Subcycle transient structures in time-dependent multiphoton-ionization rates

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We perform an ab initio and accurate exploration of the subcycle transient multiphoton-ionization dynamics of atomic and molecular systems subject to intense near-infrared laser fields on the subfemtosecond time scale. Multiple-ionization bursts within a single optical cycle are found in the time-dependent ionization rates not only for diatomic molecules H2+ and HHe2++, but also for the hydrogen atom. The analysis of the electron density reveals that several distinct density portions can be shaped and detached from the target within a half cycle of the laser field.

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I. INTRODUCTION

Multiphoton and above-threshold ionization of atoms and molecules in intense laser fields belongs to the most fundamental in addition as well as explored and understood strong-field phenomena (see the review papers [1,2]). Multiphoton ionization (MPI) is also an initial step in many other processes such as high-harmonic generation [3] and high-order above-threshold ionization [4]. Novel phenomena including generation of attosecond pulses [5,6], ultrafast molecular imaging [7,8], attosecond photoelectron holography [9], and electron diffraction [10,11] (see the review in Ref. [12]) are also closely related to multiphoton ionization. Regarding the MPI measurements, since the early experiments on above-threshold ionization (ATI) [13], research has focused on the properties of the emitted electrons in the energy domain (electron energy spectra, which manifest the famous ATI peak structure). However, recent advances in laser technology opened the possibility of clocking the electron dynamics on an attosecond scale in the time domain [14,15], thus introducing a concept of attosecond metrology [12]. The time-domain analysis can uncover different features in the well-researched phenomenon of multiphoton ionization.

Recently, a theoretical study on H2+ in an intense infrared laser field [16,17] revealed multiple ionization bursts within a half cycle of the laser-field oscillation. The phenomenon was explained by transient electron localization near one of the nuclei on the attosecond time scale [16], which is in turn related to the existence of two electronic states with opposite parities strongly coupled by the field (the charge resonance states [18]). Here we show that multiple ionization bursts per half cycle of the laser field can exist not only in homonuclear molecules with odd number of electrons, which possess the charge resonance states, but also in heteronuclear molecules and even in atoms.

II. THEORETICAL AND COMPUTATIONAL METHOD

In this paper we analyze the time-dependent MPI rates of three one-electron systems: the hydrogen atom and molecul-
back to the core, thus imposing the outgoing-wave boundary conditions.

For the time evolution of the wave function, we employ the following split-operator second-order short-time propagation formula:

\[
\Psi(r,t + \Delta t) = \exp \left( -\frac{i}{2} \Delta t H_0 \right) \times \exp \left[ -i \Delta t V \left( r, t + \frac{1}{2} \Delta t \right) \right] \times \exp \left( -\frac{i}{2} \Delta t H_0 \right) \Psi(r,t) + O((\Delta t)^3). \tag{4}
\]

Here \( \Delta t \) is the time propagation step and \( H_0 \) is the unperturbed electronic Hamiltonian, which includes the kinetic energy and the core potential. The operator \( \exp(-\frac{i}{2} \Delta t H_0) \) is constructed by the spectral expansion

\[
\exp \left( -\frac{i}{2} \Delta t H_0 \right) = \sum_n \exp \left( -\frac{i}{2} \Delta t E_n \right) |\psi_n \rangle \langle \psi_n|, \tag{5}
\]

where \( \psi_n \) and \( E_n \) are the eigenvectors and eigenvalues, respectively, of the unperturbed Hamiltonian \( H_0 \). In practical calculations, the summation in (5) includes all eigenvectors with the energies \( E_n < E_b \), where the upper limit \( E_b \) should be large enough to describe all relevant physical processes. With the control of high-energy contributions to the propagator matrix, we can avoid population of physically irrelevant regions of the energy spectrum and improve numerical stability of the computations. In the present work we use \( E_b = 10 \) a.u.; this is a reasonable value for the carrier frequency and intensities of the laser field used in the present calculations. For the given \( \Delta t \), the propagator matrix \( \exp(-\frac{i}{2} \Delta t H_0) \) is time independent and constructed only once before the propagation process starts. The matrix \( \exp[-i \Delta t V (r, t + \frac{1}{2} \Delta t)] \) is time dependent and must be calculated at each time step. However, for the interaction with the laser field in the length gauge, this matrix is diagonal in the GPS method and its calculation is not time consuming (all potential terms are represented by their values on the coordinate grid and appear as diagonal matrices in the GPS method; no calculation of potential energy matrix elements is required). In the present work we use 4096 time steps per optical cycle; this is enough to achieve convergence for the intensities and wavelengths used in the calculations.

