Optical vortices discern attosecond time delay in electron emission from magnetic sublevels

J. Wätzel and J. Berakdar
Institute for Physics, Martin-Luther-University Halle-Wittenberg, 06099 Halle, Germany
(Dated: July 9, 2018)

Photoionization from energetically distinct electronic states may have a relative time delay of tens of attoseconds. Here we demonstrate that pulses of optical vortices allow measuring such attoseconds delays from magnetic sublevels, even from a spherically symmetric target. The difference in the time delay is substantial and exhibits a strong angular dependence. Furthermore, we find an atomic scale variation in the time delays depending on the target orbital position in the laser spot. The findings offer thus a qualitatively new way for a spatio-temporal sensing of the magnetic states from which the photoelectrons originate, with a spatial resolution way below the diffraction limit of the vortex beam. Our conclusions follow from analytical considerations based on symmetry, complemented and confirmed with full numerical simulations of the quantum dynamics.

I. INTRODUCTION

The development of attosecond (as) optical sources is a major achievement. Beside technological applications, attosecond spectroscopy and metrology shed light on new and old fundamental problems that were hitherto experimentally inaccessible (cf. [1]). An illuminating example is the recent revival of the issues of time and time delay in tunneling and photoionization [2–7] which dates back to early applications of quantum mechanics to study the variation of the scattering-amplitude phase with the wave vector during collision processes [8–10]. Combining as XUV pulses and infrared (IR) streaking fields, the relative delay time of photo emitted electrons from different atomic levels was reported [11] (for an overview, see e.g. [2, 12, 13]). The finding triggered theoretical activities with a varying level of success in reproducing the experiments [14–25] but pointing out the role of electronic correlations, the directional dependence of the emitted electrons, laser fields effects, as well as the influence of resonances and Cooper minima.

Here we draw attention to another aspect of time-resolved photoelectron chronoscopy when utilizing spatially phase-structured (singular) laser fields, i.e. optical vortices [26–33]. Such beams can transfer orbital angular momentum (OAM) when interacting with matter [34–40] and have found numerous applications in a number of fields in science [41–53]. The OAM phase front forms a helical shape characterized by exp(imOAMϕ), where ϕ is the azimuthal angle with respect to the propagation direction, and mOAM is an integer winding number called the topological charge. OAM carrying laser beams are routinely realized, e.g. as Laguerre-Gaussian (LG) modes. Each photon may transfer a quantized OAM of mOAMℏ.

Beams with more than mOAMℏ = 300 were demonstrated offering the opportunity to access excitations way beyond the limit set by the conventional optical propensity rules [54, 55] (degeneracy of involved states is also important [56]). Hence, vortices offer a new optical key to access magnetic sublevels [56] which is the starting idea of this work.

We consider an XUV, OAM carrying LG beam ionizing an initially completely symmetric target such as Ar atoms or C60 molecules. For the experimental feasibility and trapping properties of LG beams we refer to [57] and others [58–63]. As the amount of transferred OAM depends strongly on the orbital location in the laser spot [55, 56, 64–66], and the predicted time delay is explicitly related to the transferred OAM we predict a spatial resolution on orbitals having time-delay.

A. Background

The quantity of interest is the dependence of the time delay τ in photoionization on the light topological charge. Usually, in the experiment τ receives two contributions τW and τCLC. The Wigner time delay τW is related to the photoionization process triggered by the XUV pulse. The Coulomb-laser coupling term τCLC is akin to photoelectron motion in the combined Coulomb-streaking field, and hence is a setup-dependent quantity [20, 67]. We concentrate here on Wigner time delay as a system-sensitive quantity [93]. The time delay of a specific subshell is the average contributions over all magnetic sub-states, labelled mi. For linearly polarized light the photoionization probabilities of states with ±mi are equal and so are their contributions to the time delay. Also the angular dependence of photoelectrons emitted from these states are identical. Irradiation with OAM beams allows for transitions involving a change in magnetic quantum numbers by a maximal amount set by mOAM. We will show explicitly for Ar atom and a fullerene cluster that a short XUV-OAM pulse ([69–71]) ionizes preferentially specific magnetic sublevels. Consequently, in certain directions the photoionization (and hence the time delay) is dominated by a specific magnetic sublevel, depending on the atom position in the beam. The time delay may serve so as a tool to identify the origin of the photoelectron in energy, magnetic state, and space.

