A central achievement of strong-field physics is the ability to resolve ultrafast physical processes in atoms and molecules on the attosecond time scale. In particular, several methods have been developed to measure ionization times, i.e. to answer the question at precisely what time an electron is released from an atom in single-photon or strong-field ionization. Shafir et al. have used an orthogonal two-color field in high-harmonic generation as a gate to measure ionization time as a function of harmonic order [1]. Schultze et al. have measured a time delay of electron emission from the neon 2p subshell relative to the neon 2s subshell using extreme-ultraviolet-induced ionization in combination with the attosecond streak camera [2]. Klünder et al. have measured a similar time delay in argon [3]. A conceptually elegant approach to measure ionization times is attosecond angular streaking implemented by Eckle et al. [4], also known as the ‘attoclock’. The idea behind the attoclock is that in strong-field ionization with a circularly polarized laser pulse the time of ionization is mapped to the detection angle of the photoelectron. In fact, the strong-field approximation (SFA), in which the atomic potential is neglected, provides a mapping from the photoelectron momentum distribution (PMD) to complex ionization time in a way that the real part of a given ionization time corresponds to exactly one angle [5, 6]. If one breaks the rotational symmetry of the PMD by using a short pulse (or a slightly elliptically polarized field), the maximum of the SFA signal exactly corresponds to ionization at the time of peak field strength and it is obtained in the direction perpendicular to the electric field at the ionization time, provided that the envelope is chosen symmetric and the initial state is compatible with that symmetry. The maximum is found at the same position when a short-range potential is used in a numerical solution of the time-dependent Schrödinger equation (TDSE) [7]. In reality, the long-range atomic potential plays an important role and one finds that the PMD is rotated forward with respect to the handedness of the electric field [8, 9]. This could be caused by delayed ionization but also by the influence of the atomic potential on the electron after ionization. The latter prevents reading the ionization time simply from the hand of the clock. Instead, measurements have to be cleared of this effect to make the ionization time accessible again. Often, a semi-classical model consisting of a tunneling step and subsequent motion on a classical trajectory in the combined potential generated by the laser field and the atom is used for this purpose. In this way Eckle et al. could give a small upper limit on delay times in helium in a narrow range of intensities in the near infrared [8]. Pfeiffer et al. included the Stark shift and used initial conditions derived from a separation of the Schrödinger equation in parabolic coordinates (TIPIS) to get vanishing ionization times in helium and argon within the experimental accuracy over a wide range of intensities [10]. Later, Landsman et al. obtained a small positive tunneling delay using the same method [11]. Camus et al. also measured positive time delays in rare-gases [12], but using a different theoretical model that predicts nonvanishing parallel velocities at the tunnel exit. Recently, analytical R-matrix (ARM) theory was used to evaluate Coulomb corrections to ionization times in an attoclock setup [7, 13]. Another theoretical method is classical backpropagation [14]. In both cases vanishing ionization time delay in the hydrogen atom was concluded. In rare-gas atoms there is the question whether multielectron dynamics have an additional effect on the angular offset, but at least for the helium atom this is not the case [15, 16].

All attoclock-based determinations of ionization times require a theoretical model to map a given electron momentum to its ionization time. Once such a model is available, one may check, e.g., whether the momentum at the maximum signal corresponds to ionization at the peak of the pulse. The notion of some sort of electron trajectory is common to all previously used attoclock models. By contrast, in this work we present a method without trajectories to retrieve ionization times. Trajectory-free methods were also presented by Yuan et al. and Teeny et al. [17, 18]. The former consists of observing the instantaneous overlap with the bound states of the field-free system; the latter observes the probability flow through the tunnel exit. Both give large positive ionization time delays for their respective definition of the maximum instantaneous ionization rate, but they do not offer a momentum-resolved retrieval, which is the content of our work.
The method is based on finding stationary points of the exact (non-SFA) Dyson integral. Starting from the time-dependent Schrödinger equation in the single-active-electron approximation (atomic units are used unless stated otherwise),

\[ i \frac{\partial}{\partial t} \langle \psi(t) \rangle = \left( \frac{1}{2} \mathbf{p}^2 + V(\mathbf{r}) \right) \langle \psi(t) \rangle + H_I(t) \langle \psi(t) \rangle, \tag{1} \]

with the interaction Hamiltonian

\[ H_I(t) = \begin{cases} \mathbf{E}(t) \cdot \mathbf{r}, & \text{length gauge} \\ \mathbf{A}(t) \cdot \mathbf{p} + \mathbf{A}(t)^2 / 2, & \text{velocity gauge} \end{cases} \tag{2} \]

