

Geometry of chiral temporal structures. I. Physical effects

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In nonrelativistic physics, the concepts of geometry and topology are usually applied to characterize spatial structures or structures in momentum space. We introduce the concept of temporal geometry, which encompasses the geometric and topological properties of temporal shapes, i.e., trajectories traced by the tip of a time-dependent vector. We apply it to electric field polarizations controlling ultrafast electron currents or induced polarization in chiral molecules. The central concepts of temporal geometry—Berry curvature and Berry connection—emerge as ubiquitous features of photoexcited, nonequilibrium, chiral *electron* dynamics. We demonstrate that the Berry curvature and Berry connection (1) rely on the polarization properties of light pulses, (2) can be introduced for multiphoton processes, and (3) control enantiosensitive geometric observables via nonequilibrium electronic dynamics excited by tailored laser fields. Our findings may open a way to ultrafast, topologically nontrivial, and enantiosensitive chemical dynamics.

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I. INTRODUCTION

Synthetic chiral light [1] is an example of a locally chiral object: the Lissajous figure of its electric field vector at every point in space draws a chiral three-dimensional trajectory in time which cannot be superimposed onto its mirror image. Since its chirality is local, it can induce chiral interactions with electrons in molecules within the electric-dipole approximation [2], promising enhancement of the chiral response by orders of magnitude compared to standard methods based on inefficient interactions of electrons with the magnetic field component of light. Three-color electromagnetic fields with mutually orthogonal polarizations, as introduced in the pioneering work of Kral and Shapiro [3] used to harvest the electric-dipole chiral response in the microwave region [4–6], also belong to this family.

Locally chiral temporal structures do not have to be limited to the one traced by the tip of the light polarization vector. Electronic polarization or electronic currents induced in chiral molecules [7,8] can also trace temporal chiral structures,

even if the driving field is not chiral. That is, the respective vectors—current or induced polarization—trace a chiral trajectory as they evolve in time. The chiral shape outlined by this trajectory is local because it is encoded in the temporal evolution of the vector, rather than in its spatial evolution. The specific chiral shape is defined by the mutual orientations of the molecule and light's polarization vector: each orientation will give rise to a different temporal chiral shape. Thus, the temporally chiral shape is defined in the configuration space of molecular orientations. If several orientations contribute to the measured response, e.g., photoionization from the current carrying superposition of states, then the set of different temporal shapes corresponding to the underlying orientations may also combine into a nontrivial global structure.

This poses two pertinent questions: (1) how is the temporal chiral geometry connected for two different orientations, and (2) how does this connection quantify the global response of a full set of orientations? Here, we address these questions by identifying the Berry connection and Berry curvature associated with the *temporal geometry* of the attosecond electronic response of chiral molecules to light. The realization of this program requires the implementation of geometric and topological concepts into the ultrafast electronic response in chiral molecules.

While topological aspects of nuclear dynamics at conical intersections in molecules are well known [9], the connection between topology and chirality in the light-induced electronic response of gas-phase chiral molecules is an emergent topic [10–14]. In these pioneering works, the respective configu-

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ration or parameter spaces range from inverse lattice vectors (in the case of periodic chiral arrangement of atoms) [12] to parameters of electromagnetic waves triggering the response [11] to propagation vectors of nonlinear response [14]. The desire to invoke geometric concepts such as the Berry curvature, Berry connection, and geometric phase is hardly surprising as it often enables one to identify novel properties of matter. Examples range from the emergence of the Fermi antisymmetrization principle from the topology of configuration space [15] to topological materials [16,17], anyons and topological quantum computing [18], twisted light [19], topological photonics, and topological lasers [20].

The topological aspects of the *electronic* response have so far been mainly harvested in condensed matter systems and have yet to find their room in the gas and liquid phases. Since topology has an attractive property of robustness to external perturbations and noise, one may be able to create efficient and robust new enantiosensitive observables by combining chirality and topology in the ultrafast electronic and optical response of chiral gases and liquids. Relevant experimental imperfections in gas-phase experiments involve fluctuations of laser parameters, sensitivity and instrument response of photoelectron detectors, challenges in sample preparation, dilute samples, and small or fluctuating enantiomeric excess in a sample. In the combination of efficiency and robustness that we are aiming to achieve, the efficiency comes from driving an ultrafast nonlinear response enabling chiral detection via electric-dipole interactions [2], whereas robustness comes from topological concepts represented locally via Berry curvature and Berry connection in relevant configuration or parameter spaces.

We have recently identified a manifestation of the Berry connection and Berry curvature in the one-photon ionization of chiral molecules [13]. Here, we extend these concepts to two-photon ionization and focus on opportunities to control the Berry curvature and the observables it induces by controlling light's polarization. We identify and describe enantiosensitive observables enabled by these generalizations. As a corollary of our approach, we establish the geometric origin of the photoexcitation circular dichroism (PXCD) [7] and its detection via photoionization with linearly polarized light (PXECD) [7]. Our findings establish geometrical concepts, such as the Berry curvature and the geometric phase, as the key quantities underlying the temporally chiral electronic response. It means that (1) there is a well-defined functional dependence of the response on these quantities, (2) the understanding of these quantities leads to a deeply illuminating understanding of the response, and (3) those quantities can be used as effective means of detection of molecular chirality. This may open a way to generate a topologically nontrivial electronic response in photoexcited bound states of chiral molecules via tailored light fields. As a guiding example, we analyze three pump-probe scenarios: linear-circular, circular-linear, and circular-circular polarizations. In the first case the Berry curvature emerges from the temporal geometry of continuum states, in the second from bound states, and in the third we show the interplay of both contributions.

The paper is organized as follows. In Sec. II we outline the concept of *temporal geometry* in the interaction of molecules with laser pulses and present expressions for the

Berry connection, Berry curvature, and vectorial and scalar observables relying on the Berry curvature. In Sec. III we use these expressions to provide a new general (i.e., using the Berry connection and Berry curvature from the outset) derivation of the geometric effect—photoionization molecular orientation circular dichroism (PI-MOCD) [13]. We show that the direction of the Berry curvature defines the direction of molecular orientation and is a direct experimental observable. This approach shows how geometric quantities may appear in multiphoton processes and verifies our new method by comparison with the earlier results [13]. It also establishes the path to derive our new results identifying the Berry curvature in bound states and in “mixed” bound and continuum states in Sec. IV. Last but not least, we show how the efficient enantiosensitive observables generated by *temporal geometry*, such as enantiosensitive molecular orientation, can be controlled via excitation of nonequilibrium dynamics. In Secs. II, III, and VI, using the chiral molecule propylene oxide as an example, we demonstrate that simple polarization control of laser pulses allows one to switch the direction of the Berry curvature from its bound to its continuum value and thus switch the direction of enantiosensitive orientation in PI-MOCD. Both the demonstration of the control and its fundamental understanding are new. Superscripts M and L denote that respective vectors belong to the molecular or laboratory frame, respectively. Vectors contributing to scalar products will not be marked, because the pair of such vectors can be associated with any frame.

II. TEMPORAL GEOMETRY IN CHIRAL MOLECULES

Light fields $E(t)$ interacting with molecules primarily couple to electrons and trigger their attosecond response. In the laboratory frame,¹ circularly polarized light interacts with randomly oriented molecules [Fig. 1(a)]. Since the strength of such interaction depends on the orientation of a molecule with respect to the laser field, it inevitably couples electronic and rotational degrees of freedom. This means that the electronic current excited in molecules oriented differently will also be different. It is convenient to visualize this by switching to the molecular frame, where the molecule is fixed and the field polarization takes different orientations [Fig. 1(b)]. The coupling term explicitly depends on the Euler angles, which characterize the orientation of the laser field in the molecular frame.

To illustrate the geometric origin of such coupling, it is convenient to associate the vector perpendicular to the light polarization plane in the molecular frame with a unit radius vector on a sphere characterized by the angles (θ, ϕ) . The polarization plane is tangent to this sphere. Therefore, the light's polarization vector in the molecular frame $e(\theta, \phi, \alpha)$ depends on three angles, where α describes the orientation of the polarization ellipse² in the tangent plane (Fig. 1). Any change

¹To define the laboratory frame in the electric-dipole approximation, we cannot rely on the propagation vector of the laser field. Instead, we can define the laboratory frame using the two orthogonal polarization components of the laser field together with their cross product, necessitating circularly or elliptically polarized fields.

²In the case of a circularly polarized field the angle α is redundant. We omit α in the following.

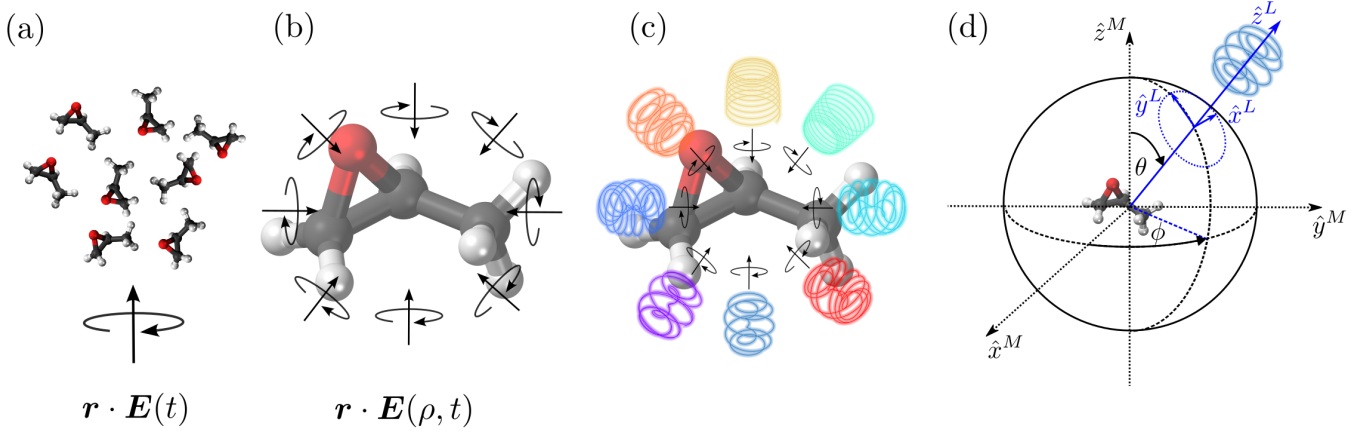


FIG. 1. The idea of temporal geometry. (a) A circularly polarized field $\mathbf{E}(t)$ incident on an ensemble of randomly oriented molecules in the laboratory frame and interacting via the dipole coupling $\mathbf{r} \cdot \mathbf{E}(t)$. In the molecular frame (b), the molecule is fixed, so it is the light $\mathbf{E}(\rho, t)$ that changes its orientation ρ . Depending on the orientation, different chiral electronic currents can be induced. They are represented by glowing curves in (c). (d) The molecular frame is defined by axes: $\hat{x}^M, \hat{y}^M, \hat{z}^M$. The laboratory frame is defined by the polarization plane $\hat{x}^L, \hat{y}^L$ and the light propagation vector $\hat{z}^L$. The polarization plane is tangent to the sphere at the points (θ, ϕ) . The third angle α (not shown) defines the orientation of the polarization ellipse, which is not relevant when considering a monochromatic circularly polarized field. The blue curve represents a chiral three-dimensional shape drawn by the electronic current excited by the laser field with polarization on the plane tangent to the sphere in points (θ, ϕ) .

in the molecular orientation will “transport” the polarization vector along the surface of the sphere, while the electronic wave function describing excited electrons will depend on this transport. At any point on the sphere, the laser field excites a geometrically different *temporally chiral* electronic response, because the orientation of the light polarization vectors as seen by the molecule [Figs. 1(b) and 1(c)], changes from one point on the sphere to another. Is there a global geometric property associated with these chiral currents for different molecular orientations?

We solve the time-dependent Schrödinger equation (TDSE) locally for each orientation characterized by a point $\rho = (\theta, \phi)$ ³ on the sphere of Euler angles in the electric dipole approximation,

$$i \frac{d}{dt} \psi_{\text{el}}^0(\mathbf{r}, \rho, t) = [H_{\text{el}} + \mathbf{r} \cdot \mathbf{E}(\rho, t)] \psi_{\text{el}}^0(\mathbf{r}, \rho, t). \quad (1)$$

We obtain an electronic wave function $\psi_{\text{el}}^0[t, \mathbf{e}(\rho), \mathbf{r}]$,³ which is “agnostic” about other light field orientations. The temporally chiral shapes are generated by the induced polarization $\mathbf{P}(\rho, t) \equiv -\langle \psi_{\text{el}}^0(t, \mathbf{e}(\rho), \mathbf{r}) | \hat{\mathbf{r}} | \psi_{\text{el}}^0(t, \mathbf{e}(\rho), \mathbf{r}) \rangle$ or current $\mathbf{j}(\rho, t) = -\frac{\partial \mathbf{P}}{\partial t}$ vectors. Thus, the question about the connection between the two currents at two different orientations reduces to the question about the connection between two wave functions for two different ρ . Can these “local” solutions be connected in any way? How is the corresponding Berry curvature related to observables, e.g., in the photoionization of randomly oriented molecules?

