Molecular alignment dependent electron interference in attosecond ultraviolet photoionization

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(Received 15 October 2014; accepted 6 January 2015; published online 30 January 2015)

We present molecular photoionization processes by intense attosecond ultraviolet laser pulses from numerical solutions of time-dependent Schrödinger equations. Simulations performed on a single electron diatomic H₂⁺ show minima in molecular photoelectron energy spectra resulting from two center interference effects which depend strongly on molecular alignment. We attribute such sensitivity to the spatial orientation asymmetry of the photoionization process from the two nuclei. A similar influence on photoelectron kinetic energies is also presented. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4906126]

I. INTRODUCTION

Real time observation of molecular structure and dynamics by photoelectron spectroscopy has attracted considerable attention lately with the rapid developments of ultrashort ultrafast laser pulses. In the past electron interference patterns in molecular photoelectron energy spectra (MPES) have been widely studied for imaging of molecular structure. The interference of electron waves emitted coherently from the two atoms in a diatomic molecule was first predicted by Cohen and Fano and Kaplan and Markin more than forty years ago in perturbative single photon ionization. The wavefunctions are described by a linear combination of the orbitals of the two separated atoms, which results in a molecular Young’s double-slit experiment. Such interference model has been extended to nonperturbative photoionization with few-cycle intense laser pulses. One can measure, in principle, molecular electronic structure and electron motion for different fixed nuclear configurations in molecular, chemical, and biochemical processes from interference patterns in molecular above-threshold ionization (MATI) spectra. A novel destructive interference in high-order angular MATI spectra of a diatomic molecule involving four geometric orbits has been found experimentally and confirmed theoretically based on molecular strong field approximation (MSFA) simulations for the suppressed ionization of the O₂ molecule. Such electron destructive interference with minima in MATI has also been investigated in circularly polarized infrared (IR) laser pulses. It has been shown that the symmetry of the electronic state and the molecular internuclear distance for both homonuclear and heteronuclear molecules determines the localization of the interference minimum in MATI spectra. Interference structure of MATI versus above-threshold detachment has also been compared. We have also investigated previously the two-center interference effects in MATI angular distributions of H₂⁺ at both equilibrium and extended internuclear distance for both linear and circular polarizations. Measuring photoelectron angular distributions of oriented molecules O₂, N₂, and CO₂, allow to study electron-ion scattering dynamics from laser induced electron diffraction (LIED).

Advanced attosecond (1 as = 10⁻¹⁸ s) laser pulses generated from high-order harmonics or free electron lasers are now proving to be a valuable tool in studying such electron interference effects by “freezing” the nuclear motion which normally occurs on femtosecond (1 fs = 10⁻¹² s)
time scale. To date, the shortest linearly polarized single pulse with duration of 67 as has been produced from high-order harmonic generation (HHG) with a few cycle intense IR laser field in atoms. With a mid-infrared femtosecond laser HHG spectra of very high order (~5000 (1.6 keV) can also be generated thus allowing for the generation of pulses as short as few attoseconds, and approaching the zeptosecond (10^{-21} s) time scale necessary for nuclear structure imaging. Circularly polarized attosecond pulses have also been proposed from circularly polarized molecular HHG, by two color counter-rotation circularly polarized laser pulse or a circularly polarized visible laser pulse combined with static or THz fields. With such ultrafast pulses on the attosecond time scale, monitoring electron motion in matter without complications from nuclear motion, imaging and the creation of electron movies become possible. With attosecond ultraviolet (UV) laser pulses, the interference effects of molecular orbital configurations in LIED have been studied by monitoring both linear and circular polarization photoelectron spectra. The interference of the electron wave packets scattered by multiple parent ions in molecular photoionization has also been investigated by measuring photoelectron momentum distributions which exhibit momentum stripes with intervals determined by the molecular internuclear distance.