and the field \( \mathbf{E}(t) = -\partial_t \mathbf{A}(t) \), the Dyson integral

\[ \mathcal{M}(\mathbf{p}) = -i \int_0^T dt \mathcal{D}(\mathbf{p}, t) \tag{3} \]

gives the momentum distribution \( |\mathcal{M}(\mathbf{p})|^2 \) of the photoelectron after ionization. The integrand is

\[ \mathcal{D}(\mathbf{p}, t) = \langle \psi(\mathbf{p}, t) | U(T, t) H_I(t) U_0(t, 0) | \psi_0 \rangle, \tag{4} \]

where \( U_0 \) denotes the field-free time-evolution operator with the Hamiltonian \( H_0 = \mathbf{p}^2 / 2 + V \) and \( U \) the full time-evolution operator. In the SFA, the scattering state \( \langle \psi(\mathbf{p}) \rangle \) is replaced by a plane wave \( \langle \mathbf{p} \rangle \) and the full time evolution operator \( \hat{U} \) is approximated by the Volkov time evolution \( \hat{U}_V \) which neglects the atomic potential. This leads to the amplitude

\[ \mathcal{M}_{\text{SFA}}(\mathbf{p}) = -i \int_0^T dt \mathcal{M}(\mathbf{p}, t) e^{-i S(\mathbf{p}, t)} \tag{5} \]

with the action

\[ S(\mathbf{p}, t) = -I_P t + \int_t^T \frac{1}{2} (\mathbf{p} + \mathbf{A}(t'))^2 \tag{6} \]

and the transition matrix element

\[ \mathcal{M}(\mathbf{p}, t) = \begin{cases} \langle \mathbf{p} + \mathbf{A}(t') | \mathbf{E}(t') \cdot \mathbf{x} | \psi_0 \rangle, & \text{length gauge} \\ \langle \mathbf{p} | \mathbf{A}(t') \cdot \mathbf{p} + \mathbf{A}(t')^2 / 2 | \psi_0 \rangle, & \text{velocity gauge} \end{cases} \tag{7} \]

The SFA amplitude (5) is frequently evaluated using the saddle-point approximation. There, the integral is replaced by a discrete sum over stationary points of the action (6) which are given by

\[ \frac{1}{2} (\mathbf{p} + \mathbf{A}(t_s))^2 + I_P = 0. \tag{8} \]

This associates a discrete set of complex ionization times \( t_s \) with every momentum \( \mathbf{p} \).

In this work we retrieve ionization times including Coulomb effects by finding the stationary points of the integrand (4) directly. To this end we solve the saddle-point equations

\[ \frac{\partial}{\partial t} \mathcal{D}(\mathbf{p}, t) \bigg|_{t=t_s} = 0. \tag{9} \]

Note that this definition gives the ionization time \( t_s \) directly and makes no assumptions or statements about the tunneling time, i.e. the time the electron spends in the classically forbidden region. Saddle-point solutions to a semiclassical approximation of the Dyson integrand (4) were also considered by Klaiber et al. [19]. There, the saddle-point evaluation was extended to the position coordinate to find initial conditions for Newtonian trajectories. This leads to saddle-point times before the peak of the field followed by a non-zero tunneling delay. Instead, we proceed with a full numerical solution here. The time-derivative on the left-hand side of (9) is evaluated using the second-order central finite difference formula. The time-derivative of the field followed by a non-zero tunneling delay. Instead, we proceed with a full numerical solution here. The time-derivative on the left-hand side of (9) is evaluated using the second-order central finite difference formula. The integrand itself, Eq. (4), is evaluated using numerical wave-function propagation starting at some time \( t \) with initial state

\[ H_I(t) U_0(t, 0) | \psi_0 \rangle \tag{10} \]

using the full time-evolution operator first down to the real axis and then along the real axis to some final time \( T \) [20]. Therefore, for each evaluation of (9) one has to solve the TDSE twice. Fortunately, solving the TDSE gives the values of \( \mathcal{D}(\mathbf{p}, t) \) for all momenta at once such that it is straightforward to find the momenta \( \mathbf{p} \) for which a given \( t_s \) is a saddle-point time.