The comparison between the electron wave function $\psi_{\text{el}}^0[t, \mathbf{e}(\rho), \mathbf{r}]$ describing the temporal geometry of chiral currents excited by the laser field fixed at a given point on the sphere $\rho_0 = (\theta_0, \phi_0)$ with its “global” counterpart $\psi_{\text{el}}[t, \mathbf{e}(\rho), \mathbf{r}]$, “informed” about all different laser geometries,

encapsulates the essence of the “connection” between different local geometries. The TDSE for the electron wavefunction $\psi_{\text{el}}^0[t, \mathbf{e}(\rho_1), \mathbf{r}]$ at some other point ρ_1 on the sphere has the same general form, but the laser field has a different orientation, leading to a different temporally chiral response. The issue arises due to the fact that these two TDSEs are completely independent, and thus each “local” electron wave function $\psi_{\text{el}}^0[t, \mathbf{e}, \mathbf{r}]$ is defined up to an arbitrary phase. Thus, one needs to find a consistent procedure to “connect” all such solutions along a given cyclic path in the configuration space, since only for closed paths the accumulated phase has a well-defined, gauge-invariant meaning. This is achieved by introducing a common phase connecting all local solutions in a well-defined way and encoded in a single, consistent “full” solution $\psi_{\text{el}}(t)$:

$$|\psi_{\text{el}}(t)\rangle = e^{-i\alpha_D(t) + iS(t)} |\psi_{\text{el}}^0(t)\rangle. \quad (2)$$

In general, the phase has a dynamical,

$$\alpha_D(t) = \int_0^t d\tau \langle \psi_{\text{el}}(\tau) | H(\tau) | \psi_{\text{el}}(\tau) \rangle, \quad (3)$$

and a geometric component,

$$S(t) = i \int_0^t d\tau \langle \psi_{\text{el}}^0(\tau) | \frac{\partial}{\partial \tau} | \psi_{\text{el}}^0(\tau) \rangle. \quad (4)$$

Our “local” solution $\psi_{\text{el}}^0(t)$ is known as a *closed lift* of the density matrix $|\psi_{\text{el}}(t)\rangle \langle \psi_{\text{el}}(t)|$ because it shares the periodicity of the Euler angles ρ (see Ref. [21] and Appendix A). The closed-lift construction employed here is naturally described within the Aharonov-Anandan fiber bundle theory, which applies to arbitrary (not necessarily adiabatic) periodic temporal evolutions of pure state density matrices and reduces to the Berry-Simons bundle in the adiabatic, parametric limit; the mathematical distinction is discussed in Appendix H. In Appendix B we show that, in the case of a periodic evolution of the polarization vector $\mathbf{e}(\rho)$, the Berry connection is a vector potential

$$\mathbf{A}(\mathbf{e}) = i \langle \psi_{\text{el}}^0(\mathbf{e}) | \nabla_{\mathbf{e}} \psi_{\text{el}}^0(\mathbf{e}) \rangle, \quad (5)$$

³For simplicity we consider a single active electron problem.

quantifying the change in the local wave function in response to the change in the laser field orientation. It specifies the geometric phase S accumulated after a full evolution cycle of $\mathbf{e}(\rho)$ in the space of Euler angles ρ as detailed in Appendix B:

$$S = \oint i \langle \psi_{\text{el}}^0(\mathbf{e}) | \nabla_{\mathbf{e}} \psi_{\text{el}}^0(\mathbf{e}) \rangle \cdot d\mathbf{e} = \oint \mathbf{A}(\mathbf{e}) \cdot d\mathbf{e}. \quad (6)$$

Equation (5) encapsulates the origin of geometric magnetism, emerging due to the necessity to “connect” the local *temporal geometry* at different points in the configuration space. The gradient with respect to the light polarization vector in Eq. (5) emphasizes the dynamical, laser-driven origin of this geometric quantity.

Due to the complex nature of the polarization vector, the Berry curvature takes the form of a skew-Hermitian rank-2 tensor, whose components can be arranged in matrix form, $\Omega^{ij} = i \langle \partial_{e_i} \psi_{\text{el}}^0(\mathbf{e}) | \partial_{e_j} \psi_{\text{el}}^0(\mathbf{e}) \rangle$. Naturally, it can be partitioned into a real-valued antisymmetric component Ω_a^{ij} and an imaginary-valued symmetric component Ω_s^{ij} . Evaluating the curl of the Berry connection, we obtain the antisymmetric part of the Berry curvature tensor (see companion paper [22]):

$$\mathbf{\Omega} = \nabla_{\mathbf{e}} \times \mathbf{A} = i \langle \nabla_{\mathbf{e}} \psi_{\text{el}}^0(\mathbf{e}) | \times | \nabla_{\mathbf{e}} \psi_{\text{el}}^0(\mathbf{e}) \rangle, \quad (7)$$

written in vector form with components Ω_l such that $\Omega_a^{ij} = \frac{i}{2} \varepsilon^{lij} \Omega_l$. As derived, Eqs. (5) and (7) appear applicable to any light-driven process, as we have so far not made any further assumptions about the wave function. Below, we use Eq. (7) to quantify the ability to control the molecular orientation in two-photon excitation for different configurations of pump- and probe- pulse polarizations. First, we derive the relationship between the antisymmetric Berry curvature [Eq. (7)] and the vectorial observables expressing the light-induced enantiosensitive molecular orientation by ionization of an initially randomly oriented ensemble of molecules, generalizing our earlier result [13], where we introduced the antisymmetric Berry curvature for one-photon ionization from a state with a stationary current. Second, we identify new regimes for observing an enantiosensitive orientation in two-photon ionization, where the selection of the preferred orientation happens at the excitation step, opening new opportunities for controlling the direction of orientation.

Specifically, we show that enantiosensitive molecular orientation can be expressed using Eq. (7) as follows (superscripts L and M stand for laboratory and molecular frames, respectively,⁴ and we consider a driving field polarized in the $x^L y^L$ plane, as shown in Fig. 1):

$$\langle \mathbf{v}_{\Omega}^L \rangle \propto \sigma \langle (\mathbf{\Omega} \cdot \hat{\mathbf{z}}) \mathbf{v}_{\Omega}^L \rangle = \sigma R^{(n,p)} \langle \mathbf{\Omega} \cdot \mathbf{v}_{\Omega} \rangle \hat{\mathbf{z}}^L. \quad (8)$$

Here, $\langle \mathbf{v}_{\Omega}^L \rangle$ is the orientationally averaged value of the unit vector $\mathbf{v}_{\Omega}^L$ in the laboratory frame. This vector is defined such that in the molecular frame it is directed along the Berry curvature ($\mathbf{v}_{\Omega} \parallel \mathbf{\Omega}$). The parameter $\sigma = \pm 1$ is the direction of rotation of the light field, $\langle \mathbf{\Omega} \cdot \mathbf{v}_{\Omega} \rangle$ is the orientationally averaged value of the scalar product $\mathbf{\Omega} \cdot \mathbf{v}_{\Omega}$, and $R^{(n,p)}$ is a

factor associated with the partial alignment of the molecular ensemble due to excitation or ionization, which depends on the number of absorbed photons n . The superscript p in $R^{(n,p)}$ indicates that it also depends on the polarizations of the absorbed photons, which may or may not break the cylindrical symmetry of the setup. We establish the molecular alignment factor $R^{(n,p)}$ (see Ref. [13]) by explicitly evaluating $\langle (\mathbf{\Omega} \cdot \hat{\mathbf{z}}) \mathbf{v}_{\Omega} \rangle$ and $\langle \mathbf{\Omega} \cdot \mathbf{v}_{\Omega} \rangle$ using Eq. (7). Importantly, the factor $R^{(n,p)}$ does not affect the direction of enantiosensitive orientation unless the excitation step strongly breaks the isotropy of the initial molecular ensemble: in this work we only capture isotropic effects. In this case, Eq. (8) shows that (1) the vector $\langle \mathbf{v}_{\Omega}^L \rangle$ orients itself along the direction of photon spin $\hat{\mathbf{z}}^L$, and that (2) the antisymmetric Berry curvature controls the direction and the degree of molecular orientation. Intuitively, the antisymmetric Berry curvature $\mathbf{\Omega}$ sets the local axis of electronic phase winding of the polarization current: the induced current loops around $\mathbf{\Omega}$. For circularly polarized light, the electric field vector rotates about the photon-spin direction $\hat{\mathbf{z}}^L$. When $\mathbf{\Omega}$ is aligned with this axis, light and intrinsic electronic motion corotate; by the usual propensity rules, corotation enhances excitation and ionization, while counter-rotation suppresses it. This preference is precisely what Eq. (8) captures. We use Eqs. (7) and (8) to evaluate the direction of enantiosensitive molecular orientation for a range of two-photon processes and compare the resulting expressions with the direct evaluation, where the antisymmetric Berry curvature is not employed. We show that the results are equivalent. Our approach not only allows us to express enantiosensitive molecular orientation in a compact way [Eq. (8)] but also uncovers its fundamental origin, appearing to be invariant for different multiphoton processes.

III. TEMPORAL GEOMETRY IN TWO-PHOTON IONIZATION

In this section, we analyze a two-photon process in which a linearly polarized pulse excites a superposition of states in a molecule and a circularly polarized pulse photoionizes this superposition [see Fig. 2(a)]. As the center of our geometrical analysis we calculate the antisymmetric Berry curvature Eq. (7). Since only spin-carrying light fields induce a temporal geometry, the linearly polarized, exciting pulse does not contribute to the Berry curvature. Thus, the curvature corresponding to this process exclusively reflects continuum state dynamics. Further, we discuss how the Berry curvature allows to infer a measure of molecular orientation.

We use perturbation theory to calculate $|\psi(\mathbf{e})\rangle$ explicitly:

$$|\psi\rangle = |\psi_0\rangle + a_1 |\psi_1\rangle + a_2 |\psi_2\rangle + \int d\theta_k a_k |\psi_k\rangle. \quad (9)$$

Here, $d\theta_k = \sin \theta_k d\theta_k d\phi_k$ and θ_k, ϕ_k are angles characterizing the direction of the photoelectron momentum $\mathbf{k}$ for fixed $k = |\mathbf{k}|$, while a_i and a_k are the amplitudes of bound ($i = 1, 2$) and continuum states:

$$a_i = i \int_0^t dt' \mathbf{d}_i \cdot \mathbf{E}_i(t') e^{i\omega_i t'} = i \mathbf{d}_i \cdot \mathbf{E}_i, \quad (10)$$

$$a_k = -(\mathbf{D}_1 \cdot \mathbf{E}_{k1})(\mathbf{d}_1 \cdot \mathbf{E}_1) e^{-i\omega_1 \tau} - (\mathbf{D}_2 \cdot \mathbf{E}_{k2})(\mathbf{d}_2 \cdot \mathbf{E}_2) e^{-i\omega_2 \tau}. \quad (11)$$

⁴Here and in the following we omit the indices M and L in scalar products, since these are rotationally invariant and can be associated with either frame.

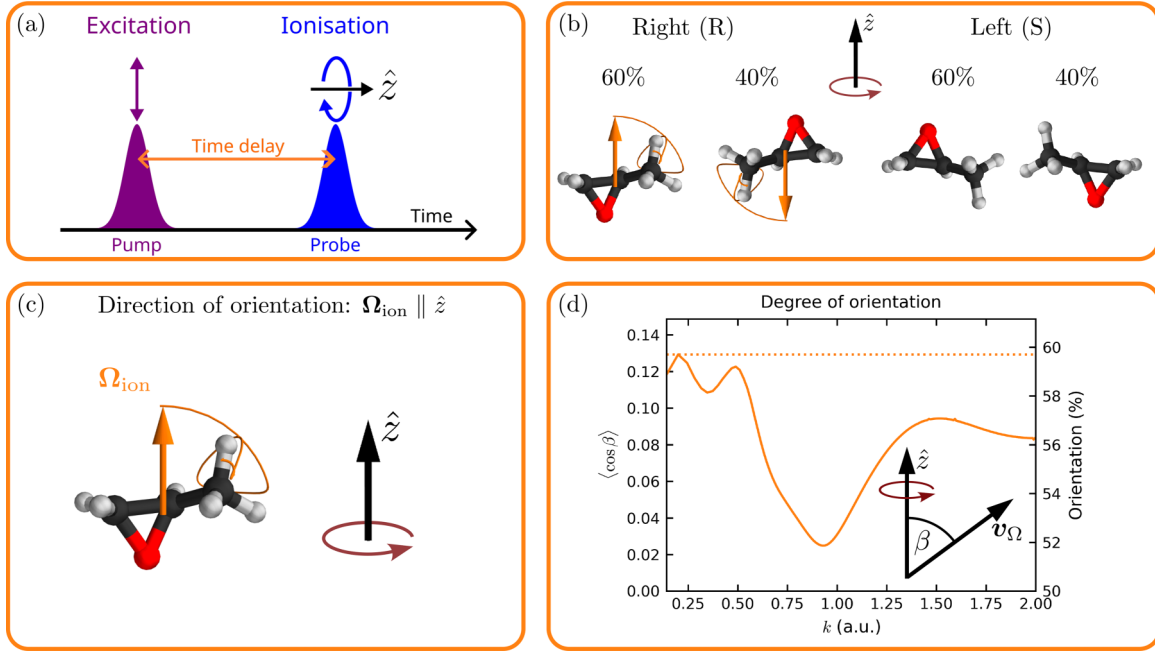


FIG. 2. Enantiosensitive molecular orientation by photoionization. (a) A linearly polarized pump pulse excites the superposition of lowest unoccupied molecular orbital (LUMO) and LUMO+1 states in propylene oxide, and then a circularly polarized probe ($\hat{z}$ is the direction of photon spin in the laboratory frame) removes the excited electron. (b) Molecules with the Berry curvature $\Omega_{\text{ion}} \parallel \hat{z}$ are preferentially ionized, leading to an enantiosensitive delay-dependent orientation of cations. Ω_{ion} depends on the excited superposition and photoelectron energy. As a function of photoelectron energy, the tip of the Berry curvature vector traces the orange curve in space. This orange curve illustrates the sequence of orientations achieved for different final photoelectron momenta, from 0.25 to 2 a.u. Estimated percentages of “up”- and “down”-oriented species correspond to the maximal value of $\langle \cos \beta \rangle \simeq 0.11$ and are obtained using the same model as in Ref. [13]. (c) The direction of molecular orientation is defined by the Berry curvature vector. (d) Expectation value $\langle \cos \beta \rangle$ as a function of photoelectron momentum k (in atomic units) for the R enantiomer. The values have been taken at the time delay that maximizes $\langle v_{\Omega}^L \rangle$ and have been normalized to the total yield averaged over the pump-probe time delay.

