Quantum Control of Electron-Proton Symmetry Breaking in Dissociative Ionization of H₂ by Intense Laser Pulses

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Forward and backward electron/proton ionization/dissociation spectra from one-dimensional non-Born-Oppenheimer H₂ molecule exposed to ultrashort intense laser pulses (I \approx 4 \times 10^{14} \text{ W/cm}^2, \lambda = 800 \text{ nm}) have been computed by numerically solving the time-dependent Schrödinger equation. The resulting above-threshold ionization and above-threshold dissociation spectra exhibit the characteristic forward-backward asymmetry and sensitivity to the carrier-envelope phase (CEP), particularly for high energies. A general framework for understanding CEP effects in the asymmetry of dissociative ionization of H₂ has been established. It is found that the symmetry breaking of electron-proton distribution with \( \pi \) periodic modulation occurs for all CEPs except for \( n \in \{ n20 - n30 \mid n = \text{integer} \} \) and the largest asymmetry coming from the CEP of \( n110 \). At least one of the electron and proton distributions is asymmetric when measured simultaneously. Inspection of the nuclear and electron wave packet dynamics provides further information about the relative contribution of the gerade and ungerade states of H₂ to the dissociation channel and the time delay of electrons in asymmetric ionization.

Introduction

Over the last few years, intense laser fields with a wide frequency range have become accessible,[1–6] in the form of short pulses having intensities of the order of the atomic unit \( I_a = 1/2 \alpha \hbar c |E_a|^2 = 3.5 \times 10^{16} \text{ W/cm}^2 \) where \( E_a = 5 \times 10^9 \text{ V/cm} \) is the strength of the Coulomb field experienced by an electron in the ground state of the hydrogen atom. Such high laser intensities are strong enough to compete with the Coulomb forces in governing the electron dynamics in molecular systems, encompassing processes of higher order than a single photon absorption/emission. The ionized electron can absorb photons in excess of the minimum number required for ionization which is called above-threshold ionization (ATI).[1–6] Radiation at higher multiple order of the laser frequency can also be emitted in intense laser fields as harmonic generation (HG).[1–6] The effect of multiphoton processes involving laser intensity much lower than that of \( I_a \) can be examined by perturbation theory. While, the processes involving laser intensities of the order of or surpassing \( I_a \) the nonperturbative methods have to be considered in analyzing its effect. So as to understand as well the dynamics of ionized electrons as they leave the laser focus, it is essential to consider the ponderomotive energy \( U_p = e^2 E_0^2 /4 \pi \alpha m_0 \) namely the cycle-averaged quiver kinetic of a free electron in the laser field (monochromatic) as an important parameter since it acts as a potential to eject electrons from regions of high intensity, that is, the laser focus.

Progress in ultrafast optics has allowed the generation of intense laser pulses comprising only a few cycles of the laser field.[6,7] Intense few-cycle laser pulses provide dependable control over the carrier-envelope phase (CEP). Indeed, a stable CEP is important for a complete control of the form of the electric field, offering a systematic control of the electron localization during the laser dissociation of molecules.[8] It has been currently an active area of research due to its potential application in controlling chemical reaction processes.

Several experimental schemes have been proposed and implemented recently to study the CEP effects in dissociation of H₂ \* and HD \*.[9] and H₂ and D₂.[10–13] In the case of atoms, it has been experimentally observed that the effects lead to an asymmetry of electron localization in the ionization of K[14] and of Rydberg states of Rb.[15] Furthermore, extensive efforts in solving the time-dependent Schrödinger equations (TDSE) for nuclear motion on two field-coupled electronic potentials have been used to understand the underlying process of the control of electron motion. Generally, all CEP-dependent effects are understood as resulting from the interference between two or more quantum channels corresponding to different numbers of absorbed photons.[16] In this view, CEP control is a form of more general coherent control.[13,17] The dependence of the asymmetry of ATI yields on the CEP of few-cycle pulses for atoms has been studied theoretically in many papers recently.[18–22] The dependence of the angular distribution of photoelectrons on the CEP has been investigated for symmetric molecules exposed to a circularly polarized few-cycle pulse, and spatial steering of low-energy photoelectrons was

