XUV ionization of the H₂ molecule studied with attosecond angular streaking

Vladislav V Serov¹ and Anatoli S Kheifets²,*

¹ General, Theoretical and Computer Physics, Saratov State University, Saratov 410012, Russia
² Research School of Physics, The Australian National University, Canberra ACT 2601, Australia

E-mail: A.Kheifets@anu.edu.au

Received 23 August 2022, revised 15 November 2022
Accepted for publication 30 November 2022
Published 23 January 2023

Abstract
We study orientation and two-center interference effects in attosecond time-resolved photoionization of the H₂ molecule. Time resolution of extreme-ultraviolet ionization of H₂ is gained through the phase retrieval capability of attosecond angular streaking demonstrated earlier by Kheifets et al (2022 Phys. Rev. A 106 033106). Once applied to H₂, this technique delivers an anisotropic phase and time delay which both depend sensitively on the molecular axis orientation. In addition, the photoelectron momentum distribution displays a very clear two-center interference pattern. When the interference formula of Walter and Briggs (1999 J. Phys. B 32 2487) is applied, an effective photoelectron momentum appears to be greater than the asymptotic momentum at the detector. This effect is explained by a molecular potential well surrounding the photoemission center.

Keywords: molecules, photoionization, time delay

Attosecond time resolved studies of molecular photoionization have become a rapidly growing field. Starting with the pioneering experiments of Haessler et al [1] on N₂ and Huppert et al [2] on H₂O and N₂O, the method of attosecond interferometry has been progressively used combining an extreme-ultraviolet (XUV) attosecond pulse train and a phase-locked infrared (IR) pulse. This technique has also been known as reconstruction of attosecond beating by interference of two-photon transitions (RABBITT) [3, 4]. Recent applications of RABBITT to molecular photoionization include attosecond time–energy structure of FEL pulses has been recently demonstrated [18, 19]. This demonstration makes FEL sources potentially suitable for attosecond time resolution of atomic and molecular photoionization. The only obstacle preventing such an application is a stochastic nature and an inherent time jitter of FEL radiation.

The method of attosecond angular streaking of XUV ionization was developed to overcome this obstacle. Prompted by theoretical works [20–23], this method was eventually implemented in practice for a shot-to-shot characterization of isolated attosecond pulses (IAPs) at FEL [18, 19]. Angular streaking of XUV ionization (ASXUVI or ASX for brevity) has common elements with the two previously

CH₃I molecule was conducted by Biswas et al [14]. Heck et al [15] presented the experimental observation of two-center interference in the ionization time delays of Kr₂. Wang et al [16] explored the role of nuclear-electronic coupling in attosecond photoionization of H₂.

The roadmap of atomic and molecular physics [17] has identified x-ray free-electron lasers (FELs) as a developing tool for resolving ultrafast molecular dynamics. Attosecond time–energy structure of FEL pulses has been recently demonstrated [18, 19]. This demonstration makes FEL sources potentially suitable for attosecond time resolution of atomic and molecular photoionization. The only obstacle preventing such an application is a stochastic nature and an inherent time jitter of FEL radiation.

The method of attosecond angular streaking of XUV ionization was developed to overcome this obstacle. Prompted by theoretical works [20–23], this method was eventually implemented in practice for a shot-to-shot characterization of isolated attosecond pulses (IAPs) at FEL [18, 19]. Angular streaking of XUV ionization (ASXUVI or ASX for brevity) has common elements with the two previously

* Author to whom any correspondence should be addressed.
developed techniques: attosecond angular streaking known as the attoclock [24, 25] and the attosecond streak camera (ASC) [26–33]. As in ASC, ASX uses XUV pulses to ionize the target. Then, similarly to the attoclock, the photoelectrons are steered by a circularly polarized laser field which makes its imprint on the photoelectron momentum distribution (PMD). This imprint is most visible in the plane perpendicular to the laser propagation direction. In its original form [18, 19, 21–23], ASX employed an intense IR laser field and was interpreted within the strong field approximation (SFA) [34]. In these strong field settings, the phase of the XUV ionization is usually neglected and the timing information associated with this phase is lost. An alternative viewpoint within the lowest order perturbation theory (LOPT) [35–37] considers IR streaking as an interference phenomenon which opens a natural access to the streaking phase $\Phi_S$. The latter is typically decomposed into the XUV ionization phase (or Wigner phase) and the continuum–continuum (CC) phase from the IR interaction. These two phases can be converted to the corresponding time delay components, which add up to the atomic time delay $\tau_0$.