II. MODEL

In a gauge where the scalar potential vanishes the interaction hamiltonian reads (atomic units are used)

\[ \hat{H}_{\text{tot}} = \hat{p} \cdot \mathbf{A}(r, t) + \mathbf{A}(r, t) \cdot \hat{p}, \]

where \( \hat{p} \) is the momentum operator and \( \mathbf{A} \) is the vector potential with polarization vector \( \mathbf{e} = (1, t) \), waist \( w_0 \), temporal envelope \( g(t) = \cos(\pi t/nT)^2 \), where \( T = 2\pi/\omega \) is the cycle duration and \( n \) is the number of optical cycles. The explicit form of \( \mathbf{A} \) is given in
We find $V(r) = -(1 + 5.4e^{-r} + 11.6e^{-3.882r})/r$, which proved useful for similar problems [73]. $V(r)$ misses correlation effects [74].

Yet the energetic position of the Cooper minimum is reasonably well reproduced [24]. Note, we consider photoemitted electrons and do not study the hole dynamics upon electron removal [75, 76]. From symmetry considerations when applying OAM beams a hole current is expected to emerge which orbitally magnetizes the residual ion. Obviously $|\Omega|^2$ has a donut shape (appendix A). An Ar atom in the donut center experiences only a weak intensity justifying so a non-relativistic perturbative treatment even for moderately intense fields (the frequency is in the XUV). As the atoms might be distributed over the beam, some would experience the peak intensity. However, as shown below these atoms show no reaction to a topological charge change and hence no time delay (because the transferrable angular momentum refers to the optical axis not the atom center). Hence the two types of atoms, located in the donut center or on its ring, should be distinguishable by measuring the time delay. Here, the electric field starts with a zero amplitude at the vortex center reaching, at a distance of 10 a.u., a peak amplitude of 1 a.u. [93]. It is important to remark that the time delay dependence on $m_{OAM}$ diminishes rapidly as the atom is displaced (say by 2 a.u.) from the vortex center so that the high intensity region is irrelevant for the time delay discussed here. We note (and explicitly demonstrate below) that due to the laser donut-type intensity profile, orbitals with larger extension as such for fullerenes show similar effect as for atoms, but at intensity orders of magnitudes smaller than needed for atoms (this difference between Ar and C_60 is two orders of magnitude).

As the effect is of a general nature, we expect the proposed scheme to be useful also for extended systems.

Concerning the emitted electron, its wave function is expressible in a standard way [77] as $\Phi(r,t) = \int dk \, a(k,t) \phi_k(r)e^{-i\omega t}$. The projection coefficients $a(k,t)$ determine the photoionization amplitude as follows: The photoinduced emission of an electron initially in the bound state labeled $|\Psi_i(r)\rangle$ with energy $\epsilon_i$ to the continuum state $\phi_k^+(r)$ with the wave vector $k$ and energy $\epsilon_k = k^2/2$ reads [77]

$$a_i(k) = -i \int_{-\infty}^{\infty} dt' \langle \phi_k^-|\hat{H}_{tot}(t)|\Psi_i\rangle e^{i(\epsilon_k - \epsilon_i)t}. \tag{1}$$

As established [20, 77–79] we expand in spherical harmonics $Y_{lm}(\Omega)$ as $|\Psi_i\rangle$, and $\phi_k^+(r) = \sum_{l,m} c_{lm} Y_{lm}(\Omega) Y_{lm}(\Omega)$. The radial wave functions $R_{k,\ell}$ normalized as $\langle R_{k,\ell}|R_{k',\ell'}\rangle = \delta(\epsilon_k - \epsilon_{k'})$. The scattering phases are given by $\delta_{l,\ell}(k) = \sigma_{l,\ell}(k) + \eta_{l,\ell}(k)$ where $\sigma_{l,\ell}(k) = \arg[\Gamma(\ell + 1 - i/\ell)]$ is the Coulomb phase shift [10]. The quantity $\eta_{l,\ell}(k)$ is due to short range phase interactions [20].