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suggested by varying the CEP.\textsuperscript{[23]} Further theoretical work has been performed to investigate the CEP dependence in molecular isomerization\textsuperscript{[24–28]} and high HG.\textsuperscript{[29]}

Dissociative ionization of the H\textsubscript{2} has been a subject of considerable interest in recent years. The breakup of the H\textsubscript{2}\textsuperscript{+} ion into proton and hydrogen atoms depends on the molecular axis orientation when the two fragments are detected in coincidence. Two single ionization channels lead from the ground H\textsubscript{2} state to the H\textsubscript{2}\textsuperscript{+} ionic gerade (1\sigma\textsubscript{g}) and ungerade (1\sigma\textsubscript{u}) states that are well separated in energy. Both ionic states hold a well-defined electron orbital symmetry which leads to a fully symmetric electron emission. However, Martin et al.\textsuperscript{[30]} observed the asymmetry distribution occurs in the proton-hydrogen ejection relative to the electron ejection direction. Attraction between the proton and the ejected electron in the region of the maximum allowed kinetic energy release could be responsible for the mechanism. In this work, we consider a different mechanism of direct electron interaction with the proton in the intense laser pulse by controlling its CEP in TDSE simulations. The Coulomb field of the ejected electron can induce transitions of the remaining H\textsubscript{2}\textsuperscript{+} ion from the gerade to the ungerade electronic state and the superposition of this process with a direct transition to vibrational continuum can produce such asymmetry. Our goal is to present a result of CEP effects for a range of energies of an ejected electron and proton for well-defined orientations of the H\textsubscript{2} molecule relative to the polarization direction of the incident radiation. In particular, evidence of CEP dependence in electron and proton asymmetries and correlation between them will be discussed as a direct consequence of the H\textsubscript{2}\textsuperscript{+} ion population in different electron state symmetries. Previous\textsuperscript{[31]} and recent\textsuperscript{[32]} non-Born-Oppenheimer simulations on H\textsubscript{2}\textsuperscript{+} dissociative ionization have partially addressed this problem. We focus in this work especially on the energies of similar effects in the two electron system, H\textsubscript{2}.

Theory

A complete one-dimensional (1D) non-Born-Oppenheimer TDSE in atomic units for a diatomic molecule driven by a linearly polarized laser field along the internuclear axis is given in the following form:

\[
\frac{i}{\hbar} \frac{\partial \psi(z_1, z_2, R, t)}{\partial t} = \left[ \hat{H}_N + \hat{N} + E(t) (z_1 + z_2) \right] \psi(z_1, z_2, R, t),
\]

(1)

where

\[
\hat{H}_N = \sum_{i=1}^{2} \left\{ -\frac{1}{2} \frac{\partial^2}{\partial z_i^2} + \frac{1}{\sqrt{(z_i \pm R/2)^2 + \epsilon}} + \frac{1}{\sqrt{(z_i - z_2)^2 + \epsilon}} \right\},
\]

\[
\hat{N} = -\frac{1}{2} \frac{\partial^2}{\partial R^2} + \frac{1}{R},
\]

(2)

(3)

\( R \) is the internuclear distance, \( z_i \) is the distance of electron \( i \) from the center of mass, \( \mu \) is the reduced mass of the two nuclei, \( E(t) \) is the laser electric field, and \( c \) and \( d \) are Coulomb softening parameters which have been set to be 0.7 and 1.2375, respectively, thus giving accurate molecular potentials. The exact time evolution of \( \psi(z_1, z_2, R, t) \) was evaluated using the split-operator spectral method\textsuperscript{[33]} for time intervals \([ t, t + \Delta t ]\) in the three dimensions \( z_1, z_2, \) and \( R \). In our simulation, the internuclear distance was varied 0 \( \leq R \leq 24 \) a.u. containing 160 grid points, whereas the electron distances \( z \) from the H\textsubscript{2} center of mass was varied \(-254 \leq z \leq 254 \) a.u. containing 1008 grid points for each electron. The grid size was chosen as large as possible to avoid the wave packet colliding at grid boundaries so that numerical results did not depend on the grid size. The grid size thus always exceeded the maximum electron excursion, \( z_0 = E/\omega^2 \) a.u. Thus at intensity \( I = 3.5 \times 10^{15} \) W/cm\textsuperscript{2}, \( E = 0.1 \) a.u. and \( \omega = 0.057 \) a.u. (\( \lambda = 800 \) nm), \( z \approx 30 \) a.u = 1.6 nm. At the grid boundaries, an absorber was used to avoid reflection.\textsuperscript{[34]}