Phase retrieval capability of ASX based on this analysis was demonstrated recently by Kheifets et al. [38]. In their numerical simulations on the hydrogen atom, they recovered accurately the streaking phase and the atomic time delay across a wide range of XUV photon energies starting from the threshold and exceeding it many times. Most importantly, this phase retrieval could be conducted from random shots of XUV radiation. This is a significant advantage over the existing interferometric techniques which require a systematic and controllable variation of the XUV/IR pulse delay in one set of measurements in order to record a streaking spectrum or a RABBITT trace. This recording requires a precise and stable temporal synchronization of the XUV/IR pulses which is not feasible at FEL at present.

In this paper, we extend ASX to molecular photoionization. We solve numerically the time-dependent Schrödinger equation (TDSE) describing the hydrogen molecule driven by a combination of the linearly polarized XUV and circularly polarized IR pulses. In our simulations, the XUV/IR pulse delay is incremented in several steps. By augmenting the isochrone analysis proposed by Kazansky et al. [21] with the energy dependent XUV ionization phase, we are able to interpret the molecular TDSE results in terms of the atomic time delay. While the phase and time delay determination is most accurate combining several increments of the XUV/IR delay, the accuracy is not significantly compromised with just a single XUV/IR delay value. We make a comparison with the previous RABBITT simulations on $\text{H}_2$ [39] and confirm validity of our interpretation and accuracy of our numerical results. We also demonstrate a strong dependence of the time delay on the molecular axis orientation discovered earlier in the $\text{H}_2^+$ ion [40, 41] and the $\text{Kr}_2$ dimer [15].

The paper is organized into the following sections. In section 1 we outline basics of the ASX method. In section 2 we describe our computational procedure. In section 3 we analyze and interpret our numerical results. In section 4 we summarize with our concluding remarks.

1. Basic considerations

The proposed phase retrieval by ASX is outlined in our preceding work [38]. The basics of the molecular ASX are essentially the same as for atoms. In brief, we apply the SFA and write the photoionization amplitude as [42]

$$a(k, \tau) = i \int_0^\infty dt E_0(t-\tau)D_0\,|k-A(t)|\,e^{-i\Phi(t)}. \quad (1)$$

Here the electric field of the XUV pulse $E_0$ is advancing the streaking pulse by the time $\tau$. Both the vector potential of the streaking field and the photoelectron momentum are confined to the polarization plane

$$A(t) = A_0 \cos(\omega t) \hat{x} + A_0 \sin(\omega t) \hat{y} \quad (2)$$

$$k = k \cos \phi \hat{x} + k \sin \phi \hat{y} \quad (3)$$

Here $\phi$ is the photoelectron emission angle. The exponential phase factor

$$\Phi(t) = \frac{1}{2} \int_t^\infty dt' |k-A(t')|^2 - E_0 t \quad (4)$$

contains the photoelectron energy in the absence of streaking $E_0 = \Omega - I_p$. The most probable photoelectron trajectory, starting at the time $t_0$, keeps the phase stationary:

$$\Phi'(t_0) = \frac{1}{2} |k-A(t_0)|^2 - E_0 = 0. \quad (5)$$

We assume that the XUV pulse is short relative to the IR pulse and shifted relative to its peak position by the time $\tau$. Under these conditions, equation (5) is transformed to the following isochrone equation [21]:

$$k^2/2 - E_0 = kA_0 \cos(\phi - \omega \tau). \quad (6)$$

Here we neglect the ponderomotive energy $U_p = A_0^2/2$ in a weak streaking field.

The above stationary phase analysis should be modified to account for the photoelectron energy dependence of the dipole matrix element [43]

$$\arg \{ D[k-A(t)] \} \propto \alpha |k-A(t)|^2/2, \quad (7)$$

where

$$\alpha = \partial \arg D(\sqrt{2E})/\partial E. \quad (8)$$

The modified stationary phase equation reads

$$\frac{1}{2} |k-A(t_0)|^2 - E_0 + \frac{\alpha}{2} \frac{d}{dt} \left[ (k-A(t_0))^2 \right] = 0. \quad (9)$$

This leads to a generalized isochrone equation

$$k^2/2 - E_0 = kA_0 [\cos(\phi - \omega \tau) - \alpha \omega \sin(\phi - \omega \tau)] \approx kA_0 [\cos(\phi - \omega \tau + \omega \alpha)]. \quad (10)$$

Here $\alpha = \Phi_S/\omega$ is related with the streaking phase $\Phi_S$ as demonstrated in [38].
2. Computational details

We solve numerically the molecular TDSE equation using the computer code [44] to obtain the ionization amplitude \( f(k) \). We use an angular basis that included spherical harmonics up to \( l_{\text{max}} = 7 \) and \( |m_{\text{max}}| = 7 \). Unlike the strict dipole selection rules in atomic XUV photoionization, the quantum numbers \( l,m \) adhere to a less restrictive parity conservation.