For an analytical model let us consider as OAM center with $\epsilon = (1,1)^T$, $m_{OAM} = 1$, and the atom is in the donut center. We find $\nabla \cdot \mathbf{A}(r,t) = 0$ and $e^{i\omega t/\sqrt{2}} = 1$ for $w_0 = 50$ nm. The angular $(\Omega = (\theta_k, \varphi_k))$ dependent projection coefficients (1) and the reduced radial matrix elements $d_{\ell m n m'}^{\text{OAM}}$ are given in appendix B. The photoionization probability $w_i(\epsilon_i, \Omega) = |a_i(k)|^2$ is peaked around the center of energy (COE) given as $\epsilon_{COE} = \omega + \epsilon_i$ and $k_{COE} = \sqrt{2\epsilon_{COE}}$.

III. RESULTS AND INTERPRETATIONS

The photoionization amplitudes from the magnetic sublevels $m_i$ of the $3p$ subshell have the structure

$$a_i(k_{COE}, \Omega) = \begin{cases} S_{m_{OAM} + 2m_{OAM}, Y_{m_{OAM} + 2m_{OAM}}}(\Omega_k) + m_i = -1, \\ S_{m_{OAM} + 2m_{OAM}, Y_{m_{OAM} - 2m_{OAM}}}(\Omega_k) \quad m_i = 0, \\ S_{m_{OAM} + 2m_{OAM} + 1, Y_{m_{OAM} + 2m_{OAM} + 1}}(\Omega_k) \quad m_i = 1, \\ S_{m_{OAM} + 2m_{OAM} + 2, Y_{m_{OAM} + 2m_{OAM} + 2}}(\Omega_k) \quad m_i = 1, \end{cases} \tag{2}$$

(cf. appendix A for $E_{\text{COE}}$). These relations impose the propensity rules $\ell - \ell_i = \Delta \ell \leq m_{OAM} + 1$ for $\ell_i + \ell + m_{OAM}$ is odd, and $m - m_i = \Delta m = m_{OAM} + 1$. Photoelectrons originating from $m_i = 0$ avoid the $x - y$ plane (i.e. $\theta_k = \pi/2$) since the spherical harmonics $Y_{\ell_i - 1}(\Omega_k)$ have a node at $\theta_k = \pi/2$. The emission probability $|a_i(k)|^2$ exhibits no angular dependence in the equatorial plane. Around the Cooper minimum transitions to lower orbital angular momenta are weaker [80]. The energetic position of the minimum depends strongly on the angular momentum of the perturbative field. Fig. 1(a) shows the radial matrix elements for $m_{OAM} = 1$. The relevant transitions according to the scheme (2) are the transitions $\ell_i = 1 \rightarrow \ell = 3$ and $\ell_i = 1 \rightarrow \ell = 1$. Around a laser frequency of $\omega = 95$ eV we find that the expected dominant $d_{\ell = 1}^{\text{OAM} = 1}$ has a comparable magnitude as $d_{\ell = 1}^{\text{OAM} = 0}$. A strong angular dependence of the time delay is expected in the energy regime where the strengths of both ionization channels are comparable, for the interference between both channels delivers eventually the angular modulation [25]. This motivates our choice of the frequency regime, both for Ar and C_60. The underlying physics of time delay both for Ar and C_60 is similar, and we will elaborate here on Ar deferring C_60 case to appendix F. For $\omega = 100$ eV the Ar photoionization probability dependence on the photoelectron emission angle $\theta_k$ is shown in Fig. 2 for different initial states $m_i$. For a topological charge $m_{OAM} = 1$ and $m_i = 1$, the ionized electron ends up in the $f$-partial wave channel with $m = 3$, while the counter-rotating photoelectron ends up in a superposition of the $p$ and $f$ partial wave channels with $m = 1$. A photoelectron lauched from $m_i = 0$ is described by the $f$ partial wave channel with $m = 2$, i.e. the node of the spherical harmonic $Y_{12}(\theta_k = \pi/2, \varphi_k)$ leads to vanishing emission in this direction. In the $x - y$ plane ($\theta_k = \pi/2$) the co-rotating electron with $m_i = 1$ relative to the circularly polarized OAM-field is dominant over the counter-rotating one with $m_i = -1$. The electron with $m_i = 0$
does not escape in this direction. Interestingly, the two types of electrons are predominantly emitted in different directions (at $\vartheta_k = 150^\circ$ the counter-rotating electron dominates the co-rotating one) allowing thus a discrimination via angular resolved photoelectron detection.