Here, $\mathbf{d}_i$ denote the bound-bound transition dipoles from the ground state to bound states ($i = 1, 2$), and $\mathbf{D}_i$ are photoionization dipoles from bound states to the continuum state $\mathbf{k}$. The quantity $\mathcal{E}_i(t')$ is the time-dependent electric field, while $\mathcal{E}_i$ and $\mathbf{E}_{k_i}$ are its Fourier components at the corresponding transition frequencies for linear and circular polarized light, respectively. The only relevant (for isotropic signal, i.e., independent on the third Euler angle α) component of the antisymmetric Berry curvature is the one in the space of circular polarization vectors $\mathbf{e}$ [22]. Writing $\mathbf{E}_{k_i} = |E_{\omega_{k_i}}| \mathbf{e}$, with $\mathbf{e} = \frac{1}{\sqrt{2}}(\hat{x} + i\sigma\hat{y})$ spanning the parameter space, the Berry curvature [Eq. (7)] in the molecular frame can be expressed as

$$\Omega_{\text{ion}}^M(k, \rho) = -|E_{\omega_{k_1}}||E_{\omega_{k_2}}|\text{Im}\left\{(d_1 \cdot \mathcal{E}_1)^*(d_2 \cdot \mathcal{E}_2)e^{i\omega_{12}\tau}\right. \\ \left. \times \int d\Theta_k \mathbf{D}_1^{*M} \times \mathbf{D}_2^M\right\}, \quad (12)$$

where the subscript “ion” emphasizes that the Berry curvature $\Omega_{\text{ion}}^M(k, \rho)$ relies on the properties of continuum states contributing to photoionization dipoles and thus manifests itself due to geometry of continuum currents during photoionization. The direction of the Berry curvature in the molecular frame is defined by the direction of the vector $\mathbf{P}_{12}^{+M}(k)$, where $\mathbf{P}_{12}^{+M}(k) \equiv \frac{1}{2}\text{Im}\{i \int d\Theta_k \mathbf{D}_1^{*M} \times \mathbf{D}_2^M\}$, and the superscript “+” indicates that only the $\mathbf{k}$ -even part of the vector product contributes to the integrated quantity (see also Ref. [13]).

We now introduce the polar unit vector $\mathbf{v}_{\Omega}^M$ along the direction of the Berry curvature $\Omega_{\text{ion}}^M(k, \rho)$ [i.e., along $\mathbf{P}_{12}^{+M}(k)$] and obtain the averaged value of $\langle \Omega_{\text{ion}} \cdot \mathbf{v}_{\Omega} \rangle$ (see Appendix E):

$$\langle \Omega_{\text{ion}}(k) \cdot \mathbf{v}_{\Omega} \rangle = -\frac{1}{3}C(d_1 \cdot d_2)(\mathbf{P}_{12}^{+}(k) \cdot \mathbf{v}_{\Omega}) \sin(\omega_{12}\tau) \\ = -\frac{1}{3}vC(d_1 \cdot d_2)|\mathbf{P}_{12}^{+}(k)| \sin(\omega_{12}\tau), \quad (13)$$

where $C \equiv |E_{\omega_{k_1}}||\mathcal{E}_{\omega_1}||E_{\omega_{k_2}}||\mathcal{E}_{\omega_2}|$. Note that $\mathbf{P}_{12}^{+}(k) \cdot \mathbf{v}_{\Omega} = v|\mathbf{P}_{12}^{+}(k)|$, where $v = \pm 1$ is a pseudoscalar characterizing the molecular handedness.

The enantiosensitive molecular orientation by ionization (PI-MOCD) for the linear pump–circular probe excitation is associated with the preferential photoionization of the molecules with the Berry curvature oriented along the photon spin, as shown in Fig. 2(b). This ‘preferential ionization’ can be made explicit by rewriting the dichroic contribution to the photoionization yield in terms of the Berry curvature (Appendix F). Using Eq. (8) together with Eq. (12) we can calculate (see Appendix E) the orientation-averaged value of $\langle v_{\Omega}^L \rangle$:

$$\langle v_{\Omega}^L \rangle^{\dagger, \odot} = N\sigma \langle (\Omega_{\text{ion}} \cdot \hat{z}) v_{\Omega}^L \rangle = N\sigma R^{(2, \dagger, \odot)} \langle \Omega_{\text{ion}} \cdot \mathbf{v}_{\Omega} \rangle \hat{z}^L. \quad (14)$$

Here, N is a normalization factor, $N^{-1} = (2\pi)^{-1} \int_0^{2\pi} d\phi_{\tau} \int d\rho W^{\dagger, \odot}(\rho)$, where $W^{\dagger, \odot}(\rho)$ is photoionization rate for a given molecular orientation ρ , $(2\pi)^{-1} \int_0^{2\pi} d\phi_{\tau}$ describes the averaging over delay τ between the pump and probe pulses. The factor $R^{(2, \dagger, \odot)}$ quantifies

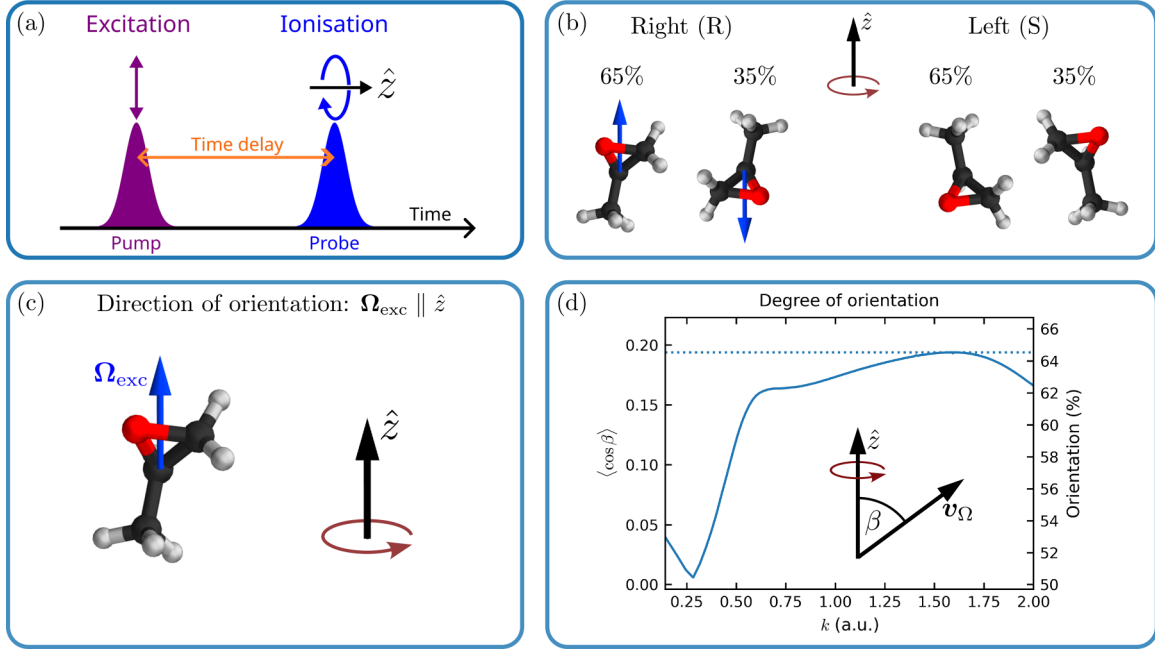


FIG. 3. Enantiosensitive molecular orientation by excitation probed via photoionization. (a) A circularly polarized pulse ($\hat{z}$ is the direction of photon spin in the laboratory frame) excites a superposition of LUMO and LUMO+1 states in propylene oxide. (b) Molecules with $\Omega_{\text{exc}} \parallel \hat{z}$ are excited preferentially. A linearly polarized probe removes the excited electron, leading to enantiosensitive delay-dependent orientation of cations. Estimated percentages of “up”- and “down”-oriented species correspond to the maximal value of $\langle \cos \beta \rangle \simeq 0.19$ and are obtained using the same model as in Ref. [13]. (c) The direction of the molecular orientation is defined by the Berry curvature vector. (d) Expectation value $\langle \cos \beta \rangle$ as a function of the photoelectron momentum k (in atomic units). The values have been taken at the time delay that maximizes $\langle v_{\Omega}^L \rangle$ and have been normalized to the total yield averaged over the pump-probe time delay.

molecular alignment,

$$R^{(2,\uparrow,\odot)} \equiv \frac{2}{5} \left[1 - \frac{1}{2} \frac{(\mathbf{d}_1 \cdot \mathbf{v}_{\Omega})(\mathbf{d}_2 \cdot \mathbf{v}_{\Omega})}{(\mathbf{d}_1 \cdot \mathbf{d}_2)} \right]. \quad (15)$$

Up to notation, Eq. (14) reproduces our earlier result for PI-MOCD [13], validating the general approach [i.e., calculating $\langle v_{\Omega}^L \rangle$ using Eqs. (7) and (8) developed here]. For completeness, we also provide the result calculated without employing the concept of the antisymmetric Berry curvature, i.e., only using the definition of the oriented vector $\langle v_{\Omega}^L \rangle^{\uparrow,\odot} = N \int d\rho W^{\uparrow,\odot}(\rho) v_{\Omega}^L$:

$$\langle v_{\Omega}^L \rangle^{\uparrow,\odot} = \frac{i\sigma}{60} NC \int d\Omega_k [4(\mathbf{d}_2 \cdot \mathbf{d}_1) \mathbf{v}_{\Omega} - (\mathbf{d}_2 \cdot \mathbf{v}_{\Omega}) \mathbf{d}_1 - (\mathbf{d}_1 \cdot \mathbf{v}_{\Omega}) \mathbf{d}_2] \cdot (\mathbf{D}_2^* \times \mathbf{D}_1) e^{i\omega_{21}\tau} \hat{z} + \text{c.c.} \quad (16)$$

Note that the first term in the expression for $R^{(2,\uparrow,\odot)}$ corresponds to the contribution to the signal from the isotropic ensemble and the second term corresponds to the contribution emerging due to the alignment of the molecular ensemble by the linearly polarized field. As long as $(\mathbf{d}_1 \cdot \mathbf{d}_2) \neq 0$, the isotropic term dominates and the orientation is controlled by the antisymmetric Berry curvature. The effect is maximized when $\mathbf{d}_1 \parallel \mathbf{d}_2$. If $(\mathbf{d}_1 \cdot \mathbf{d}_2) = 0$, the isotropic contribution vanishes and the direction of enantiosensitive orientation is controlled by vectors $\mathbf{d}_1$ and $\mathbf{d}_2$, as it is clear from the last two terms in Eq. (16).

The vector $\langle v_{\Omega}^L \rangle$ can be used to find the expectation value of $\cos \beta$, where β is the angle between the unit vector along the Berry curvature $\mathbf{v}_{\Omega}^L$ and the direction of photon spin. The curve in Fig. 2(c) shows the orientation of the Berry curvature as a

function of photoelectron momentum. The value of $\langle \cos \beta \rangle$ as a function of photoelectron momentum [see Fig. 2(d)] is given by the normalized (to the total photoionization yield averaged over the pump-probe delay) magnitude of $\langle v_{\Omega}^L \rangle$.

IV. TEMPORAL GEOMETRY IN PHOTOEXCITATION

In this section, we analyze a photoexcitation induced by a circular pump-, and followed by a circular, photoionizing probe pulse. In this setting, the Berry curvature can be associated with the excitation of the bound states, in contrast to the previous discussion of the curvature corresponding to photoionization. Importantly, the general definition Eq. (7) describes both cases, even though the specific expressions are different. This surprising result demonstrates the importance of the laser pulse polarization geometry: applying a circularly polarized pulse either to photoionize or to excite the molecule, one can address these two different facets of the Berry curvature.

Let a circularly polarized pump pulse excite a superposition of states in a chiral molecule. We now show that the subsequent photoionization by a linearly polarized probe pulse will lead to enantiosensitive orientation of ions (PI-MOCD). The pump-probe scheme is shown in Fig. 3(a). Exchanging $\mathbf{E}_{ki}$ and $\mathbf{E}_i$ in Eq. (11), using Eq. (7) and following the same steps as in the previous section, we obtain the analog of Eq. (12):

$$\Omega_{\text{exc}}^M(k, \rho) = -|E_{\omega_1}| |E_{\omega_2}| \text{Im} \left\{ \int d\Theta_k (\mathbf{D}_1 \cdot \mathbf{E}_{k1})^* \times (\mathbf{D}_2 \cdot \mathbf{E}_{k2}) e^{i\omega_{12}\tau} \right\} (\mathbf{d}_1^M \times \mathbf{d}_2^M). \quad (17)$$

Here, the subscript “exc” emphasizes the nature of the Berry curvature, which now relies on excitations in bound states.