The photoelectron momentum spectrum \( P(k) \) is obtained as the modulus squared of the ionization amplitude

\[
P(k) \propto |f(k)|^2. \tag{11}
\]

The PMD is restricted to the polarization plane \( P(k_x, k_y, k_z = 0) \) and converted to the polar coordinates \( P(k, \phi) \) where

\[
k = (k_x^2 + k_y^2)^{1/2}, \quad \phi = \tan^{-1}(k_y/k_x). \tag{12}
\]

In these coordinates, we define the directional probability of the photoelectron emission

\[
P(\phi) = \int dk P(k, \phi) \tag{13}
\]

and the mean (central) radial momentum in the given direction

\[
\bar{k}(\phi) = \int k P(k, \phi) dk / P(\phi). \tag{14}
\]

The TDSE is driven by the XUV and IR pulses with the following parameters. The XUV pulse with a Gaussian envelope has a FWHM of 2 fs and the intensity of \( 6 \times 10^{13} \text{ W cm}^{-2} \). The XUV photon energy \( \Omega \) ranges from 0.7 au to 3 au. A relatively low XUV field intensity is required to remain within the LOPT framework. A fairly large pulse duration is employed to ensure a moderately narrow spectral width to probe XUV ionization sufficiently close to the threshold at 15.6 eV (0.57 au). At the same time, the spectral width \( \Gamma \) should be kept sufficiently large to make sure the IR assisted XUV absorption process overlaps spectrally with unassisted XUV ionization [38]. This requires \( \Gamma > 2\omega \), where \( \omega \) is the laser photon energy. To satisfy this requirement, we chose a mid-IR laser pulse with \( \omega = 0.038 \) au corresponding to \( \lambda = 1200 \) nm. The pulse has a cosine squared envelope with FWHM of 25 fs and the intensity of \( 1.5 \times 10^{11} \text{ W cm}^{-2} \). The XUV pulse is linearly polarized along the \( \hat{x} \) axis whereas the IR pulse is circularly polarized in the \((xy)\) plane. At each XUV photon energy, we scan the delay between the XUV pulse and the IR laser field \( \tau \) in the range of 0–60 au in 7 increments.

3. Numerical results

We identify three regions of the photoelectron energy which display distinctively different PMD in the polarization plane. These regions can be characterized by the strength of the molecular two-center interference. The theory of this interference was proposed by Cohen and Fano [45] and Kaplan and Markin [46] and further developed for diatomic molecules fixed in space by Walter and Briggs (WB) [47]. In the latter formulation, the ionization amplitude is approximated by the following expression

\[
f_{\text{WB}}(k) \propto (\mathbf{e} \cdot \hat{k}) \cos(k \cdot \mathbf{R}/2). \tag{15}
\]

Here \( \mathbf{e} \) is the linear polarization vector of the ionizing radiation and \( \mathbf{R} \) is the vector connecting the nuclei. The first term in the RHS of equation (15) is the atomic hydrogen dipole factor whereas the second term represents the molecular two-center interference. In the following, we will use a scalar coefficient \( c = kR/2 \) to identify the strength of this interference.

3.1. Weak interference

At low photoelectron energy when \( c \ll 1 \), the PMD of H\(_2\) looks essentially atomic like with very little anisotropy seen between the parallel and perpendicular orientation of the molecular axis \( \mathbf{R} \) relative to the linear polarization axis \( \mathbf{e} \) of the XUV pulse. This behavior is featured in figure 1 which displays the PMD at \( \Omega = 0.7 \) au. The top and middle panels both illustrate the case of the parallel orientation with the XUV only pulse (top) and XUV+IR pulses (middle). The bottom panel displays the radially integrated PMD of the middle panel in the form of the angular distribution \( P(\phi) \) which is over-plotted with the analogous distribution for the perpendicular orientation. Except for an overall magnitude factor \( \times 1.8 \), the \( \perp \) angular distributions look essentially the same as the \( \parallel \) one.