In the present work, we focus on the effects of molecular alignment on the two-center electron interference in single electron photoionization with linearly polarized attosecond UV laser pulses. We simulate MPES for an aligned diatomic molecule H\(^+\)\(_2\) at equilibrium distance \(R_e\). Results of MPES exhibit doublets due to two-center electron interferences, a new type of LIED. Such interference patterns are shown to be sensitive to molecular alignment owing to the molecular Coulomb potential. Moreover, it is found that the photoelectron kinetic energy also determines the interference patterns. Simulations are performed by solving numerically the corresponding three-dimensional (3D) time-dependent Schrödinger equation (TDSE) for static nuclei. Attosecond photoionization processes can also be treated by perturbation theory or MSFA methods. We use a 3D model, restricting the electron motion in a plane with static nuclei, thus enabling to go beyond perturbation theory and independent of gauge transformations. Such a fixed nuclei approach is appropriate due to the longer femtosecond (fs) time scale of nuclear motions compares to the electron attosecond time scale. UV ultrashort laser pulses with frequency \(\hbar \omega > I_p\) (\(I_p\), the molecular ionization potential) and intensity \(I_0 = 5.0 \times 10^{14}\) W/cm\(^2\) are used in the present simulations.

The paper is arranged as follows: Sec. II introduces the computational methods for time-dependent quantum electron wave packet calculations from the corresponding TDSEs. The numerical results of the electron interference in MPES by intense ultrashort linearly polarized UV laser pulses for aligned H\(^+\)\(_2\) are shown in Sec. III. We summarize our findings in Sec. IV. Throughout this paper, atomic units (a.u.) \(\hbar = m_e = 1\) are used unless otherwise stated.

II. COMPUTATIONAL METHODS

For an aligned diatomic molecular ion H\(^+\)\(_2\) interacting with an intense ultrashort laser pulse, the corresponding TDSE with static nuclei in cylindrical coordinates is written as

\[
\imath \frac{\partial}{\partial t} \Psi(r, t) = H(r, t) \Psi(r, t),
\]

where the field-molecule Hamiltonian is \(H(r, t) = T_k(r) + V_c(r) + r \cdot E(t)\) and \(r = (\rho, \theta, z)\) with \((x = \rho \cos \theta, y = \rho \sin \theta)\). The \((x, y)\) plane is defined by the molecular \(R\) axis and the polarization of laser pulses. \(V_c(r)\) is the molecular two-center Coulomb potential. The molecular kinetic energy term (Laplacian) is

\[
T_k(\rho, \theta, z) = -\frac{1}{2\rho} \frac{\partial}{\partial \rho} \left( \rho \frac{\partial}{\partial \rho} \right) - \frac{1}{2\rho^2} \frac{\partial^2}{\partial \theta^2} - \frac{1}{2} \frac{\partial^2}{\partial z^2}.
\]
\[
V_r(\rho, \theta, z) = - \left[ \rho^2 + \frac{R^2}{4} + \rho \rho \cos(\theta - \Theta) + z^2 + z \right]^{\frac{1}{2}} - \left[ \rho^2 + \frac{R^2}{4} - \rho \rho \cos(\theta - \Theta) + z^2 + z \right]^{\frac{1}{2}},
\]

where $\Theta$ is the molecular alignment angle between the molecular $R$ axis and the $x$ axis. A regular-
ization parameter $z = 0.35$ is used to remove the singularity in the Coulomb potential in Eq.
(3), allowing the accurate reproduction of the electronic state potential energies of $\text{H}_2$.\(^\text{35}\)

Removing the Coulomb singularity allows for using efficient split operator methods to solve the
TDSE, Eq. (1) as described below. The field-molecule interaction is treated in the length gauge
with a laser field, propagating along the $z$ axis. A temporal slowly varying envelope $f(t) = \sin^2(\pi t/T)$, with one optical cycle (o.c.) period
$1\tau = 2\pi/\omega$ and total duration $T = 8\tau$ is adopted.

We solve numerically the 3D TDSE in Eq. (1) by a five-point finite difference method and fast
Fourier transform technique combined with high-order split-operator methods.\(^\text{41,42}\) The time
step is fixed at $\Delta t = 0.01$ a.u. (1 a.u. = 24 as) thus allowing maximum energy spectrum of 100
a.u., whereas the spatial discretization is $\Delta \rho = \Delta \theta = 0.25$ a.u. (1 a.u. = 1 $a_0$, Bohr radius) for ra-
dial grid sizes $0 \leq \rho \leq 128$ a.u. and $|z| \leq 64$ a.u., and angle grid size $\Delta \theta = 0.01$ rad. To prevent
unphysical effects due to the reflection of the electron wave packet from the boundary, we mul-
tiply $\psi(r, t)$ by a “mask function” with the form

\[
E(t) = E_{id}(t) \cos \omega t.
\]

A temporal slowly varying envelope $f(t) = \sin^2(\pi t/T)$, with one optical cycle (o.c.) period
$1\tau = 2\pi/\omega$ and total duration $T = 8\tau$ is adopted.