In the dipole approximation, for a particle located at the position \( z_0 \), the vector potential \( A(z_0) = A(t) \) is spatially homogeneous, that is, it depends only on the time variables so that the Coulomb gauge condition is satisfied. Defining \( A \), the vector potential with an envelope \( \epsilon(t) \) and CEP \( \phi \)

\[
A(t) = -c \epsilon(t) \sin \left[ \frac{\omega(t - t_{\text{center}}) + \phi}{\omega} \right],
\]

(4)

the electric field \( E(t) \) in the Coulomb gauge condition is then given by

\[
E(t) = -\frac{1}{c} \frac{\partial}{\partial t} A(t) = \epsilon(t) \cos \left[ \frac{\omega(t - t_{\text{center}}) + \phi}{\omega} \right] + E_{\text{cor}},
\]

(5)

where

\[
E_{\text{cor}} = \frac{\sin \left[ \frac{\omega(t - t_{\text{center}}) + \phi}{\omega} \right]}{\omega} \frac{\partial}{\partial t} \epsilon(t)
\]

(6)

comes from the derivative of the envelope \( \epsilon(t) \) of the vector potential \( A \). \( E_{\text{cor}} \) is small near the pulse maximum and is negligible for long pulses. The few-cycle laser pulse has a cosine square envelope

\[
\epsilon(t) = E_0 \cos^2 \left[ \frac{\pi(t - t_{\text{center}})}{t_{\text{f}}} \right],
\]

(7)

where \( E_0 = \sqrt{I/I_{\text{thr}}} \), \( I \) is the laser intensity expressed in W/cm\textsuperscript{2}, \( I_{\text{thr}} = 3.51 \times 10^{16} \) W/cm\textsuperscript{2} is an atomic unit of laser intensity and a peak intensity \( I = 4 \times 10^{14} \) W/cm\textsuperscript{2}. The laser wavelength is \( \lambda = 800 \) nm with the pulse duration \( t_{\text{f}} \) is six optical cycles with period \( \tau = 2.67 \) fs. The electron ponderomotive radius and ponderomotive energy are \( z_0 = 2 \) nm and \( U_p = 0.88 \) a.u. = 23.92 eV, respectively.

The ATI spectra of the ionized electrons in the left (backward) \( S_{\text{d}}^0 \) and right (forward) \( S_{\text{d}}^1 \) sides are calculated according to the formulas

\[
S_{\text{d}}^0(E_d) = \frac{1}{|p_{\text{rel}}|} \int_{-\infty}^{\infty} dR \int_{-z_0}^{0} dz_1 |\psi_\omega(p_0, z_1, R)|^2
\]

(8)

where the Fourier transform \( \psi(p_0, z_1, R) \) of \( \psi(z_1, z_2, R, t) \) can be propagated to some final time \( t_{\text{f}} \) using the expression
The above-threshold dissociation (ATD) spectra for the protons in the left (backward) $S^N_-$ and right (forward) $S^N_+$ sides are calculated in the following way:

$$S^N_+(E_\text{N}) = \frac{\mu}{p_{\text{el}}} \left[ \int_{-\infty}^{Z_0} dz_2 |\psi_+(p_\text{N}, z_2)|^2 + \int_{Z_0}^{\infty} dz_2 |\psi_+(p_\text{N}, z_2)|^2 \right].$$  \hspace{1cm} (11)