### IV. ATTOSECOND TIME DELAY

The Wigner time delay is

$$\tau'_{W}(\varepsilon_k, \Omega_k) = \frac{\partial}{\partial \varepsilon_k} \mu_i(\varepsilon_k, \Omega_k), \text{ where } \mu_i(\varepsilon_k, \Omega_k) = \text{arg } [a_i(k)],$$

or

$$\tau'_{W}(\varepsilon_k, \Omega_k) = \Im \left[ \frac{1}{a_i(k)} \frac{\partial a_i(k)}{\partial \varepsilon_k} \right]. \tag{3}$$

The analytical expressions for $\partial a(k, \Omega_k)/\partial \varepsilon_k$ are in appendix D. Evaluating eq. (3) on the energy shell $\varepsilon_k = \varepsilon_{\text{COE}}$ reveals angular modulations with the azimuthal angle of the form $\exp[i(2m_{\text{COE}} + 2)\varphi]$, while the amplitude of this modulation depends on $\partial \varepsilon_z/\partial \varepsilon_k |_{\varepsilon = \varepsilon_{\text{COE}}} \cdot \partial \varepsilon_z/\partial \varepsilon_k |_{\varepsilon = \varepsilon_{\text{COE}}} \cdot \varepsilon_{\text{COE}}$.

In addition to this quasi analytical model we solved the three-dimensional Schrödinger equation numerically using the matrix iterative method [81, 82]. This numerical algorithm was already tested and implemented in time delay calculations [83, 84] (cf. appendix E for details). The time delays in fig. 2 show, depending on the emission direction, a large difference between the photoionization process from initial states with $m_i = 1$ and $m_i = -1$.s. The photoelectron originating from $m_i = 1$ dominates the photoionization probabilities (cf. fig. 1) at the angle $\vartheta_k = 90^\circ$, while at $\vartheta_k = 150^\circ$ the counter-rotating electron ($m_i = -1$) delivers the largest contribution. The small angular variations in the time delay (in $\varphi_k$) smoothen very fast (without affecting the magnitude of the time-delay) for longer pulses (cf. appendix C-E). Experimentally advantageous is the large difference between both cases where the co-rotating or the counter-
rotating electrons dominate the photoionization process. The averaged time delay \( \tau^m_W = 10.7 \text{ as} \) which coincides almost with the value of \( \tau^m_W = 8.7 \text{ as} \). The time delay \( \tau^m_W = -1 \) being related to the counter-rotating electron is only a minor contribution to the full subshell delay due to the lower photoionization probability. The electron ionized from the initial state with \( m = 0 \) has no influence on the resulting time delay because we find no photoionization probability in the equatorial plane. The differences between the analytical model and the numerical propagation are vanishingly small giving further credibility to the analytical explanations.

In contrast at \( \theta_k = 150^\circ \) the fully averaged, subshell time delay \( \tau^3_p = -23.5 \text{ as} \) is mainly characterized by \( \tau^m_W = -27 \text{ as} \), where the influences of the co-rotating electron \( \tau^m_W = 3.0 \text{ as} \) and the electron ionized from the initial state with \( m = 0 \) \( \tau^m_W = 4.0 \text{ as} \) play a minor role. Thus, we find a large difference of 34.2 as between both cases where either the co-rotating \( m = 1 \) electron or the counter-rotating electron \( m = -1 \) dominates. With this configuration it is so possible to pinpoint the origin of the time delay, i.e. a time delay measurement identifies from which initial magnetic sublevel the photoelectron were launched. From the analytical and symmetry considerations it is conceivable that these findings are of a general nature and are akin to quantized systems with spherical symmetry. This is indeed confirmed by corresponding results (Fig. 2c, d) for ionization of \( C_{60} \) from the highest occupied molecular levels (HOMO) (see appendix F for full technical details). The 5 electrons in HOMO (or the 5h state) occupy the magnetic sublevels \( m_i = \pm 2, \pm 1, 0 \) which are degenerate but their photoionization probabilities exhibit crossly different angular behavior, as for Ar: In certain directions the photoionization is dominated by emission from specific initial magnetic sublevels of HOMO. As a result, if for instance \( \theta_k = 90^\circ \) or \( \theta_k = 180^\circ \) are chosen where photoionization stems largely from \( m = -1 \) or \( m = -2 \) respectively, we observe the azimuthal time delay behavior as depicted in Fig. 2c, d. The interpretation goes along the lines as for Ar. The time delays averaged over the initial degeneracies are governed by contributions from the \( m_i \) states that dominate the photoionization.

