Dynamics of the Molecular Geometric Phase

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The fate of the molecular geometric phase in an exact dynamical framework is investigated with the help of the exact factorization of the wave function and a recently proposed quantum hydrodynamical description of its dynamics. An instantaneous, gauge-invariant phase is introduced for arbitrary paths in nuclear configuration space in terms of hydrodynamical variables, and shown to reduce to the adiabatic geometric phase when the state is adiabatic and the path is closed. The evolution of the closed-path phase over time is shown to adhere to a Maxwell-Faraday induction law, with nonconservative forces arising from the electron dynamics that play the role of electromotive forces. We identify the pivotal forces that are able to change the value of the phase, thereby challenging any topological argument. Nonetheless, negligible changes in the phase occur when the local dynamics along the probe loop is approximately adiabatic. That is, the geometric phase effects that arise in an adiabatic limiting situation remain suitable to effectively describe certain dynamic observables.

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Introduction.—Geometric phases are fundamental concepts in physics and chemistry, with wide-ranging implications. They are closely associated with various phenomena, such as the quantum Hall effect, the quantum anomalous Hall effect, and the quantum spin Hall effect [1,2], the exotic physics of topological insulators [3,4], dielectric polarization in crystals [2,5–9], the Aharonov-Bohm effect [10], and conical intersections (CIs) in molecules [11–13]. Geometric phases usually emerge when the Hamiltonian of a system depends on a set of "environmental" parameters $\mathbf{x}$ that are allowed to change adiabatically, as in Berry's original work [14], but they remain well-defined concepts for nonadiabatic, noncyclic, and nonunitary evolutions as well [15–18]. In the case of molecules, geometric phases play a critical role around an intersection between two or more potential energy surfaces. Even when the molecular dynamics remains nearly adiabatic, the presence of a CI can significantly impact the outcome of a chemical reaction [19–21] because of the quantum interference of wave packets encircling the CI, which crucially depends on the geometric phase [22,23]. In these molecular problems, the Berry phase is often not just geometric but also topological, that is, it is independent of both the dynamics and the path (as long as homotopic paths are compared). In fact, it is the phase introduced as early as 1958 by Longuet-Higgins [24,25] that is known to control the energy level ordering in, e.g., Jahn-Teller systems. However, these intriguing properties depend critically on the adiabatic approximation and it is uncertain whether and how they persist when the *exact* quantum dynamics is considered. Recent works [26,27] have shown that the topological character of the phase is an artifact of the adiabatic approximation and suggest, more generally, that the geometric phase in molecules may be a less useful concept than previously believed.

The purpose of this Letter is to shed light on these issues and to reconcile the adiabatic perspective with the exact dynamical evolution. To this end we will first show that a geometric phase is yet meaningful when the full electron-nuclear (*e-n*) system is in a pure state. We will use the framework of the exact factorization (EF) of the molecular wave function [28,29] since this construction extends the fiber structure of the adiabatic approximation to arbitrary states, thereby enabling a natural extension of the Berry phase [30]. This feature has already been used in previous works on the geometric phase, namely in Refs. [26,27] in a time-independent framework and, more recently, in Ref. [31] in a time-dependent context. Subsequently, we will explore the exact dynamical evolution of this phase. This task is challenging when using the original equations of motion of the EF approach due to their inherent *gauge* freedom. However, a recently developed quantum hydrodynamical (QHD) description of the EF dynamics [32] makes this step feasible. QHD offers an alternative formulation for the *e-n* dynamics, relying on EF while employing only *gauge*-invariant variables [32]. Within this QHD-EF framework we will identify the key factors influencing the evolution of the geometric phase and we will analyze a model two-state problem for illustration.