where $E_\text{N}=p_\text{N}^2/(2\mu)$ is the nuclear energy, $\mu=m_p/2$ is the proton reduced mass, and

$$\psi_+(p_\text{N}, z_2) = \frac{1}{\sqrt{2\pi R_0}} \int_{Z_0}^{\infty} dR \exp \left(-ip_\text{N}R\right) z_2^2 \phi_+(z_1, R) \psi(z_1, z_2, R, t_{\text{final}}).$$  \hspace{1cm} (12)

$$\psi_-(p_\text{N}, z_2) = \frac{1}{\sqrt{2\pi R_0}} \int_{-\infty}^{Z_0} dR \exp \left(-ip_\text{N}R\right) z_2^2 \phi_-(z_1, R) \psi(z_1, z_2, R, t_{\text{final}}).$$  \hspace{1cm} (13)

$R_0=10$ a.u. is the distance at which H + p may be considered as dissociated and $\phi_\pm(z_1, R)$ are the electron wave function of $H_2^+$ localized at the left or right proton, that is, at $z_1=-R/2<0$ for $\phi_+$ or at $z_1=R/2>0$ for $\phi_-$. The sign ($\pm$) also means the proton is at $z_1>0$ or at $z_1<0$. At very large $R$ they are simply the 1D hydrogen atom wave functions located at the left or right protons which can be constructed using the combination of the $H_2^+$ two lowest eigenstates (gerade and ungerade $\phi_g$ and $\phi_u$).

$$\psi_+(p_\text{e}, z_1, R) = \frac{1}{\sqrt{2\pi z_0}} \int_{Z_0}^{\infty} dz_2 \exp \left(-ip_\text{e}z_2\right) \psi(z_1, z_2, R, t_{\text{final}})$$

for $p_\text{e}>0$,

$$\psi_-(p_\text{e}, z_1, R) = \frac{1}{\sqrt{2\pi z_0}} \int_{-\infty}^{Z_0} dz_2 \exp \left(-ip_\text{e}z_2\right) \psi(z_1, z_2, R, t_{\text{final}})$$

for $p_\text{e}<0$,  \hspace{1cm} (10)

where $E_\text{el}=p_\text{e}^2/(2\mu)$ and $\psi_-$ and $\psi_+$ are the wave functions corresponding to the electron moving in the negative (backward) and positive (forward) directions along the z axis, respectively.

The asymmetries for nuclear (proton) $A_N$ and electron $A_{\text{el}}$ distribution for a series of CEP, $\phi$, can be calculated from Eqs. (8) and (11) based on the following expression

$$A_{N/\text{el}} = \frac{S^{N/\text{el}}_- - S^{N/\text{el}}_+}{S^{N/\text{el}}_+ + S^{N/\text{el}}_-}.  \hspace{1cm} (15)$$

Integrating out the electron and nuclear spectra over all energies (or over momenta), the total asymmetries for nuclear $A_{N_{\text{tot}}}$ and electron $A_{\text{el_{tot}}}$ distribution for a series of CEP, $\phi$, can be calculated from

$$A_{N/\text{el_{tot}}} = \frac{\rho^{N/\text{el}}_+ - \rho^{N/\text{el}}_-}{\rho^{N/\text{el}}_+ + \rho^{N/\text{el}}_-}.  \hspace{1cm} (16)$$

where

$$\rho^{N/\text{el}}_{\pm} = \int_{E_{\text{min}}}^{\infty} dE_{\text{N/\text{el}}} S^{N/\text{el}}_{\pm}(E_{\text{N/\text{el}}}).$$  \hspace{1cm} (17)

and $E_{\text{min}}=0.01$ a.u. for protons and 0.1 a.u. for electrons. Finally, using Eq. (16) the asymmetry for electron-proton distribution is defined as

$$A_{\text{tot}} = |A_{\text{el_{tot}}}-A_{N_{\text{tot}}}|.  \hspace{1cm} (18)$$

All these quantities were calculated at the final time $t_{\text{final}}$ few cycles longer than the pulse duration $t_{\text{tot}}$, for example, at $t_{\text{final}}=t_{\text{tot}}+4$ cycles, or more to allow the molecule to
dissociate. Therefore $R_{\text{max}}$ should be larger than 20 a.u. and $z_{\text{max}} > 200$ a.u. The electron spectra at earlier times are calculated, that is, at $t_{\text{final}} = t_{\text{tot}}$ to catch the fastest electrons which are probably missing in spectra calculated at $t_{\text{final}} = t_{\text{tot}} + 4$ because of the boundary absorption.

