

Revealing the wave-function-dependent zeptosecond birth time delay in molecular photoionization with double-slit interference minima

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We study the photoionization of molecule H_2^+ in an XUV pulse by numerically solving the time-dependent Schrödinger equation simulation and focus on a zeptosecond birth time delay of a photoelectron from the different cores. We propose a simple and robust method to extract accurately the zeptosecond birth time delay with double-slit interference minima. Based on this extraction method, our results show that the birth time delay is strongly affected by the initial bound-electron wave function due to the deviation of the electron emission position from the central core. Furthermore, an experimental scheme is also proposed to testify this wave-function-dependent zeptosecond birth time delay. Our study sheds more light on the ultrafast molecular photoionization dynamics on the zeptosecond timescale.

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I. INTRODUCTION

As one of the most famous physical phenomena in history, the photoelectric effect has been attributed to the energy transfer from a photon to an electron bound in an atom or a molecule. This hypothesis has advanced the foundation of quantum physics. In general, this effect is assumed to occur instantaneously. Recent advances in ultrafast laser science have made it possible to trace the photoionization dynamics. For example, an isolated sub-100-attosecond ($1 \text{ as} = 10^{-18} \text{ s}$) extreme ultraviolet (XUV) pulse has been produced via high-order harmonic generation [1–5]. Such an ultrashort XUV pulse is taken as a precise trigger for timing the electronic ionization and the corresponding time is recorded with a weak near-infrared (NIR) field, which forms an attosecond streaking camera [6,7]. By using this technology, a time delay of about 20 as between the emission of electrons from the $2p$ and $2s$ orbitals in a neon atom has been observed in experiments [8]. In addition, an attosecond angular streaking (or attoclock) [9,10] technique has been developed. In this scheme, the photoionization process of atoms and molecules in an intense laser field occurs via tunneling [11,12] and the attoclock attempts to relate the tunneling ionization time to the offset angle of the peak photoelectron momentum distribution in the polarization plane of the laser pulse. Recent attoclock experiments have shown dispersive results of the tunneling ionization time for various atomic and molecular systems [13–16].

Very recently, a much smaller time delay, i.e., on the zeptosecond ($1 \text{ zs} = 10^{-21} \text{ s}$) timescale, in molecular photoionization has been revealed in experiments. When a molecule interacts with a laser field, the electron wave packets may be emitted from the different cores, forming a double-slit

interference pattern in the photoelectron momentum distribution [17–23]. Usually, these electron wave packets are assumed to be launched simultaneously. But, due to the travel of the photon across the molecules, there is a very small birth time delay between the electron emission, leading to an angular shift of the double-slit interference pattern in the forward direction with respect to the photon propagation. This scheme has been demonstrated by Grundmann *et al.* [24] by studying the ionization of the hydrogen molecule under a circularly polarized laser field with a photon energy of 800 eV. The angular shift of the double-slit interference pattern in the forward direction is clearly observed in the photoelectron momentum spectra. By fitting the shifted angular position of the zeroth-order interference maximum, a birth time delay on the order of a few hundred zeptoseconds for the molecular hydrogen has been extracted. This is in qualitative agreement with R/c (R is the molecular internuclear separation and c is the speed of light).

It is worthy noting that in Grundmann *et al.*'s work, the electron wave packets are assumed to be emitted from the central position of each core and, accordingly, the birth time delay is given by R/c . However, the emission positions might deviate from the central positions of the cores, because the initial bound-electron wave function is usually not completely concentrated at the center of the core, but has a spatial distribution. Thus, to what extent the assumption taken in the seminal work by Grundmann *et al.* can be justified, and, equally importantly, how the emission positions are affected by the initial electron wave function and whether the birth time delay is changed accordingly are still open questions. In order to address these questions, it is critically required to accurately extract the birth time delay from the double-slit interference patterns. In Grundmann *et al.*'s work, the birth time delay is extracted by measuring the angular shift of the double-slit interference maxima. However, due to the influence of the photoionization cross section of the constituent atoms

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inside the molecule, the interference maxima will be imposed with an additional angular shift [24], which makes it difficult to accurately construct the relation between the angular shift and the birth time delay, and hence, hinders the study of the influence of the initial electron wave functions on the ultrafast zeptosecond molecular photoionization dynamics.

