i H_{nuc}' t} K_{0} | \psi_{t-l'} \rangle | u_0 \rangle dt'
$$

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

$$
H^+ \approx \frac{1}{2} \sum_{ij} \xi_{ij} \hat{\pi}_i^+ \hat{\pi}_j + (E_0(x) + \phi^+)
$$
resembles closely the adiabatic Hamiltonian $H^0$; 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.,

$$A^0_k = i \langle u_0|\partial_k u_0 \rangle \rightarrow$$

$$A_k = A^0_k + i \langle u_0|\partial_k \Delta u_0 \rangle + i \langle \Delta u_k|\partial_k u_0 \rangle$$

$$= A^0_k + 2\Im \langle \partial_k u_0|\Delta u_0 \rangle$$

where $\partial_k \langle (u_0|\Delta u_0) \rangle = 0$ has been used in the last line. In fact, it turns out that the main modification is precisely the time-dependent term

$$\delta A_k = A_k - A^0_k$$

$$= 2\Im \left( \frac{i}{\hbar} \int_0^\infty \langle \partial_k u_0 e^{\mp H_0 t'} K_0[\psi_{t-t'}]|u_0 \rangle dt' \right)$$

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

$$F_k = \frac{\partial \hat{\pi}_k^+}{\partial t} + \frac{i}{\hbar} [H^+, \hat{\pi}_k] = -\hbar \frac{\partial}{\partial t} \delta A_k + \frac{i}{\hbar} [H^+, \hat{\pi}_k]$$

$$\approx -\hbar \frac{\partial}{\partial t} \delta A_k$$

where $\hat{\pi}_k^+ = \hat{\rho}_k - \hbar A^0_k$ is the adiabatic momentum. Here, the line hand holds if we retain only terms that contain up to three spatial derivatives of the electronic state at a time, e.g., of the form

$$-\partial_k \phi_0 = -\hbar \frac{2}{i} \sum_{ij} \xi_{ij} \partial_k R \langle \partial_k u_0|Q_0|\partial_j u_0 \rangle$$

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

$$[\hat{\pi}_k^+, \hat{\pi}_j^+] \approx [\hat{\pi}_k^0, \hat{\pi}_j^0] \phi^+ \approx \phi^0$$

which can be summarized by stating that the geometric properties are the same as in the adiabatic limit, $q_{ij} \approx q_{ij}^0$.

Let us then take a closer look at the correction $\delta A_k$ to the vector potential. From the definition of $K_0$ we have

$$\delta A_k = -2 \sum_j \Im \int_0^\infty \langle \partial_k u_0 e^{\mp H_0 t'} Q_0|\partial_j u_0 \rangle V_{j-t',t'} \rangle \langle \partial_k u_0|e^{-\mp H_0 t'} R|u_0 \rangle dt'$$

$$+ 2\Re \int_0^\infty \langle \partial_k u_0 e^{\mp H_0 t'} R|u_0 \rangle \langle \partial_k u_0|e^{-\mp H_0 t'} Q_0|\partial_j u_0 \rangle V_{j-t',t'} \rangle \langle \partial_k u_0|e^{-\mp H_0 t'} R|u_0 \rangle dt'$$

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

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

and integrating by parts we find

$$\delta A_k = -2 \sum_j \Im \langle q_{ij}^0 X^j \rangle$$

$$+ \frac{2}{\hbar} \sum_j \Re \left( \int_0^\infty \langle \partial_k u_0|\Gamma(t')|\partial_j u_0 \rangle X^j_{t-t'} dt' \right)$$

where $\Gamma(t) = H'_e e^{-iH'_e t} Q_0$ has been introduced. In the Markov limit we have

$$\int_0^\infty \langle \partial_k u_0|\Gamma(t')|\partial_j u_0 \rangle X^j_{t-t'} dt \approx$$

$$X^j_0 \int_0^\infty \langle \partial_k u_0|\Gamma(t')|\partial_j u_0 \rangle dt$$

where, as seen above,

$$\lim_{\epsilon \to 0^+} \int_0^\infty e^{-\epsilon t} \Gamma(t) dt = -i h \left( 1 + i \pi H' e \delta(H'_e) \right) Q_0$$

Hence, in this limit, we find the following simple “frictional correction” to the adiabatic dynamics

$$\delta A_k = 2\pi \sum_j \Re \left( \langle \partial_k u_0|H'_e \delta(H'_e)|\partial_j u_0 \rangle X^j_0 \right)$$

It is not hard to show that these expressions for $\delta A_k$ give exactly the correction to the forces discussed above. In the Markov limit, for instance, $F_k = F^0_k + \delta F_k$ where

$$\delta F_k = - \sum_j \gamma'_{kj} R V^j_0 + \sum_j \gamma''_{kj} \Im V^j_0$$

and $\gamma'$ and $\gamma''$ are, respectively, the real and imaginary parts of the kernel

$$\gamma_{kj} = 2\pi \hbar \langle \partial_k u_0|H'_e \delta(H'_e)|\partial_j u_0 \rangle$$

In the Markov limit, in the simplest case where $\xi_{ij} = \delta_{ij} M^{-1}$, if $\gamma_{kj}$ can be taken diagonal and uniform in the configuration space of the system where the dynamics occurs, we can write

$$\delta A_k = \Re \langle \gamma X^k \rangle \approx \partial_k \Re \left( -i h M^{-1} \gamma \int_{-\infty}^t \ln \psi(t,x) dt \right)$$

if we neglect the contribution of the vector potential to the velocity field. We thus see that $\delta A_k$ becomes longitudinal and can be replaced by an appropriate scalar field

$$\delta \phi = h M^{-1} \Im (\ln \psi(t,x))$$

When setting $\gamma'' \approx 0$ the resulting Hamiltonian $H = H^0 + \delta \phi$ is the Kostin Hamiltonian which is a simple way to introduce dissipation into a Schrödinger-like equation by adding a simple “phase potential” (depending on the phase of the system wavefunction in the position representation).