Parity is of fundamental importance in many areas of physics, e.g., atomic and molecular physics, cosmology, and particle physics. It is conserved in electromagnetism, strong interactions, and gravity, but not in weak interactions. In quantum mechanics, it mostly relates to the symmetry of wave functions representing microscopic particles, and to quantum phase differences. For an atom or molecule interacting with a strong laser field, the parity of electronic orbitals governs many phenomena such as resonant multiphoton transitions, molecular ionization suppression, and the phase differences acquired by the tunneling wave packet. Following tunneling, the electron can be driven back by the laser field to recollapse with its parent ion and initiate many interesting strong field phenomena. Laser-driven recollision is the basis of a myriad of techniques for probing the dynamic structure of atomic or molecular systems with attosecond temporal resolution and Angstrom spatial resolution. One such technique is ultrafast photoelectron holography. Thereby, a probe and a reference wave are employed to reconstruct a target by recording phase differences between them. Both probe and reference stem from qualitatively different ionization pathways, which can be associated to interfering electron wave packets. This phase encoding makes it an ideal tool to probe the parity of the atomic and molecular orbitals (for a review see ).

Since its inception, ultrafast photoelectron holography has been used for extracting not only structural information, but also for visualizing the attosecond dynamics of valence electron motion, and revealing the coupled electronic and nuclear dynamics of molecules. Furthermore, sculpted driving fields have been adopted to resolve different interference structures and unravel novel holographic patterns. So far various interference patterns have been observed in the photoelectron momentum distributions. Prominent examples are the spider-like structure that forms around the polarization axis, the carpet-like structure in the region approximately perpendicular to the laser polarization, and the near-threshold fan-shaped structure. The spider and in particular the fan are caused by the interplay between the residual Coulomb potential and the laser field. Recently, a novel orbit-based approach that incorporates the Coulomb potential and the laser field on equal footing, the Coulomb quantum-orbit strong-field approximation (CQSFA) simulation, has offered a transparent picture of different interference structures. It was shown that the fan-shaped structure is a subcycle time-resolved holographic structure, whose high-energy limit gives the interference carpets.

In this paper we demonstrate, both experimentally and theoretically, that photoelectron holography is a sensitive tool for probing the parity of atomic and molecular orbitals. The basic strategy is illustrated in Fig. 1. Let us consider an atomic or molecular orbital of odd parity. When irradiated by an intense laser pulse, the tunnel ionized electrons ending up with same final momentum lead to various interference patterns in the photoelectron momentum distribution. Within the CQSFA, each trajectory carries a phase that can be separated into two parts, i.e., the initial phase which includes the parity of the atomic or molecular orbital and the phase accumulated along the pathway from the origin until the detector. For each given final momentum, the electron trajectories can be distinguished into four groups, as introduced in CQSFA or trajectory-based Coulomb-strong-field approximation theory. For type-I trajectories, the electron moves directly to the detector without revisiting its parent core. For type-II and type-III trajectories, the electron first moves away from the detector and then turns around and finally arrives at the detector. For type-IV trajectories, the electron initially moving to the detector goes around the core and then again moves...
TABLE I. Summary of the phase shifts expected for different types of orbits and initial bound states of different parity.

| Structure | Orbits   | Parity | Shift |
|-----------|----------|--------|-------|
| Fan       | I, II    | even/odd | 0/π   |
| Spider    | II, III  | even/odd | 0/0   |
| Carpet    | III, IV  | even/odd | 0/π   |

To experimentally realize the strategy, we introduce a differential holographic method, in which we use Ar as a reference atom to reveal information about the target molecule \( \text{N}_2 \). One important reason for this target choice is that the ground state \( 3p \) of Ar and the highest-occupied molecular orbital (HOMO) of \( \text{N}_2 \) have odd and even parities, respectively. Additionally, according to the CQSFA theory [26, 37], for each type of trajectory in identical laser fields, the phase obtained along the continuum propagation is expected to be nearly identical for Ar and \( \text{N}_2 \) due to their close ionization potentials and similar long-range Coulomb effects, as we will see below. The initial phase encoding the parity of the atomic or molecular orbital is thus accessed by comparing the holographic patterns of the two targets. We find that the measured fan-shaped (and carpet-like) patterns show out of phase features for Ar and \( \text{N}_2 \), whereas the spider-like patterns are in phase under identical laser conditions. The observations are reproduced by a numerical solution of the time-dependent Schrödinger (TDSE) equation, as well as the CQSFA simulation. In terms of the CQSFA theory, we demonstrate that our findings can be ascribed to the different parities of the \( 3p \) orbital of Ar and the HOMO of \( \text{N}_2 \).