The orientationally averaged expression for the scalar product $\mathbf{\Omega} \cdot \mathbf{v}_\Omega$, where $\mathbf{v}_\Omega$ is oriented along the direction of $(\mathbf{d}_1 \times \mathbf{d}_2)$ in the molecular frame, can be derived in the same way as in the previous section:

$$\begin{aligned} & \langle \mathbf{\Omega}_{\text{exc}}(k) \cdot \mathbf{v}_\Omega \rangle \\ &= -\frac{1}{3} C \text{Re} \left\{ \int d\Theta_k \mathbf{D}_1^* \cdot \mathbf{D}_2 \right\} (\mathbf{d}_1 \times \mathbf{d}_2) \cdot \mathbf{v}_\Omega \sin(\omega_{12}\tau), \end{aligned} \quad (18)$$

where $C \equiv |\mathcal{E}_{\omega_{k1}}| |E_{\omega_1}| |\mathcal{E}_{\omega_{k2}}| |E_{\omega_2}|$. Moreover, we took into account that for the excited states ψ_1 and ψ_2 , time-reversal symmetry implies that (see Appendix C):

$$\text{Im} \left\{ \int d\Theta_k \mathbf{D}_1^* \cdot \mathbf{D}_2 \right\} = 0. \quad (19)$$

Using Eq. (8) together with Eq. (17), we can calculate (see Appendix E) the orientation-averaged value of

$$\langle \mathbf{v}_\Omega^L \rangle^{\odot, \dagger} = N \sigma \langle (\mathbf{\Omega}_{\text{exc}}^L \cdot \hat{\mathbf{z}}^L) \mathbf{v}_\Omega^L \rangle = N \sigma R^{(2, \odot, \dagger)} \langle \mathbf{\Omega}_{\text{exc}} \cdot \mathbf{v}_\Omega \rangle \hat{\mathbf{z}}^L, \quad (20)$$

where $N^{-1} = \int_0^{2\pi} d\phi_\tau (2\pi)^{-1} \int d\rho W^{\odot, \dagger}(\rho, \tau)$ is a normalization factor, $(2\pi)^{-1} \int_0^{2\pi} d\phi_\tau$ is the averaging over a cycle of the pump-probe delay, $W^{\odot, \dagger}(\rho, \tau)$ is the ionization rate for a given orientation ρ , and

$$R^{(2, \odot, \dagger)} \equiv \frac{2}{5} \left[1 - \frac{1}{2} \frac{\text{Re} \{ \int d\Theta_k (\mathbf{D}_1^* \cdot \mathbf{v}_\Omega) (\mathbf{D}_2 \cdot \mathbf{v}_\Omega) \}}{\text{Re} \{ \int d\Theta_k (\mathbf{D}_1^* \cdot \mathbf{D}_2) \}} \right]. \quad (21)$$

Evaluating it explicitly gives

$$\langle \mathbf{v}_\Omega^L \rangle^{\odot, \dagger} = N \int d\rho W^{\odot, \dagger}(k, \rho) \mathbf{v}_\Omega^L, \quad (22)$$

and we get the expression equivalent to Eq. (20), up to rearrangement of terms:

$$\begin{aligned} \langle \mathbf{v}_\Omega^L \rangle^{\odot, \dagger} &= \frac{i\sigma}{60} C N \int d\Theta_k [4(\mathbf{D}_2^* \cdot \mathbf{D}_1) \mathbf{v}_\Omega^M \\ &\quad - (\mathbf{D}_2^* \cdot \mathbf{v}_\Omega) \mathbf{D}_1^M - (\mathbf{D}_1 \cdot \mathbf{v}_\Omega) \mathbf{D}_2^{*M}] (\mathbf{d}_2^M \times \mathbf{d}_1^M) \\ &\quad \times e^{i\omega_{21}\tau} \hat{\mathbf{z}} + \text{c.c.} \end{aligned} \quad (23)$$

Equation (20) together with Eq. (18) show that PI-MOCD can also emerge due to the Berry curvature in bound states: molecules, in which the Berry curvature is oriented along the photon spin are preferentially excited [see Figs. 3(b) and 3(c)].

Thus, photoionization following photoexcitation creates enantiosensitive orientation of both neutrals and cations. The expectation value of $\cos \beta$ is shown in Fig. 3(d), where β is the angle between the unit vector along the Berry curvature $\mathbf{v}_\Omega^L$ and the direction of photon spin is given by the normalized (to the total photoionization yield averaged over the pump-probe

delay) magnitude of $\langle \mathbf{v}_\Omega^L \rangle$. The antisymmetric Berry curvature describes the orientation of cations in the dominant isotropic case. In the rare cases when the first, isotropic, term in Eq. (23) vanishes, the latter two terms originating from the alignment of the molecular ensemble define the direction of the enantiosensitive orientation.

V. INTERPLAY OF BOUND AND CONTINUUM TEMPORAL GEOMETRIES

In the previous two sections, we considered photoexcitation followed by photoionization induced by pairs of pump-probe pulses with linear-circular or circular-linear polarizations, correspondingly. In the first case, the Berry curvature emerged due to the temporal geometry in photoelectron continuum states. In the second case, it emerged due to the temporal geometry in bound states. What happens if both the pump and the probe pulses are circularly polarized [see Fig. 4(a)]?

To answer this question, we need to apply Eqs. (7) to Eqs. (9)–(11), where the Fourier components of the linearly polarized fields $\mathcal{E}_2$ and $\mathcal{E}_1$ are substituted by the Fourier components of circularly polarized fields: $\mathcal{E}_2 \rightarrow \mathbf{E}_2$ and $\mathcal{E}_1 \rightarrow \mathbf{E}_1$. Here, we have to evaluate the gradients in Eq. (7) with respect to both the pump field components and the probe field components. It leads to the following expression for the Berry curvature (see Appendix G):

$$\mathbf{\Omega}^M(k, \rho) = \mathbf{\Omega}_{\text{exc}}^M(k, \rho) + \mathbf{\Omega}_{\text{ion}}^M(k, \rho) + \mathbf{\Omega}_{\text{mix}}^M(k, \rho), \quad (24)$$

where

$$\begin{aligned} \mathbf{\Omega}_{\text{exc}}^M(k, \rho) &= -2C \text{Im} \left\{ \int d\Theta_k (\mathbf{D}_1 \cdot \mathbf{e})^* (\mathbf{D}_2 \cdot \mathbf{e}) \right. \\ &\quad \times e^{i\omega_{12}\tau} \left. \right\} (\mathbf{d}_1^M \mathbf{d}_2^M), \end{aligned} \quad (25)$$

$$\begin{aligned} \mathbf{\Omega}_{\text{ion}}^M(k, \rho) &= -2C \text{Im} \left\{ (\mathbf{d}_1 \cdot \mathbf{e})^* (\mathbf{d}_2 \cdot \mathbf{e}) e^{i\omega_{12}\tau} \right. \\ &\quad \times \left. \int d\Theta_k \mathbf{D}_1^{*M} \times \mathbf{D}_2^M \right\}. \end{aligned} \quad (26)$$

$$\begin{aligned} \mathbf{\Omega}_{\text{mix}}^M(k, \rho) &= -2C \text{Im} \left\{ \int d\Theta_k (\mathbf{d}_1 \cdot \mathbf{e}) (\mathbf{D}_2 \cdot \mathbf{e})^* (\mathbf{D}_1^{*M} \times \mathbf{d}_2^M) e^{i\omega_{12}\tau} \right\} \\ &\quad - 2C \text{Im} \left\{ \int d\Theta_k (\mathbf{D}_1 \cdot \mathbf{e})^* (\mathbf{d}_2 \cdot \mathbf{e}) (\mathbf{d}_1^M \times \mathbf{D}_2^M) e^{i\omega_{12}\tau} \right\}. \end{aligned} \quad (27)$$

Here, $C \equiv |E_{\omega_{k1}}| |E_{\omega_1}| |E_{\omega_{k2}}| |E_{\omega_2}|$. Equation (24) combines bound and continuum Berry curvatures as detailed in Eqs. (12) and (17), and also contains “mixed” terms, relying on both bound and continuum Berry curvatures.

The orientationally averaged scalar product of the Berry curvatures and a unit vector $\mathbf{v}_\Omega$ are

$$\langle \mathbf{\Omega}_{\text{exc}}(k, \rho) \cdot \mathbf{v}_\Omega \rangle = -\frac{1}{3} C \text{Re} \left\{ \int d\Theta_k (\mathbf{D}_1^* \cdot \mathbf{D}_2) \right\} (\mathbf{d}_1 \times \mathbf{d}_2) \cdot \mathbf{v}_\Omega \sin(\omega_{12}\tau), \quad (28)$$

$$\langle \mathbf{\Omega}_{\text{ion}}(k, \rho) \cdot \mathbf{v}_\Omega \rangle = -\frac{1}{3} C (\mathbf{d}_1 \cdot \mathbf{d}_2) \mathbf{P}_{12}^+(k) \cdot \mathbf{v}_\Omega \sin(\omega_{12}\tau). \quad (29)$$

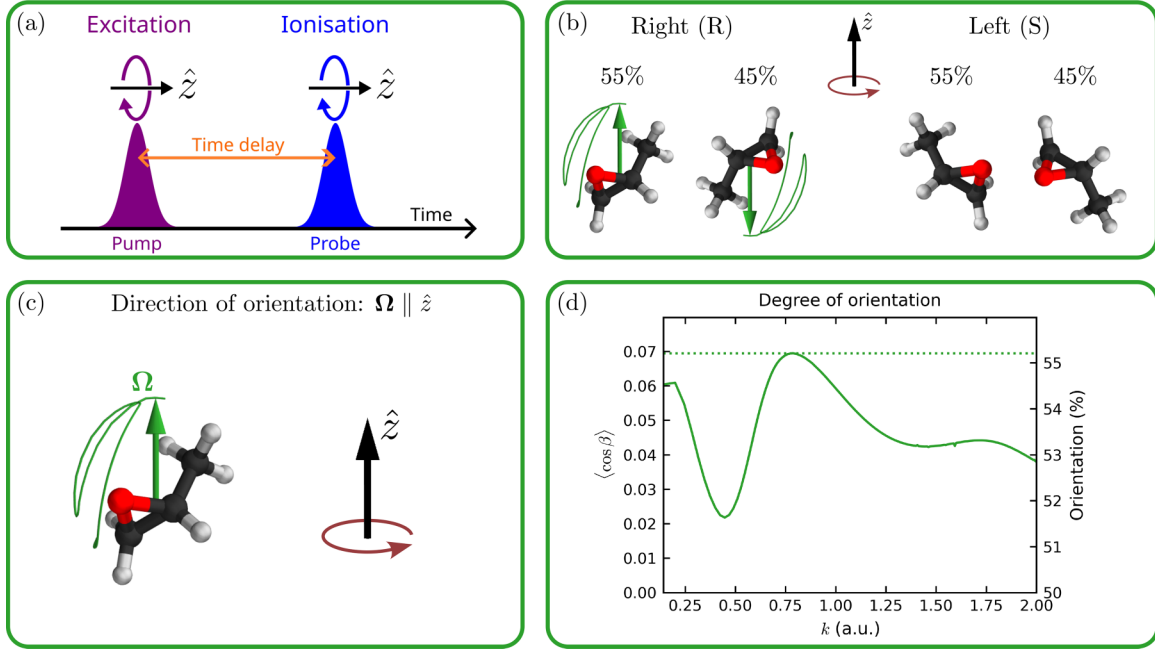


FIG. 4. Enantiosensitive molecular orientation by excitation probed via photoionization. (a) A circularly polarized pulse ($\hat{z}$ is the direction of photon spin in the laboratory frame) excites a superposition of LUMO and LUMO+1 states in propylene oxide. (b) A circularly polarized probe removes the excited electron, leading to enantiosensitive delay-dependent orientation of cations. Molecules with $\Omega \parallel \hat{z}$ are excited and ionized preferentially. The green curve represents the trajectory traced by the tip of the Berry curvature vector in space as a function of photoelectron energy, from 0.25 to 2 a.u. It shows how different photoelectron momenta lead to different orientation of the cation. Estimated percentages of “up”- and “down”-oriented species correspond to the maximal value of $\langle \cos \beta \rangle \simeq 0.07$ and are obtained using the same model as in Ref. [13]. (c) Direction of molecular orientation is defined by the Berry curvature vector. (d) Expectation value $\langle \cos \beta \rangle$ as a function of the photoelectron momentum k (in atomic units). The values have been taken at the time delay that maximizes $\langle v_{\Omega}^L \rangle$ and have been normalized to the total yield averaged over the pump-probe time delay.

$$\begin{aligned} \langle \Omega_{\text{mix}}(k, \rho) \cdot v_{\Omega} \rangle = & -\frac{1}{3} C \text{Im} \left\{ \int d\Theta_k (d_1 \cdot D_2^*) (D_1^* \times d_2) \cdot v_{\Omega} e^{i\omega_{12}\tau} \right\} \\ & - \frac{1}{3} C \text{Im} \left\{ \int d\Theta_k (D_1^* \cdot d_2) (d_1 \times D_2) \cdot v_{\Omega} e^{i\omega_{12}\tau} \right\}. \end{aligned} \quad (30)$$

Evaluating $\langle v_{\Omega}^L \rangle^{\odot}$ explicitly without involving the Berry curvature yields

$$\begin{aligned} \langle v_{\Omega}^L \rangle^{\odot} = & \frac{i\sigma}{30} C N \int d\Theta_k \{ (d_2 \cdot d_1) [v_{\Omega} \cdot (D_2^* \times D_1)] + (D_2^* \cdot D_1) [v_{\Omega} \cdot (d_2 \times d_1)] \\ & + (d_2 \cdot D_1) [v_{\Omega} \cdot (D_2^* \times d_1)] + (D_2^* \cdot d_1) [v_{\Omega} \cdot (d_2 \times D_1)] \} e^{i\omega_{21}\tau} \hat{z} + \text{c.c.} \end{aligned} \quad (31)$$

Comparing it to

$$\langle v_{\Omega}^L \rangle^{\odot, \odot} = N \sigma \langle (\Omega^L \cdot \hat{z}^L) v_{\Omega}^L \rangle = N \sigma R^{(2, \odot, \odot)} \langle \Omega \cdot v_{\Omega} \rangle \hat{z}^L, \quad (32)$$

where Ω is defined by Eq. (24), we find that the factor $R^{(2, \odot, \odot)} = \frac{1}{10}$ is purely numerical due to preserved cylindrical symmetry. In summary, when both pump and probe are circularly polarized, the enantiosensitive orientation is governed by the vector sum of the three Berry curvatures—bound, continuum, and mixed—appearing in Eqs. (24–27). Molecules for which the net curvature Ω is aligned with the photon spin are excited and ionized preferentially [Fig. 4(b)]. The direction of this orientation is set by the net Berry-curvature vector, which traces a curve as a function of photoelectron momentum [Fig. 4(c)], while the expectation value $\langle \cos \beta \rangle$ quantifies its angle to the photon spin [Fig. 4(d)].