Electron asymmetry distribution as a function of time $A_{\text{el}}(t)$ is calculated in the following way

$$A_{\text{el}}(t) = \frac{P_{\text{el}}^{+}(t) - P_{\text{el}}^{-}(t)}{P_{\text{el}}^{+}(t) + P_{\text{el}}^{-}(t)}$$

(19)

by projecting the wave function $\psi(z_1, z_2, R, t)$ on the electronic states $\varphi_{\pm}(z_1, R)$ defined in Eq. (14) where

$$P_{\text{el}}^{\pm}(t) = \int_{R_1}^{R_1} dR \left\{ \int_{-\infty}^{z_0} dz_2 |\varphi_{\pm}(z_2, R, t)|^2 + \int_{z_0}^{\infty} dz_2 |\varphi_{\pm}(z_2, R, t)|^2 \right\}$$

(20)

and

$$\bar{\psi}_{+}(z_2, R, t) = \int_{-z_0}^{0} dz_1 \varphi_{+}(z_1, R) \psi(z_1, z_2, R, t),$$

(21)

$$\bar{\psi}_{-}(z_2, R, t) = \int_{0}^{z_0} dz_1 \varphi_{-}(z_1, R) \psi(z_1, z_2, R, t).$$

(22)

The time monitoring electron distribution $P_{\text{el}}$ is calculated based from the following equation

$$P_{\text{el}}^{\pm}(z_1, t) = \int_{R_1}^{\infty} dR \left\{ \int_{-\infty}^{z_0} dz_2 |\psi(z_1, z_2, R, t)|^2 + \int_{z_0}^{\infty} dz_2 |\psi(z_1, z_2, R, t)|^2 \right\}.$$ 

(23)

The time evolution of the nuclear wave packets on the gerade (g) and ungerade (u) surfaces in $H_2^+$ is calculated by considering $P_g(R, t)$ and $P_u(R, t)$ at intervals $(1/8)$ of the cycle to make the contour graph of these functions:

Figure 2. a) Gerade $\varphi_g(z, R)$ and b) Ungerade $\varphi_u(z, R)$ electronic functions of $H_2^+$.

Figure 3. a) $\varphi^+_g(z, R)$ and b) $\varphi^+_u(z, R)$ electron wave functions of $H_2^+$ localized at the left and right proton.
Apart from the reduced dimensionality used, the only approximations made in our calculations are the dipole approximation in describing the laser-molecule interaction. In previous work, this method has been shown to yield integral and differential cross sections for dissociative ionization of H$_2$ and D$_2$ in good agreement with various experimental measurements.$^{[11,34,35]}$

Figure 1 shows the wave form of the six cycles electric field of a linearly polarized laser pulse whose carrier wavelength is $\lambda = 800$ (period $\tau = 2.67$ fs) and whose intensity profile is proportional to Eq. (5), where $\epsilon(t)$ is a cosine envelope function.
given by Eq. (7) such that $\epsilon_2(t)$ is a function with 5 fs full width at half maximum. At the middle of Figure 1, a CEP of $\phi=0$ corresponds to a “cosine-like” pulse, while $\phi=\pm \pi/2$ corresponds to a “sine-like” pulse. The chosen field intensity is such that “bond softening” occurs where distortion of the $H_2^+$ potentials by the external field are important.\textsuperscript{36} Figures 2(a) and 2(b) show the contour plots of the gerade $\varphi_g$ and ungerade $\varphi_u$ states of $H_2^+$, respectively, as a function of electron and internuclear coordinates. Figures 3(a) and 3(b) show the contour plots of the electron wave functions $\varphi_+$ and $\varphi_-$ of $H_2^+$ localized at the left of proton and at the right of proton, respectively. The plots are obtained based on Eq. (14).