In this paper, we investigate the photoionization of the simplest prototype molecule, i.e., H_2^+ , and address the relevance of the zeptosecond birth time delay with the initial electron wave functions. By considering the propagation of the photon across the molecule in the time-dependent Schrödinger equation (TDSE) simulation, we well reproduce the double-slit interference pattern in the photoelectron momentum spectra with a clear angular shift induced by the birth time delay. Furthermore, we propose and demonstrate a robust method to extract accurately the birth time delay, which is based on the double-slit interference minima and has its advantage of being free from the influence of the photoionization cross section of the constituent atoms inside the molecule. With this simple and robust method, we reveal that the emission position depends strongly on the initial bound-electron wave function. Accordingly, this will give rise to a significant dependence of the birth time delay on the initial wave function. Furthermore, in order to explain this intriguing effect, an experimental scheme based on the inner-shell ionization of a diatomic molecule is proposed.

This paper is organized as follows. In Sec. II, we briefly introduce the TDSE with considering the propagation of the photon across the molecule. In Sec. III, we present the TDSE simulations of the photoelectron momentum distributions in an XUV laser field. Subsequently, we propose a simple method to extract accurately the zeptosecond birth time delay with double-slit interference minima and the influence of the initial bound-electron wave function on the birth time delay is discussed. Finally, in Sec. IV our conclusions are given. Atomic units (a.u.) are used unless stated otherwise.

II. THEORETICAL METHODS

The photoionization of molecules in an XUV pulse has been studied by solving the TDSE [21–23]. However, in these works, the angular shift of the double-slit interference pattern found in Ref. [24] has not been observed in the photoelectron momentum spectra. The reason is that the dipole approximation is used in these works, within which the electron wave packets from the different cores are assumed to be emitted simultaneously. In our work, we will consider the nondipole effect during the propagation of the laser pulse across the molecules [25,26]. The corresponding vector potential $\mathbf{A}(z, t)$ of a linearly polarized XUV pulse with a sine-square envelope is written as

$$\begin{aligned} \mathbf{A}(z, t) = & A_0 \sin^2 \left[\frac{\omega_e}{c} (z + a_0) - \omega_e t \right] \sin \left[\frac{\omega}{c} (z - ct) \right] \hat{x} \\ & \times [\theta_H(z - ct + \pi c/\omega_e + a_0) - \theta_H(z - ct + a_0)], \end{aligned} \quad (1)$$

where \hat{z} is the light propagation direction, \hat{x} denotes the polarization direction, θ_H is the Heaviside or step function, $\omega_e = \omega/2N_{\text{cyc}}$ with the cycle number N_{cyc} and the frequency ω , and a_0 is the initial distance between the pulse and the

molecule. The photoionization of the H_2^+ in the XUV pulses is simulated by numerically solving the TDSE in the velocity gauge,

$$i \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \left[\frac{1}{2} \left(\mathbf{p} - \frac{1}{c} \mathbf{A}(z, t) \right)^2 + V(\mathbf{r}) \right] \Psi(\mathbf{r}, t), \quad (2)$$

where $V(\mathbf{r})$ is the Coulomb potential. For simplicity, the electron wave function is limited in the two-dimensional space and the Coulomb potential is written as $V(\mathbf{r}) = \frac{-1}{\sqrt{(z-R/2)^2 + x^2 + a}} + \frac{-1}{\sqrt{(z+R/2)^2 + x^2 + a}}$, where a is a soft-core parameter. For $a = 4.33$, the ground-state energy matches the H_2^+ value of about 15.8 eV. In this work, the initial states of H_2^+ are obtained with the imaginary-time propagation method and the propagation of the electron wave function is implemented with the second-order split-operator method [27]. Due to the z -dependent vector potential, a propagation term of $\exp[i\mathbf{p} \cdot \mathbf{A}(z, t)\Delta t/c]$ cannot be simply evaluated in the momentum space as usual, but should be solved alternately in the position space and the momentum space in terms of the Taylor expansion: $\exp[i\mathbf{p} \cdot \mathbf{A}(z, t)\Delta t/c] = \sum_{n=0}^N [i p_x A(z, t)\Delta t/c]^n / n!$. In practice, we employ an XUV pulse with an intensity of 1.0×10^{14} W/cm², a central wavelength of 5 nm, corresponding to a photon energy of about 248 eV, $N_{\text{cyc}} = 30$, and $a_0 = 10$ a.u. For such an XUV pulse, our simulation shows that the choice of $N = 6$ in the Taylor expansion is adequate to obtain a converged electron wave function at each time step Δt . By performing the Fourier transform of the final wave function in the region far away from the two cores, the photoelectron momentum spectra can be obtained. Due to the high-energy photon of the XUV pulse, the photoelectron momentum spectra are dominant by the one-photon ionization of H_2^+ .