Meanwhile, the PMD of the top panel (XUV only) and the middle panel (XUV+IR) differ by a noticeable displacement of the radial momentum by the vector-potential \( A_{2R} \) of the streaking field. To quantify this displacement, we use the central photoelectron momenta (14) in the downwards (–) and upwards (+) shifted lobes of the PMD

\[
k_- \equiv \bar{k}(\phi = 0), \quad k_+ \equiv \bar{k}(\phi = \pi). \tag{16}
\]

These momenta \( k_{\pm}(\tau) \), which depend sensitively on the XUV/IR time delay \( \tau \), are then used to obtain the isochrone phase offset:

\[
k_{\pm}(\tau)/2 - E_0 = \pm A_0 \Phi_{\pm}(\tau) \cos(\omega \tau + \Phi_{\parallel}). \tag{16}
\]

This determination is illustrated in the top panel of figure 2. Here we determine \( \Phi_{\parallel} \approx -0.216 \pm 0.003 \) rad by fitting either of the \( k_{\pm}(\tau) \) branches with a common streaking phase value over the whole set of the time delays \( \tau \). Alternatively, we can apply equation (16) to individual \( \tau \) values and to determine the instantaneous \( \Phi_{\parallel}(\tau) \). These values are displayed along with the average streaking phase on the bottom panel of figure 2. Even though the variation of \( \Phi_{\parallel}(\tau) \) exceeds the error bars of the average value, the accuracy of the instantaneous streaking phase determination is not significantly compromised.

3.2. Moderate interference

This region is characterized by a moderate interference factor \( c \lesssim 1 \). A typical PMD in this region is presented in the top
Figure 1. PMD of H$_2$ at $\Omega = 0.7$ au in the parallel field orientation with the XUV only pulse (top) and the XUV+IR pulses (middle). The horizontal dashed line visualizes the photoelectron momentum $k_0 = \sqrt{2(\Omega - I_p)}$ from the energy conservation. The vertical dashed line marks the half of the angular width. Bottom: angular profile $P(\phi)$ (13) corresponding to the XUV+IR ionization in the parallel (middle panel) and perpendicular (not shown) orientations.
and middle panels of figure 3. Here the XUV photon energy $\Omega = 1.5 \text{ au}$ and the molecule is oriented parallel (top) and perpendicular (middle) to the polarization axis. Both panels visualize single-photon XUV ionization. Adding the IR streaking field does not change the PMD structure except for a vertical up and down displacement by the vector potential $A_{\text{IR}}$ as in the middle panel of figure 1.

The case of $c \lesssim 1$ differs from $c \ll 1$ by a significant deviation of the PMD shapes corresponding to the parallel and perpendicular orientations. The PMD lobes are noticeably elongated for the parallel orientation and hence acquire a greater angular width. The photoelectron angular distribution shown in the bottom panel is markedly different for the $\parallel$ and $\perp$ orientations. While the latter retains the atomic like structure, the former widens significantly and becomes drastically, by a factor $\times 10$, suppressed. This parallel emission suppression is documented in the literature and termed the ‘confinement effect’ [48, 49]. This corresponds to the dominant photoelectron $p$-wave being trapped inside a one-dimensional box of length $R$ when the momentum quantization condition $kR = \pi$ satisfied at $c = \pi/2$.

3.3. Strong interference

This region is characterized by a large interference factor $c \gtrsim \pi/2$. In this region, the shape distortion of PMD is most graphical as shown in figure 4 for $\Omega = 2.5 \text{ au}$. While the perpendicular orientation (middle panel) retains an atomic like shape, the parallel orientation (top panel) displays very clear interference fringes. These fringes are also seen in the angular resolved cross-section exhibited in the bottom panel of figure 4.

To quantify the two-center interference effects across a wide range of the photon energies, we plot in the bottom panel of figure 5 the half width of the PMD lobes. The atomic like half width of $45^\circ$ corresponds to the dipole $\cos^2 \phi$ angular shape. It is retained consistently over the whole photon energy range in the perpendicular molecular orientation for XUV only photoionization. Adding a streaking IR field reduces this width insignificantly for the $\perp$ orientation. Meanwhile, the $\parallel$ orientation, both in XUV and XUV+IR fields, displays a broad widening of the width in the range of moderate to strong two-center interference.

To understand the nature of this oscillation, we note that the amplitude (15) for the parallel orientation is reduced to

$$f_{\text{WB}}^\parallel(\phi) \propto \cos \phi \cdot \cos (0.5kR \cos \phi).$$

This amplitude can be expanded over the spherical harmonics with the expansion coefficients given by the following expression [50]

$$A_\ell(c) = \langle Y_{00}|f_{\text{WB}}^\parallel|Y_{\ell\ell}\rangle = \sqrt{2\pi} \int_{-1}^{1} P_\ell(\eta) \eta \cos(c\eta) d\eta.$$  (18)

Here $P_\ell(\eta)$ are the normalized Legendre polynomials which depend on $\eta = \cos \phi$. The expansion coefficients (18) for various $\ell$ are plotted in the top panel of figure 5. From this graph we see clearly that $c \approx 1$ corresponds to a noticeable contribution of the $f$-wave whereas at $c \approx \pi/2$ the $p$- and $f$-wave contributions become of the same magnitude. These two boundaries correspond to the region of moderate and strong two-center interference according to our classification in sections 3.2 and 3.3. In the meantime, the weak interference $c \ll 1$ considered in section 3.1 corresponds to a nearly sole contribution of the $p$-wave.