VI. OPPORTUNITIES FOR CONTROL OF GEOMETRIC OBSERVABLES

Photoionization molecular orientation circular dichroism (PI-MOCD) is the first geometric observable that is directly proportional to the antisymmetric Berry curvature, relying on the geometry of either bound or continuum states. Importantly, the antisymmetric Berry curvature is a dynamical property, as it relies on the excitation of currents and reflects their temporal geometry. The studied dynamics offer several opportunities for control. We showed that the direction of enantiosensitive molecular orientation is defined by the direction of the antisymmetric Berry curvature vector in the molecular frame. The Berry curvature vectors relying on the vector product of bound or continuum dipoles naturally have different directions: $\Omega_{\text{exc}} \parallel d_1 \times d_2$ and $\Omega_{\text{ion}} \parallel$

$\text{Re}\{\int d\Theta_k \mathbf{D}_1^* \times \mathbf{D}_2\}$. Moreover, both orientations are state specific [see Figs. 2 and 3(b) for propylene oxide], which presents several opportunities for controlling the enantiosensitive direction of molecular orientation.

First, by changing the frequency of the pump pulse, one can address different bound states and thus control both the magnitude and direction of the Berry curvature. Second, controlling the polarization of the pump-probe pulse sequence also allows us to control the magnitude and the direction of the enantiosensitive molecular orientation by switching the Berry curvature between its form defined by the geometry of the excited bound states to the one defined by the geometry of the continuum states. Figures 2 and 3 illustrate how the direction of the Berry curvature and respective molecular orientation changes if one switches polarizations of pump and probe pulses from circular (linear) to linear (circular). Third, by changing the frequency of the probe pulse in the case of linear-circular pulse sequence, one can change the direction of the Berry curvature as shown in Fig. 2(b).

For a given set of intermediate bound states excited by a pump pulse and continuum states populated by the probe pulse, the magnitudes of Ω_{ion} and Ω_{exc} differ only in their dipole factors. The bound transition dipole contributions to the magnitudes of Ω_{ion} and Ω_{exc} are $\mathbf{d}_1 \cdot \mathbf{d}_2 = -7.3 \times 10^{-2}$ a.u. and $|\mathbf{d}_1 \times \mathbf{d}_2| = 4.9 \times 10^{-2}$ a.u., respectively. The continuum dipole contributions $\text{Re}\{\int d\Theta_k \mathbf{D}_1^* \cdot \mathbf{D}_2\}$ and $|\text{Re}\{\int d\Theta_k \mathbf{D}_1^* \times \mathbf{D}_2\}|$ change as a function of the photoelectron energy and are shown in Fig. 5. These two parameters determine the k dependence of the expectation value of the degree of orientation in Figs. 2 and 3(c).

VII. CONCLUSION AND OUTLOOK

We introduce the notion of *temporal geometry* for ultrafast electronic dynamics in chiral molecules, identify the Berry connection and the (antisymmetric) Berry curvature as the operative quantities, and show that PI-MOCD is a direct, experimentally accessible probe of this curvature. We derive expressions for the antisymmetric Berry curvature and disentangle continuum, bound, and mixed curvature contributions across three pump-probe scenarios: linear-circular, circular-linear, and circular-circular. This establishes a unified geometric language for fragment- and photoelectron-based observables and connects enantiosensitive orientation directly to ultrafast current dynamics.

Geometric magnetism in chiral molecules appears to be a ubiquitous phenomenon, which can be controlled by tailoring light pulses and by addressing various molecular states. The linear-circular and circular-linear pump-probe sequences have been used experimentally to observe time-resolved photoelectron circular dichroism (TR-PECD) [23,24] and photoexcitation circular dichroism (PXCD) [7] in chiral molecules via detection of angular distribution of photoelectrons. We show that in both cases, detection of molecular fragments would lead to a complementary geometric observable, directly proportional to the antisymmetric Berry curvature related to currents in continuum or bound states.

Our results show that the temporal evolution of angular distribution of fragments [Eqs. (18) and 20)] and the angular distribution of photoelectrons produced after inducing

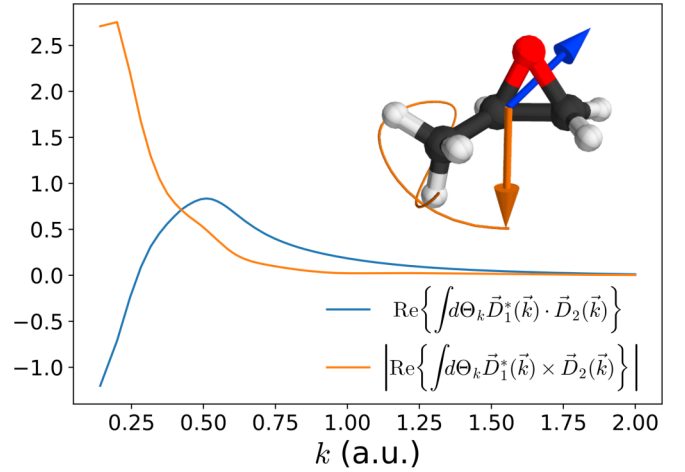


FIG. 5. Photoelectron momentum dependent terms $\text{Re}\{\int d\Theta_k \mathbf{D}_1^* \cdot \mathbf{D}_2\}$ and $|\text{Re}\{\int d\Theta_k \mathbf{D}_1^* \times \mathbf{D}_2\}|$, controlling the PI-MOCD in the case of circular-linear pulse sequence (blue) and linear-circular pulse sequence (orange). The inset shows the molecule together with the molecular axis getting oriented in each case; $\mathbf{d}_1 \times \mathbf{d}_2$ in the circular-linear case (blue arrow) and $\text{Re}\{\int d\Theta_k \mathbf{D}_1^* \times \mathbf{D}_2\}$ in the linear-circular case (orange arrow). The latter changes as a function of photoelectron momentum k and is shown for $k=0.2$ a.u. As k increases, the tip of the orange arrow traces the orange curve.

the photoexcitation circular dichroism (circular-linear pump-probe sequence) [7] and controlled by the term $\int d\Theta_k \mathbf{k}(\mathbf{D}_1^* \cdot \mathbf{D}_2)$ have fundamentally different properties.

The former is proportional to the current in the bound states $\propto \sin(\omega_{12}\tau)$ and thus vanishes at zero pump-probe delay $\tau = 0$, while the latter also includes terms $\propto \cos(\omega_{12}\tau)$ and does not vanish at $\tau = 0$. This property establishes PI-MOCD as a direct probe of charge-directed reactivity: PI-MOCD is proportional to the Berry curvature (either in bound or in continuum states) and as such relies on time-reversal symmetry breaking, which can be introduced by exciting a current prior to photoionization [13]. The direction of the current at the moment of ionization defines the orientation of molecular cations and therefore the direction of molecular fragmentation, highlighting the ability of the ultrafast electron dynamics to control subsequent dynamics of the nuclei. Simulations [24] show that enantiosensitive fragment asymmetry resulting from excitation of the electronic wave packet in Rydberg states in methyl lactate molecule in linear-circular polarization sequence reaches 20%, confirming strong enantiosensitivity of the Berry curvature-driven geometric observables.

The control over the directions of enantiosensitive orientations of molecular ions suggests new opportunities. For example, in the linear-circular sequence of the pulses the tip of the Berry curvature vector traces the orange curve in space [Fig. 2(c)] as a function of photoelectron energy. This orange curve illustrates the sequence of orientations of the Berry curvature vector achieved for different final photoelectron momenta from 0.25 to 2 a.u. Since enantiosensitive molecular orientation follows the orientation of the Berry curvature vector, polarization-controlled pulses at free electron lasers (FELs), such as chirped circularly polarized pulses, can be

used to force molecular ions to draw the trajectory shown in Fig. 2(c) in a single experiment. Alternatively, a set of experiments where the frequency of the circularly polarized probe light is varied by several tens of electron volts would produce a variety of well-controlled molecular orientations.

In summary, we have shown that enantiosensitive observables in ultrafast chiral dynamics are inherently linked to the antisymmetric Berry curvature, establishing their geometric origin. This insight defines temporal geometry as a unifying framework for ultrafast chiral light-matter interactions, with PI-MOCD providing a robust, experimentally accessible probe of electronic currents in both bound and continuum states. Beyond clarifying the relation between TR-PECD, PXCD, and fragment observables, this connection opens practical routes for geometric control and for discovering further curvature-driven observables.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

APPENDIX A: CLOSED LIFT FOR A PURE DENSITY MATRIX $|\psi_{\text{el}}(t)\rangle \langle \psi_{\text{el}}(t)|$

The closed lift is a concept from fiber bundle theory that allows one to identify the geometric phase outside the approximation of an adiabatic evolution. As shown in Fig. 6, in the Aharonov-Anandan fiber bundle theory, one introduces the base space in which all pure density matrices $|\psi_{\text{el}}(t)\rangle \langle \psi_{\text{el}}(t)|$ live. By definition, the density matrices do not possess any phase. Thus, when the system evolves along the closed contour $\gamma(t)$ in the base space, the density matrix remains the same after this cyclic evolution along the contour: $|\psi_{\text{el}}(t)\rangle \langle \psi_{\text{el}}(t)| = |\psi_{\text{el}}(t+T)\rangle \langle \psi_{\text{el}}(t+T)|$.

Wave functions corresponding to density matrices $|\psi_{\text{el}}(t)\rangle \langle \psi_{\text{el}}(t)|$ at every point in base space $|\psi_{\text{el}}(t)\rangle e^{i\phi}$ “live” on a fiber, which “grows vertically” from the base space while the phase ϕ is taking all possible values along this vertical direction (the fiber). These wave functions are said to constitute “lifts” of the density matrix $|\psi_{\text{el}}(t)\rangle \langle \psi_{\text{el}}(t)|$ from the base space into the fiber space (at every point on the contour γ in the base space). Any wave function that does not accumulate a phase throughout a cyclic evolution of a state

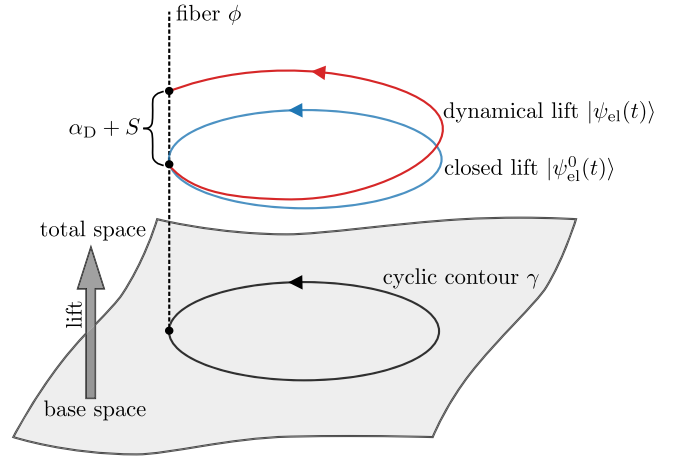


FIG. 6. The figure illustrates the fiber-bundle structure: the base space is formed by all pure state density matrices $|\psi_{\text{el}}\rangle \langle \psi_{\text{el}}|$, and attached to each point of the base is a fiber ϕ representing the possible phases of the state. A cyclic contour γ in the base space (black solid line) can be lifted to the total space in several ways. The closed lift (blue) corresponds to the state $|\psi_{\text{el}}^0(t)\rangle$, which traces a closed curve in the total space. The dynamical lift [see Eq. (2)], shown in red, is the full solution of the Schrödinger equation. It acquires a dynamical and geometric phase. The figure is inspired by Ref. [25].

on the contour γ such that $|\psi_{\text{el}}^0(t)\rangle = |\psi_{\text{el}}^0(t+T)\rangle$ is called a closed lift (see Fig. 6).