We analyzed the symmetry breaking of the electron and proton distributions simultaneously resulting from dissociative ionization of $H_2$ by the intense laser pulses described by Eqs. (5–7). The backward-forward (or left-right) asymmetry of electron distribution in molecules that dissociatively ionize is a process\textsuperscript{37–39} that arises from the superposition of two states with different parity. In our scheme from the electron momenta and based on Eq. (8), we calculated for various CEP the ATI spectra separately for an electron emitted in two opposite directions along the laser polarization axis and with respect to the center of mass of $H_2$. Figures 4(a) and 4(b) show the contour plots of both spectra $S_1^\text{el}$ and $S_2^\text{el}$ of the ionized electron integrated out over $z_0 \geq 15$.
From those spectra, we have mapped electron localization induced by the laser pulse by obtaining energy and CEP-dependent asymmetry $A_{el}$ from Eq. (15), as plotted in Figure 5. Apparently, there are two pronounced energy regions (below and above $U_p$) characterized by different pattern of CEP-dependent directionality of ejected electron. Above $U_p$, the electron distribution asymmetry exhibits smoothly periodic CEP-dependence with $\pi$ periodicity. By simulations at higher energy, the asymmetry remains constant indicating now that the electron is moving favorably in the forward or backward direction. High-energy ATI spectra also generate a high degree of asymmetry with values greater or less than 0.5 or $-0.5$. After the cut at $t_{tot}=6$ of the laser pulse. The figure also displays the CEP cut through of the contour spectra for three selected CEP showing two distinct cutoff energies of the plateau in the low-energy ATI spectra at about 12 eV ($0.5U_p$) and 24 eV ($U_p$). The spectra show a strong sensitivity to the variation of CEP. In this region, the ATI exhibits periodic dependence on the CEP with $\pi$ periodicity, for example, the spectra for $160^\circ$ is similar to that of $340^\circ$. In high-energy region above $U_p$, the ATI spectra are not much sensitive to the CEP and the cutoff energy disappears into the background.

Figure 6. A contour plot of electron asymmetry distribution $A_{el}(E_{el}, \phi) = (S_{el}^2(E_{el}, \phi) - S_{el}^1(E_{el}, \phi)) / (S_{el}^2(E_{el}, \phi) + S_{el}^1(E_{el}, \phi))$ in the low energy ATI spectra and its curves from a cut through of the plot at various CEP $\phi$ and energy, included together with a curve of total asymmetry distribution $A_{el}^{tot}(\phi) = (P_{el}^2(\phi) - P_{el}^1(\phi)) / (P_{el}^2(\phi) + P_{el}^1(\phi))$. 

a.u. and $z_0 \leq -15$ a.u. at 10 cycles (26.7 fs) ($t_{final}=t_{tot}+4$ where $t_{tot}=6$) of the laser pulse.
Nonetheless, using Eq. (16), our calculations predict only a small modulation in the total asymmetry $A_{\text{el}}^\text{tot}$, namely between 0.2 and 20.2. The total asymmetry of electron distribution is shown in the same figure, as a function of CEP with also periodic modulation. Conversely, the presence of complex asymmetry structures shown in Figure 6 in the low-energy ATI spectra suggest interferences between energy degenerate paths. By looking at the lower panel of Figures 5 and 6, it is clear that the low-energy channels have minimum modulation depth of the sharp noticeable asymmetry obtained for the dominant high-energy channels. The pronounced asymmetry in the high-energy ATI spectra for the CEP ranging from 0 to $\pi$ essentially results from the existence of a symmetric potential well, similar to that of atoms.\textsuperscript{[18–22]} The forward-backward asymmetry of high-energy photoelectrons has been used to measure and stabilize the CEP\textsuperscript{[40]} and to measure the Gouy phase shift.\textsuperscript{[41]} While these experiments demonstrated that the results can vary with the CEP of few-cycle pulses, the determination of its actual phase has to rely on the prediction of theoretical calculations.