Fitting the numerical TDSE results for the photoelectron angular distributions with the squared amplitude (17) gives systematically higher effective momenta $k_{\text{eff}}$ in comparison with the nominal momenta $k$ determined by the energy conservation. We find $k_{\text{eff}}$ from the moduli ratio of the $f$- and $p$-waves

$$\left| \frac{A_3(c_0)}{A_1(c_0)} \right| = \left| \frac{\langle Y_{00}|f(k)| \rangle}{\langle Y_{10}|f(k)| \rangle} \right|.$$  (19)

This ratio equates the expansion coefficients $A_\ell$ from equation (18) evaluated at $c_0 = k_{\text{eff}}/R$ with the corresponding
Figure 3. PMD of H$_2$ at $\Omega = 1.5$ au for the parallel (top) and perpendicular (middle) field orientation with the XUV only pulse. The horizontal dashed line visualize the photoelectron momentum $k_0$ while the vertical line marks half of the angular width. Bottom: angular profile $P(\phi)$ (13) corresponding to the parallel (top panel) and perpendicular (middle panel) orientations. The Legendre polynomial fitting using equation (18) is shown for the parallel orientation.
expansion coefficients of the exact numerical amplitude $f(k)$ found by the TDSE solution.

The deviation $k_{\text{eff}}$ from $k$ displayed in the top panel of figure 6 can be explained by the effective potential of the ion remainder. Due to this potential, the momentum of the electron near the nucleus is greater, and, accordingly, a larger phase difference between the emitting centers is accumulated. We can introduce an average effective potential related to the effective momentum through the following expression

$$k_{\text{eff}}/k = \sqrt{1 + 2|\bar{U}_{\text{eff}}|/k^2}.$$

The values of $\bar{U}_{\text{eff}}$ are presented in the bottom panel of figure 6. A gradual reduction of $\bar{U}_{\text{eff}}$ with a decreasing XUV photon energy can be understood as follows. By the uncertainty principle, a slower photoelectron has a larger birthplace area across which the ionic potential is sampled. Therefore, its effective depth becomes smaller.

### 3.4. Streaking phase and time delay

The streaking phase results for the $H_2$ molecule in the $\parallel$ and $\perp$ orientations are summarized in the top panel of figure 7 where they are compared with the corresponding values of the H atom. While the molecular $\Phi_S$ in the $\perp$ orientation is very similar to the atomic one, the $\parallel$ orientation displays a systematically higher values, especially at the onset of the strong interference when the $c$ factor approaching $\pi/2$. The atomic time

---

**Figure 4.** Same as figure 3 for $\Omega = 2.5$ au.

**Figure 5.** Top: expansion coefficients of the ionization amplitude over the spherical harmonics (18) plotted as functions of the interference factor $c = kR/2$. Bottom: angular half width of the PMD lobes as a function of the photoelectron energy $E = \Omega - I_p$. The upper horizontal scale marks the corresponding interference factors.

---

**Figure 6.** H$_2$ XUV $\Omega = 2.5$ au parallel and perpendicular. The deviation $k_{\text{eff}}$ from $k$ displayed in the top panel can be explained by the effective potential of the ion remainder. Due to this potential, the momentum of the electron near the nucleus is greater, and, accordingly, a larger phase difference between the emitting centers is accumulated. We can introduce an average effective potential related to the effective momentum through the following expression

$$k_{\text{eff}}/k = \sqrt{1 + 2|\bar{U}_{\text{eff}}|/k^2}.$$

The values of $\bar{U}_{\text{eff}}$ are presented in the bottom panel of figure 6. A gradual reduction of $\bar{U}_{\text{eff}}$ with a decreasing XUV photon energy can be understood as follows. By the uncertainty principle, a slower photoelectron has a larger birthplace area across which the ionic potential is sampled. Therefore, its effective depth becomes smaller.