The time propagation is performed using the split-operator method with step size \( dt = 0.01 \) on a two-dimensional cartesian grid with 2048 points and a box size of 400 a.u. in each direction. We use the soft-core potential

\[ V(\mathbf{r}) = \frac{-1}{\sqrt{\mathbf{r}^2 + \alpha}}, \tag{11} \]

where \( \alpha = 0.64 \) is chosen in order to reproduce approximately the ionization potential \( I_P = 0.5 \) of hydrogen. The vector potential is

\[ \mathbf{A}_x(t) = -A_0 \cos(\omega t/4)^4 \cos(\omega t) \]
\[ \mathbf{A}_y(t) = -A_0 \cos(\omega t/4)^4 \sin(\omega t) \tag{12} \]

representing a two-cycle circularly polarised laser pulse with \( \omega = 0.05695 \) corresponding to 800 nm wavelength. The field is chosen exactly as in [7]. We solve the TDSE both on the real axis to obtain momentum distributions for various intensities and in the complex plane to find the ionization times. Time-propagation is always performed in velocity gauge. To evaluate \( \mathcal{D}(\mathbf{p}, t) \) in length gauge we apply the interaction operator \( H_I(t) \) in length gauge and perform a gauge transformation to velocity gauge at time \( t \). Starting from this complex time \( t \) we propagate the states first down to the real axis and then along the real axis to the final time \( T = 1000 \). While propagating along the real axis, outgoing parts of the wave function are projected onto Volkov-states starting at a distance of 150 a.u. from the atom [21].

The momentum distribution for the field strength \( E_0 = 0.05 \) \((1.75 \times 10^{14} \text{ W/cm}^2)\) is shown in Fig. 1(a). The
distribution is clearly rotated towards positive angles. Since the maximum of the momentum distribution is expected to be formed by ionization close to the time of peak field strength we begin by asking what momentum corresponds to ionization at the center of the pulse. To this end we solve the saddle-point equation (9) for the momentum $p$ at $\text{Re}(t) = 0$ and varying imaginary parts $\text{Im}(t)$. It is convenient to consider the logarithmic time-derivative
\[
\frac{\partial}{\partial t} \log(D(p, t)) = \frac{1}{D(p, t)} \frac{\partial}{\partial t} D(p, t)
\] (13)
which can also be calculated for all $p$ at once.

Logarithmic derivatives for two different imaginary times are depicted in Figs. 1(b,c). For small imaginary times, no saddle points are found. For a critical value of the imaginary time a saddle point emerges (b), which then splits into two separate saddle points for higher values of the imaginary time (c). Comparing with Fig. 1(a) we see that the saddle points are rotated in the same direction as the momentum distribution is. The exact values of these angles and the corresponding imaginary times are shown in Figs. 1(d,e) as a function of the absolute value of the momentum for both length and velocity gauge. In length gauge, saddle points emerge at much smaller imaginary times compared to velocity gauge. The velocity-gauge saddle points are closer to the original SFA saddle points that take only the action into account. (For a strict comparison with the SFA one would have to find saddle points of the entire SFA integrand, not just the action). However, the rotation angles are not so different in both gauges, especially in the region where the momentum distribution is actually concentrated. Still, for the purpose of interpreting the saddle points as ionization times, we believe that length gauge should be favored over velocity gauge. This is because in length gauge, the form of the integrand (4) in the Dyson integral is closer to our interpretation of the time evolution of a bound electron until time $t$ followed by ionization and subsequent propagation in both laser field and potential. The reason is that the state $U_0(t, 0)|\psi_0\rangle$ which appears in $D(p, t)$ in both gauges is a good approximation for the bound state

FIG. 1. (a) Photoelectron momentum distribution for $E_0 = 0.05$, normalized to maximum signal 1.0. (b,c) Absolute value of logarithmic derivative (13) at time zero for different imaginary times (length gauge, log-scale in arb. units). (b) $\text{Im}(t) = 198$ as. (c) $\text{Im}(t) = 213$ as. (d) Imaginary times of saddle points versus absolute value of the momentum. (e) Rotation angles of saddle points versus absolute value of the momentum.
in the presence of the field only in length gauge [22].