For an intense laser pulse, a quite large grid range must be used to obtain via Fourier trans-
form the high energy of the ejected electron in the ionization spectra. In the present work, we
use an efficient method by calculating a radial flux (electron current density) $S_{\rho}(t)$ to describe
the ionization spectra, where the high kinetic energy of the ionized electron can be accurately
calculated.\(^\text{35}\) At an asymptotic point $\rho_f = 100$ a.u., the electron wave function $\psi(r, t)$ generates
the flux $S_{\rho}(t)$ in the molecular and laser polarization ($x$, $y$) plane before the grid absorption
at boundary. For attosecond photoionization processes, the laser duration $T \leq 400$ as is very short.
At such large asymptotic point $\rho_f$, the angular flux distributions can be ignored, i.e.,
$1/\rho_f \partial / \partial \rho \rho \psi \ll \partial / \partial \rho \rho \psi \rho$. As a result, we only need to consider the radial part of the elec-
tronic flux along the radial direction, \(\partial / \partial \rho \rho \psi \rho \). The time-independent energy-resolved angular
differential yield (photoelectron spectra) is obtained by a Fourier transform from the exact time
dependent functions:\(^\text{35}\)

\[
\psi(\theta, E_e)_{|\rho_f} = \int_{\rho_f}^{\infty} \psi(\theta, t)_{|\rho_f} e^{iE_e t} dt,
\]

\[
\psi'(\theta, E_e)_{|\rho_f} = \int_{\rho_f}^{\infty} \frac{\partial \psi(\theta, t)_{|\rho_f}}{\partial \rho} e^{iE_e t} dt,
\]

\[
S_{\rho}(\theta, E_e) \sim \text{Re} \left[ \frac{1}{2} \psi'(\theta, E_e)_{|\rho_f} \psi(\theta, E_e)_{|\rho_f} \right],
\]

where $t_p$ is time after pulses switch off. $E_e = p_e^2/2$ (in a.u.) is the kinetic energy of an ionized
electron with wave vector $k = p_e = 2\pi/\lambda_e$ (in a.u.), $p_e = (p_x^2 + p_y^2)^{1/2}$ is the momentum of a
of the field vector. Since only the radial electronic flux is taken into account, we can also define \( \theta \) as the angle between the photoelectron momentum \( p_x \) and the \( x \) axis. With the transformation \( p_x = p_x \cos \theta \) and \( p_y = p_x \sin \theta \), we then obtain the 2D momentum distributions of photoelectrons from Eq. (6).

**III. NUMERICAL RESULTS AND DISCUSSIONS**

We present the two-center interference in photoionization by intense attosecond UV laser pulses. Due to effects of the molecular potential, interference patterns are shown to be sensitive to molecular alignment. We choose a single photon ionization, \( \omega > I_p \), to eliminate the effects of the resonant intermediate electronic states. High-order MATI spectra can also be observed in UV laser fields but the spectrum intensity decreases rapidly as the photoelectron kinetic energy increases.\(^{44}\) For higher-order MATI spectra, \( E_e \gg I_p \), Coulomb effects on photoionization become weak and thus can be ignored in molecular UV photoelectron processes.\(^{45}\) Therefore, in the present work we mainly focus on the interference patterns in the first order MATI spectra, i.e., \( E_e = \omega - I_p \). In these simulations, the Keldysh parameter\(^{46}\) \( \gamma = \sqrt{I_p/2U_p} \gg 1 \), where \( I_p \) is the molecular ionization potential and \( U_p = E_\text{p}^2/4\alpha^2 \) is the ponderomotive energy, indicates a multi-photon ionization process regime. Moreover, the molecular alignment during ionization can be readily achieved with current orientational laser technology.\(^{47}\)