### 3.4. Streaking phase and time delay

The streaking phase results for the $H_2$ molecule in the $\parallel$ and $\perp$ orientations are summarized in the top panel of figure 7 where they are compared with the corresponding values of the H atom. While the molecular $\Phi_S$ in the $\perp$ orientation is very similar to the atomic one, the $\parallel$ orientation displays a systematically higher values, especially at the onset of the strong interference when the $c$ factor approaching $\pi/2$. The atomic time
delay derived from the streaking phase $\tau_a = \Phi_S/\omega$ is shown in the bottom panel of figure 7 where it is compared with the corresponding values returned by the RABBITT simulations [39]. Numerical $\tau_a$ values from the ASX and RABBITT simulations are slightly different because of a difference in the wavelength $\lambda = 1200$ nm in the former and 800 nm in the latter. The IR photon wavelength and energy affect the CC component of the atomic time delay [36, 51] which becomes particularly noticeable close to the threshold. Nevertheless, the qualitative behavior of $\tau_a$ is very similar in both sets of simulations. The atomic time delay in the H atom and the $\text{H}_2$ molecule in the $\parallel$ orientation remain negative in the studied XUV photon energy range. At the same time, the $\parallel$ orientation displays a sharp rise of the time delay to positive values. This effect is also recorded in the $\text{H}_2^+$ ion [40, 41]. It was attributed in [40] to the destructive two-center interference. We offer a more physically appealing interpretation of the positive time delay due to the trapping the photoelectron in the molecular potential well. From the condition of this trapping $k_{\text{eff}}R = \pi$ occurring at $KR \simeq 2.4$ we can estimate $|U_{\text{eff}}| \simeq 1$ au. This determination is consistent with the values of $U_{\text{eff}}$ presented in the bottom panel of figure 6.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure6.png}
\caption{Top: the effective momentum $k_{\text{eff}}/k$. Bottom: effective potential $U_{\text{eff}}$.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure7.png}
\caption{Top: the streaking phase $\Phi_S$ as a function of the photoelectron energy for the hydrogen atom and the $\text{H}_2$ molecule in the $\parallel$ and $\perp$ orientations. Bottom: the atomic time delay derived from the streaking phase $\tau_a = \Phi_S/\omega$ is compared with the corresponding values returned from the RABBITT simulations [39].}
\end{figure}

4. Conclusions

In the present work, we employed the angular streaking of XUV ionization of the $\text{H}_2$ molecule to determine the streaking phase and time delay corresponding to various orientations of the inter-nuclear axis relative to the polarization axis of ionizing radiation. The ASX technique was originally developed to characterize IAPs from FEL source on the shot-to-shot basis. This technique was adapted to determine the streaking phase and applied in our previous work [38] to the atomic hydrogen. In the present work we expand this technique to diatomic homonuclear molecules. We converted the streaking phase to the atomic time delay and found it in good agreement with our earlier RABBITT simulations [39]. Unlike RABBITT, which requires an accurate and stable synchronization of the ionizing XUV and probing IR pulses, ASX can determine the streaking phase and time delay from random shots of XUV ionization. This is essential in FEL sources with their inherent time jitter.

As in earlier works [39–41] we observe a strong orientation dependence of the molecular time delay. In most cases, $\tau_a$...
remains negative in H, H₂ and H³⁺ due to a large negative CC component. However, τₐ becomes positive in H₂ and H³⁺ in the parallel orientation R || e. This occurs when the photoelectron in the dominant p-wave becomes trapped in the molecular potential well. From the condition of this trapping we can estimate the depth of this well U₀₂₂.

While the streaking phase retrieval by ASX was demonstrated for a diatomic homo-nuclear molecule H₂, the proposed method should work for arbitrary molecular targets. A preliminary report by Driver et al [52] demonstrates an application of ASX to measure the time delay in the shape resonance region of NO. The usage of ASX with FEL will be particularly beneficial for studying inner shell ionization in atomic and molecular targets which cannot be ionized at present with conventional laser HHG sources.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Acknowledgments

The authors are grateful to James Cryan and Taran Driver for very stimulating discussions. We thank Rickson Wiellian for reviewing the literature. This work is supported by the Discovery Grant DP190101145 of the Australian Research Council. Resources of National Computational Infrastructure facility (NCI Australia) have been employed.