V. SPATIAL DEPENDENCE OF TIME DELAY

Another interesting aspect is the dependence of the time delay in photoionization on the position \( r_0 \) of the atom in the OAM XUV laser spot, i.e. away from the optical axis. When the atom is in the donut center the transfer of OAM from the light beam to the photoelectron is maximal, decreasing with enhancing the distance between the atom and optical axis \( r_0 \) [56]. This is due to the vast difference in the spatial extension...
of the atom and the laser spot. Roughly speaking, when the atom is at the peak intensity \( r_0 \approx w_0 / \sqrt{2} \) only the beam local spatial structure is relevant, which resembles locally a Gaussian beam [94]. In fig. 3 we show the time delay corresponding to cases where either the co-rotating electron (\( \vartheta_k = 90^\circ \)) or the counter-rotating electron (\( \vartheta_k = 150^\circ \)) dominates the photoionization process, as delivered from the full numerical simulations. The numbers at \( r_0 = 0 \) belong to the results of fig. 2. Surprisingly, even at small distances \( r_0 = 1 \) a.u. the transfer of OAM diminishes rapidly. At distances \( r_0 > 10 \) a.u. both time delays are nearly indistinguishable. So we argue that measurements of the time delay as a function of the topological charge allows accessing magnetic information with an atomic size spatial resolution using optical beams. This is not a violation of the diffraction limit, as these information are carried by the photoelectron and are not gained via optical microscopy.

VI. CONCLUSIONS

Summarizing, the time delays in photoionization are substantially different for co-rotating (relative to the OAM field) or counter-rotating emitted electrons, even for spherically symmetric targets. The time delay carry atomic-scale information on the orbital position in the beam spot. Including spin-orbital coupling, e.g., as done in [85] should yield spin-dependent time delays offering a tool for polarized electron burst [86] by short OAM pulses. Combined with the possible spatial resolution on the magnetic states, this may offer a novel technique for spatio-temporal mapping of spin dynamics.

ACKNOWLEDGMENTS

The work is supported by the DFG through SPP 1840. We thank Olga Smirnova and Ingo Barth for interesting discussions.

Appendix A: Modelling propagating OAM beams

The OAM beam vector potential in the coordinate frame of the atom with the \( z \) axis being parallel to the light propagation (with a wave vector \( q_z \)) is [87]

\[
A(r, t) = \hat{e} A_0 f_{\text{OAM}}^p(r) e^{i \varphi'(r) - \omega t} \hat{g}(t) e^{i \varphi z(r)} + \text{c.c.} \quad (A1)
\]

The polarization vector is taken \( \hat{e} = (1, i, 0)^T \), and for the pulse temporal envelope we take

\[
\hat{g}(t) = \cos[\pi t/nT]^2,
\]

where \( T = 2\pi/\omega \) is the cycle duration and \( n \) is the number of optical cycles. \( \varphi'(r) \) is the electron azimuthal angle relative to the optical axis of the laser field. If the atom is in the beam center we write \( \varphi'(r) = \varphi \). For the photon energies of concern here \( q_z z'(r) \ll 1 \) applies, i.e. the dipole approximation is acceptable along the \( z \) axis. The radial structure is described by the function

\[
f_{\text{OAM}}^p(r) = e^{-\frac{r^2}{w_0^2}} \left( \frac{\sqrt{2} \rho'(r)}{w_0} \right)^{|m_{\text{OAM}}|} L_p^{|m_{\text{OAM}}|} \left( \frac{2 \rho'(r)^2}{w_0^2} \right). \quad (A2)
\]