We adopt the exactly solvable photoionization model of \( \text{H}_2^+ \) by a linearly polarized delta function pulse which has been previously used successfully to describe LIED\(^{12}\) to derive the two-center interference model, as derived in the Appendix. From Eq. (A8) where the photoionization distribution is \( A^{\sigma_e}(p_e) = (2\pi)^{-3/2} \sqrt{2} \cos(\mathbf{F} \cdot \mathbf{p}_e + R/2) / \sqrt{C_{14}} \), one can see that the effect of the delta pulse is to shift the total momentum distribution by the total amplitude of the field vector \( \mathbf{F} \). For the 1s\(\sigma_e \) state since the initial orbitals are concentrated equally at the two nuclei which are separated by \( R \), the cosine term represents the interference of two outgoing electron wave packets emanating from the two-centers. This is reminiscent of electron interference and diffraction through a double slit.\(^{10-12}\) The pulse field amplitude \( \mathbf{F} \) can be ignored to describe the two-center interference patterns since the chosen intensities produce negligible ponderomotive energies \( U_p = E_\text{p}^2/4\alpha^2 \ll I_p \) and \( F \ll p_e \). Then the photoionization distributions can be expressed as

\[
A^{\sigma_e}(p_e) = (2\pi)^{-3/2} \sqrt{2} \cos(p_e R \cos \vartheta/2) / \sqrt{C_{14}}, \quad (7)
\]

where \( \vartheta \) is the angle between the momentum \( p_e \) of the ejected electron and the molecular \( R \) axis. For the 1s\(\sigma_e \) state of \( \text{H}_2^+ \) at internuclear distance \( R \), Eq. (7) yields constructive interference at the condition \( p_e R \cos \vartheta/2 = n\pi \), \( n = 0, \pm 1, \pm 2, \ldots \), and destructive case at \( p_e R \cos \vartheta/2 = (n + 1/2)\pi \). For photoelectron distributions at certain momentum \( p_e \), the

![FIG. 1. (a) Photoionization for the ground 1s\(\sigma_e \) state of the \( \gamma \)-aligned (\( \Theta = 90^\circ \)) molecular ion \( \text{H}_2^+ \) at equilibrium by linearly \( x \)-polarized attosecond UV laser pulses at intensity \( I_0 = 5 \times 10^{14} \text{W/cm}^2 \), wavelengths \( \lambda = 12.5 \text{nm} \), and durations \( T = 8t = 333.6 \text{ as} \). \( \mathbf{p} \) indicates the photoelectron momentum at the critical angle \( \vartheta_c \). (b) Photoelectron energy spectra at the critical angle \( \vartheta_c = 44^\circ \) (\( \vartheta = 46^\circ \)). (c) Angle \( \vartheta \) resolved photoelectron energy spectra around the critical angle \( \vartheta_c \). Signal intensities of the ionization spectra are on a logarithmic scale in arbitrary units.](image-url)
TABLE I. Classic momenta $p_e$ and wavelengths $\lambda_e$ of a photoelectron calculated by $p_e^2/2 = \omega - I_e$ and $\lambda_e = 2\pi/p_e$ for the ground $1s\sigma_g$ electronic state of the aligned molecular ion $\text{H}_2^+$ at equilibrium $R_e = 2$ a.u. by varying the wavelength $\lambda$ (angular frequency $\omega$) of UV laser pulses.

| UV pulses | Photoelectron |
|-----------|---------------|
| $\lambda$ (nm) | $\Omega$ (a.u.) | $p_e$ (a.u.) | $\lambda_e$ (a.u.) |
| 12.5 | 3.65 | 2.26 | 2.78 |
| 19.5 | 2.34 | 1.57 | 4.0 |
| 3.75 | 12.1 | 4.70 | 1.34 |

constructive interference yields multiple angle nodes at critical angle $\vartheta_e$, i.e., LIED;\textsuperscript{12} whereas minima are produced in the destructive interference patterns.\textsuperscript{48}

Figure 1 shows results of photoionization for the perpendicular $y$-aligned ($\Theta = 90^\circ$) $\text{H}_2^+$ ground $1s\sigma_g$ electronic state at equilibrium $R_e = 2$ a.u. in ultrashort intense linearly polarized UV laser pulses with wavelength $\lambda = 12.5$ nm (angular frequency $\omega = 2\pi c/\lambda = 3.65$ a.u.), duration $T = 8\tau = 13.8$ a.u. = 333.6 as, and intensity $I_0 = 5 \times 10^{14}$ W/cm$^2$ ($E_0 = 0.12$ a.u.).