In our experiments, intense laser pulses at a central wavelength of 788 nm were generated by a commercial Ti:Sapphire femtosecond laser system (100 kHz, 100 \( \mu J \), 45 fs, Wyvern-500, KMLabs). The laser beam was then focused by a spherical concave mirror \(( f = 60 \text{ mm}) \) onto a cold supersonic jet of mixture of Ar and \( \text{N}_2 \) inside the main chamber of a Cold Target Recoil Ion Momentum Spectroscopy (COLTRIMS) reaction microscope [42]. The use of a mixture gas jet substantially reduces the systematic uncertainties resulting from the absolute determination of each gas target density as well as the laser intensity, and beam pointing fluctuations during long-time measurements. The laser intensity in the interaction region was calibrated by measuring the “donut”-shape momentum distribution of singly charged Ne\(^+\) ions with circular polarized light [43]. We did not align the \( \text{N}_2 \) molecules throughout our measurements.

We employed the COLTRIMS setup to simultaneously measure the three-dimensional momentum distributions of the electrons and ions from ionization of Ar and \( \text{N}_2 \). The photoelectrons and photoions were guided by homogeneous electric (27.6 V/cm) and magnetic (9.5 G) fields towards two microchannel plate detectors equipped with delay-line anodes [44] in order to obtain the positions of impinging particles. The spectrometer consisted of an ion arm with a 18.2 cm acceleration region and a 40.0 cm drift region, and an electron arm with an acceleration region of 7.8 cm. By checking for momentum conservation between the detected electrons and the singly charged ions, the events arising from false coincidences were suppressed substantially.

In Figs. 2(a) and 2(b) we present the measured photoelectron momentum distributions of Ar and \( \text{N}_2 \), respectively. One can find distinct fan-shaped interference patterns near the ionization threshold (enclosed by the half circles), i.e., four smaller lobes distributed symmetrically with respect to \( p_z = 0 \) a.u. for Ar and five lobes with the middle one along \( p_z = 0 \) a.u. for \( \text{N}_2 \). For the spider-like structures, the constructive interferences, i.e.,
respectively. The experimental differential hologram is a.u., the carpet-like structures as revealed in previous rings exhibit minima for Ar but maxima for N\textsubscript{2}.

The numbers represent the orders of ATI rings. Here \(D_{\text{Ar}}\) denotes the photoelectron distribution for Ar and \(D_{\text{N}_2}\) for \(N_2\) (confined by the rectangles). For an intensity of \(2\times10^{13}\) W/cm\(^2\), the rectangles cover a number of ATI rings ranging from the 4th to the 7th order. The carpet-like structures clearly exhibit different features for Ar and \(N_2\). To highlight this discrepancy, we produced a differential hologram by calculating the normalized difference \(\frac{D_{\text{Ar}}(p) - D_{\text{N}_2}(p)}{[D_{\text{Ar}}(p) + D_{\text{N}_2}(p)]}\), where \(D_{\text{Ar}}\) and \(D_{\text{N}_2}\) denotes the photoelectron distribution for Ar and \(N_2\), respectively. Here \(D_{\text{Ar}}\) and \(D_{\text{N}_2}\) has been normalized to the corresponding maximum photoelectron yield, respectively. The experimental differential hologram is displayed in Fig. 3(a). This hologram reveals that, among \(p_z = 0\) a.u., every odd-order (the 5th and 7th orders) ATI rings exhibit minima for Ar but maxima for \(N_2\). While for every even-order ATI rings (the 4th, 6th, and 8th orders), maxima for Ar but minima for \(N_2\) are observed. In general, when comparing Ar and \(N_2\), both the fan-shaped and carpet-like interferences are out of phase while the spider-like interferences are in phase.

To simulate our data, we first solved the full-dimensional time-dependent Schrödinger equation (TDSE). The details about the TDSE simulations are provided elsewhere [28, 45]. For Ar, the simulation was performed within the single-active-electron approximation for an effective model potential \(V(r) = -(1 + a_1e^{-a_2r} + a_3e^{-a_4r} + a_5e^{-a_6r})/r\) with \(a_1 = 16.039, a_2 = 2.007, a_3 = -25.543, a_4 = 4.525, a_5 = 0.961\), and \(a_6 = 0.443\) considering a 3p \((m = 0)\) orbital neglecting spin orbit interaction. For \(N_2\) we only considered the HOMO in the simulation, and used the linear combination of atomic orbitals (LCAO) approximation [47]. The calculated results are shown in Figs. 2(c) and 2(d). Many key features of the experimental results, as described above, are satisfyingly reproduced by our simulations. More lobes for the fan-shaped structures around \(p_z = 0\) a.u. in the simulations are not well resolved in the experiments due to the insufficient momentum resolution along the transverse direction.