Gauge-invariant EF dynamics.—In the exact factorization approach [28,29] the wave function is represented exactly as

$$|\Psi\rangle = \int_X d\mathbf{x}\, \psi(\mathbf{x})|u(\mathbf{x})\rangle|\mathbf{x}\rangle, \tag{1}$$

where $\{|\mathbf{x}\rangle\}$ is the position basis of the nuclear variables $\mathbf{x} \in \mathcal{M} \cong \mathbb{R}^N$, $|u(\mathbf{x})\rangle$ is the conditional electronic state at $\mathbf{x}$, and $\psi(\mathbf{x})$ is the marginal probability amplitude for the nuclei, i.e., the "nuclear wave function." The latter two can be obtained, up to a *gauge* choice [33], by singling out a normalized electronic wave function from the total probability amplitude at $\mathbf{x}$, i.e.,

$$\langle \mathbf{x}|\Psi\rangle_X = \psi(\mathbf{x})|u(\mathbf{x})\rangle \equiv |\mathbf{\Psi}(\mathbf{x})\rangle \ \langle u(\mathbf{x})|u(\mathbf{x})\rangle_{\mathrm{el}} = 1, \tag{2}$$

where the subscript X (el) indicates that integration is performed over nuclear (electronic) variables only. In the EF approach $\psi(\mathbf{x})$ and $|u(\mathbf{x})\rangle$ evolve in time according to equations of motion that can be derived from either the variational principle [28,29] or projection operator techniques [34,35]. In the QHD description of the dynamics [32] the nuclear wave function is replaced by a probability fluid with density $n(\mathbf{x}) = |\psi(\mathbf{x})|^2$ and velocity field $\boldsymbol{v} = \{v^k(\mathbf{x})\}$, and the electronic state is described by conditional density operators $\rho_{\mathrm{el}}(\mathbf{x}) = |u(\mathbf{x})\rangle\langle u(\mathbf{x})|$. The equations of motion consist of a continuity equation for the density, $\partial_t n + \sum_k \partial_k(n v^k) = 0$, a momentum equation,

$$\dot{\pi}_k = -\mathrm{Tr}_{\mathrm{el}}(\rho_{\mathrm{el}}\partial_k H_{\mathrm{el}}) - \frac{\hbar^2}{n}\sum_{ij}\xi^{ij}\partial_i(n g_{kj}) - \partial_k Q, \tag{3}$$

and a Liouville–von Neumann-like equation,

$$i\hbar\dot{\rho}_{\mathrm{el}} = [H_{\mathrm{el}} + \delta H_{\mathrm{en}}, \rho_{\mathrm{el}}]. \tag{4}$$

Here, the dot denotes the material (or convective) derivative, ξ^{ij} is the inverse mass tensor of the nuclear system, $Q = -\hbar^2/2\sum_{ij}\xi^{ij}n^{-1/2}\partial_i\partial_j n^{1/2}$ is the Bohm quantum potential [36], $H_{\mathrm{el}} = H_{\mathrm{el}}(\mathbf{x})$ is the local electronic Hamiltonian, and δH_{en} is the *e-n* coupling, $\delta H_{\mathrm{en}} = -\hbar^2/(2n)\sum_{ij}\xi^{ij}\partial_i(n\partial_j\rho_{\mathrm{el}})$. Furthermore, g_{kj} is the Fubini-Study metric [37], which is the real part of the quantum geometric tensor [14] $q_{kj} = \mathrm{Tr}_{\mathrm{el}}(\rho_{\mathrm{el}}\partial_k\rho_{\mathrm{el}}\partial_j\rho_{\mathrm{el}})$.