The corresponding photoelectron momentum and wavelength calculated by $p_e^2/2 = \omega - I_p$ and $\lambda_e = 2\pi/p_e$ are, respectively, $p_e = 2.26$ a.u. and $\lambda_e = 2.78$ a.u., as listed in Table I. It has been recently found that high frequency imaging of polyatomics through photoelectron angular distributions occurs mainly from bond direction of ionized electron.\textsuperscript{49}

From Fig. 1(c), we see that the MPES are sensitive to the angle $\theta$ between the momentum $p_e$ of the ejected electron and the $x$ axis, the laser polarization direction (Fig. 1(a)). At small or large angles $\theta = 35^\circ$ and $60^\circ$, a single peak structure is obtained whereas MPES split into two separated sub-peaks around a specific angle $\theta = 46^\circ$, i.e., $\vartheta_e = 44^\circ$. Such doublets in MPES mainly result from the destructive interference effects of electron wave packets emitted separately from the two nuclei. According to the interference model in Eq. (A8), the destructive interference with minima occurs at condition $p_e R_e \cos \vartheta/2 = (n + 1/2)\pi$, $n = 0, \pm 1, \pm 2, \cdots$. With the electron momentum $p_e = 2.26$ a.u. at the pulse wavelength $\lambda = 12.5$ nm (Table I), destructive interference of the photoelectron is predicted at angles $\vartheta = n\pi \pm 0.2557\pi$ for $R_e = 2$ a.u., see Eq. (A8). For $n = 0$, the interference angle is then $\vartheta_e = 46^\circ$. This is in good agreement with the numerical results illustrated in Fig. 1(b) at the critical angle $\vartheta_e = 44^\circ$ ($\theta = 46^\circ$), with a pronounced double peak structure.

We next show effects of molecular alignment on the two center interference. We present results of MPES at different molecular alignment angles $\Theta = 45^\circ$. Fig. 2, and $\Theta = 0^\circ$, Fig. 3 in the $\text{H}_2^+$ $1s\sigma_g$ state with a linearly $x$-polarized attosecond UV laser pulse. The laser pulse is the same as Fig. 1, thus an interference minimum should be predicted at a critical angle $\vartheta = 46^\circ$ from Eq. (A8).

![Figure 2](image_url)

FIG. 2. (a) Photoionization for the ground $1s\sigma_g$ state of the $\Theta = 45^\circ$ aligned molecular ion $\text{H}_2^+$ at equilibrium by linearly $x$-polarized attosecond UV laser pulses at intensity $I_0 = 5 \times 10^{14}$ W/cm$^2$, wavelengths $\lambda = 12.5$ nm, and durations $T = 333.6$ as. p indicates the photoelectron momentum at the critical angle $\vartheta_e$. (b) Photoelectron energy spectra at the critical angle $\vartheta_e = 50^\circ$ ($\theta = 0^\circ$). (c) Angle $\theta$ resolved photoelectron energy spectra around the critical angle $\vartheta_e$. Signal intensities of the ionization spectra are on a logarithmic scale in arbitrary units.
At $\Theta = 0^\circ$ for the ionized electron with the ejection angle $175^\circ$, the corresponding momentum of the ionized electron is predominantly molecular. The asymmetry therefore leads to a decrease of the electron interference. Rotating the ground $1^g$ molecular axis further, the asymmetry between the two centers increases as well. As the molecular $R$ axis rotates with respect to the $x$ polarization axis, the two interferences become weak. Results in Fig. 1 at the $y$ aligned molecular angle $\Theta = 90^\circ$ exhibit a clear interference pattern with deep minima in MPES. However, at $\Theta = 45^\circ$ one sees that the amplitude of the interference patterns in MPES decreases. At angle $\vartheta_\pi = 50^\circ$ ($\vartheta = 175^\circ$) strong asymmetric sub-peaks are obtained as illustrated in Fig. 2(b). Due to the asymmetric Coulomb force, spatial asymmetry of the ionization probability from the left ion and the right ion is induced following the $x$ polarization. As illustrated in Fig. 2(a) for the ionized electron with the ejection angle $175^\circ$, the ionization from the left center dominates. The asymmetry therefore leads to a decrease of the electron interference. Rotating the molecular $R$ axis further, the asymmetry between the two center photoionization increases as well. At $\Theta = 0^\circ$, the ionization mainly comes from one center. The angles $\vartheta$ and $\vartheta$ are same. The strongly asymmetric amplitudes of the two outgoing electron wave packets can not trigger sufficiently an efficient interference to produce a minimum in the energy spectra around the critical angle $\vartheta_\pi = \vartheta = 46^\circ$ predicted from Eq. (A8). Therefore, only one broad peak is obtained in MPES in Fig. 3. For the ionization at $\Theta = 90^\circ$, the asymmetric Coulomb force essentially does not influence the molecular ionization. Therefore, as shown in Fig. 1 a pronounced interference pattern at $\vartheta = 46^\circ$ ($\vartheta_\pi = 44^\circ$) is observed. Of note is that due to the asymmetric ionization from the two nuclear centers, the numerical results of the critical angle shift slightly comparing to the predictions in Eq. (A8).