where \( \rho'(r) \) is the radial distance to the optical axis. If the atom is in the beam center then \( \rho'(r) = r \sin \vartheta \). The number of nodes in the beam radial profile is indexed by \( p \) and \( L_p^{|m_{\text{OAM}}|}(x) \) are the generalized Laguerre polynomials. We consider the experimentally important case \( p = 0 \) for which \( L_p^{|m_{\text{OAM}}|}(x) = 1 \). Calculations for \( p \neq 0 \) are feasible but are not expected to yield any sizable effect on the time delay (the beam radial variation is on the scale of tens of nanometers, i.e. far off the electron wavelength). \( w_0 \) stands for the beam waist. Typical values that we employed in the calculations are in the range of \( w_0 = 50 \) nm (940 a.u.). Obviously \( |A|^2 \) possess a donut shape for \( p = 0 \) and intercalated rings for \( p > 1 \).

Appendix B: Transition amplitude

For the analytical model and the situation detailed in the main text the optical-vertex matrix elements between the initial and final states are (we exploited \( p = -|\hat{L}_0, r| \))

\[
\langle \varphi_k^- | \hat{H}_{\text{int}}(t) | \Psi_i \rangle = i (\varepsilon_i - \varepsilon_k) \langle \varphi_k^- | r \cdot A(r, t) | \Psi_i \rangle. \quad \text{After the laser}
\]
pulse is off we infer

\[ a_i(k) = (e_i - e_k) \sum_{l=0}^{\infty} \sum_{m=-l}^{l} i^{-l} e^{-i \delta(k)} d_{l,m}^{\text{OAM}} Y_{lm}(\Omega_k) \]

\[ \times \left( \mathcal{E}_-(e_k - e_i) \left( \frac{\ell}{l} \frac{m_{\text{OAM}} + 1}{m_{\text{OAM}} + 1} \ell_i \right) + \mathcal{E}_+(e_k - e_i) \left( \frac{\ell}{l} \frac{m_{\text{OAM}} + 1}{-m_{\text{OAM}} - 1} \ell_i \right) \right), \]

where \( \mathcal{E}_\pm(e) = E_0 \int_0^{\infty} dt g(t)e^{i(e(t)/a_0)} \) and \( E_0 = A_0 \left( \frac{\sqrt{2}}{e_0} \right)^3 \).

The reduced radial matrix elements are given by

\[ d_{l,n,l_i}^{m_{\text{OAM}}} = \sqrt{\frac{(2\ell + 1)(2m_{\text{OAM}} + 3)(2\ell_i + 1)}{3}} \times \left( \frac{\ell}{l} \frac{m_{\text{OAM}} + 1}{0} \ell_i \right) \int dr r^{3m_{\text{OAM}}} R_{\ell n}(r) R_{\ell_i}(r). \]

**Appendix C: Details to the numerical propagation scheme**

Numerically, we follow a standard matrix iterative method: The time dependent wave function is expanded in spherical harmonics, i.e., \( \Psi(r, t) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} Y_{lm}(\Omega) Y_{lm}(r) \) with \( \lim_{t \to \infty} \Psi(r, t) = \Psi(r, t) \). Every initial state of Ar 3p subshell is propagated from \( t = -0.5T \) to \( 0.5T \) in the presence of the OAM laser field. At a time where the photoelectron wave packet is fully formed, the solution \( \Psi(r, t > 0.5T) \) is then projected onto a set of field-free scattering wave function \( \varphi_k^{-1}(r) \) and we obtain the photoionization amplitudes \( a_i(k) \) associated with the specific initial state \( i \), which are further analyzed to extract the time delay.