The momentum field $\boldsymbol{\pi} = \{\pi_k(\mathbf{x})\}$ is related to the velocity field through the inverse mass tensor, $v^k = \sum_j \xi^{kj}\pi_j$, and is connected to the EF wave function by $\pi_k = \Re(\hat{p}_k\psi/\psi) - \hbar A_k$, where $\hat{p}_k = -i\hbar\partial_k$ is the canonical momentum operator and A_k is the Berry connection, $A_k = i\langle u|\partial_k u\rangle$. It can also be obtained from the total *e-n* wave function, without referring to the EF, since

$$\pi_k(\mathbf{x}) = \Re\frac{\langle\mathbf{\Psi}(\mathbf{x})|\hat{p}_k|\mathbf{\Psi}(\mathbf{x})\rangle_{\mathrm{el}}}{\langle\mathbf{\Psi}(\mathbf{x})|\mathbf{\Psi}(\mathbf{x})\rangle_{\mathrm{el}}}, \tag{5}$$

where $|\mathbf{\Psi}(\mathbf{x})\rangle$ was introduced in Eq. (2). The circulation of $\boldsymbol{\pi}$ around arbitrary closed paths γ in $\mathcal{M}$ satisfies a quantization condition,

$$\sum_k \oint_\gamma (\pi_k + \hbar A_k)dx^k = 2\pi\hbar\nu \quad \nu \in \mathbb{Z}, \tag{6}$$

which merely expresses the fact that the nuclear wave function ψ must be smooth around any loop [38]. This condition needs to be imposed at the initial time only [with a smooth choice of the phases of the nuclear and electronic wave functions in Eq. (2)], since Kelvin's circulation theorem holds for the fluid dynamics described here [39]. In the following we shall focus on a given instant of time and investigate the geometric properties of the instantaneous fiber bundle induced by the EF of the total wave function [40].

Nonadiabatic geometric phase.—The quantization condition of Eq. (6) formalizes earlier observations that the geometric phase is related to the circulation of the momentum field in a dynamical context [31,41–43]. More than that, since $\boldsymbol{\pi}$ is *gauge*-invariant, Eq. (6) shows how to define an instantaneous, *gauge*-invariant "phase" for arbitrary paths γ in $\mathcal{M}$,

$$\Gamma[\gamma] = -\frac{1}{\hbar}\sum_k \int_\gamma \pi_k dx^k. \tag{7}$$

For loops, $\Gamma[\gamma]$ reduces, by construction, to the holonomy of the vector bundle defined by EF, namely

$$-\frac{1}{\hbar}\sum_k \oint_\gamma \pi_k dx^k = \oint_\gamma A_k dx^k \mod 2\pi, \tag{8}$$

while more generally, for an open curve γ that connects $\mathbf{x}_a$ to $\mathbf{x}_b$, it turns out to be the sum of two contributions that are separately invariant,

$$\Gamma[\gamma] = -\Theta_{ba} + \Gamma_{\mathrm{el}}[\gamma]. \tag{9}$$

Here, $\Theta_{ba} = \arg\langle\mathbf{\Psi}(\mathbf{x}_a)|\mathbf{\Psi}(\mathbf{x}_b)\rangle$ is the Pancharatnam phase difference of the total *e-n* wave function between b and a, while $\Gamma_{\mathrm{el}}[\gamma]$ reads as

$$\Gamma_{\mathrm{el}}[\gamma] = \arg\langle u(\mathbf{x}_a)|u(\mathbf{x}_b)\rangle + \sum_k \int_\gamma A_k dx^k \tag{10}$$

and is the Pancharatnam phase accumulated by the electronic vector when parallel transported from $\mathbf{x}_a$ to $\mathbf{x}_b$ along γ [15,17,18,44,45] [46]. In a sense, $-\Gamma[\gamma]$ is a *nuclear* phase, i.e., the phase difference of the total wave function minus that of the electronic one. That is, $\Theta_{ba} = -\Gamma[\gamma] + \Gamma_{\mathrm{el}}[\gamma]$ is a decomposition of the total phase difference into nuclear and electronic contributions. For a loop $\Theta_{ba} \equiv 0$ and the nuclear phase difference is the opposite of the

electronic one, i.e., Eq. (10) with only the second term on the rhs surviving.