We can show that the wave function $\psi_{\text{el}}^0(t, \mathbf{e}(\rho), \mathbf{r})$ defined by Eq. (1) does not accumulate a phase as a result of cyclic evolution of rotational degrees of freedom and therefore presents the closed lift of the density matrix $|\psi_{\text{el}}(t)\rangle \langle \psi_{\text{el}}(t)|$.

In our case, one cycle of evolution corresponds to one full rotation of the molecular frame $\psi_{\text{el}}^0(t, \mathbf{e}(\rho), \mathbf{r})$ from some initial orientation characterized by Euler angles $\rho_0 = \{\theta_0, \phi_0, \alpha_0\}$ with respect to the laboratory frame to the exact same orientation $\rho_0 + 2\pi = \{\theta_0 + 2\pi, \phi_0 + 2\pi, \alpha_0\}$. The wave functions $\psi_{\text{el}}^0[t, \mathbf{e}(\rho_0), \mathbf{r}]$ and $\psi_{\text{el}}^0[t, \mathbf{e}(\rho_0 + 2\pi), \mathbf{r}]$ can be obtained from the same laboratory-frame wave function using an appropriate unitary transformation, such as, e.g., rotation around $\hat{n}$ axes by the angle ξ : $\psi_{\text{el}}^0[t, \mathbf{e}(\rho_0 + 2\pi), \mathbf{r}] = e^{-i\xi(\hat{n} \cdot \mathbf{L})} \psi_{\text{el}}^0[t, \mathbf{e}(\rho_0), \mathbf{r}] = \psi_{\text{el}}^0[t, \mathbf{e}(\rho_0), \mathbf{r}]$. Since these unitary transformations do not impart any relative phases on the transformed wave functions $\psi_{\text{el}}^0[t, \mathbf{e}(\rho_0 + 2\pi), \mathbf{r}]$ and $\psi_{\text{el}}^0[t, \mathbf{e}(\rho_0), \mathbf{r}]$, and the same arguments remain valid for every point ρ_0 , the wave function $\psi_{\text{el}}^0[t, \mathbf{e}(\rho), \mathbf{r}]$ presents a closed lift.

APPENDIX B: DERIVATION OF EQ. (6)

Previously, we have derived Eqs. (5) and (7) using the concept of adiabatic evolution of the rotational degree of freedom, introducing two different time scales for the evolution of electronic and rotational degrees of freedom. We now extend our derivation to a general case, including nonadiabatic evolution. We follow the arguments of Ref. [21] and introduce a rotational Hamiltonian $H_{\text{rot}}(t)$, responsible for the cyclic nonadiabatic evolution of the rotational wave function $\psi_{\text{rot}}(\rho, t)$,

$$i \frac{d}{dt} \psi_{\text{rot}}(\rho, t) = H_{\text{rot}}(t) \psi_{\text{rot}}(\rho, t). \quad (\text{B1})$$

For example, $H_{\text{rot}}(t)$ could encapsulate a sequence of microwave fields driving resonant transitions in three rotational levels of a chiral molecule. Since our focus is laser-induced coupling between electronic and rotational degrees of freedom, which arises due to the sensitivity of the electronic dynamics to the mutual orientation between the molecule and the laser field, we omit the standard Coriolis coupling between electronic and rotational degrees of freedom in the zero approximation.

Starting from the TDSE for the full wave function including the electronic and rotational degrees of freedom

$$i \frac{d}{dt} \Psi(\mathbf{r}, \rho, t) = [H_{\text{el}} + \mathbf{r} \cdot \mathbf{E}(\rho, t) + H_{\text{rot}}(t)] \Psi(\mathbf{r}, \rho, t) \quad (\text{B2})$$

and using the ansatz

$$\Psi(\mathbf{r}, \rho, t) = \psi_{\text{el}}(\mathbf{r}, \rho, t) \psi_{\text{rot}}(\rho, t), \quad (\text{B3})$$

we obtain

$$\begin{aligned} i \psi_{\text{rot}}(\rho, t) \frac{d}{dt} \psi_{\text{el}}(\mathbf{r}, \rho, t) + i \psi_{\text{el}}(\mathbf{r}, \rho, t) \frac{d}{dt} \psi_{\text{rot}}(\rho, t) \\ = [H_{\text{el}} + \mathbf{r} \cdot \mathbf{E}(\rho, t) + H_{\text{rot}}(t)] \psi_{\text{el}}(\mathbf{r}, \rho, t) \psi_{\text{rot}}(\rho, t). \end{aligned} \quad (\text{B4})$$

Multiplying this TDSE by $\psi_{\text{rot}}^*(\rho, t)$ from the left and integrating over ρ yields the following equation:

$$\begin{aligned} i \int d\rho |\psi_{\text{rot}}(\rho, t)|^2 \frac{d}{dt} \psi_{\text{el}}(\mathbf{r}, \rho, t) \\ + i \int d\rho \psi_{\text{el}}(\mathbf{r}, \rho, t) \psi_{\text{rot}}^*(\rho, t) \frac{d}{dt} \psi_{\text{rot}}(\rho, t) \\ = \int d\rho \psi_{\text{rot}}^*(\rho, t) [H_{\text{el}} + \mathbf{r} \cdot \mathbf{E}(\rho, t)] \psi_{\text{el}}(\mathbf{r}, \rho, t) \psi_{\text{rot}}(\rho, t) \\ - i \int d\rho \frac{d}{dt} [\psi_{\text{rot}}^*(\rho, t)] \psi_{\text{el}}(\mathbf{r}, \rho, t) \psi_{\text{rot}}(\rho, t), \end{aligned} \quad (\text{B5})$$

where we have used the adjoint of Eq. (B1) in the last term applying the rotational Hamiltonian $H_{\text{rot}}(t)$ to the bra vector on the left:

$$\psi_{\text{rot}}^*(\rho, t) H_{\text{rot}}(t) = -i \frac{d}{dt} \psi_{\text{rot}}^*(\rho, t). \quad (\text{B6})$$

Note that in doing so we have avoided the assumption of the adiabatic decoupling of the electronic and rotational degrees of freedom. Indeed, the adiabatic decoupling implies that H_{rot} does not affect the electronic wave function, while here it clearly does so via the last term in Eq. (B5). In the following we shall use the adiabatic decoupling to derive the equation for the closed lift solution [see Eqs. (B10)–(B12)].

Equation (B5) takes the following form:

$$\begin{aligned} i \int d\rho |\psi_{\text{rot}}(\rho, t)|^2 \frac{d}{dt} \psi_{\text{el}}(\mathbf{r}, \rho, t) \\ + i \int d\rho \psi_{\text{el}}(\mathbf{r}, \rho, t) \frac{d}{dt} |\psi_{\text{rot}}(\rho, t)|^2 \\ = \int d\rho [H_{\text{el}} + \mathbf{r} \cdot \mathbf{E}(\rho, t)] \psi_{\text{el}}(\mathbf{r}, \rho, t) |\psi_{\text{rot}}(\rho, t)|^2. \end{aligned} \quad (\text{B7})$$

We shall now assume that the rotational wave packet is narrow. This assumption can be realized in an experiment by preparing a narrow rotational wave packet with a pump

pulse and using a short probe pulse with time-dependent polarization, rotating with respect to the frame established by the pump pulse. The center of the rotational wave packet may be defined as $\bar{\rho}(t) \equiv \int d\rho \rho |\psi_{\text{rot}}(\rho, t)|^2$. Introducing $\dot{\bar{\rho}}(t) = \int d\rho \frac{d}{dt} |\psi_{\text{rot}}(\rho, t)|^2 \rho = \frac{d}{dt} \int d\rho \rho |\psi_{\text{rot}}(\rho, t)|^2 \rho = \frac{d}{dt} \bar{\rho}(t)$ and expanding $E_i(\rho, t) = E_i(\rho_0, t) + \nabla_{\rho_0} E_i(\rho_0, t)(\rho - \rho_0)$, and $\psi_{\text{el}}(\mathbf{r}, \rho, t)$ up to the first order around $\bar{\rho}(t)$, we obtain for the integral $\int d\rho \psi_{\text{el}}(\mathbf{r}, \rho, t) \frac{d}{dt} |\psi_{\text{rot}}(\rho, t)|^2$ the following expansion:

$$\begin{aligned} \int d\rho \psi_{\text{el}}(\mathbf{r}, \rho, t) \frac{d}{dt} |\psi_{\text{rot}}(\rho, t)|^2 \\ = \int d\rho \psi_{\text{el}}(\mathbf{r}, \bar{\rho}(t), t) \frac{d}{dt} |\psi_{\text{rot}}(\rho, t)|^2 \\ + \nabla_{\bar{\rho}} \psi_{\text{el}}[\mathbf{r}, \bar{\rho}(t), t] \cdot \dot{\bar{\rho}}(t). \end{aligned} \quad (\text{B8})$$

Here, we took into account that $\int d\rho |\psi_{\text{rot}}(\rho, t)|^2 = 1$, which leads to $\frac{d}{dt} \int d\rho |\psi_{\text{rot}}(\rho, t)|^2 = 0$. Combining this term with the other terms, we obtain the following TDSE for the “global” wave function $\psi_{\text{el}}(\mathbf{r}, \bar{\rho}(t), t)$:

$$\begin{aligned} i \frac{\partial}{\partial t} \psi_{\text{el}}(\mathbf{r}, \bar{\rho}(t), t) + i \nabla_{\bar{\rho}} \psi_{\text{el}}(\mathbf{r}, \bar{\rho}(t), t) \cdot \dot{\bar{\rho}}(t) \\ = [H_{\text{el}} + \mathbf{r} \cdot \mathbf{E}(\bar{\rho}(t), t)] \psi_{\text{el}}(\mathbf{r}, \bar{\rho}(t), t). \end{aligned} \quad (\text{B9})$$

Note that $\bar{\rho}(t) = \int d\rho \rho |\psi_{\text{rot}}(\rho, t)|^2$ follows the evolution of the center of the rotational wave packet and therefore is controlled by $H_{\text{rot}}(t)$.

Let us derive an approximate solution $\psi_{\text{el}}^0(\mathbf{r}, \rho, t)$ for the case when the rotational Hamiltonian itself does not affect the electronic dynamics, i.e.,

$$H_{\text{rot}}(t) \psi_{\text{el}}^0(\mathbf{r}, \rho, t) \psi_{\text{rot}}(\rho, t) = \psi_{\text{el}}^0(\mathbf{r}, \rho, t) H_{\text{rot}}(t) \psi_{\text{rot}}(\rho, t). \quad (\text{B10})$$

Applying this condition to Eq. (B4) yields

$$\begin{aligned} i \psi_{\text{rot}}(\rho, t) \frac{d}{dt} \psi_{\text{el}}^0(\mathbf{r}, \rho, t) \\ = [H_{\text{el}} + \mathbf{r} \cdot \mathbf{E}(\rho, t)] \psi_{\text{el}}^0(\mathbf{r}, \rho, t) \psi_{\text{rot}}(\rho, t), \end{aligned} \quad (\text{B11})$$

demonstrating that $\psi_{\text{el}}^0(\mathbf{r}, \rho, t)$ solves the “local” TDSE for fixed ρ :

$$i \frac{d}{dt} \psi_{\text{el}}^0(\mathbf{r}, \rho, t) = [H_{\text{el}} + \mathbf{r} \cdot \mathbf{E}(\rho, t)] \psi_{\text{el}}^0(\mathbf{r}, \rho, t). \quad (\text{B12})$$

Comparing Eq. (B9) with Eq. (B11), we find that the “global” and the “local” solutions are related as follows:

$$\psi_{\text{el}}[\mathbf{r}, \bar{\rho}(t), t] = e^{iS[\bar{\rho}(t)]} \psi_{\text{el}}^0[\mathbf{r}, \bar{\rho}(t), t]. \quad (\text{B13})$$

Substituting Eq. (B13) into Eq. (B9), we find

$$S[\bar{\rho}(t)] = i \int_{\bar{\rho}(t_0)}^{\bar{\rho}(t)} d\rho' \cdot \langle \psi_{\text{el}}^0(\mathbf{r}, \rho', t) | \nabla_{\rho'} \psi_{\text{el}}^0(\mathbf{r}, \rho', t) \rangle. \quad (\text{B14})$$

Note that, by the virtue of Eqs. (B10) and (B11), the only reason why $\psi_{\text{el}}^0(\mathbf{r}, \rho, t)$ depends on ρ is because the laser field in the molecular frame depends on ρ , i.e., $\psi_{\text{el}}^0(\mathbf{r}, \rho, t) \equiv \psi_{\text{el}}^0[\mathbf{r}, \mathbf{e}(\rho), t]$.