Because of the absorber, the normalization integral of the wave function \( \Psi(r,t) \) decreases in time. The parts of the wave packet absorbed in the layer between the distance values \( R_a \) and \( R_b \) describe unbound states populated during the ionization process. The time-dependent ionization rate can be defined as a logarithmic derivative of the time-dependent population \( P(t) \):

\[
P(t) = \int_{r < R_a} d^3r |\Psi(r,t)|^2, \tag{6}
\]

\[
\Gamma(t) = -\frac{d}{dt} \ln P(t). \tag{7}
\]

III. RESULTS AND DISCUSSION

We have performed a series of calculations on H, H\(_2\)\(^{+}\), and HHe\(^{2+}\) for the laser fields with several intensities and wavelenghts in the near-infrared range (780–1064 nm). The subcycle structures appear as a universal feature of multiphoton ionization and become well pronounced for sufficiently strong laser fields. Here we report some representative results. For the diatomic molecules H\(_2\)\(^{+}\) and HHe\(^{2+}\), we report the time-dependent MPI rates obtained from the Floquet states in the monochromatic laser field. The scheme for the calculation of the Floquet states is similar to that for the calculation of ordinary time-dependent wave functions but includes an additional procedure for construction and diagonalization of the one-optical-cycle propagator (see Ref. [23]). For H\(_2\)\(^{+}\), we choose a stretched configuration for the ground electronic 1\( \sigma_g \) state with the internuclear separation \( R = 3 \) a.u. This makes the ionization potential lower and allows us to obtain noticeable ionization rates for moderate laser intensities. In Fig. 1 we show the results for the field with the wavelength 800 nm and intensity 1 \( \times 10^{14} \) W/cm\(^2\), with the molecular axis orientation parallel to the laser field. In this calculation, we use \( R_a = 50 \) a.u. and \( R_b = 30 \) a.u. As expected, the MPI rate has two main maxima per optical cycle, corresponding to the peak values of the laser field. However, each maximum is split in two subpeaks with the local minimum between them.

For HHe\(^{2+}\), the bonding orbital is not the ground electronic state but the first excited state 2\( \sigma_g \). We have performed the calculations for the internuclear separation of 4 a.u., which is close to the equilibrium distance. The laser field has the wavelength 780 nm and intensity 5 \( \times 10^{13} \) W/cm\(^2\) and is directed along the molecular axis. Here we use \( R_a = 40 \) a.u. and \( R_b = 20 \) a.u. The results for the MPI rate are shown in Fig. 2. As for the H\(_2\)\(^{+}\) molecule, we can see two main maxima per optical cycle corresponding to the peak values of the laser field. However, unlike the H\(_2\)\(^{+}\) case, the MPI rates at these maxima are different: The positive and negative directions of the field are not equivalent for HHe\(^{2+}\) because of its heteronuclear nature. Each main maximum is again split into subpeaks. Since HHe\(^{2+}\) is a heteronuclear diatomic molecule with a highly asymmetric electron density distribution, we can conclude that the fine subpeak structure of the time-dependent MPI rate is not related to the two-center nature of the molecule.
but shaped in the vicinity of one nucleus only. This observation is confirmed by our calculations of the hydrogen atom in the laser field.

In Fig. 3 we show the time-dependent MPI rates for the hydrogen atom initially in the ground state. The laser field has a carrier wavelength 800 nm and the peak intensity $5 \times 10^{13}$ W/cm$^2$. We use the values $R_0 = 60$ a.u. and $R_b = 40$ a.u. The field is switched on during the first 5 optical cycles with the $\sin^2$ ramp until it reaches the peak intensity. Then the intensity is kept constant for the next 15 optical cycles. Thus the total time for the propagation of the wave function is 20 optical cycles. We should note that the resulting wave function at the end of the propagation time differs very little from the Floquet state in the monochromatic field with the same wavelength and intensity. We perform the MPI rate analysis on the last optical cycle, approximately between the time moments 50.7 and 53.4 fs. For a better understanding of the electron dynamics during this period of time, in Fig. 3(a) we show the force experienced by the electron from the laser field. For the first half cycle, the force is negative, pushing the electron to the negative side of the z axis; for the second half cycle, the picture is reversed.

The MPI rate is defined by Eqs. (6) and (7) for the whole spherical volume with the radius $R_b$ where the time-dependent Schrödinger equation is solved. However, we can also define the MPI rate on the boundary of a smaller spherical volume with the radius $R_0 < R_b$. Defined in this way, the quantity $dP/dt$ represents the electron current through the sphere of radius $R_0$, which is the observable that can be measured experimentally if the detector is placed at the distance $R_0$ from the target. In Fig. 3(b) the time-dependent MPI rates of the hydrogen atom are shown for two different spherical volumes, with the radii $R_0 = 20$ and 40 a.u. As in the case of diatomic molecules, the maxima of the MPI rates exhibit a fine subpeak structure. In Fig. 3(b) one can see three distinct subpeaks corresponding to each maximum. The shape of the subpeaks depends, however, on the radius $R_0$ (which is the distance from the nucleus) where the rate is measured. Their position on the time scale is shifted from that of the field peak values and also depends on $R_0$. To get a better understanding of this phenomenon, it is instructive to study the electron density evolution subject to the influence of both the nucleus and the laser field.