When comparing the saddle points with the rotation angle from the momentum distribution, care must be taken in defining that angle. The most likely momentum is given by the maximum of the cartesian distribution |M(p)|^2. However, in a semiclassical picture with an ionization and a propagation step, the momentum that corresponds to the highest instantaneous ionization rate is the maximum of the cylindrical distribution |p|M(p)|^2 rather than that of the cartesian distribution because one has to take the Jacobian of the deflection function [23] into account, which in the plane of polarization is given semiclassically by ωp for a circularly polarized field in both two and three dimensions when any additional influence by the atomic potential is neglected. In the recent study using ARM theory the maximum of the spherical distribution p^2|M(p)|^2 was used [7]. Many experiments on the other hand use the maximum of the angular distribution to define the rotation angle [8, 11, 12], which in our 2D case reads

$$w(\phi) = \int_0^\infty dp |M(p, \phi)|^2.$$  \hspace{1cm} (14)

The angles we obtain from the momentum distribution according to the different criteria are shown in Fig. 1(e). We find that the angle of the cartesian distribution is larger than the angle of the cylindrical distribution, which in turn is larger than the angle of the spherical distribution. This can be intuitively understood as a consequence of the momentum factors in the definitions of the different distributions pushing the maximum of the momentum distribution to higher momenta where the rotation angle is smaller. The angle obtained for the angular distribution (not shown here) agrees well with the cylindrical distribution. The differences between the various options are not negligible. For example, the angles from |M(p)| and |p|M(p)| differ by Δφ = 3.42° corresponding to a time difference of Δφ/ω = 25.4 as. In other words, the location of the maximum in a momentum distribution is influenced significantly by geometrical arguments and not only by the instantaneous ionization rate. This was also observed in [13], but its significance for the ionization-time retrieval was not addressed.

Since the angles extracted from the saddle points are almost constant as a function of radial momentum in the vicinity of the maxima we can assign a single rotation angle to time zero, which for simplicity we take to be the one at the radial momentum given by the maximum of the cylindrical distribution. The angles obtained in this way are shown in Fig. 2(a) as a function of intensity in comparison with the angles extracted directly from the momentum distributions. For the latter, we see that the choice of prescription (cartesian, cylindrical, spherical) has a non-negligible effect. We find good agreement between both length and velocity gauge saddle points and the maxima from the momentum distributions at small to intermediate field strengths. At high intensities there is disagreement. This is not surprising considering that the PMD is strongly affected by depletion whereas the ionization times are not (see Fig. 2(b)).

We also provide the time-zero angles and imaginary times from ARM theory, which we have calculated by full numerical solution of the saddle-point equations [7, 24]

$$-\frac{1}{2}(p + A(t_s))^2 - I_p$$
$$+ \frac{\partial}{\partial t} \int_{t_s}^T dt' V(r(p, t'), t)|_{t=t_s} = 0,$$  \hspace{1cm} (15)
where

\[ r(p, t', t) = \int_t^{t'} dt'' (p + A(t'')) \]  

(16)

is the Coulomb-free trajectory of an electron in the laser field and \( V \) is the 2D soft-core potential (11). Torlina et al. solved these equations for the 3D Coulomb potential approximately via a first-order expansion around the solution of the Coulomb-free case and found that the maxima of the PMDs correspond well to time zero [7]. Here, we find that the rotation angle corresponding to time zero in ARM theory is much smaller than what it would have to be to associate the maximum of the PMD with ionization at the peak of the pulse when the ARM saddle-point equations (15) are solved exactly, see Figs. 1(e) and 2(a). To highlight the difference, we include the rotation angles from the linearized ARM theory in Fig. 2(a), showing that the time-zero angles of the saddle points become much larger compared to the full solution.

Finally, we proceed in analogy with previous attoclock studies [7, 8] to retrieve the ionization time from the location of the peak of the PMD. Specifically, we match the saddle point in length gauge to the maximum of the cation of the peak of the PMD. Specifically, we match studies [7, 8] to retrieve the ionization time from the location of the maxima of the exact distributions. The comparison with ARM and SFA theories is also shown in Fig. 2(c). These models underestimate or neglect the Coulomb correction to the ionization time and therefore yield positive time delays when used to retrieve ionization times from the location of the maxima of exact distributions.

In conclusion, we have obtained momentum-resolved ionization times without resorting to electron trajectories. The theory is independent of assumptions on initial conditions for Newtonian motion, which have often been a cause of major discussion in previous work. In the future, we plan to apply our method to strong-field ionization in other types of laser pulses, such as bicircular fields. Since the Dyson integral is a rather general concept in quantum mechanics, we believe that our proposal may have applications even outside strong-field ionization. It could reveal temporal aspects of bound-state dynamics or photochemistry, for example.

ACKNOWLEDGMENTS

We acknowledge the fruitful discussions with Simon Brennecke. This work has been supported by the Deutsche Forschungsgemeinschaft through the Priority Programme Quantum Dynamics in Tailored Intense Fields (QUTIF).