Indeed, $\psi_{\text{el}}^0(\mathbf{r}, \rho, t)$ satisfies the TDSE for the electronic degrees of freedom Eq. (B12). This equation, by definition, has no information about the rotational degree of freedom. Thus, the gradient of $\psi_{\text{el}}^0(\mathbf{r}, \rho, t)$ with respect to ρ can be rewritten in

an equivalent form, $\nabla_{\rho} \psi_{\text{el}}^0(\mathbf{r}, \rho, t) = \nabla_{\mathbf{e}} \psi_{\text{el}}^0(\mathbf{r}, \rho, t) \frac{\partial \mathbf{e}}{\partial \rho}$, as long as the laser field polarization $\mathbf{e}$ can be used to unambiguously define the laboratory frame with respect to which the molecular orientation ρ is expressed. For example, the polarization vector $\mathbf{e}$ of a circularly (elliptically) polarized field satisfies this requirement. Hence, the derivative should be taken with respect to $\mathbf{e}$. This leads to the following equivalent expression for the geometric phase:

$$\begin{aligned} S[\bar{\rho}(t)] &= i \int_{\mathbf{e}(t_0)}^{\mathbf{e}(t)} \langle \psi_{\text{el}}^0(\mathbf{r}, \rho', t) | \nabla_{\mathbf{e}} \psi_{\text{el}}^0(\mathbf{r}, \rho', t) \rangle \cdot d\mathbf{e} \\ &\equiv \int_{\mathbf{e}(t_0)}^{\mathbf{e}(t)} \mathbf{A}(\mathbf{e}) \cdot d\mathbf{e}, \end{aligned} \quad (\text{B15})$$

where $\mathbf{A}(\mathbf{e}) = i \langle \psi_{\text{el}}^0(\mathbf{r}, \mathbf{e}, t) | \nabla_{\mathbf{e}} \psi_{\text{el}}^0(\mathbf{r}, \mathbf{e}, t) \rangle$.

APPENDIX C: TIME REVERSAL IN TWO-PHOTON PROCESSES

Inspired by Ref. [26], consider

$$\begin{aligned} \mathcal{D}_{ij}^{\pm} &\equiv i^{(1\mp 1)/2} \int d\Theta_k (D_{1,i}^* D_{2,j} \pm D_{1,j}^* D_{2,i}) \\ &= i^{(1\mp 1)/2} \int d\Theta_k \left(\langle \psi_1 | x_i | \psi_k \rangle \langle \psi_k | x_j | \psi_2 \rangle \right. \\ &\quad \left. \pm \langle \psi_1 | x_j | \psi_k \rangle \langle \psi_k | x_i | \psi_2 \rangle \right) \\ &= \langle \psi_1 | (x_i P_k x_j \pm x_j P_k x_i) | \psi_2 \rangle \\ &= \langle \psi_1 | G_{ij}^{\pm} | \psi_2 \rangle, \end{aligned} \quad (\text{C1})$$

where x_i is the position operator of the i th Cartesian coordinate and we defined

$$G_{ij}^{\pm} \equiv i^{(1\mp 1)/2} (x_i P_k x_j \pm x_j P_k x_i), \quad (\text{C2})$$

$$P_k \equiv \int d\Theta_k |\psi_k\rangle \langle \psi_k|. \quad (\text{C3})$$

Since the position operators x_i and the projector P_k are Hermitian, $G_{ij}^{\pm}$ is also Hermitian,

$$\begin{aligned} G_{ij}^{\pm\dagger} &= \pm i^{(1\mp 1)/2} (x_j P_k x_i \pm x_i P_k x_j) \\ &= G_{ij}^{\pm}. \end{aligned} \quad (\text{C4})$$

Furthermore, since x_i and P_k are time even (i.e., commute with the time-reversal operator T), G_{ij}^+ is time even and G_{ij}^- is time odd,

$$\begin{aligned} T G_{ij}^{\pm} &= \pm i^{(1\mp 1)/2} (x_i P_k x_j \pm x_j P_k x_i) T \\ &= \pm G_{ij}^{\pm} T. \end{aligned} \quad (\text{C5})$$

Therefore, for time-even states $|\psi_1\rangle$ and $|\psi_2\rangle$ we have $\langle \psi_1 | G_{ij}^{\pm} | \psi_2 \rangle = \pm \langle \psi_1 | G_{ij}^{\pm} | \psi_2 \rangle^*$. That is, $\text{Im}\{\langle \psi_1 | G_{ij}^+ | \psi_2 \rangle\} = 0$ and $\text{Re}\{\langle \psi_1 | G_{ij}^- | \psi_2 \rangle\} = 0$ (see e.g. [27]). In terms of $\bar{D}_1$ and $\bar{D}_2$, we get

$$\text{Im} \left\{ \int d\Theta_k (D_{1,i}^* D_{2,j} + D_{1,j}^* D_{2,i}) \right\} = 0, \quad (\text{C6})$$

$$\text{Re} \left\{ i \int d\Theta_k (D_{1,i}^* D_{2,j} - D_{1,j}^* D_{2,i}) \right\} = 0. \quad (\text{C7})$$

The latter can be rewritten as

$$\text{Im} \left\{ \int d\Theta_k (D_{1,i}^* D_{2,j} - D_{1,j}^* D_{2,i}) \right\} = 0 \quad (\text{C8})$$

Adding Eqs. (12) and (14) we obtain

$$\text{Im} \left\{ \int d\Theta_k D_{1,i}^* D_{2,j} \right\} = 0 \quad (\text{C9})$$

Using this fundamental property, we can derive others such as:

$$\begin{aligned} \text{Im} \left\{ \int d\Theta_k \bar{D}_1^* \times \bar{D}_2 \right\} &= \text{Im} \left\{ \epsilon_{lij} \hat{x}_l \int d\Theta_k D_{1,i}^* D_{2,j} \right\} \\ &= \epsilon_{lij} \hat{x}_l \text{Im} \left\{ \int d\Theta_k D_{1,i}^* D_{2,j} \right\} \\ &= 0, \end{aligned} \quad (\text{C10})$$

which was derived in a similar but less general way in Ref. [13], and

$$\begin{aligned} \text{Im} \left\{ \int d\Theta_k \bar{D}_1^* \cdot \bar{D}_2 \right\} &= \text{Im} \left\{ \int d\Theta_k D_{1,i}^* D_{2,i} \right\} \\ &= 0, \end{aligned} \quad (\text{C11})$$

which we use in Eq. (19) of the main text.

APPENDIX D: CONNECTION BETWEEN THE CORIOLIS COUPLING AND TEMPORAL GEOMETRY

In this work we focus on the new, light-driven and light-controlled, mechanism of coupling between the electronic and rotational degrees of freedom, which is complementary to the well-known Coriolis coupling between the electronic and rotational degrees of freedom. Formally, the difference between the standard Coriolis coupling and light-driven coupling can be seen from the following formal expressions. The electronic wave functions in the laboratory frame $|\Psi\rangle^L$ and in the molecular frame $|\Psi\rangle^M$ are related by the unitary transformation encoding the set of Euler angles R , which characterizes their mutual orientation $U(R)$:

$$|\Psi\rangle^L = U(R) e^{-i \int \hat{H}^M dt} |\Psi\rangle^M. \quad (\text{D1})$$

Since R can depend on time, we obtain

$$i \langle \Psi | \frac{d}{dt} | \Psi \rangle^L idt = {}^M \langle \Psi | U^\dagger \frac{dU}{dt} | \Psi \rangle^M idt + {}^M \langle \Psi | \frac{d}{dt} | \Psi \rangle^M idt. \quad (\text{D2})$$

Here, the first term describes the Coriolis coupling, while the second term describes the coupling due to temporal geometry: the dependence on the Euler angles comes from the laser field orientation, which appears as an argument of the electronic wave function in the molecular frame $|\Psi\rangle^M$ because it also depends on Euler angles.

APPENDIX E: ORIENTATIONAL AVERAGING, DERIVATION OF EQS. (13) AND (14)

The average over a set of Euler angles is given by the Haar measure $\int d\mathbf{g} = \int_0^{2\pi} \int_0^\pi \int_0^{2\pi} d\phi d\theta d\alpha \sin \theta$. Let $l_{i\alpha} \in \text{SO}(3)$ be a

rotation matrix constituting the rotation between molecular and laboratory frame, such that $v_i^L = l_{i\alpha} v_\alpha^M$ for $\mathbf{v} \in \mathbb{R}^3$. Greek indices denote molecular frame vectors and Latin indices denote laboratory frame vectors, respectively. We employ the following identity [28]:

$$\int d\varrho l_{i\alpha} l_{j\beta} l_{k\gamma} l_{l\delta} = \frac{1}{30} (\delta_{ij}\delta_{kl} \quad \delta_{ik}\delta_{jl} \quad \delta_{il}\delta_{jk}) \begin{pmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & 4 \end{pmatrix} \begin{pmatrix} \delta_{\alpha\beta}\delta_{\gamma\delta} \\ \delta_{\alpha\gamma}\delta_{\beta\delta} \\ \delta_{\alpha\delta}\delta_{\beta\gamma} \end{pmatrix} \quad (\text{E1})$$

$$= \frac{1}{30} [4\delta_{ij}\delta_{kl}\delta_{\alpha\beta}\delta_{\gamma\delta} - \delta_{ik}\delta_{jl}\delta_{\alpha\beta}\delta_{\gamma\delta} - \delta_{il}\delta_{jk}\delta_{\alpha\beta}\delta_{\gamma\delta} \quad (\text{E2})$$

$$- \delta_{ij}\delta_{kl}\delta_{\alpha\gamma}\delta_{\beta\delta} + 4\delta_{ik}\delta_{jl}\delta_{\alpha\gamma}\delta_{\beta\delta} - \delta_{il}\delta_{jk}\delta_{\alpha\gamma}\delta_{\beta\delta} \quad (\text{E3})$$

$$- \delta_{ij}\delta_{kl}\delta_{\alpha\delta}\delta_{\beta\gamma} - \delta_{ik}\delta_{jl}\delta_{\alpha\delta}\delta_{\beta\gamma} + 4\delta_{il}\delta_{jk}\delta_{\alpha\delta}\delta_{\beta\gamma}], \quad (\text{E4})$$

i.e.,

$$\begin{aligned} \int d\rho (a^L \cdot u^L)(b^L \cdot v^L)(c^L \cdot w^L)x^L &= \frac{1}{30} [4(a^L \cdot b^L)c^L(u^M \cdot v^M)(w^M \cdot x^M) - (a^L \cdot c^L)b^L(u^M \cdot v^M)(w^M \cdot x^M) \\ &\quad - (b^L \cdot c^L)a^L(u^M \cdot v^M)(w^M \cdot x^M) - (a^L \cdot b^L)c^L(u^M \cdot w^M)(v^M \cdot x^M) \\ &\quad + 4(a^L \cdot c^L)b^L(u^M \cdot w^M)(v^M \cdot x^M) - (b^L \cdot c^L)a^L(u^M \cdot w^M)(v^M \cdot x^M) \\ &\quad - (a^L \cdot b^L)c^L(u^M \cdot x^M)(v^M \cdot w^M) - (a^L \cdot c^L)b^L(u^M \cdot x^M)(v^M \cdot w^M) \\ &\quad + 4(b^L \cdot c^L)a^L(u^M \cdot x^M)(v^M \cdot w^M)]. \end{aligned} \quad (\text{E5})$$

We derive Eq. (14), which we list here for completeness:

$$\langle v_\Omega^L \rangle^{\dagger, \odot} = \sigma \langle (\mathbf{\Omega}_{\text{ion}} \cdot \hat{\mathbf{z}}) v_\Omega^L \rangle = \sigma R v \langle \mathbf{\Omega}_{\text{ion}} \cdot \mathbf{v}_\Omega \rangle \hat{\mathbf{z}}^L, \quad (\text{E6})$$

where

$$\begin{aligned} \mathbf{\Omega}_{\text{ion}}(k, \rho) &= -|E_{\omega_{k1}}||E_{\omega_{k2}}|(\mathbf{d}_1 \cdot \mathbf{\mathcal{E}}_1)^*(\mathbf{d}_2 \cdot \mathbf{\mathcal{E}}_2) \mathbf{P}_{12}^+(k) \sin(\omega_{12}\tau) \quad (\text{E7}) \end{aligned}$$

[Eq. (12)]. Substituting Eq. (E7) into Eq. (E6), we obtain

$$\begin{aligned} \langle v_\Omega^L \rangle^{\dagger, \odot} &= -|E_{\omega_{k1}}||E_{\omega_{k2}}| \sin(\omega_{12}\tau) \\ &\quad \times \int d\rho (\mathbf{d}_1 \cdot \mathbf{\mathcal{E}}_1)^*(\mathbf{d}_2 \cdot \mathbf{\mathcal{E}}_2) (\mathbf{P}_{12}^+(k) \cdot \hat{\mathbf{z}}) v_\Omega^L. \end{aligned} \quad (\text{E8})$$

Applying Eq. (E5) to Eq. (E8), we obtain

$$\begin{aligned} \langle v_\Omega^L \rangle^{\dagger, \odot} &= \frac{\sigma}{30} C [4(\mathbf{d}_2 \cdot \mathbf{d}_1) \mathbf{v}_\Omega - (\mathbf{d}_2 \cdot \mathbf{v}_\Omega) \mathbf{d}_1 - (\mathbf{d}_1 \cdot \mathbf{v}_\Omega) \mathbf{d}_2] \\ &\quad \cdot \mathbf{P}_{12}^+(k) \sin(\omega_{12}\tau) \hat{\mathbf{z}}^L, \end{aligned} \quad (\text{E9})$$

which is equivalent to Eq. (14) and (15) up to the notation $\mathbf{P}_{12}^+(k) = v|\mathbf{P}_{12}^+(k)|\mathbf{v}_\Omega$ and normalization.

