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RESEARCH ARTICLE

Ionisation effect on the electron localisation in the subcycle waveform shaping scheme

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We have theoretically studied the ionisation effect on the asymmetric dissociation of H$_2^+$ exposed to the synthesised multicycle infrared pulses of different wavelengths by solving the time-dependent Schrödinger equation without using the Born–Oppenheimer approximation. Our simulations are performed at two different pulse intensities of 1 × 10$^{14}$ and 3 × 10$^{14}$ W/cm$^2$. In both cases, the electron localisation is significantly enhanced in the synthesised pulses compared to that in the one-colour (OC) field. But due to the ionisation effect, the physical mechanisms responsible for the enhancement are different. Our results confirm that the ionisation slightly influences the electron localisation of the high vibrational states for the relatively lower intensity and the enhancement mechanism is consistent with the work of Ref. [31]. For the relatively high pulse intensity, we find that the ionisation saturation occurs when the initial state is higher than a critical vibrational state, leading to

1. Introduction

The interaction of ultrashort intense laser pulses with matter has been a very important subject in current research of attosecond physics [1–5]. Many efforts have been made to study the ultrafast molecular dynamics in the strong field [6–12]. A wealth of phenomena responsible for the laser-induced dynamics of the molecule have been discovered in theoretical and experimental studies, including the generation of higher order harmonics [13–17] and attosecond pulses [18–22], molecular dissociation [23], electron diffraction [24], and angular streaking [25].

The control of the electron localisation in the dissociation of molecules has recently become one of the exciting goals of molecular research [11,26], thanks to its potential possibility of selectively breaking and forming molecular bonds in chemical reactions. In 2004, Roudnev et al. [9] proposed that the electron between nuclei during the dissociation of H$_2^+$ and HD$^+$ can be steered by using a few-cycle carrier-envelope phase (CEP) stabilised femtosecond laser pulse. This control scheme has been achieved in experiment by Kling et al. [11], which is a key step forward in the direction of electron localisation. In their work, the CEP serves as the only control parameter, thus limiting the control of electron localisation. An alternative approach to steer the electron in molecular dissociation has been reported, i.e. by using two-colour fields [27–30], where two control parameters, the time delay and the CEP, can be used to control the asymmetric dissociation. Although the degree of the control over the electron localisation has been improved with this approach, the total dissociative probability is still low [27].

In a recent work, Lan et al. [31] proposed a method, named subcycle waveform shaping (SWS), to enhance electron localisation by synthesising multicycle infrared pulses of different wavelengths. However, their theoretical results are based on the two-level model, which ignores the ionisation process. It is shown that the high ionisation probability would lead us to the significant reduction in the electron localisation on the dissociating nuclei [32]. Thus, the use of two-level model would be questionable and it leaves the question: Can the SWS scheme still control the electron localisation efficiently in higher pulse intensity, where the ionisation would be more significant? Therefore, for a better understanding of the molecular dynamics in the SWS scheme, it is necessary to provide a more realistic simulation that includes the ionisation effect. In this paper, we have investigated the asymmetric dissociation of H$_2^+$ in the synthesised multicycle pulses via solving the time-dependent Schrödinger equation (TDSE) without using the Born–Oppenheimer approximation. Our simulations are performed at two different pulse intensities of 1 × 10$^{14}$ and 3 × 10$^{14}$ W/cm$^2$. In both cases, the electron localisation is significantly enhanced in the synthesised pulses compared to that in the one-colour (OC) field. But due to the ionisation effect, the physical mechanisms responsible for the enhancement are different. Our results confirm that the ionisation slightly influences the electron localisation of the high vibrational states for the relatively lower intensity and the enhancement mechanism is consistent with the work of Ref. [31]. For the relatively high pulse intensity, we find that the ionisation saturation occurs when the initial state is higher than a critical vibrational state, leading to
weak electron localisation for the high vibrational states. In this case, the enhancement of final electron localisation results from the enhanced, phase-synchronised localisation asymmetry in the lower vibrational states.