For these ionization processes, the dominant ionization is along the $x$ polarization axis. The electron is initially localized on the two nuclei, and then ionized to the continuum by the field. Therefore, the orientation ionization probabilities from the two centers are influenced by the asymmetric Coulomb force and the polarization direction of the driving pulses. Comparison of Figs. 1–3 shows that the interference patterns are strongly influenced by the molecular alignment angle $\Theta$. As the molecular $R$ axis rotates with respect to the $x$ polarization axis, the two interferences become weak. Results in Fig. 1 at the $y$ aligned molecular angle $\Theta = 90^\circ$ exhibit a clear interference pattern with deep minima in MPES. However, at $\Theta = 45^\circ$ one sees that the amplitude of the interference patterns in MPES decreases. At angle $\vartheta_\pi = 50^\circ$ ($\vartheta = 175^\circ$) strong asymmetric sub-peaks are obtained as illustrated in Fig. 2(b). Due to the asymmetric Coulomb force, spatial asymmetry of the ionization probability from the left ion and the right ion is induced following the $x$ polarization. As illustrated in Fig. 2(a) for the ionized electron with the ejection angle $175^\circ$, the ionization from the left center dominates. The asymmetry therefore leads to a decrease of the electron interference. Rotating the molecular $R$ axis further, the asymmetry between the two center photoionization increases as well. At $\Theta = 0^\circ$, the ionization mainly comes from one center. The angles $\vartheta$ and $\vartheta$ are same. The strongly asymmetric amplitudes of the two outgoing electron wave packets can not trigger sufficiently an efficient interference to produce a minimum in the energy spectra around the critical angle $\vartheta_\pi = \vartheta = 46^\circ$ predicted from Eq. (A8). Therefore, only one broad peak is obtained in MPES in Fig. 3. For the ionization at $\Theta = 90^\circ$, the asymmetric Coulomb force essentially does not influence the molecular ionization. Therefore, as shown in Fig. 1 a pronounced interference pattern at $\vartheta = 46^\circ$ ($\vartheta_\pi = 44^\circ$) is observed. Of note is that due to the asymmetric ionization from the two nuclear centers, the numerical results of the critical angle shift slightly comparing to the predictions in Eq. (A8).