Starting from

$$\begin{aligned} \mathbf{\Omega}_{\text{ion}}(k, \rho) \cdot \mathbf{v}_\Omega &= -|E_{\omega_{k1}}||E_{\omega_{k2}}|(\mathbf{d}_1 \cdot \mathbf{\mathcal{E}}_1)^*(\mathbf{d}_2 \cdot \mathbf{\mathcal{E}}_2) \\ &\quad \times (\mathbf{P}_{12}^+(k) \cdot \mathbf{v}_\Omega) \sin(\omega_{12}\tau), \end{aligned} \quad (\text{E10})$$

we shall now evaluate $\langle \mathbf{\Omega}_{\text{ion}} \cdot \mathbf{v}_\Omega^M \rangle$. Note that we only need to average the part that depends on mutual orientations of the pump pulse and molecule:

$$\begin{aligned} \int d\rho (\mathbf{d}_1 \cdot \mathbf{\mathcal{E}}_1)^*(\mathbf{d}_2 \cdot \mathbf{\mathcal{E}}_2) &= \frac{1}{3} (\mathbf{d}_1 \cdot \mathbf{d}_2) (\mathbf{\mathcal{E}}_1^* \cdot \mathbf{\mathcal{E}}_2) = \frac{1}{3} (\mathbf{d}_1 \cdot \mathbf{d}_2) |\mathcal{E}_{\omega_1}| |\mathcal{E}_{\omega_2}|, \end{aligned} \quad (\text{E11})$$

yielding Eq. (13):

$$\langle \mathbf{\Omega}_{\text{ion}}(k) \cdot \mathbf{v}_\Omega \rangle = -\frac{1}{3} v C (\mathbf{d}_1 \cdot \mathbf{d}_2) |\mathbf{P}_{12}^+(k)| \sin(\omega_{12}\tau). \quad (\text{E12})$$

APPENDIX F: CONNECTION BETWEEN THE BERRY CURVATURE AND THE PHOTOIONIZATION YIELD

In this section, we calculate the photoionization yield $W \equiv \int |a_k|^2 d\Theta_k$ for two-photon processes considered in this work. For example, consider a sequence of linear and circularly polarized pulses:

$$\mathbf{\mathcal{E}}_i^L = \mathcal{E}_{\omega_i} \hat{\mathbf{x}}^L, \quad \mathbf{E}_j^L = E_{\omega_{jk}} \frac{1}{\sqrt{2}} (\hat{\mathbf{x}}^L + i\sigma \hat{\mathbf{y}}^L). \quad (\text{F1})$$

The photoionization amplitude $|a_k|^2$ can be written as

$$\begin{aligned} |a_k|^2 &= \frac{1}{2} [|E_{\omega_{1k}}|^2 |(\mathbf{d}_1^L \cdot \mathbf{\mathcal{E}}_1^L)|^2 [|\mathbf{D}_1^L \cdot \hat{\mathbf{x}}^L|^2 + |\mathbf{D}_1^L \cdot \hat{\mathbf{y}}^L|^2 + i\sigma (\mathbf{D}_1^{*L} \times \mathbf{D}_1^L) \cdot \hat{\mathbf{z}}^L] \\ &\quad + \frac{1}{2} [|E_{\omega_{2k}}|^2 |(\mathbf{d}_2^L \cdot \mathbf{\mathcal{E}}_2^L)|^2 [|\mathbf{D}_2^L \cdot \hat{\mathbf{x}}^L|^2 + |\mathbf{D}_2^L \cdot \hat{\mathbf{y}}^L|^2 + i\sigma (\mathbf{D}_2^{*L} \times \mathbf{D}_2^L) \cdot \hat{\mathbf{z}}^L] \\ &\quad + \text{Re}\{E_{\omega_{1k}}^* E_{\omega_{2k}} (\mathbf{d}_1^L \cdot \mathbf{\mathcal{E}}_1^L)^* \cdot (\mathbf{d}_2^L \cdot \mathbf{\mathcal{E}}_2^L) [(\mathbf{D}_1^{*L} \cdot \hat{\mathbf{x}}^L)(\mathbf{D}_2^L \cdot \hat{\mathbf{x}}^L) + (\mathbf{D}_1^{*L} \cdot \hat{\mathbf{y}}^L)(\mathbf{D}_2^L \cdot \hat{\mathbf{y}}^L) + i\sigma (\mathbf{D}_1^{*L} \times \mathbf{D}_2^L) \cdot \hat{\mathbf{z}}^L]\}]. \end{aligned} \quad (\text{F2})$$

The dichroic (i.e., proportional to σ) photoionization yield is

$$\int |a_k|^2 d\Theta_k = \sigma \text{Re} \left\{ E_{\omega_{1k}}^* E_{\omega_{2k}} (\mathbf{d}_1^L \cdot \boldsymbol{\varepsilon}^L)^* \cdot (\mathbf{d}_2^L \cdot \boldsymbol{\varepsilon}^L) \left[e^{i\omega_{12}\tau} \int i(\mathbf{D}_1^{*L} \times \mathbf{D}_2^L) d\Theta_k \right] \right\} \cdot \hat{\mathbf{z}}^L = \sigma \boldsymbol{\Omega}^L \cdot \hat{\mathbf{z}}^L, \quad (\text{F3})$$

where $\boldsymbol{\Omega}$ is given by Eq. (12).

APPENDIX G: ANTISYMMETRIC BERRY CURVATURE FOR CIRCULAR PUMP AND PROBE FIELDS: DERIVATION

The wave function expressed in first-order perturbation theory is

$$|\psi\rangle = |0\rangle + i \sum_j \mathbf{d}_j \cdot \mathbf{E}_j |k\rangle - \sum_j \int d\Theta_k (\mathbf{D}_j \cdot \mathbf{E}_{kj}) (\mathbf{d}_j \cdot \mathbf{E}_j) e^{-i\omega_j\tau} |k\rangle. \quad (\text{G1})$$

The corresponding antisymmetric Berry curvature is

$$\boldsymbol{\Omega} = i \langle \nabla_e \psi | \times | \nabla_e \psi \rangle \quad (\text{G2})$$

with

$$|\nabla_e \psi\rangle = i \sum_j |E_{\omega_j}| \mathbf{d}_j |k\rangle - \sum_j |E_{\omega_j}| |E_{\omega_{kj}}| \times \int d\Theta_k [\mathbf{D}_j (\mathbf{d}_j \cdot \mathbf{e}) + (\mathbf{D}_j \cdot \mathbf{e}) \mathbf{d}_j] e^{-i\omega_j\tau} |k\rangle. \quad (\text{G3})$$

Using the orthogonality of the basis, we get

$$\begin{aligned} -i\boldsymbol{\Omega} &= \sum_j |E_{\omega_j}| \mathbf{d}_j^* \times \mathbf{d}_j + \sum_{jl} |E_{\omega_j}| |E_{\omega_{kj}}| |E_{\omega_l}| |E_{\omega_{kl}}| \\ &\times \int d\Theta_k [\mathbf{D}_j^* (\mathbf{d}_j \cdot \mathbf{e})^* + (\mathbf{D}_j \cdot \mathbf{e})^* \mathbf{d}_j^*] \\ &\times [\mathbf{D}_l (\mathbf{d}_l \cdot \mathbf{e}) + (\mathbf{D}_l \cdot \mathbf{e}) \mathbf{d}_l] e^{i\omega_{jl}\tau}. \end{aligned} \quad (\text{G4})$$

Since the dipole moments $\mathbf{d}_l$ are real, the curvature simplifies to

$$\begin{aligned} -i\boldsymbol{\Omega} &= \sum_{jl} |E_{\omega_j}| |E_{\omega_{kj}}| |E_{\omega_l}| |E_{\omega_{kl}}| \\ &\times \int d\Theta_k [\mathbf{D}_j^* (\mathbf{d}_j \cdot \mathbf{e}^*) + (\mathbf{D}_j \cdot \mathbf{e})^* \mathbf{d}_j] \\ &\times [\mathbf{D}_l (\mathbf{d}_l \cdot \mathbf{e}) + (\mathbf{D}_l \cdot \mathbf{e}) \mathbf{d}_l] e^{i\omega_{jl}\tau}. \end{aligned} \quad (\text{G5})$$

Equation (G5) yields:

$$\begin{aligned} -i\boldsymbol{\Omega} &= \sum_{j,l} |E_{\omega_j}| |E_{\omega_{kj}}| |E_{\omega_l}| |E_{\omega_{kl}}| \\ &\times \int d\Theta_k [(\mathbf{d}_j \cdot \mathbf{e}^*) (\mathbf{d}_l \cdot \mathbf{e}) (\mathbf{D}_j^* \times \mathbf{D}_l) \\ &+ (\mathbf{d}_j \cdot \mathbf{e}^*) (\mathbf{D}_l \cdot \mathbf{e}) (\mathbf{D}_j^* \times \mathbf{d}_l) \\ &+ (\mathbf{D}_j \cdot \mathbf{e})^* (\mathbf{d}_l \cdot \mathbf{e}) (\mathbf{d}_j \times \mathbf{D}_l) \\ &+ (\mathbf{D}_j \cdot \mathbf{e})^* (\mathbf{D}_l \cdot \mathbf{e}) (\mathbf{d}_j \times \mathbf{d}_l)] e^{i\omega_{jl}\tau}. \end{aligned} \quad (\text{G6})$$

Due to the antisymmetry of the cross product, the Berry curvature can be expressed as

$$\begin{aligned} \boldsymbol{\Omega} &= -2C \int d\Theta_k [\text{Im}\{(\mathbf{d}_1 \cdot \mathbf{e}^*) (\mathbf{d}_2 \cdot \mathbf{e}) (\mathbf{D}_1^* \times \mathbf{D}_2) e^{i\omega_{12}\tau}\} \\ &+ \text{Im}\{(\mathbf{d}_1 \cdot \mathbf{e}^*) (\mathbf{D}_2 \cdot \mathbf{e}) (\mathbf{D}_1^* \times \mathbf{d}_2) e^{i\omega_{12}\tau}\} \\ &+ \text{Im}\{(\mathbf{D}_1 \cdot \mathbf{e})^* (\mathbf{d}_2 \cdot \mathbf{e}) (\mathbf{d}_1 \times \mathbf{D}_2) e^{i\omega_{12}\tau}\} \\ &+ \text{Im}\{(\mathbf{D}_1 \cdot \mathbf{e})^* (\mathbf{D}_2 \cdot \mathbf{e}) (\mathbf{d}_1 \times \mathbf{d}_2) e^{i\omega_{12}\tau}\}], \\ &- 2 \sum_j \int d\Theta_k \text{Im}\{(\mathbf{d}_j \cdot \mathbf{e}^*) (\mathbf{D}_j \cdot \mathbf{e}) (\mathbf{D}_j^* \times \mathbf{d}_j)\} \end{aligned} \quad (\text{G7})$$

where the diagonal terms do not contribute to orientation averaged Eqs. (24)–(30) and we defined

$$C = |E_{\omega_1}| |E_{\omega_{k1}}| |E_{\omega_2}| |E_{\omega_{k2}}|. \quad (\text{G8})$$

APPENDIX H: MATHEMATICAL DIFFERENCE BETWEEN THE AHARONOV-ANANDAN AND BERRY-SIMONS BUNDLE

Let us consider a Hamiltonian $h[\mathbf{R}(t)]$ which induces a closed path of period T in the space of pure state density matrices Λ such that

$$\Lambda(0) \equiv |\psi(0)\rangle \langle \psi(0)| = |\psi(T)\rangle \langle \psi(T)|. \quad (\text{H1})$$

The wave function (dynamical lift) corresponding to this path is quasi-periodic, i.e., is periodic up to a phase factor which can be decomposed into a dynamical and a geometric contribution. In general, the dependence of the density matrix at time t on the path $\mathbf{R}(t)$ is functional, which means that it depends on the whole history of $\mathbf{R}$ and not just on its value at time t . In this case, the underlying structure is the Aharonov-Anandan (AA) fiber bundle. The whole fiber space is the Hilbert space $\mathcal{H}$. The projection map

$$\pi : |\psi\rangle \rightarrow |\psi\rangle \langle \psi| \quad (\text{H2})$$

takes us to the base space of the AA bundle, the space of pure state density matrices. The Berry connection in the AA bundle is

$$\mathcal{A} = i \langle \phi(t) | \frac{d}{dt} | \phi(t) \rangle dt, \quad (\text{H3})$$

where $|\phi(t)\rangle$ is the closed lift. It is defined such that

$$|\phi(0)\rangle = |\phi(T)\rangle. \quad (\text{H4})$$

In some physical situations the dependency of the density matrix on $\mathbf{R}(t)$ is parametric, as, e.g., in our case three Euler angles specifying a molecular rotation, governing the time evolution of the Hamiltonian. Above all, an adiabatic

approximation with respect to the parameters $\mathbf{R}$ or a perturbative treatment of the wave function are to be listed here. Consequently, the $\mathbf{R}$ -parameter space becomes isomorphic to the density matrix space and may, from a perspective of fiber bundle theory, be treated as the base space of the fiber bundle. In this case, the closed lifts are the instantaneous eigenstates of the Hamiltonian and the AA connection reduces to the Berry-Simons (BS) connection. This can be easily seen when writing down the expression for the geometric

phase:

$$\gamma = \oint i \langle \phi(t) | \frac{d}{dt} | \phi(t) \rangle dt \stackrel{\text{parametric dependence}}{=} \oint i \langle \phi(\mathbf{R}) | \nabla_{\mathbf{R}} \times | \phi(\mathbf{R}) \rangle d\mathbf{R}. \quad (\text{H5})$$

This bundle is commonly referred to as the BS bundle. Note that the formation of BS bundles solely depends on a parametric description of the underlying geometric problem and not on a cyclic evolution of the density matrix.

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