Importantly, $\Gamma[\gamma]$ is only indirectly tied to the connection defined by the EF: it is a property that relies on EF but does not require that the EF of the wave function is performed. It is an integral property of the momentum field which, as mentioned above, can be obtained from the total *e-n* wave function without performing its EF [Eq. (5)]. Its definition is further consistent with the fluid dynamics: for stationary loops the quantization condition [Eq. (6)] possibly jumps by $\pm 2\pi$ during the dynamics (every time a wave function node crosses the loop [32]) but this does not affect the above interpretation.

Dynamics.—We now focus on the phase defined by Eq. (7), evaluated for a loop γ, fixed in time, and use the symbol $\Gamma_O[\gamma]$ to emphasize that the path is closed. The dynamical evolution of $\Gamma_O[\gamma]$ is determined by Eq. (3), upon observing that the advection term can be rearranged as [47] $\sum_j v^j \partial_j \pi_k = \sum_j v^j B_{kj} + \sum_j v^j \partial_k \pi_j$ in order to display the kj component of the curvature tensor $B_{kj} = -2\hbar \Im q_{kj}$ and the kth derivative of the classical kinetic energy $T = 1/2 \sum_{ij} \xi^{ij} \pi_i \pi_j$. The result for the rate of change of the phase shows three distinct, *gauge*-invariant contributions, namely

$$-\frac{d\Gamma_O[\gamma]}{dt} = \mathfrak{E}^{\mathrm{NBO}} + \mathfrak{E}^{\mathrm{el}} + \mathfrak{E}^{\mathrm{mag}}, \tag{11}$$

where

$$\mathfrak{E}^{\mathrm{NBO}} = -\frac{1}{\hbar} \oint_\gamma \sum_k \mathrm{Tr}_{\mathrm{el}}(\rho_{\mathrm{el}} \partial_k H_{\mathrm{el}}) dx^k \tag{12}$$

depends on the electronic Hamiltonian, and

$$\mathfrak{E}^{\mathrm{el}} = -\hbar \oint_\gamma \sum_{ijk} \frac{\xi^{ij}}{n} \partial_i (n g_{kj}) dx^k \tag{13}$$

$$\mathfrak{E}^{\mathrm{mag}} = -\frac{1}{\hbar} \oint_\gamma \sum_{jk} v^j B_{kj} dx^k \tag{14}$$

are geometric and related to the *gauge* fields acting on the nuclei. Equation (12) represents a genuine non-Born-Oppenheimer (NBO) contribution entirely due to the nonconservative part of the Ehrenfest force $F_k^{\mathrm{Eh}} = -\mathrm{Tr}_{\mathrm{el}}(\rho_{\mathrm{el}} \partial_k H_{\mathrm{el}})$ appearing in Eq. (3). It disappears when the system is in an adiabatic state. The second contribution, Eq. (13), is generally nonvanishing, and it depends on the (instantaneous) electronic state through the metric properties of the EF fiber bundle [48] and on the nuclear state through the density n. The third contribution, Eq. (14), on the other hand, is (possibly) nonvanishing only when the nuclear state is current-carrying. It appears here only because we fixed the loop [49]: if we allowed the loop to follow the fluid dynamics we would find

$$-\frac{d\tilde{\Gamma}_O[\gamma]}{dt} = \mathfrak{E}^{\mathrm{NBO}} + \mathfrak{E}^{\mathrm{el}}, \tag{15}$$

where now $\tilde{\Gamma}_O[\gamma]$ refers to the geometric phase along a dynamical loop γ in motion with the fluid [50].