**Appendix D: Time Delay**

The Wigner time delay in photoionization is given by

\[ \tau_W(e_k, \Omega_k) = \frac{\partial}{\partial e_k} \mu(e_k, \Omega_k), \]

where \( \mu(e_k, \Omega_k) = \arg [a_i(k)] \) or by

\[ \tau_W(e_k, \Omega_k) = \Im \left[ \frac{1}{a_i(k)} \frac{\partial a_i(k)}{\partial e_k} \right]. \]

Taking into account that \( \partial \mathcal{E}_- / \partial e_k = 0 \) (absorption) while \( \partial \mathcal{E}_+ / \partial e_k \neq 0 \) (emission) at \( e_k = e_{\text{COE}} \), we find the following expression for the energy derivative of the amplitude in case of \( m_i = 1 \)

\[ \frac{\partial a_i(k, \Omega_k)}{\partial e_k} \bigg|_{e_k = e_{\text{COE}}} = \frac{\partial S_{m_{\text{OAM}} + 2, m_{\text{OAM}} + 2}^{2, \text{OAM}} Y_{m_{\text{OAM}} + 2, m_{\text{OAM}} + 2}(\Omega_k)}{\partial e_k} \]

\[ + F_{m_{\text{OAM}} - m_{\text{OAM}}}(Y_{m_{\text{OAM}} - m_{\text{OAM}}}(\Omega_k)) + F_{m_{\text{OAM}} + 2, m_{\text{OAM}}}(Y_{m_{\text{OAM}} + 2, m_{\text{OAM}}}(\Omega_k)). \]

**Appendix E: Analytical vs. numerical results**

To facilitate the comparison between the analytical and the numerical results for the delay time as the pulse duration varies we refer to Fig. 4 of this supplementary materials that should be compared with Fig 2 of the main text. It is obvious that for longer pulse durations (meaning more optical cycles \( n \)) the small variations in the dependence on the azimuthal angle \( \varphi_k \) diminish.

**Appendix F: Time delay in photoionization of C_{60} molecule**

Due to the vast difference between the atomic orbital extent and the focused, but diffraction limited laser spot the predicted effects for atoms require highly intense laser pulses. For instance, the Ar calculations in the main text were performed for a peak intensity of \( 5.6 \times 10^{19} \text{W/cm}^2 \) at \( e_0/\sqrt{2} \). For more extended orbitals similar effects in photoionization are achieved at lower peak intensity which is advantageous from an experimental point of view. To endorse and quantify this statement we considered C_{60} as the next step from atoms towards extended systems. The radius of the carbon cage of C_{60} is \( R_{\text{C}_{60}} = 6.745 \text{a}_B \). Assuming an \( A_0 = 0.05 \text{a}_u \) at \( R_{\text{C}_{60}} \) we find a peak intensity of \( 3.2 \times 10^{17} \text{W/cm}^2 \) at \( e_0/\sqrt{2} \). In principle, one may consider C_{240} to lower the peak intensity even more.

To apply our theory we describe the molecule with an effective single particle potential that captures the valence electronic structure with its characteristics as derived accounting for the \( l_{t0} \)-symmetry. Technically, as an input we use the correlated, ab-initio calculated, single particle density \( n(r) \) which incorporates the underlying ionic structure to construct a local single particle (orbital-dependent) potential [88–90]. This
potential is utilized for the driven electron dynamics [89, 91].
Using the constructed potential, the electronic wave function
\( \Psi(r) \) of the fullerene valence shell is expressible as a product
of a radial part \( R_{n}(r) \) with \( n = 1 \) nodes, and an angular part
characterized by the spherical harmonics \( Y_{l,m}(\Omega_{k}) \) with
the orbital and magnetic quantum numbers \( \ell_{i} \) and \( m_{i} \). The
corresponding energies (degenerate in \( m_{i} \)) are \( \epsilon_{n,\ell_{i}} \). Within this
model the occupied valence states form two radial (\( \sigma \) and \( \pi \))
subbands. The wave functions are shown in fig. 5. The occu-
pation of the single-particle orbitals were discussed in Ref.
[92] with the HOMO orbital \( (n_{i} = 2, \ell_{i} = 5) \) being occupied by
5 electrons. \( C_{60} \) has a diamagnetic character with the HOMO
magnetic sublevels \( m_{i} = -2, -1, 0, 1, 2 \) being populated.
In fig. 6(a) we present the radial matrix elements which are
relevant for the photoionization process of the HOMO orbital.
For the same reason as in the main text we choose
a frequency regime where the matrix elements have simi-
lar magnitudes (in which case \( \hbar \omega_{XUV} = 60 \text{eV} \)). In panel
fig. 6(b) we show the corresponding photoionization probabil-
ities \( |\mu_{\ell_{i}=5,m_{i}}(k,\varphi_{k},\theta_{k})|^{2} \) of the different initial states from the
\( 5h \) orbital in \( C_{60} \) in dependence on the polar angle \( \theta_{k} \) relative
to the optical axis of the vortex field. The figure demonstrates
the significantly different angular distributions for photoelec-
trons originating from different initial states which endorses
the generality of the predicted effect. Clearly, one may follow
the arguments made for Ar in the main text and reach the same
conclusions for \( C_{60} \): We find directions where the photoion-
ization process is totally dominated by some specific initial
magnetic sublevel of the HOMO. This has also a direct con-
sequence for the time delay depicted in panel fig. 6(c) and (d).
FIG. 6. (a) Reduced radial matrix elements for the partial wave functions with the orbital angular momenta $\ell = 5$ and $\ell = 7$. (b) Angular dependent photoionization probabilities for the different initial states of the 5h subshell (HOMO) in CO. (c)-(d) The time delays vary with the azimuthal angle $\varphi_k$ at the polar angle $\vartheta_k$. The left column corresponds to the photoionization process for $\vartheta_k = 90^\circ$ (electrons with $m_i = -1$ are dominant), while the right column is associated with $\vartheta_k = 180^\circ$ (electrons with $m_i = -2$ are dominant). Time delays for the 5h subshell averaged over the initial states degeneracies are also shown.