III. RESULTS AND DISCUSSIONS

Figure 1(a) shows the molecule-frame photoelectron momentum spectra from the one-photon ionization of H_2^+ initialized from its ground state. A clear double-slit interference pattern of the electron wave packets from the different cores can be well observed, which is qualitatively consistent with the experimental and theoretical results [17–23]. A closer inspection reveals that, different from the previous calculations within the dipole approximation [21–23], the position of the zeroth-order maximum of the double-slit interference pattern in our simulations deviates from the direction perpendicular to the molecular axis, i.e., $\alpha = \pi/2$. In order to more clearly identify the positions of the interference fringes, we present the photoelectron momentum spectra of H_2^+ with respect to $\cos \alpha$ in Fig. 1(b) and the corresponding radially integrated photoelectron angular distribution (PAD) is shown in Fig. 1(c). It is clearly shown that the value of $\cos \alpha_0$ of the zeroth-order maximum is slightly larger than zero [28]. Our simulation is in good agreement with the measurement reported by Grundmann *et al.* [24], in which the angular shift of the interference fringes is ascribed to the birth time delay between the electron emission.

Here, we propose an extraction scheme of the birth time delay from the PAD. In Grundmann *et al.*'s work [24], the birth time delay is extracted based on the double-slit interference maxima in the PAD. However, in the measured

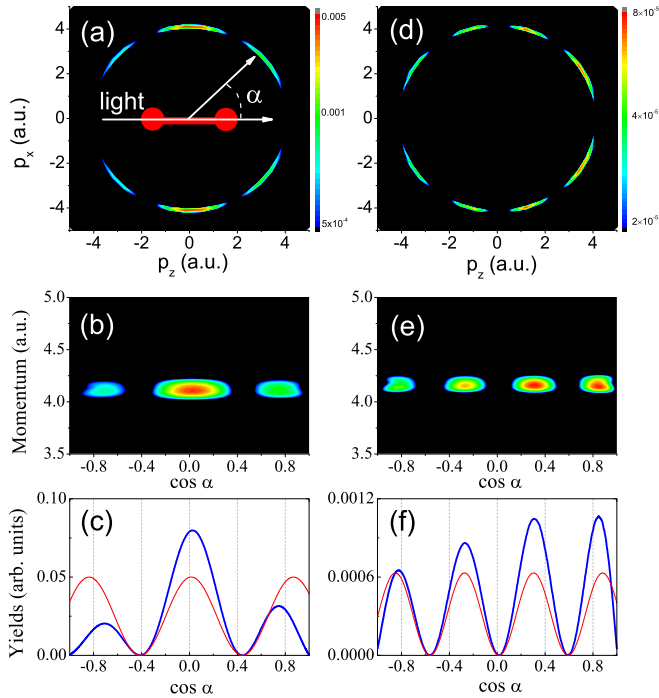


FIG. 1. (a) and (d) TDSE simulated molecule-frame photoelectron momentum distributions of H₂⁺ initialized from its ground state and first excited state, respectively. The two red circles in (a) denote the molecular cores and the angle α is the photoelectron momentum direction with respect to the molecular axis, which is aligned parallel to the light propagation direction. (b) and (e) The photoelectron momentum spectra of H₂⁺ with respect to $\cos\alpha$. (c) and (f) The corresponding radially integrated PADs (blue curves). The red thin curve denotes the fitted double-slit interference pattern, which is used to obtain the birth time delay by fitting the interference minima. For more details, see the text.

photoelectron momentum spectra, the double-slit interference patterns are entangled with the background signal, that is, the photoionization cross section of the constituent atoms inside the molecule [29]. The superposition of the double-slit interference pattern and the background signal leads to an angular shift of the interference maxima toward the direction with a larger photoionization cross section. Thus, to extract the birth time delay from the angular shift, *a priori* knowledge of the photoionization cross section of the constituent atoms needs to be derived as a prerequisite. Different from the method in Ref. [24], we propose a simple and robust extraction scheme of the birth time delay with the double-slit interference minima. For the interference minima, their positions are almost unaffected by the background signal, due to the vanishing amplitude of the interference minima. Thus, the angular shift of the interference minima is only related to the birth time delay. Therefore, the use of the interference minima for the extraction of the birth time delay can avoid the complexities caused by the atomic photoionization cross section.