ORCID iD

Anatoli S Kheifets https://orcid.org/0000-0001-8318-9408

References

[1] Haessler S et al 2009 Phase-resolved attosecond near-threshold photoionization of molecular nitrogen Phys. Rev. A 80 011404
[2] Huppert M, Jordan I, Baykusheva D, von Conta A and Wörner H J 2016 Attosecond delays in molecular photoionization Phys. Rev. Lett. 117 093001
[3] Muller H 2002 Reconstruction of attosecond harmonic beating by interference of two-photon transitions Appl. Phys. B 74 s17
[4] Toma E S and Muller H G 2002 Calculation of matrix elements for mixed extreme-ultraviolet-infrared-two-photon above-threshold ionization of argon J. Phys. B 35 3435
[5] Cattaneo L, Vos J, Bello R Y, Palacios A, Heuser S, Pedrelli L, Luccini M, Kheifets A, Martin F and Keller U 2018 Attosecond coupled electron and nuclear dynamics in dissociative ionization of H₂ Nat. Phys. 14 733
[6] Vos J, Cattaneo L, Patchkovskii S, Zimmermann T, Cirelli C, Luccini M, Kheifets A, Landsman A S and Keller U 2018 Orientation-dependent stereo Wigner time delay in a small molecule Science 360 1326
[7] Liao Y, Zhou Y, Pi L-W, Ke Q, Liang J, Zhao Y, Li M and Lu P 2021 Two-center interference and stereo Wigner time delay in photoionization of asymmetric molecules Phys. Rev. A 104 013110
[8] Nandi S et al 2020 Attosecond timing of electron emission from a molecular shape resonance Sci. Adv. 6 eaba7762
[9] Loriot V, Marciniak A, Nandi S, Karras G, Hervé M, Constant E, Pléziat E, Palacios A, Martin F and Lépine F 2021 Attosecond ionization time delay around a shape resonance in nitrogen measured by the RABBIT-2ω method 2021 Conf. on Lasers and Electro-Optics Europe & European Quantum Electronics Conf. (Munich, Germany, 21–25 June 2021) (CLEO/Europe-EQEC) p 1
[10] Kamalov A, Wang A L, Bucksbaum P H, Haxton D J and Cryan J P 2020 Electron correlation effects in attosecond photoionization of CO₂ Phys. Rev. A 102 023118
[11] Gong X, Jiang W, Tong J, Quang J, Lu P, Ni H, Lucchese R, Ueda K and Wu J 2022 Asymmetric attosecond photoionization in molecular shape resonance Phys. Rev. X 12 011002
[12] Heck S, Baykusheva D, Han M, Ji J-B, Perry C, Gong X and Wörner H J 2021 Attosecond interferometry of shape resonances in the recoil frame of CF₄ Sci. Adv. 7 eabd8121
[13] Ahmadi H, Pléziat E, Moioli M, Frassetto F, Poletto L, Deleva P, Schröter C D, Pfeiffer T, Moshhammer R and Palacios A et al 2022 Attosecond photoionisation time delays reveal the anisotropy of the molecular potential in the recoil frame Nat. Commun. 13 1242
[14] Biswas S et al 2020 Probing molecular environment through photoemission delays Nat. Phys. 16 778
[15] Heck S, Han M, Jelovina D, Ji J-B, Perry C, Gong X, Lucchese R, Ueda K and Wörner H J 2022 Two-center interference in the photoionization delays of Kr₂ Phys. Rev. Lett. 129 133002
[16] Wang A L, Serov V V, Kamalov A, Bucksbaum P H, Kheifets A and Cryan J P 2021 Role of nuclear-electronic coupling in attosecond photoionization of H₂ Rev. Phys. A 104 063119
[17] Young L et al 2018 Roadmap of ultrafast x-ray atomic and molecular physics J. Phys. B 51 032003
[18] Hartmann N et al 2018 Attosecond time-energy structure of x-ray free-electron laser pulses Nat. Photon. 12 215
[19] Duris J et al 2020 Tunable isolated attosecond x-ray pulses with gigawatt peak power from a free-electron laser Nat. Photon. 14 30
[20] Zhao Z X, Chang Z, Tong X M and Lin C D 2005 Circularly-polarized laser-assisted photoionization spectra of argon for attosecond pulse measurements Opt. Express 13 1966
[21] Kazansky A K, Bozhevolnov A V, Sazhina I P and Kabachnik N M 2016 Interference effects in angular streaking with a rotating terahertz field Phys. Rev. A 93 013407
[22] Li S, Guo Z, Coffee R N, Hegazy K, Huang Z, Natan A, Osipov T, Ray D, Marinelli A and Cryan J P 2018 Characterizing isolated attosecond pulses with angular streaking Opt. Express 26 4531
[23] Kazansky A K, Sazhina I P and Kabachnik N M 2019 Fast retrieval of temporal characteristics of FEL pulses using streaking by THz field Opt. Express 27 12939
[24] Eckle P, Smolarski M, Schlup P, Biegert J, Staudte A, Schoffler M, Muller H G, Dorner R and Keller U 2008 Attosecond angular streaking Nat. Phys. 4 565