To further gain physical insight, we resort to the CQSFA, which describes ionization in terms of quantum orbits from the saddle-point evaluation of the Coulomb-distorted transition amplitude. In an exact form, the ionization amplitude reads

\[
M(p_f) = -i \lim_{t \to \infty} \int_{-\infty}^{t} dt_0 \langle \psi_{p_f}(t) | \hat{U}(t, t_0) \hat{H}_I(t_0) | \psi_0(t_0) \rangle,
\]

where \(\psi_0(t_0) = e^{i\hat{p}_0 \cdot \hat{r}} | \psi_0 \rangle\) is the initial bound state and the final state \(| \psi_{p_f}(t) \rangle\) is a continuum state with momentum \(p_f\). \(\hat{U}(t, t_0)\) is the time-evolution operator of the Hamiltonian \(\hat{H}(t) = \hat{p}^2/2 + V(\hat{r}) + \hat{H}_I(t)\), with \(\hat{H}_I(t) = -\hat{r} \cdot \hat{E}(t)\) and the Coulomb potential \(V(\hat{r})\). Using the Feynman path-integral formalism [48, 49] and the saddle-point approximation [50, 51], Eq. (1) can be rewritten as [20, 57]

\[
M(p_f) \propto -i \lim_{t \to \infty} \int_{-\infty}^{t} dt_0 \left\{ \det \left[ \frac{\partial \rho_s(t)}{\partial \tau_s(t_0, s)} \right] \right\}^{-1/2} \times C(t_0, s) e^{i S(p_f, \vec{r}, t_0, s, t)},
\]

FIG. 2. (a) and (b) Measured photoelectron momentum distributions (in logarithmic scale) from ionization of Ar and randomly aligned \(N_2\) in identical laser fields of a peak intensity of \(6.5 \times 10^{13}\) W/cm\(^2\), respectively. The laser central wavelength is 788 nm. The abscissa \(p_z\) and ordinate \(p_\perp = \sqrt{p_\parallel^2 + p_\perp^2}\) denotes the momentum parallel and perpendicular to the laser polarization, respectively. The fan-shaped structures close to the ionization threshold are enclosed by half circles. The minima of the spider-like structures are indicated with dotted lines. The rectangles mark the carpet-like structures, including several ATI rings along the transverse direction. The numbers represent the orders of ATI rings covered in the rectangles. (c) and (d) TDSE simulations. (e) and (f) CQSFA simulations. To compare with the data, the focal volume effect has been considered in both TDSE and CQSFA simulations. The calculated results for \(N_2\) molecules have been averaged over the random alignment of the internuclear axis. The color scales have been adjusted to highlight the interference structures.

FIG. 3. (a) Blow-up of the experimental normalized momentum difference spectrum between Ar [Fig. 2(a)] and \(N_2\) [Fig. 2(b)]. The numbers represent the orders of ATI rings. (b) The corresponding CQSFA calculation.
\[
C(t_{0,s}) = \sqrt{2\pi i/(\partial^2 S(\tilde{p}_r, r_s, t_{0,s}, t)/\partial t^2)_{t=t_0}}
\]
\[\times (p_s(t_{0,s}) + A(t_{0,s}) |\hat{H}_I(t_{0,s})| \psi_0) \]
\]
where \(t_{0,s}\) is a prefactor, \(\partial p_s(t)/\partial r_s(t_{0,s})\) is related to the stability of the trajectory, and

\[
S(\tilde{p}, r, t_0, t) = I_p t_0 - \int_{t_0}^t d\tau [\tilde{p} \cdot \dot{r}(\tau) + \tilde{p}^2/2 + V(r)]
\]

denotes the action, where \(I_p\) is the ionization potential, \(\tilde{p}\) is the field-dressed momentum and \(\tilde{p} = p + A(\tau)\) with \(t_0 < \tau < t\), is the electron velocity. Eq. (2) indicates that there are in principle many trajectories along which the electron may be ionized. For the same final momentum, the corresponding transition amplitudes will interfere.