In the following, we will demonstrate this extraction method of the birth time delay in the photoionization of H₂⁺ with the double-slit interference minima. In terms of the path-length difference between the two emitted electron wave packets [24], the double-slit interference pattern in the

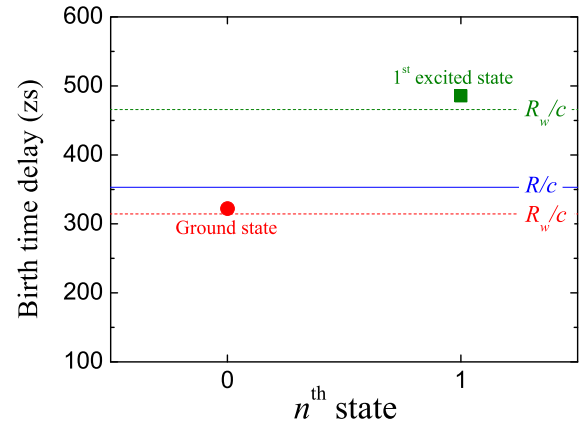


FIG. 2. The fitted birth time delay for the ground state (red circle) and the first excited state (green square), respectively. The red and green dashed lines denote the times of R_w/c for the ground state ($R_w = 1.77$ a.u.) and the first excited state ($R_w = 2.64$ a.u.), respectively. The blue line is the time of R/c .

photoelectron momentum spectrum of H₂⁺ initialized from its ground state can be described by

$$f(\cos\alpha) = 1 + \cos\left[2\pi\left(\frac{\cos\alpha R_w}{\lambda} - \frac{\tau_b v_{\text{ph}}}{\lambda}\right)\right], \quad (3)$$

where τ_b is the birth time delay we focus on, R_w is the separation of the electron emission positions, λ is the electron's de Broglie wavelength, and $v_{\text{ph}} = E/p$ is the phase velocity of the electron with the energy E and the momentum p . The theoretical model in Eq. (3) is different from that in Ref. [24], in which the electron wave packets are assumed to be emitted from the central positions of the cores, i.e., $R_w = R$. Here, we will first show that R_w usually deviates from R . According to Eq. (3), the oscillation period $T_{\cos\alpha}$ of the double-slit interference pattern with respect to the variable of $\cos\alpha$ is given by λ/R_w and thus $R_w = \lambda/T_{\cos\alpha}$. The value of $T_{\cos\alpha}$ can be obtained directly by measuring the interval of the interference minima near $\cos\alpha = \pm 0.4$ shown in Fig. 1(c). Note that the minima near $\cos\alpha = \pm 1$ are due to the atomic photoionization cross section. Inserting the measured value of $T_{\cos\alpha}$, R_w is equal to 1.77 a.u., which is smaller than R ($=2$ a.u.). Therefore, our result clearly shows that the emission positions of the electron wave packets deviate from the central positions of the cores, which goes beyond the assumption in Ref. [24]. The origin of the deviation between R_w and R will be further discussed later.

After obtaining the value of R_w , we will extract the birth time delay in the photoionization of H₂⁺, by fitting the positions of the interference minima in the PAD with Eq. (3). The thin red curve in Fig. 1(c) exhibits the fitted double-slit interference pattern. It clearly shows that the positions of the interference minima near $\cos\alpha = \pm 0.4$ in the PAD are well fitted, while the interference maxima in the fitted interference pattern significantly deviate from that in the PAD, which is due to the influence of the photoionization cross section of the constituent atoms inside the molecule. In Fig. 2, we present the corresponding fitted birth time delay τ_b . For H₂⁺ initialized from its ground state (red circle), the time is clearly smaller than the value of R/c (blue line). On the other side,

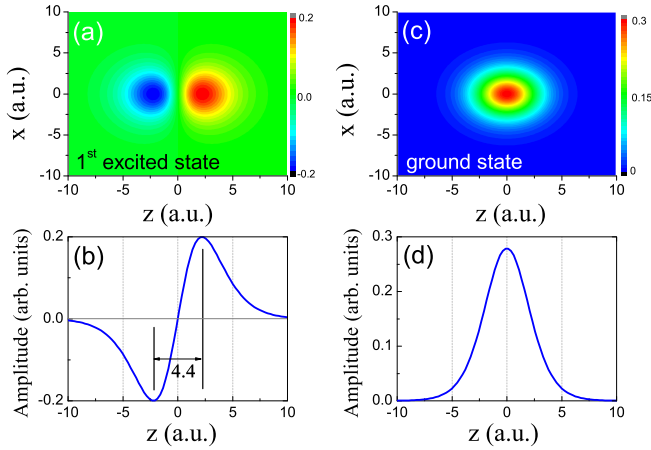


FIG. 3. (a) and (c) Wave functions of the first excited state and the ground state of H_2^+ , respectively. (b) and (d) The corresponding amplitude distributions along the z axis.

it is found that such a time delay qualitatively agrees well with R_w/c , indicating that the birth time delay in molecular photoionization actually corresponds to the travel time of the photon across the separation R_w of the electron emission positions, rather than the core separation.

