Breakdown of odd-harmonic rule in the high harmonic generation spectra of the hydrogen molecular ion

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Abstract. We numerically solve the fully-dimensional electronic time-dependent Schrödinger equation for an H$_2^+$ molecular ion. The occurrence of electron localization is investigated to better understand the complex patterns appearing in the high-order harmonic generation (HHG) spectrum. Our studies show that changing trends of electronic acceleration are affected by electron localization at large enough internuclear distances. This effect leads to the complex patterns in the HHG spectrum.

1. Introduction

According to the odd-harmonic rule, the harmonic angular frequencies, $n\omega_0$, of photons produced by recollision of the electron with the parent ion in an intense laser field are odd multiples of the laser angular frequency, $\omega_0$, but some irregularities have been seen in high harmonic generation (HHG) spectra.

Different studies have been carried out to explain the origin of these complex patterns. Martin’s group reported that these patterns result from electron localization, which induces a permanent dipole during dissociation, even for pulses containing tens of laser cycles. They claimed that the permanent dipole associated with the linear Stark effect leads to a relative phase between the two consecutive electron round trips initiated in the adjacent laser half-cycles. As this phase approaches $\pi$, the odd harmonics are replaced by the even ones [1-2].

Ahmadi et al. discussed elaborately in Ref. [3] that these complexities (non-adiabatic frequency redshift of the harmonics and spatially asymmetric emission along the z direction) are related to the falling edge of the laser pulse. According to Ahmadi et al., the H$_2^+$ system responds non-adiabatically to the rapidly changing laser field, and the emission along the polarization direction is spatially asymmetric in this region.

In this work, we investigate the HHG of the H$_2^+$ molecular ion exposed to an intense laser field with a 2-8-2 trapezoidal envelope, $I = 3 \times 10^{14}$ Wcm$^{-2}$ intensity, and 800 nm wavelength, by solving the time-dependent Schrödinger equation numerically for the fully-dimensional electronic dynamics without nuclear dynamics, i.e., with a fixed $R_0$ inter-nuclear distance. We choose three different $R_0$ and study the effect of increasing $R_0$ on electronic population, electronic acceleration and HHG in the simulation box. Throughout this paper, atomic units (a.u.) with $e = \hbar = m_e = 1$, will be used, unless otherwise stated.
2. Computational method

After separating the center-of-mass motion and ignoring the nuclear dynamics, the time-dependent Schrödinger equation (TDSE) for a hydrogen molecular ion can be written, in terms of the electron’s coordinates $z$ and $\rho$, as [4-5]

$$i \frac{\partial \psi(z, \rho; R_0, t)}{\partial t} = \hat{H}(z, \rho; R_0, t) \psi(z, \rho; R_0, t),$$

(1)

where $R_0$, to be treated as a parameter, denotes the internuclear distance (parallel to both electronic coordinate $z$ and the laser polarization direction) and $\hat{H}$ is the Hamiltonian, given by

$$\hat{H}(z, \rho; R_0, t) = -\frac{2m_N + m_e}{4m_N m_e} \left[ \frac{\partial^2}{\partial z^2} + \frac{\partial^2}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial}{\partial \rho} \right] + V_C(z, \rho; R_0, t),$$

(2)

with

$$V_C(z, \rho; R_0, t) = -\frac{1}{\sqrt{(z + \frac{R_0}{2})^2 + \rho^2}} - \frac{1}{\sqrt{(z - \frac{R_0}{2})^2 + \rho^2}} + \left( \frac{2m_N + 2m_e}{2m_N + m_e} \right) z E_0 f(t) \cos(\omega t).$$

(3)

In the above equations, $E_0$ is the laser peak amplitude, $m_e$ and $m_N$ are masses of the electron and single nucleus, respectively, $\omega$ is the laser angular frequency, and $f(t)$ is the laser pulse envelope. The envelope rises linearly during the first two cycles, then remains constant for eight cycles and decreases during the last two cycles.