The sum in Eq. (2) is over the semi-classical trajectories starting from position \(r(t_{0,s})\) at time \(t_{0,s}\) and end at momentum \(p(t)\) at time \(t \to \infty\). The index \(s\) denotes the different trajectories satisfying three saddle-point equations:

\[
[p_0 + A(t_0)]^2/2 + I_p = 0,
\]
\[
\dot{p}(\tau) = -\nabla r V[r(\tau)],
\]
\[
\dot{r}(\tau) = p(\tau) + A(\tau).
\]

These equations are solved using an iteration scheme for any given final momentum \(37\) under the assumption that the electron is ionized by tunneling from \(t_0\) to \(t_0^f = \text{Re}[t_0]\) and then reaches the detector at a final (real) time \(52\), \(53\). For simplicity, we used \(-1/r\) as the form of Coulomb potential for both Ar and N\(_2\) in the simulations. Close to the origin, a regularisation procedure was implemented to treat the Coulomb singularities in the complex time plane (See \(54\) and references therein). The GAMESS code \(55\) was adopted to calculate the exact wave functions of the \(3p, m = 0\) state for Ar, neglecting spin orbit interaction and the HOMO of N\(_2\). The calculated results shown in Figs. (2c) and (2f) agree well with our observations and also the TDSE simulations. The main features of the fan-shaped, spider- and carpet-like structures for Ar and N\(_2\) are faithfully reproduced. Figure 3(b) displays the calculated differential hologram highlighting the difference of the carpet structures. Again, we find very good agreement between the experiment and simulation.

Encouraged by the overall agreement, we further explore the physical origin of our observations. From Eq. (2) we learn that the interference patterns are closely related to the phase \(\text{Re}[S]\), which is accumulated along the pathway starting from the original position, and the prefactor \(C(t_{0,s})\) associated with the atomic or molecular orbital \(\psi_0\) [Eq. (3)]. The stability factor \(\partial p_s(t)/\partial r_s(t_{0,s})\) is a real term and contains no phase information. In identical laser fields, we find that the difference between phase \(\text{Re}[S]\) for different types of trajectory is nearly identical for Ar and N\(_2\), due to their nearly identical ionization potentials (see Supplementary Material \([56\) for details]). Moreover, the simulations without inclusion of the prefactor \(C(t_{0,s})\) reveal practically identical features for Ar and N\(_2\) (not shown here). Therefore, our observations can be attributed to the different prefactors for Ar and N\(_2\).

Physically, the prefactor \(C(t_{0,s})\) contains the tunneling probability \(\sqrt{2\pi i/(\partial^2 S(\tilde{p}_r, r_s, t_{0,s}, t)/\partial t^2)}\) and the tunneling matrix element \((p_s(t_{0,s}) + A(t_{0,s}) |\hat{H}_I(t_{0,s})| \psi_0). For each trajectory type, the phase of the prefactor, i.e., \(\Phi_{0,s} = \arg[C(t_{0,s})]\), is related to the parity of the atomic and molecular orbital. The tunneling probability term has a simple phase that will not be affected by this parity. Here \(s = 1, 2, 3,\) and 4 correspond to types I, II, III, and IV trajectories, respectively, as depicted in Fig. 1. In the Supplementary Material \([56\), we explain how \(\Phi_{0,s}\) leads to the phase differences (or absence thereof) in specific holographic structures. The analysis verifies the physical picture illustrated in Fig. 1: Both the carpet-like and fan-shaped interference structures are sensitive to the parity of the electronic orbital of the target.

In summary, we show that the parity of atomic and molecular orbitals can be inferred from ultrafast holographic patterns. Our comparative and differential measurements show that holography patterns such as fan-shaped and carpet-like structures are dephased, while the spider-like fringes show in phase features when comparing Ar and N\(_2\) with identical laser conditions. Our data is well reproduced by focal- and alignment-averaged TDSE and CQSFA simulations. Using the CQSFA, we trace back the above-mentioned dephasing to parity-related phase differences in the interfering quantum orbits. These phases can be attributed to the different parity of the \(3p\) orbital for Ar and the HOMO of N\(_2\). The current work introduces a novel differential holographic method, in which we use a reference atom to reveal information about the target molecule, and gives access to the parity of the orbitals of atoms and molecules. This method also permits ultrafast detection of the parity of multielectron wavefunctions or multiple orbitals, which play significant roles in more complex molecules \([10\]. This will be particularly useful for interpreting complex electron dynamics such as charge migration in polyatomic and biological molecules.

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