The success of our extraction method of the zeptosecond birth time delay allows us to further investigate whether the zeptosecond birth time is dependent on the initial bound-electron wave function of the molecules. For this purpose, we also simulate the photoelectron momentum spectra of H_2^+ initialized from, e.g., its first excited state; see Figs. 1(d) and 1(e). We find that the zeroth-order region of the double-slit interference pattern becomes the interference minimum, which is due to the antisymmetric initial wave function of the first excited state. In Fig. 1(f), we present the corresponding radially integrated PAD, in which the angular shift of the zeroth-order minimum induced by the birth time delay can be also observed. Similarly, we extract the birth time delay by fitting the positions of the interference minima with Eq. (3). Due to the antisymmetric initial wave function, an additional initial phase difference of π between the emitted wave packets should be added into the cos term in Eq. (3). Figure 1(f) shows the fitted double-slit interference pattern with $R_w = \lambda/T_{\cos\alpha} = 2.64$ a.u. As expected, all of the interference minima in the PAD can be well fitted, while there is a significant deviation for the interference maxima due to the influence of the photoionization cross section of the constituent atoms inside the molecule. The corresponding fitted birth time delay is present in Fig. 2 (green square), which is clearly larger than the value of R/c , but qualitatively agrees well with R_w/c . Therefore, our result shows that the birth time delay in molecular photoionization depends strongly on the initial electronic wave function of the molecule.

Such wave-function-dependent birth time delay can be qualitatively well understood from their initial electron distributions. Figure 3(a) shows that, for the first excited state of H_2^+ , the electron is in an antibonding orbital, which forces the electron wave-packet density to be in a region away from the central position. In Fig. 3(b), we present the corresponding amplitude distribution along the z axis. It is clearly shown that

the spatial interval between the two peaks of the wave function is about 4.4 a.u., much larger than molecular internuclear separation, leading to an increase of the emission position separation R_w with respect to R and hence an increase of the birth time delay. In contrast, for the ground state, the electron is in a bonding orbital [see Figs. 3(c) and 3(d)], which concentrates the electron wave-packet density in a region between the two cores. The shrinkage of the wave function of the ground state results in a decrease of R_w in comparison with R and hence the decrease of the birth time delay. It is worth noting that, in the comparison with the real H_2^+ , the deviation of the peaks of the wave function from the cores for the first excited state and the shrinkage of the wave function for the ground state are significant, because a relatively large soft-core parameter in the two-dimensional Coulomb potential is used in our simulation to match the ground-state energy of H_2^+ , which results in more pronounced dependence of the emission position separation and the corresponding birth time delay on the initial electron wave function.

Finally, we further propose a feasible experimental scheme to testify this wave-function-dependent zeptosecond birth time delay. When a diatomic molecule interacts with an XUV laser pulse from, e.g., a free-electron laser system, the inner-shell electron may be significantly ionized by absorbing one high-energy photon [30]. For the different shell states in the molecule, the corresponding wave functions have different symmetries. For example, the highest occupied molecular orbital (HOMO) in molecule O_2 is $1\pi_g$, which is an antibonding orbital, while for the HOMO-1 it is $1\pi_u$, a bonding orbital. According to our discussion above, the different symmetrical structures affect the initial electron distributions and hence the birth time delay. Therefore, we can experimentally measure the photoelectron momentum spectra from the different shells of the prealigned diatomic molecule and obtain the birth time delay from the corresponding double-slit interference patterns to testify the relevance of the birth time delay with the initial wave function. Moreover, we expect that this birth time delay, once being derived experimentally, may be taken as a sensitive probe of the ground-state electronic wave function of a complex molecule.

IV. CONCLUSIONS

In summary, we have studied the photoionization of molecule H_2^+ in an XUV pulse and focus on the zeptosecond birth time delay of the photoelectron from the different cores due to the travel of the photon across the molecules. By analyzing the angular shift of the photoelectron momentum spectra, we propose and demonstrate a simple and robust method to extract accurately the birth time delay with the double-slit interference minima, which is free from the influence of the photoionization cross section of the constituent atoms inside the molecule. Based on the advantage of this extraction method, we predict that the emission position depends strongly on the initial bound-electron wave function and the birth time delay corresponds to the travel time of photon across the separation of the emission positions. Furthermore, we propose a feasible experimental scheme based on the inner-shell ionization of the diatomic molecule to testify this wave-function-dependent birth time

delay. Our study sheds more light on the zeptosecond birth time delay in molecular photoionization.

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