2. Theoretical model

In numerical simulations, we have used a reduced-dimensionality model of H$_2^+$ to solve the TDSE without using the Born–Oppenheimer approximation. This model agrees reasonably with the three-dimensional model [9], even though some quantitative deviations still exist [33]. The model consists of one-dimensional motion of the nuclei and one-dimensional motion of the electron [33,34]. Thus, both the ionisation and dissociation processes can be well described in the model. Here, we assumed that the electronic and nuclear motion are restricted along the polarisation direction of the laser pulse. Since the time scale of nuclear rotation is several hundred femtoseconds, the nuclei do not have time to rotate during the time of interaction. Thus, the nuclear rotation after the pulse is not significant [35]. The reduced-dimensional TDSE can be written as (atomic units, \( e = m = \hbar = 1 \) are used throughout unless otherwise indicated)

\[
i \frac{\partial}{\partial t} \Psi(R, z; t) = \left[ -\frac{1}{2\mu} \frac{\partial^2}{\partial R^2} - \frac{1}{2\mu e} \frac{\partial^2}{\partial z^2} + V_C(z, R) + V(t) \right] \Psi(R, z; t),
\]

where \( R \) is the internuclear distance, \( z \) is the electron position measured from the centre of mass of the protons, \( \mu_e = 2m_p/(2m_p + 1) \) and \( \mu_R = m_p/2 \) are the reduced masses with \( m_p \) as the mass of the proton. The Coulomb potential is given by

\[
V_C(z, R) = -\frac{1}{\sqrt{(z - R/2)^2 + \alpha(R)}} - \frac{1}{\sqrt{(z + R/2)^2 + \alpha(R)}} + \frac{1}{R},
\]

where \( \alpha(R) \) is the soft-core parameter [33]. The interaction with the laser is (in the dipole approximation and length gauge)

\[
V(t) = \left( 1 + \frac{1}{2m_p + 1} \right) z E(t),
\]

with \( E(t) = E_1 \sin(\pi t / \tau_1) \sin(\omega_1 t + \phi_{PE}) + E_2 \sin(\pi t / \tau_2) \sin(\omega_2 t + \phi_{PE}) \) as the electric field of the two-colour laser pulse. Here, the subscript \((1, 2)\) means the two laser-pulse components. \( E, \tau, \) and \( \omega \) are the peak electric field amplitude, pulse duration and angular frequency, respectively. \( \phi_{PE} \) denotes the CEP of the laser pulse.

We have solved the TDSE by using the Crank–Nicolson method [36]. The initial states are chosen as the vibrational bound states of H$_2^+$ and are propagated in the field-free Schrödinger equation in imaginary time [37], respectively. In the simulation, the wavefunction is discrete on a two-dimensional grid, which ranges in the \( R \) direction from 0.05 to 50 au, for \( z \) from \(-90 \) to 90 au with 1000 and 900 points, respectively. The outgoing parts of the wavefunction have been absorbed at the boundaries of the grid by using the \( \cos^{1/6} \) — masking functions. During the evolution of the wavefunction, we have defined the time-dependent dissociative wavefunction by \( \Psi_{DWP}(R, z; t) = \Psi(R, z; t) - \sum_{n=0}^{N-1} \langle \psi_n(R, z) | \Psi(R, z; t) \rangle \nu_n(R, z) \) with \( \nu_n \) as the vibrational bound states and \( N = 20 \) as the number of \( \nu_n \) in our model. The time-dependent probabilities of the dissociative wavepackets localised on the left \((P_l(t))\) or on the right \((P_r(t))\) nucleus can be estimated by integrating the corresponding regions of the grid as follows:

\[
P_{i,t}(t) = \int_0^\infty dR \int_{-\infty}^{\infty} dz |\Psi_{DWP}(R, z; t)|^2 + \int_{-\infty}^{R_{max}} dR \int_{-\infty}^{\infty} dz |\Psi_{DWP}(R, z; t)|^2,
\]

where \( R_{max} \) corresponds to the boundary of \( R \). The evolution of the wavefunction in the external field has been continued with a time step of \( \delta t = 0.05 \) au until \( P_{i,t}(t) \) are converged. Besides the absorbed contributions in the \( R \) dimension have been stored and added to the corresponding localisation probabilities. We estimate the ionisation probability by storing the absorbed wavepackets reaching the boundary in the \( z \) direction. The kinetic energy release (KER) spectrum \( S_{i,t}(E_k) \) is obtained by Fourier analysis of the real-space wavefunction with the bound states projected out [34]. What we need to pay attention to is the preparation mechanism of a H$_2^+$ ion beam generally indicates an incoherent Franck–Condon (FC) distribution of vibrational states in experiments [38]. Thus, it is necessary to average the observables over the initial vibrational states weighted by FC factors [38], i.e.,

\[
\eta = \sum_{\nu} \eta_{\nu} F_{\nu},
\]

where \( \eta_{\nu} \) denotes the observable calculated for the vibrational states \( \nu \) and \( F_{\nu} \) is the corresponding FC factor (see the inset of Figure 5(a)).