The TDSE is numerically integrated using unitary split-operator methods [6-7]. Details of the numerical procedure are described in our previous work [8-9]. The finest grid size values in our numerical integration are, respectively, 0.13 and 0.2 for $z$ and $\rho$ coordinates and the time steps are 0.02. The size of the simulation box is chosen as $z_{\text{max}} = 150$ and $\rho_{\text{max}} = 125$.

An HHG spectrum is calculated as the square of the windowed Fourier transform of the dipole acceleration $a_z(t)$ in the electric field direction ($z$), or

$$S(\omega) = \left| \int_0^T \left< \psi(z, \rho; R_0, t) | a_z(t) \right| \psi(z, \rho; R_0, t) >_{z, \rho} \times H(t) \exp[-i\omega t] dt \right|^2,$$

where

$$H(t) = \frac{1}{2} \left[ 1 - \cos(2\pi t/T) \right],$$

(4)

is the Hanning function and $T$ is the total pulse duration. The Hanning filter reduces the effect of nondecaying components in the dipole acceleration that last after the laser pulse is switched off [10].

3. Results and discussions

Ahmadi et al. reported that for the 14-cycle trapezoidal laser pulses with $I = 3 \times 10^{14}$ Wcm$^{-2}$ intensity and 800 nm wavelength, no considerable final electron localization was achieved and the HHG spectrum was dominated by the odd harmonic orders [3]. As is shown in figure 1 for $R_0 = 2.08$, the odd harmonic orders are distinct. However, by increasing the distance between the hydrogen nuclei, the HHG spectra become complicated. For $R_0 = 3.66$, the peaks become multiple and a red-shift to even harmonic orders is seen.

In order to investigate the origin of these complexities, we consider total acceleration in the $z$ direction and also the acceleration in the left and right sides of the simulation box. According to figure 2, the variation of total acceleration at $R_0 = 2.08$ follows the pattern of laser field. However, the pattern of total acceleration changes becomes complicated by increasing $R_0$. 
Figure 1. High harmonic generation spectra of $\text{H}_2^+$ system with different internuclear distances ($R_0 = 2.08, 3.13$ and $3.66$) under 12-cycle trapezoidal laser pulse of 800 nm wavelength and $I = 3 \times 10^{14}$ W cm$^{-2}$ intensity.

Interestingly, the total acceleration intensity decreases gradually at $R_0 = 3.66$ due to the decline of electronic population in the simulation box. It seems that the doublet peaks appearing in the HHG spectrum of $\text{H}_2^+$ at $R_0 = 3.13$ and $R_0 = 3.66$ (see figure 1) are related to doublet peaks of the total acceleration at similar internuclear distances.

Left- and right-accelerations (Acceleration(L) and Acceleration(R)) are obtained, respectively, by integration over the left and right parts of the simulation box. The changes of Acceleration(R) and Acceleration(L) are shown in Fig. 3. At $R_0 = 2.08$, these changes follow the laser field pattern. But at $R_0 = 3.13$, two periodic trends could be detected in them. One is dominated by the laser field and the other is controlled by electron localization (this trend could also be found in figure 2 for $R_0 = 3.66$). The changing trends at $R_0 = 3.66$ are similar to $R_0 = 3.13$, but the structure of the left and right accelerations get more complex.

In figure 4, Acceleration(R) and population of the right side of the simulation box (Population(R)) are displayed with the laser field. In order to compare these graphs more easily, we raise the intercept of Acceleration(R) and laser field graphs. According to this figure, when the laser field increases in the positive direction, the population in the right side of the simulation box decreases but the acceleration of electrons increases in that side of the simulation box.
Figure 3. Acceleration of H$_2^+$ system in the left (blue) and right (red) side of simulation box. From top to bottom, the graphs are related to internuclear distances of 2.08, 3.13 and 3.66, respectively. Laser parameters are the same as in figure 1.

Figure 4. Changing of Acceleration(R) with respect to Population(R). From top to bottom, the graphs are related to internuclear distances of 2.08, 3.13 and 3.66, respectively. Laser parameters are the same as in figure 1.

4. Conclusions
At the lowest internuclear distance ($R_0 = 2.08$), the pattern of total acceleration and left and right accelerations follows the laser field. By increasing $R_0$, these patterns become more complex and another periodic trend appears which is governed by electron localization.

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