[25] Pfeiffer A N, Cirelli C, Smolarski M, Dimitrovski D, Abu-samha M, Madsen L B and Keller U 2012 Attoclock reveals natural coordinates of the laser-induced tunnelling current flow in atoms Nat. Phys. 8 76
[26] Constant E, Taranukhin V D, Stolow A and Corkum P B 1997 Methods for the measurement of the duration of high-harmonic pulses Phys. Rev. A 56 3870
[27] Itatani J, Quéré F, Yudin G L, Ivanov M Y, Krausz F and Corkum P B 2002 Attosecond streak camera Phys. Rev. Lett. 88 173903
[28] Goulielmakis E et al 2004 Direct measurement of light waves Science 305 1267
[29] Kienerber R et al 2004 Atomic transient recorder Nature 427 817
[30] Yakovlev V S, Bammer F and Scrinzi A 2005 Attosecond streaking measurements J. Mod. Opt. 52 395
[31] Frühling U et al 2009 Single-shot terahertz-field-driven x-ray streak camera Nat. Photon. 3 523
[32] Zhang C-H and Thumm U 2011 Streaking and Wigner time delays in photoemission from atoms and surfaces Phys. Rev. A 84 033401
[33] Ivanov M and Smirnova O 2011 How accurate is the attosecond streak camera? Phys. Rev. Lett. 107 213605
[34] Zhao X, Li S, Driver T, Hoang V-H, Le A-T, Cryan J P, Marinelli A and Thumm U 2011 How accurate is the attosecond streak camera? Phys. Rev. A 84 033401
[35] Dahlström J M, Huillier A L and Maquet A 2012 Introduction to attosecond delays in photoionization J. Phys. B 45 183001
[36] Dahlström J M, Guénot D, Klünder K, Gisselbrecht M, Mauritsson J, Huillier A L, Maquet A and Taïeb R 2013 Theory of attosecond delays in laser-assisted photoionization Chem. Phys. 414 53
[37] Maquet A, Caillat J and Taïeb R 2014 Attosecond delays in photoionization: time and quantum mechanics J. Phys. B 47 204004
[38] Kheifets A S, Wielian R, Serov V V, Ivanov I A, Wang A L, Marinelli A and Cryan J P 2022 Ionization phase retrieval by angular streaking from random shots of XUV radiation Phys. Rev. A 106 033106
[39] Serov V V and Kheifets A S 2017 Time delay in XUV/IR photoionization of H2O J. Chem. Phys. 147 204303
[40] Ning Q-C, Peng L-Y, Song S-N, Jiang W-C, Nagele S, Pazourek R, Burgdörfer J and Gong Q 2014 Attosecond streaking of Cohen-Fano interferences in the photoionization of H2+ Phys. Rev. A 90 013423
[41] Serov V V and Kheifets A S 2016 Angular anisotropy of time delay in XUV+IR photoionization of H2+ Phys. Rev. A 93 063417
[42] Kitzler M, Milosevic N, Scrinzi A, Krausz F and Brabec T 2002 Quantum theory of attosecond XUV pulse measurement by laser dressed photoionization Phys. Rev. Lett. 88 173904
[43] Schultz M et al 2010 Delay in photoemission Science 328 1658
[44] Serov V V 2011 Calculation of intermediate-energy electron-impact ionization of molecular hydrogen and nitrogen using the paraxial approximation Phys. Rev. A 84 062701
[45] Cohen H D and Fano U 1966 Interference in the photo-ionization of molecules Phys. Rev. 150 30
[46] Kaplan I G and Markin A P 1969 Interference phenomena in photoionization of molecules Sov. Phys. - Dokl. 14 36 (available at: www.mathnet.ru/eng/dan/v184/i1/p66
[47] Walter M and Briggs J 1999 Photo-double ionization of molecular hydrogen J. Phys. B 32 2487
[48] Fernández J, Fojin O, Palacios A and Martín F 2007 Interferences from fast electron emission in molecular photoionization Phys. Rev. Lett. 98 043005
[49] Fernández J, Yip F L, Rescigno T N, McCurdy C W and Martín F 2009 Two-center effects in one-photon single ionization of H2+, H2 and Li2+ with circularly polarized light Phys. Rev. A 79 043409
[50] Serov V V, Ivanov I A and Kheifets A S 2012 Single-photon double ionization of H2 away from equilibrium: a showcase of two-center electron interference Phys. Rev. A 86 025401
[51] Serov V V, Derbov V L and Sergeeva T A 2015 Interpretation of the time delay in the ionization of Coulomb systems by attosecond laser pulses Advanced Lasers: Laser Physics and Technology for Applied and Fundamental Science (Dordrecht: Springer) pp 213–30
[52] Driver T, Champenois E G, Cryan J P, Li S, Marinelli A, Rosenberger P, Kling M F, Ortmann L and Landsman A 2020 Attosecond electron correlation and molecular resonance in K-shell photoexcitation of nitric oxide 51st Annual Meeting of the APS Division of Atomic, Molecular and Optical Physics