3. Results and discussions

First of all, we simulate the asymmetric dissociation of H$_2^+$ in the SWS field with the intensity of \( 1 \times 10^{14} \) W/cm$^2$ via solving the TDSE without using the Born–Oppenheimer approximation. In the calculation, all the vibrational states...
are considered and propagated in the laser fields independently. To calculate the final electron localisation probability, FC averaging is performed for these vibrational states by using Equation (5). The electric field has been illustrated in Figure 1. In this paper, the SWS pulse is synthesised by 800-nm pulse and 1200-nm pulse. The pulse durations are 15 and 25 fs, respectively. The laser intensity is \(1 \times 10^{14} \text{ W/cm}^2\) with an intensity ratio of 15%. In our scheme, the phases in the two pulses change synchronously. Here, \(\phi_{PE} = 0\).

In this case, the underlying enhancement mechanism of the electron localisation is consistent with that in the work of Ref. [31]. However, we can find that the CEP-dependent asymmetries in this work are not absolutely same with the results of Ref. [31]. This is because the two-level model used in Ref. [31] ignores the ionisation process. According to the previous research [32], the ionisation process may influence the electron localisation in the laser pulse with high intensity or long pulse duration. Note that their calculations were performed at a pulse with rather high intensity (\(1 \times 10^{14} \text{ W/cm}^2\)) and long duration (25 fs), where the probability for the ionisation in the high vibrational states should not be negligible. Therefore, the use of two-level model in Ref. [31] would be still questionable. We are wondering whether the SWS scheme still can control the electron localisation efficiently in higher pulse intensity, where the ionisation would be more significant. To understand the molecular dynamics in the scheme better, we present additional simulations for the electron localisation asymmetry of the \(\text{H}_2^+\) in the SWS field and the OC field with the intensity of \(3 \times 10^{14} \text{ W/cm}^2\). For the SWS field, other laser parameters are the same as those in Figure 1 except for the intensity. The central wavelength and pulse duration of the

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**Figure 1.** The electric field of the SWS pulse. The SWS pulse (blue solid line) is synthesised by 800-nm pulse (red dash-dot line) and 1200-nm pulse (green dash-dotted line). The laser intensity is \(1 \times 10^{14} \text{ W/cm}^2\) with an intensity ratio of 15%. The pulse durations are 15 fs and 25 fs, respectively. In our scheme, the phases in the two pulses change synchronously. Here, \(\phi_{PE} = 0\).

**Figure 2.** (a) Shows the CEP dependence of the FC-averaged electron localisation asymmetry. Also shown is the absolute asymmetry parameter \(A(E_k, \phi_{PE})\) as a function of the CEP and the kinetic energy release (KER) in (b) and the absolute asymmetry map as a function of the vibrational states and CEP in (c). The laser parameters are the same as those in Figure 1.
Figure 3. The CEP dependence of the FC-averaged localisation asymmetry for the 5-fs OC field (a) and the SWS field (b). And the absolute asymmetry map as a function of the vibrational states and CEP in (c) 5-fs pulse and (d) SWS pulse. For the SWS field, other laser parameters are the same as those in Figure 1 except for the intensity of the laser pulses. The central wavelength and pulse duration of the OC pulse are 800 nm and 5 fs, respectively.

Figure 4. Evolution of the field (green line) and the expectation value of the internuclear distance (blue line) for (a) 5-fs field and (b) SWS field. The red arrows mark the position of the \( R = 5 \text{ au} \). Here, \( \nu_{10} \) is selected, \( \phi_{PE} = 0 \), and other laser parameters are the same as those in Figure 3.

Meanwhile, several interesting phenomena are observed in \( 3 \times 10^{14} \text{ W/cm}^2 \) field. From the results of Figure 3(c) and 3(d), we can find two main characteristics: (1) in the 5-fs OC field, the electron localisation asymmetries are negligible for the low vibrational states, but are very strong for the high vibrational states. (2) In contrast, in the SWS field, the electron localisation asymmetries mainly distribute in the lowest five vibrational states but almost disappear for the high vibrational states. Here, we show the CEP-averaged ionisation probability \( (P_i) \) and electron localisation probability \( (P_l + P_r) \) in the two cases (see Figure 5(a) and 5(b)). Compared to the low vibrational states, the high vibrational states have larger dissociation probabilities and ionisation probabilities in both cases. This is determined by the energy curves of the \( \text{H}_2^+ \).