We choose here as examples the polar angles $\vartheta_k = 90^\circ$ and $\vartheta_k = 180^\circ$, where according to the photoionization probabilities are dominated by emission from respectively the $m_i = -1$ and $m_i = -2$ states. The duration of the pulse is $n = 3$ optical cycles. The small variations as the azimuthal angle $\varphi_k$ varies decrease for longer pulses. We show only time delays of electrons which have a photoionization probability $|d_{i=5,m_i(kCOE,\vartheta_k)}|^2 > 0$. The time delay averaged over initial state degeneracies receives major contributions from specific magnetic sublevels at certain directions as in the case of Argon atom.

[1] Attosecond photonics (focus issue) *Nat. Photon.* **8**, 161-264 (2014).
[2] R. Pazourek, S. Nagele, J. Burgdörfer, Attosecond chronoscopy of photoemission. *Rev. Mod. Phys.* **87**, 765 (2015).
[3] L. Torlina, *et al.*, Interpreting attoclock measurements of tunnelling times. *Nat. Phys.* **11**, 503–508 (2015).
[4] A. Maquet, J. Caillat, R. Taieb, Attosecond delays in photoionization. *Time and quantum mechanics. J. Phys. B: At. Mol. Opt. Phys.* **47**, 204004 (2014).
[5] J. Dahlström, A. LHuillier, A. Maquet, Introduction to attosecond delays in photoionization. *J. Phys. B: At. Mol. Opt. Phys.* **45**, 183001 (2012).
[6] A. S. Landsman, U. Keller, Attosecond science and the tunnelling time problem. *Phys. Rep.* **547**, 1–24 (2015).
[7] J. Su, H. Ni, A. Becker, A. Jarôi-Becker, Numerical simulation of time delays in light-induced ionization. *Phys. Rev. A* **87**, 033420 (2013).
[8] L. E. Eisenbud, *PhD thesis* (Princeton University, 1948).
[9] E. P. Wigner, Lower limit for the energy derivative of the scattering phase shift. *Phys. Rev.* **98**, 145–147 (1955).
[10] C. Joachain, *Quantum collision theory* (North-Holland, Amsterdam, 1975).
[11] M. Schultz, *et al.*, Delay in photoemission. *Science* **328**, 1658–1662 (2010).
[12] K. Klünder, *et al.*, Probing single-photon ionization on the attosecond time scale. *Phys. Rev. Lett.* **106**, 143002 (2011).
[13] D. Guénot, *et al.*, Photoemission-time-delay measurements and calculations close to the 3 s-ionization-cross-section minimum in ar. *Phys. Rev. A* **85**, 053424 (2012).