In this work, we have also calculated the ATD energy spectra from the proton momenta for various CEP as described by Eq. (11), for a proton emitted on the right $S^\text{R}$ and on the left $S^\text{L}$ of the center of mass. Figures 7(a) and 7(b) show the contour plots of the spectra as a function of energy and CEP. For convenience, the contours have been cut through along the CEP coordinates showing two distinct energy regions namely below and above 2 eV. The spectra are very sensitive to the CEP above 2 eV and exhibit periodic dependence on the CEP with $\pi$ periodicity. In this region, the spectra increase to a maximum around 4 eV. We note that the bond dissociation energy for H$_2$ is 4.52 eV. From these spectra, we obtain energy- and CEP-dependent proton asymmetry distribution $A^\text{N}$ and the total asymmetry $A_{\text{tot}}^\text{N}$ shown in Figure 8. The asymmetries are calculated based on Eqs. (15) and (16), respectively. Displayed are also the cut through of contour plot for various CEP and energies. Below 2 eV, the energy generates a high degree of asymmetry which its value greater or less than 0.5 or $-0.5$. The highest and the lowest peak in this region is around 1.4 eV. This modulation depth is significantly larger than the theoretical prediction in the work by Hua and Esry for H$_2$\textsuperscript{[42]} However, the modulation of the asymmetry decreases slowly as the energy increases, implying that the two proton dissociation directions, forward and backward, become indistinguishable. CEP control with few-cycle pulses was first demonstrated experimentally by Kling et al.\textsuperscript{[12]} where they demonstrated significant CEP-controlled asymmetry of deuteron emission for only the higher energy above dissociation channels $>3$ eV. However, no noticeable asymmetry was reported for the dominant low-energy channels. More recently, Kremer et al.\textsuperscript{[43]} observed a significant asymmetry for low-energy channels in H$_2$ between 0.5 and 2.5 eV. Our simulations show that the total asymmetry of proton distribution $A_{\text{tot}}^\text{N}$ predicts a small modulation between 0.2 and $-0.2$ with $\pi$ periodicity.

An important aspect of the CEP control scheme noticed before and further considered in this work is that dissociative ionization involves H$_2^+$ electronic states of different parity, $\varphi_{u}$ and $\varphi_{g}$.$^{[31,32]}$ A coherent superposition of these states has been observed in our calculations thus distinguishing between electron or proton emitted forward and electron or proton emitted backward. Because proton dissociation is fast
compared with molecular rotation, the direction of fragmentation of two nuclei coincides with the molecular axis at the instant of ionization. One striking observation obtained from the coincidence studies was the breaking of the electron emission symmetry with respect to the proton dissociation. One can observe that, for a chosen CEP of \(20^\circ\) – \(30^\circ\) and its \(\pi\) multiple angles as in Figure 9, electron-proton distributions become nearly symmetric when the electron and proton directionality are the same. Elsewhere, the electron-proton distributions become asymmetric, that is, both electron and proton move in opposite directions. Indeed, Figure 9 shows that the largest asymmetry at CEP of \(110^\circ\) and its \(\pi\) multiple angles occurs associated with the smallest overlap of the two channels, electron or proton. Thus, observation of a pronounced asymmetry in the electron-proton distribution at a given CEP is a direct measure of the symmetry breaking in the dissociative ionization process.