The low vibrational states are relatively stable, thus the vibrational wavepackets of these states can be hardly dissociated. In contrast, the high vibrational states are considerably active and the vibrational wavepackets of these states can be easily dissociated even ionised. Therefore, the phenomena exhibited in Figure 3(c) and 3(d) are well explained.

Note that the final electron localisation asymmetry should be averaged over all vibrational states as described in Section 2. The corresponding weights of the high vibrational states (see the inset of Figure 5(a)) are seriously suppressed. Thus, in the 5-fs OC field, the electron localisation asymmetry after FC averaging shown in Figure 3(a) has been smeared out. For the SWS field, however, the weights of the low vibrational states (see the inset of Figure 5(a)) are much larger than those of the high vibrational states. In addition, the electron localisation asymmetries of the five lowest vibrational states are phase-synchronised and enhanced. Thus, in the SWS field, a large FC-averaged

OC pulse are 800 nm and 5 fs, respectively. We find that the ionisation effect on the electron localisation enhances remarkably. Figure 3 shows the results of the higher intensity laser pulses. The left and the right columns correspond to the OC-5-fs field and the SWS field, respectively. A larger asymmetry with an amplitude of 0.3928, corresponding to an electron localisation probability of about 70%, is obtained in the case of SWS, but it has been significantly smeared out in the OC field. In order to qualitatively interpret the increase of the asymmetry in the multicycle laser pulse, we have given the evolution of the fields and the expectation value of the internuclear distances for Figure 4(a) 5-fs field and Figure 4(b) SWS field. Here, \( \nu_{10} \) is selected, and \( \phi_{PE} = 0 \). The red arrows indicate the positions of the \( R = 5 \text{ au} \). The internuclear distances gradually increase with the evolution of the fields in both cases, leading to the dissociation of the \( \text{H}_2^+ \) ultimately. At the same time, something different has happened in the processes, i.e. when \( R > 5 \text{ au} \), (1) in the OC field, the wavepackets can be pumped to the upper state \( (2p\sigma_u) \) only by the absorption of 800-nm photon; (2) in the SWS field, the wavepackets can be pumped to the upper state by absorbing the photons of 800 or 1200 nm. In addition, when the internuclear distance is stretched to 5 au, the OC pulse already becomes very weak and cannot efficiently pump the wavepackets to the upper state, as a result of a weak interference and a small electron localisation asymmetry. In contrast, in the SWS field, the tail pulse remains very strong and very long when \( R > 5 \text{ au} \). Therefore, a lot of wavepackets can be coupled to the upper state, resulting in a large electron localisation asymmetry.
Figure 5. Red and blue bars: probabilities of ionisation ($P_i$) and electron localisation ($P_l$) after CEP averaging for different vibrational states for (a) 5-fs field and (b) SWS field. The inset in (a) shows the FC distribution of vibrational states.

In order to compare the ionisation effect on electron localisation in the two SWS pulses with different pulse durations, we present additional simulations for the asymmetry electron localisation in the SWS field with the short duration. We chose the durations of the 800-nm pulse and 1200-nm pulse as 10 and 15 fs, respectively. Other laser parameters are the same those in Figure 1. The results are shown in Figure 6. It is found that the obvious electron localisation asymmetries mainly distribute in more vibrational states and wider CEP than in 25-fs field. As a result a sine-like curve and a larger FC-averaged asymmetry amplitude are obtained in Figure 6(a). This is because the ionisation is lower in the 15-fs field than in the 25-fs field. It is noteworthy that the underlying mechanisms are the same in the 15-fs field and 25-fs field.

4. Conclusion
In conclusion, the electron localisation in dissociating $H_2^+$ in the SWS control scheme has been studied by solving the TDSE without using the Born–Oppenheimer approximation. The ionisation effect on the electron localisation is found to be insignificant in the case of relatively low...
pulse intensity, whereas it becomes much more significant as the pulse intensity is increased. Although the electron localisation is enhanced in the synthesised pulses under different intensities, the underlying mechanism is quite different because of the ionisation effect. For the relatively low intensity, the enhancement of final electron localisation results from the almost phase-synchronised localisation asymmetry in the high vibrational states, which is consistent with the published work [31]. On the contrary, due to the ionisation, very few wavepackets are localised on the dissociating nuclei for the critical vibrational states and higher vibrational states at the relatively high intensity. The enhancement that survives in this case is related to the enhanced, phase-synchronised localisation asymmetry in the lower vibrational states, of which the FC factor is larger.

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**References**