In Fig. 4 we show the electron density evolution within the 0.7-fs time interval corresponding to multiple current density bursts on the spherical surface with the radius 20 a.u. [see Fig. 3(b)]. The evolution of the density for the full optical cycle is presented as a motion picture in Ref. [24]. In both Fig. 4 and Ref. [24], one can clearly see the formation of distinct density portions and their motion in the negative-z direction where the force from the laser field is directed for this time interval. At the time 51.68 fs, the force is near the peak value and the first portion of the density is approaching but not yet crossing the spherical surface at 20 a.u. The ionization rate has its minimum at this time moment. The next time moment, 51.83 fs, corresponds to the maximum of the ionization rate. The first portion of the electron density is crossing the boundary while the second one is clearly seen between the $z$ values $-15$ and $-10$ a.u. At the time 51.97 fs, the first portion has already moved beyond the boundary, the second portion
has approached the boundary but not crossed it, and the third portion is shaped and clearly seen at \( z = -10 \) a.u. This is again a minimum in the ionization rate. The force from the laser field is still negative but close to zero. At the next time moment, 52.08 fs, the force is also weak but has already changed the sign, now pointing in the positive-\( z \) direction. Nevertheless, the second portion of the electron density continues moving in the negative-\( z \) direction and passes the boundary at 20 a.u. In Fig. 3(b) this time moment corresponds to the second maximum of the ionization rate. At the time 52.25 fs, the third portion of the electron density has approached but not yet crossed the boundary; the ionization rate has its minimum. Finally, at 52.39 fs, the third portion of the density crosses into the outer domain giving rise to the third maximum in the ionization rate. However, the force from the laser field has already been positive for some time and becomes quite strong by this moment. That is why the negative velocity of the third portion of the density has become small and the third maximum in the ionization rate is quite weak.

As the analysis of the time evolution of the electron density reveals, several distinct density portions are shaped and detached from the target within a half cycle of the laser field. These portions of the electronic wave packet contain contributions with various energies, which move with different velocities when leaving the core. Thus it is not surprising that the shape of the structures changes as the ionized wave packet moves away from the nucleus. Therefore, the transient structures in time-dependent multiphoton ionization rates (including the number of subpeaks) depend on the radius \( R_0 \) of the sphere where the electron current is measured. Eventually, as \( R_0 \) becomes very large, one may expect a rearrangement in the time-dependent rates according to the energies of the outgoing electrons, with the fast electrons arriving at the detector first and slower electrons arriving later. The asymptotic (large \( R_0 \)) time-dependent rates should correspond to the well-known ATI structures in the energy domain with the peaks separated by the photon energy. However, this large-\( R_0 \) behavior of the ionization rates is beyond the scope of our study; we focus on the nanometer length scale where the physical picture is quite different.

The subcycle transient structures in the time-dependent MPI rates depend also on the wavelength and intensity of the laser field. In Fig. 5 we show the MPI rates of \( \text{H}_2^+ \) and atomic hydrogen at different wavelengths and intensities. The data are obtained from the Floquet state corresponding to the ground electronic state of the target. For the box size and absorber position, we use the values \( R_0 = 60 \) a.u. and \( R_a = 40 \) a.u., respectively. For \( \text{H}_2^+ \), the calculations are performed for the equilibrium internuclear separation \( R = 2 \) a.u., laser wavelength 800 nm, and two intensities \( 3 \times 10^{14} \) and \( 5 \times 10^{14} \) W/cm\(^2\). For the hydrogen atom, we fix the intensity at \( 5 \times 10^{13} \) W/cm\(^2\) and perform the calculations for two different wavelengths, 780 and 1064 nm. As Fig. 5 shows, the subcycle structures change their form significantly when the wavelength or intensity of the laser field is changed. However, we do not see any simple rule that can describe the correspondence between the subcycle pattern (including the number of subpeaks) and the laser field parameters.
IV. CONCLUSION

In summary, we have performed a computational study of the multiphoton-ionization dynamics on the subfemtosecond time scale for the hydrogen atom and two one-electron molecular systems, H$_2^+$ and HHe$_2^+$, subject to intense near-infrared laser fields. Our calculations show a multiple-peak structure of the time-dependent multiphoton-ionization rate within a single optical cycle. The nature of this phenomenon is revealed by the analysis of the time-dependent electron density, which exhibits multiple portions of the density detached from the core at different times, not necessarily when the external field reaches its maximum values. The oscillations of the electron density are caused by transitions to excited bound and continuum states in the laser field. A large dynamic polarizability of the initial state may play a role here. However, at this time we cannot suggest a simple model explaining the phenomenon.

We note that the structures of the multiphoton-ionization rates in the time domain discussed in this paper are not related to the above-threshold peak structures of the electron spectra in the energy domain. When created under the influence of the external field, the portions of the outgoing wave packet are localized in space and time but contain various energy contributions. That is why the shape of the structure is changed as the outgoing wave packet moves away from the core. The structures described above can be observed on the nanometer length scale. Certainly, recording the time information close to the target is a very difficult experimental task. Possibly, it can be done by the experimental methods mapping time into momentum such as streak camera or reconstruction of attosecond beating by two-photon interference. Measurements could be more feasible at sufficiently large distances from the target. Of course, in the far asymptotic region, the time-dependent signal would be reshaped according to the time of flight of the electrons with different energies. In this case, a theoretical reconstruction procedure could help, which maps the properties of the outgoing-wave packet at large distances to earlier times and smaller distances.

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