The above findings are general, and hold for arbitrary states. For cases where Stokes' theorem applies they can be anticipated by the Maxwell-Faraday induction law,

$$-\partial_t \mathcal{B} = d\mathcal{E}, \tag{16}$$

which holds for the *gauge* fields governing the nuclear dynamics in the EF approach [32]. Here, d denotes the exterior derivative, $\mathcal{B} = d\omega$ is the Berry curvature two-form, $\omega = \hbar \sum_k A_k dx^k$ is the one-form associated with the Berry connection, and $\mathcal{E} = i\hbar d\langle u|\partial_t u\rangle - \partial_t \omega = \sum_k E_k dx^k$ is the *gauge*-invariant one-form defining the *pseudo*electric field E_k [51]. Indeed, application of Stokes' theorem to an open surface having γ as a boundary, and identification of the *pseudo*electric field E_k acting on the nuclei [see Sec. III. A of Ref. [32] and, in particular, Eq. (59)] leads again to Eqs. (11)–(14). This agrees with previous findings for a particle in three dimensions [52]. Compared to the Maxwell-Faraday induction law of classical electromagnetism, though, here there is no varying magnetic flux inducing an electromotive force on a circuit. Rather, it is the *pseudo*magnetic flux (i.e., the geometric phase) of the electronic subsystem that changes *because* of the nonconservative work done by the electrons on the nuclei around the loop γ in nuclear configuration space. That is, Eq. (16) becomes a reversed induction law.

Of main interest here is the analysis of the adiabatic geometric phase, when the system is found in an adiabatic state and, in particular, when the phase is topological. In this situation, as mentioned above, the NBO circulation of Eq. (12) vanishes since the Ehrenfest force becomes conservative. However, also the "drift," *pseudo*magnetic term of Eq. (14) disappears since $\mathcal{B} \equiv 0$ (almost everywhere) if the phase is topological. Hence, we are left with the electromotive force of Eq. (13), which thus represents the key factor that converts a phase that is topological in the adiabatic approximation into a geometric phase. Indeed, the curvature departs from zero according to the induction law, Eq. (16), driven by the local vorticity of the *pseudo*electric field, which is generally nonzero. Hence, $\mathcal{B}$ becomes nonzero and the phase cannot remain topological.

Model two-state problem.—We now consider a two-state model that highlights the key features of a molecular problem involving a CI. The electronic Hamiltonian takes the general form (in a diabatic basis [53]) $H_{\mathrm{el}} = A(\mathbf{x})\sigma_0 + \mathbf{B}(\mathbf{x})\boldsymbol{\sigma}$, where $A(\mathbf{x})$ is a scalar, $\mathbf{B}(\mathbf{x}) \in \mathcal{N} \cong \mathbb{R}^3$ is an effective magnetic field, $\sigma_0 = \mathbb{I}_2$ is the 2×2 unit matrix and $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ is the vector of Pauli matrices. The geometric properties of the adiabatic bundles are well-known [14,54] and can be "pulled back" from the

problem of a spin in a slowly varying magnetic field, with $\mathcal{N}$ as parameter space [55]. In a typical molecular problem, one of the $\mathbf{B}$ components identically vanishes because of time-reversal symmetry. Hence, the curvature in nuclear configuration space vanishes everywhere except at the CI seam, and the Berry phase becomes topological.

In the adiabatic approximation the magnetic field $\mathbf{B}$ fully characterizes the electron dynamics and the structure of the relevant bundle. For an exact dynamics we further need the polarization vector $\mathbf{s}(\mathbf{x}) \in \mathcal{N}$ that characterizes the conditional density matrix, $\rho_{\rm el}(\mathbf{x}) = (\sigma_0 + \mathbf{s}(\mathbf{x})\boldsymbol{\sigma})/2$ ($\|\mathbf{s}\| = 1$ for a pure state). Equation (4) gives its dynamical equation in the form

$$\dot{\mathbf{s}} = (\Omega\mathbf{b} + \boldsymbol{\tau}) \times \mathbf{s} - \hbar/2 \sum_{ij} \xi^{ij} \partial_i (\mathbf{s}_j \times \mathbf{s}), \qquad (17)$$