It is also found that the interference patterns are a function of the photoelectron kinetic energies. In Fig. 4, we compare the results at different photoelectron kinetic energies $E_e$ for the ground $1^s\sigma_x$ state. Figure 4(a) shows MPES at $\vartheta_\pi = \vartheta = 0^\circ$ in the $1^s\sigma_x$ state with intensity $I_0 = 5 \times 10^{14}$ W/cm$^2$ linearly $x$ polarized attosecond UV laser pulses. The pulse duration is $T = 8\tau = 20.4$ a.u. $= 493.7$ as. The molecular axis is aligned the $x$ polarization axis, i.e., $\Theta = 0^\circ$. The corresponding momentum of the ionized electron is $p_e \approx \pi/2$ a.u. (Table I). According to the two-center ionization model in Eq. (A8), destructive interference patterns with minimum in MPES should be expected at $\vartheta = 0^\circ$. It is, however, found that in Fig. 4(a) no splitting and minimum occur again and the energy spectra only exhibit a single peak around the photoelectron energy $E_e = 1.24$ a.u., the same as Fig. 3(b). For comparison, in Fig. 4(b), we also display the corresponding results by a higher frequency laser pulse. The laser wavelength $\lambda = 3.75$ nm ($\omega = 12.1$ a.u.) and duration $T = 100$ as are adopted. With such laser pulses, the momentum of the ionized electron is $p_e \approx 3\pi/2$ a.u. ($n = 1$), as listed in Table I. Contrary to the previous result ($n = 0$) in Fig. 4(a), the expected double peak structure predicted in Eq. (A8) is now obtained due to the two-center destructive interference.

**FIG. 3.** (a) Photoionization for the ground $1^s\sigma_x$ state of the $x$-aligned ($\Theta = 0^\circ$) molecular ion $\text{H}_2^+$ at equilibrium by linearly $x$-polarized attosecond UV laser pulses at intensity $I_0 = 5 \times 10^{14}$ W/cm$^2$, wavelengths $\lambda = 12.5$ nm, and durations $T = 333.6$ as. $p$ indicates the photoelectron momentum at the critical angle $\vartheta_\pi$. (b) Photoelectron energy spectra at the “critical” angle $\vartheta_\pi = \vartheta = 46^\circ$ predicted from Eq. (A8). (c) Angle $\vartheta$ resolved photoelectron energy spectra around the “critical” angle $\vartheta_\pi$. Signal intensities of the ionization spectra are on a logarithmic scale in arbitrary units.
The absence of the doublet in MPES for the $1\sigma_g$ state in Fig. 4(a) mainly results from the asymmetric ionization for the two centers due to the molecular Coulomb potential, the same as Fig. 3. At such low kinetic energies ($E_e = 2.55$ a.u. and $I_p = 1.1$ a.u.), the two outgoing electron wave packets from the two nuclei do not match each other in amplitude, as illustrated in Fig. 3(a). Efficient destructive interference cannot be induced, therefore leading to a single peak in MPES. For the higher energy photoelectron, effects of Coulomb potential on the electron interference can be ignored. For $\omega \gg I_p$, the spatial asymmetry of the two-center ionization is weak. Therefore, in Fig. 4(b) where $E_e = 11.04$ a.u. $\gg I_p$, we can observe interference patterns in the MPES only at $\vartheta_e = 0'$. The similar processes have also been predicted in the rotation of molecular circular polarization photoelectron angular distributions in MATI for $H^+_2$, and the rotation angle arising from the Coulomb effects is absent in the high kinetic energy region ($E_e \gg I_p$). The dependence on the photoelectron kinetic energy $E_e$ of the interference patterns confirms the effects of the spatial orientation asymmetry of the two center photoionization as functions of angle.

IV. CONCLUSIONS

Effects of molecular alignment on electron interference in intense high frequency laser photoelectron energy spectra of a single electron molecular ion $H^+_2$ are investigated by intense linearly polarized attosecond UV laser pulses from numerical solutions of the corresponding TDSEs for static nuclei at equilibrium $R_e = 2$ a.u. Single photon ionization processes are simulated in the ultrashort attosecond laser pulses with frequencies $\omega > I_p$. At critical ejection angles $\vartheta$ of the ionized electrons with respect to the molecular internuclear $R$ axis, photoelectron energy spectra exhibit generally a doublet structure in molecular linear polarization ionization processes. We attribute these minima to effects of the destructive interference between the electron wave packets ionized separately from the two nuclear centers. It is found that the interference patterns are sensitive to the molecular alignment angle $\Theta$ with respect to the laser polarization. This mainly results from a spatial orientation asymmetry of the two outgoing electron from the two nuclear centers due to effects of the molecular Coulomb potential. At high photoelectron kinetic energy $E_e$, suppression of such interference occurs due to decreasing Coulomb potential effects.