In this work, we have shown that by studying the variation of the electron asymmetry distribution with time can also provide a clear image of the time evolution of the electron wave packet generated by the pulse. This is relevant because such evolution will support the information provided by the ATI
spectra. Figure 10, obtained from Eqs. (19) and (23) shows the contour map of snapshots of an electron wave packet $P_{el}$ plotted together with the time-dependent electron asymmetry distribution $A_{el}^{\delta}(t)$. The wave packet was obtained by integrating out over all electron coordinates using Eq. (23). The observed behavior in the total asymmetry $A_{el}^{\delta}$ (lower panel of Fig. 5) is the direct consequence of the evolution of the proton vibrational wave packet projected on the field-free molecular state. Figure 10 shows this wave packet after its creation at 4 cycles laser pulse. At $t=4-6$ cycles, there is an almost perfect one-to-one correspondence in the field region between the asymmetry distribution $A_{el}^{\delta}$ and the position of the vibrational wave packet associated with its ratio in the forward and backward ejection pathways. In this region, the asymmetry yields maximum value but as mentioned in the theory section, this should be coupled to the electron distribution in the field-free region. Taking CEP equal to 90° for instance, after $t_{tot}=6$ cycles (16 fs) of laser pulse duration, one observes that in the field-free evolution the wave packet starts to spread and split into two directions. The variation of the asymmetry $A_{el}^{\delta}(t)$ only can be seen after the time delay of 2 cycles namely at $t=8$ cycles. At $t_{final}=10$, it is clearly shown that the electron is more favorable to propagate towards the forward direction indicated by its positive $A_{el}^{\delta}(t)$. On the contrary, CEP of 270° yields negative $A_{el}^{\delta}(t)$. Accordingly, the sign for each value of $A_{el}^{\delta}(t)$ corresponding to these CEPs are in agreement with $A_{tot}^{\delta}$ (as depicted in Fig. 5).

In this work, we have also focused on the nuclear wave packet generated in the electronic excited states of H$_2$. Figure 11 shows the contour plots of snapshots of time evolution for nuclear wave packets $P_{Ng}^\delta$ and $P_{Nu}^\delta$ on the gerade and ungerade surfaces of H$_2^+$. Both plots are constructed based on Eqs. (25) and (27). The figure shows the contributions of the dissociation channels associated with the ground $\varphi_g$ and first excited $\varphi_u$ states of H$_2^+$. At $t_{tot}=6$ cycles pulse, ionization via the $\varphi_g$ state is the major contributor to dissociation.
channel, indicated by its significantly higher intensity of the wave packet $P_9$ compared to the one created in the $\varphi_u$ state. As time increases, one observes that contribution from the $P_u$ in the field-free region becomes progressively delocalized faster than the $P_9$. Hence, the two cycles of time delay (6 fs) prior to the electron being asymmetrically distributed for certain CEPs is a measure of the traveling time of the localized nuclear wave packet in the two molecular states. The electron-proton asymmetry in dissociative ionization means that the asymptotics of the wave function of the state with fixed ionized electron energy and a fixed proton kinetic energy release is nonsymmetric in the coordinates of the bound electron. From the mathematical point of view, this means that the bound electron is in a superposition of gerade and ungerade H$_2^+$ wave functions. In contrast with the electron wave packet in which a single channel is involved, dissociative ionization resulting from the present scheme involves not only the $\varphi_g$ but also the $\varphi_u$ channel. Contributions from both channels overlap in the whole ATD spectrum. This problem is even more dramatic when the wave packets created in the both states approach the outer classical turning point namely for a time larger than 10 cycles, because structures due to interferences with direct ionization channels are prominent.

**Conclusion**

In summary, we have investigated from TDSE numerical simulations the ATI and ATD spectra of a 1D H$_2$ molecule driven by a linearly polarized laser pulse. The phase dependence of the high-energy ATI spectra and steering off electron emission in space can be achieved by controlling the CEP of the laser pulse. The electron forward-backward asymmetry is particularly pronounced for the CEP ranging from 0 to $\pi$ for symmetric molecules such as H$_2$ molecule. The field-free evolution of the electron wave packet has also been used to study the variation of this asymmetry with time. We have also presented the study of CEP effects in the laser-induced dissociation of the molecule by numerically evaluating the forward-backward asymmetry of proton ejection from ATD spectra, originating from the coherent superposition of two electronic states of different inversion symmetry. The evolution of nuclear wave packets in these states has been constructed to gain insightful details on the dynamics involved. All the asymmetry distributions from electron to proton allowed to examine CEP effects on the dissociative ionization of H$_2$ beyond the Born-Oppenheimer approximation.

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