where $\Omega = 2B/\hbar$ is the Larmor precession frequency, $\mathbf{b} = \mathbf{B}/B$, $\mathbf{s}_j = \partial_j \mathbf{s}$, and $\boldsymbol{\tau} = \sum_j u^j \mathbf{s}_j$ is the "nuclear torque," an effective field due to the e-n coupling, in which $u^j = -\hbar/2 \sum_k \xi^{jk} \partial_k \ln n$. The bundle structure, on the other hand, is characterized by the quantum geometric tensor, $q_{kj} = [\mathbf{s}_k \mathbf{s}_j + i\mathbf{s}(\mathbf{s}_k \times \mathbf{s}_j)]/4$, and the contributions appearing in Eq. (11) take the form of integrals of simple one-forms, i.e., $\mathfrak{G}^{\rm X} = \oint_\gamma \Phi^{\rm X}$ (for X = NBO, el, and mag), where $\Phi^{\rm NBO} = \hbar^{-1} \mathbf{B} d\mathbf{s}$, $\Phi^{\rm el} = 1/2 \boldsymbol{\tau} d\mathbf{s} - \hbar/4 \sum_{ij} \xi^{ij} \partial_i \mathbf{s}_j d\mathbf{s}$, and $\Phi^{\rm mag} = 1/2 (\boldsymbol{\nu} \times \mathbf{s}) d\mathbf{s}$, upon defining $\boldsymbol{\nu} = \sum_j v^j \mathbf{s}_j$ [50]. The circulations are therefore all mapped on the Bloch sphere $S^2 \subset \mathcal{N}$, where $\mathbf{s}(\mathbf{x})$ traces a curve $\tilde{\gamma}$ when $\mathbf{x}$ moves along the curve γ. The results for an adiabatic state follow upon setting $\mathbf{s} = \pm\mathbf{b}$ for the upper and lower adiabatic states, respectively.

For concreteness, we consider $2 + 1$ nuclear degrees of freedom ($\mathcal{M} \cong \mathbb{R}^3$) mimicking a one-dimensional CI seam, with parameter values typical of a molecular problem and a diagonal mass tensor, $\xi^{ij} = \delta^{ij} M^{-1}$ (with $M = 1$ amu). Upon taking $A(\mathbf{x})$ independent of z the problem becomes effectively two-dimensional. Specifically, setting $A(\mathbf{x}) = \frac{1}{2} M\omega_x^2 x^2 + \frac{1}{2} M\omega_y^2 y^2$ ($\omega_x = \omega_y = \omega = 1000$ cm^{-1}) and employing a linear vibronic coupling $\mathbf{B} = \kappa_x x \mathbf{e}_1 + \kappa_y y \mathbf{e}_2$ ($\kappa_x = \kappa_y = \kappa = 0.1$ a.u.) the problem becomes a standard, linear $E \otimes e$ Jahn-Teller model (Fig. 1). We solved the time-dependent Schrödinger equation for this problem using a numerically exact method and computed the geometric phase along a number of paths fixed in time [50]. Figure 1 shows the main results of our numerical investigation. The wave packet, prepared in the adiabatic ground state, spreads along the valley of the "Mexican hat" potential and its trailing edges meet each other and interfere at time $t \approx 75$ fs, after which the wave packet covers more or less uniformly the valley, with a time-varying interference pattern [panels (b)–(d)]. Figure 1(e) shows the evolution of the geometric phase (in π units) along three significant paths, i.e., three different circles on the valley floor. The behavior of the phase at short time ($t \lesssim 20$ fs) is to some extent undetermined due to regions of near-vanishing nuclear density that impose intrinsic limits on the numerical implementation [50]. After this transient, the phase is seen to undergo an evident variation, which is