ACKNOWLEDGMENTS

The authors thank RQCHP and Compute Canada for access to massively parallel computer clusters and NSERC, FQRNT for financial support in ultrafast science program.
APPENDIX: TWO CENTER INTERFERENCE MODELS IN MOLECULAR ATTOSECOND PHOTOIONIZATION

According to the attosecond perturbative theory developed recently by Starace and coworkers,\textsuperscript{50} the differential probability for ionization with momentum $p$ into the solid angle $d\Omega$ and the energy interval $dE$ is given in the electric dipole approximation (in the first order in laser intensity)

$$
\frac{d^2P}{d\Omega dE} \sim |\langle \psi' | F(E - E_i) \cdot \mathbf{r} | \psi_0 \rangle|^2,
$$

(A1)

where $E = p^2/2m$ and $\psi'$ and $\psi_0$ are the final continuum and initial electronic states, respectively. $F(E)$ is an energy Fourier transform of the ionizing pulse

$$
F(E) = \int e^{iEt} E(t) dt
$$

(A2)

and $E_i$ is the eigenenergy of the initial electronic state. From Eq. (A1), one sees that the photoelectron distribution is product of an electronic Franck-Condon factor (photoionization probability) $A$ and the pulse spectral width $F(E - E_i)$. Then, Eq. (A1) can be written as

$$
\frac{d^2P}{d\Omega dE} = |A F(E - E_i)|^2,
$$

(A3)

with

$$
A = \langle \psi' | \mathbf{F} \cdot \mathbf{r} | \psi_0 \rangle,
$$

(A4)

and $F(E) = F(E)/F_0$, where $F$ is the pulse maximum amplitude. We see that the MPES strongly depend on the bandwidth of the laser pulse $F(E - E_i)$. The relation of the photoelectron momentum and the angle between the momentum $p_e$ and the molecular $\mathbf{R}$ axis is determined by the transition amplitude $A$, and the pulse bandwidth $F(E)$ decides the position of the photoelectron energy spectra.

Taking into account an impulsive field model,\textsuperscript{51} the wavefunction in momentum space right after the pulse is given by

$$
\psi(p_e, 0^+) = \psi_0(p_e + \mathbf{F}),
$$

(A5)

where $\psi_0(p_e)$ is the wavefunction of the ground electronic state in momentum space. Transforming the wavefunction $\psi(p_e, 0^+)$ to coordinate space, we then get

$$
\psi(r, 0^+) = (2\pi)^{-3/2} \int dp_e e^{-ip_e \cdot r} \psi(p_e, 0^+) = e^{-iFr} \psi_0(r).
$$

(A6)

The transition amplitude $A(p_e)$ to a continuum state can be expressed as

$$
A(p_e) = (2\pi)^{-3/2} \int dr e^{-ip_e \cdot r} \psi(r, 0^+).
$$

(A7)

For the initial ground $1s\sigma_g$ electronic states of $\text{H}_2^+$ at internuclear distance $\mathbf{R}$, the corresponding wavefunction is $\psi_{1s\sigma_g} = \psi_{1s}( - \mathbf{R}/2) + \psi_{1s}( \mathbf{R}/2)/\sqrt{2}$, i.e., linear combinations of hydrogenic $1s$ orbital located at $\pm \mathbf{R}/2$. Then the transition amplitude $A$, i.e., the momentum distribution of photoelectron in Eq. (A7) can be written as

$$
A^{1s}(p_e) = (2\pi)^{-3/2} \sqrt{2} \cos(|\mathbf{F} + p_e| \cdot \mathbf{R}/2) \psi_{1s}( |\mathbf{F} + p_e|).
$$

(A8)
For the excited $2\sigma_s^a$ electronic state with wavefunction $\psi_{2\sigma_s^a} = |\psi_{1s}(−R/2) − \psi_{1s}(R/2)|/\sqrt{2}$, the corresponding distributions exhibit a strong phase difference as

$$A^\alpha(p_s) = (2\pi)^{−3/2} \sqrt{2} \sin((F + p_s) \cdot R/2) |\psi_{1s}(F + p_s)|.$$  

(A9)