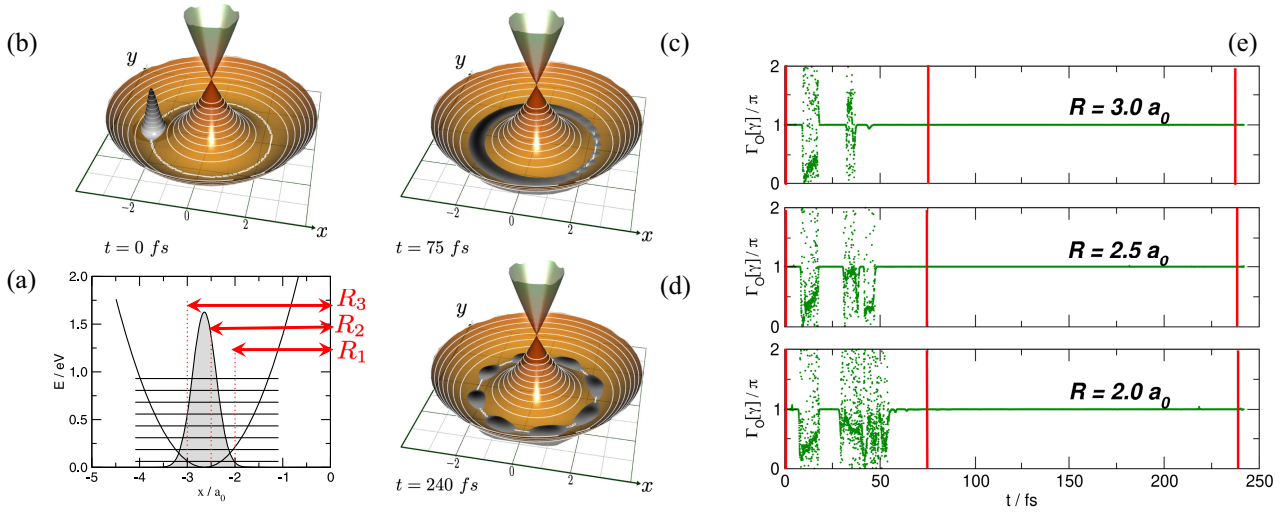

FIG. 1. Exact quantum dynamical results for the two-dimensional, two-state model problem described in the main text. (a) Nuclear density at $t = 0$ along the x coordinate. Also shown is the adiabatic ground-state potential and the ladder of vibrational states of the diabatic potential. The arrows denote the radii of some circular paths, centered at the CI point, along which the geometric phase was computed. (b)–(d) Snapshots of the nuclear density at three significant times, $t = 0$, 75, and 240 fs, as indicated, along with the adiabatic potential energy surfaces intersecting at the origin of the coordinate system. The density is nodeless, even though it is seen to decrease to small values. (e) Evolution of the geometric phase of Eq. (7) (in π units) along the three paths marked in (a), namely for circles of radius $R = 2.0$, 2.5, and $3.0 a_0$ (from bottom to top, as indicated). The red vertical bars denote the three times chosen for panels (b)–(d). See text for details.

numerically robust, when the wave packet edges start to interfere, and later gets back to the value expected for an adiabatic dynamics [Fig. 1(e)]. This provides direct evidence for the transition between the geometric and topological phase from the vantage point of exact quantum dynamics. Analysis of the contributions to the electromotive force confirms that the NBO component contributes little to the phase change, while the *pseudo*electric one plays the major role [50].

Conclusions.—We have shown that the molecular geometric phase of the adiabatic approximation can be seamlessly extended to exact quantum dynamics. The generalized phase is shown to be related to the circulation of the mechanical momentum, it is time-dependent and its evolution is governed by a (reversed) Maxwell-Faraday induction law, with nonconservative forces arising from the electron dynamics that play the role of electromotive forces. Though generally evolving in a complicated way, this geometric phase remains highly relevant when the dynamics is close to adiabatic and a physically motivated choice of the path is performed.

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[38] Here, ν is the topological value that describes the way the wave function phase winds around a singularity of the momentum field (for instance, a wave function node). In fact, ν can be nonzero only in a multiply connected domain, when γ cannot be shrunk to a single point.

[39] The theorem guarantees that the circulation of Eq. (6) is constant in time when the loop is let evolve in tandem with the nuclear probability fluid. It can be extended to stationary loops provided one accounts for the possibility that nodal lines cross the loop during the dynamics. A proof that Kelvin's theorem holds for the nuclear probability fluid of the electron-nuclear problem is provided in Appendix A of Ref. [32].

[40] This is the bundle $p: E \to \mathcal{M}$, where $\mathcal{M}$ is the nuclear configuration space and the fundamental bundle projection p is defined such that $p^{-1}(\mathbf{x})$ is the ray of the EF conditional electronic state at the configuration $\mathbf{x} \in \mathcal{M}$.

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[46] Indeed, $\pi_k \equiv \hbar\partial_k\theta - \hbar A_k$ (where $\theta = \arg\psi$) and the phase change of the nuclear wave function at the endpoints of the curve, $\Delta\theta = \theta_b - \theta_a$, can be written as $\Delta\theta = \arg(\psi_a^*\psi_b\langle u_a|u_b\rangle) - \arg(\langle u_a|u_b\rangle)$, where $\psi(\mathbf{x})|u(\mathbf{x})\rangle = |\mathbf{\Psi}(\mathbf{x})\rangle$.

[47] We exploit here the identity $\partial_j\pi_k - \partial_k\pi_j = B_{kj}$, that can be directly obtained from Eq. (5). In terms of differential forms this identity reads as $d\pi = -\mathcal{B}$, where $\pi = \hbar\Im\langle\Psi|d\Psi\rangle_{\rm el}/\langle\Psi|\Psi\rangle_{\rm el}$, and can be considered a precursor of the induction law discussed below [Eq. (16)].

[48] We refer to the quantum metric $g = \sum_{kj}\Re q_{kj}dx^k dx^j$ induced in the tangent bundle $T\mathcal{M}$ by the EF fiber structure [37].

[49] The phase is tied to the local electronic states that, in turn, move in tandem with the fluid elements describing the nuclear probability density.

[50] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.132.243002 for details about some formal results and the numerical investigation presented in the main text.

[51] There is some freedom in defining this field, since one can add any *gauge*-invariant closed form to $\mathcal{E}$ without altering the induction law and its *gauge* invariance. For instance, one can choose to add conservative forces in the form $\mathcal{F} = d\mathcal{V}$, where $\mathcal{V}$ is a (*gauge*-invariant) scalar potential acting on the nuclei. The important, nonconservative, part of $\mathcal{E}$ is the electron dynamical force $F_k^{\rm ED}$ first introduced in Ref. [34]: in the adiabatic approximation $F_k^{\rm ED} \equiv 0$ and the geometric phase is stationary.

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[55] More precisely, the quantum geometric tensor q in parameter space $\mathcal{M}$ is the pullback by the magnetic field $\beta: \mathcal{M} \to \mathcal{N}$ of the fundamental geometric tensor $\tilde{q}$ in $\mathcal{N}$, i.e., $q_{\mathbf{x}}(\mathbf{u},\mathbf{v}) = (\beta^*\tilde{q})_{\mathbf{x}}(\mathbf{u},\mathbf{v}) \equiv \tilde{q}_{\beta(\mathbf{x})}[d\beta_{\mathbf{x}}(\mathbf{u}), d\beta_{\mathbf{x}}(\mathbf{v})]$ for $\mathbf{x} \in \mathcal{M}$ and $\mathbf{u},\mathbf{v} \in T_{\mathbf{x}}\mathcal{M}$. Here, $\beta: \mathbf{x} \to \mathbf{B}(\mathbf{x})$ specifies the magnetic field and q, $\tilde{q}$ are sections of $T^*\mathcal{M} \otimes T^*\mathcal{M}$ and $T^*\mathcal{N} \otimes T^*\mathcal{N}$, respectively (see Ref. [50] for details).