Effects of Bounding Potential on High-Order Harmonic Generation with H$_2^+$ *

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We present harmonic spectra from hydrogen molecular ions with different ionization energy I_p. By comparing the recombination matrix element from helium ions and hydrogen molecular ions, we verify that the interference effect in high-order harmonic generation originates from the recombination interference. A numerical study on recombination matrix elements in 1D shows that $\omega = E_k + I_p$ holds only when an exact continuum wavefunction is used, and the positions of extrema in harmonic spectra can be predicted accurately. We demonstrate that the positions of extrema in harmonic spectra are mainly affected by bounding potential dependence of the recombination interference.

High-order harmonic generation (HHG) is one of the most studied nonlinear phenomena of strong field physics in the last two decades.[1−7] In this process multiple photon energies are converted to the harmonics via a strong laser-driven atomic or molecular system. In this viewpoint, the HHG is well explained by the so-called three-step model, also known as the simple-men's model.[8] First, the electron is released due to the tunnel ionization process; second, it is accelerated by the oscillating laser field; and finally the electron recombines with its parent ion to emit coherent radiation. Due to the additional nuclear degrees of freedom and more complicated symmetries, high-order harmonic spectra from molecules show more complicated structures. The discovery of the interference effect in HHG was a significant breakthrough. Particularly, Lein *et al.*[9] found that the intensity of the harmonic spectra from diatomic molecules is minimized at some critical angle between the molecular axis and the polarization of the laser pulses. They showed that it arose from the destructive interference when the electron recombined with the two-center ion. By aligning molecules with a short pump pulse and measuring the generated harmonic yields from a probe pulse, the interference effect in the harmonic spectrum from CO_2 had been observed experimentally.[10,11] Kamta *et al.* also found that both odd and even harmonics were emitted from each nucleus but even harmonics are destroyed by interferences between contributions of each nucleus.[12] Then dependence of the harmonic spectra on the internuclear distance[9,13−15] and the relative orientation between molecules and the laser polarization[16−18] is studied extensively. Since harmonic spectra carry information on the molecular structure, it becomes an ideal tool to probe molecular structures and electronic dynamics, as shown in Ref. [19].

In Ref. [9] the authors predicted the positions of minima by the simple double-slit interference model. Using the linear combination of atomic orbitals (LCAO) and the plane wave approximation to describe the recombination matrix element in velocity gauge, simple formulae can be obtained to predict the extrema positions. Destructive interference for hydrogen molecular ions occurs when (atomic units are used unless stated otherwise)

$$R\cos\theta = (2m+1)\lambda/2, \quad m = 0, 1, \cdots, \qquad (1)$$

where $R\cos\theta$ is the projected internuclear distance and λ is the electron wavelength.

Constructive interference occurs when

$$R\cos\theta = m\lambda, \quad m = 0, 1, \cdots. \qquad (2)$$

However, it is found that positions of minima in harmonic spectra obtained by numerical simulations are different from those predicted by these simple formulae.[9]

According to the Lewenstein model, the interference effect occurs in the recollision process when the electron recombines with its parent ion along with the generation of harmonics. It is obvious that two factors are involved in the recombination process. Firstly the molecular ground state has to be described precisely. When molecular orbitals are calculated with LCAO, different atomic orbital components would have a π phase difference. Therefore the analysis of constructive or destructive interference is meaningful only when one particular atomic orbital dominates, which fortunately is usually the case. Secondly, the continuum electron wavefunction can be approximated as a plane wave only when the electronic wavelength is much shorter than the molecular size. Otherwise, the multi-center and long-range characteristics of the potential need to be taken into account. Great efforts have been devoted to exactly describe the continuum electron in the presence of the molecular potential, such as the two-center continuum Coulomb wavefunction[20,21] and modified two-center

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continuum wavefunction.[23] It is found that using the two-center Coulomb wavefunction for the continuum electron state gives a more accurate prediction of the two-center interference effect.[21]

In the present work, our goal is to further investigate the interference effect in HHG through numerical study on the recombination matrix element, and to study whether the interference effect depends on the soft-core parameter, i.e., on the ionization energy. It is found that the positions of the minima shift slightly with different ionization energy. By comparing recombination matrix elements from the helium ion and hydrogen molecular ion, we verify that the interference effect in HHG originates from the recombination interference. Through numerical study on recombination matrix elements in 1D, it is shown that $\omega = E_k + I_p$ holds only when exact continuum wavefunctions are used. Here ω is the harmonic frequency where the interference minimum appears, and E_k is the electron kinetic energy corresponding to the recombination interference. It can be used to predict the positions of extrema in harmonic spectra accurately. Finally, we demonstrate that the positions of extrema in harmonic spectra are mainly affected by the bounding potential dependence of the recombination interference.

Since we do not aim to investigate the effect of molecular orientation, and previous simulations of H_2^+ have shown that the interference effects are not very sensitive to the dimensionality of the system, a one dimensional calculation is sufficient.[9] In this model, the molecular axis is aligned with the polarization axis and the two nuclei are placed at the position of $x_{1/2} = \pm\frac{R}{2}$. The Hamiltonian for H_2^+ with fixed nuclear separation is

$$H = -\frac{1}{2}\nabla_x^2 + V_c(R, x) + V_I(x, t), \qquad (3)$$

with

$$V_c(R, x) = -\sum_{i=1,2} \frac{1}{\sqrt{(x - x_i)^2 + \sigma(R)}}, \qquad (4)$$

where R and x are the internuclear distance and the electron coordinate, respectively. The softening parameter $\sigma(R)$ is chosen to mimic the lowest Born-Oppenheimer potential of the hydrogen molecular ion.[24] Applying the dipole approximation, the laser-molecule interaction is given in the length gauge $V_I(x, t) = -xE(\boldsymbol{t})$. The harmonic spectrum is obtained from the Fourier transformation of the dipole acceleration

$$S(\omega) = \left| \int \langle \Psi(t)|\frac{d}{dx}V_c - E(t)|\Psi(t)\rangle e^{i\omega t} dt \right|^2. \quad (5)$$

The time-dependent Schrödinger equation (TDSE) is solved numerically by the split-operator technique[25] with 2048 time steps per laser cycle. The laser pulse applied in the calculation has a wavelength of 800 nm with a trapezoidal envelope. The total duration of the laser pulse is 10 optical cycles with 2 cycles turn-on

and turn-off respectively.

In Fig. 1, we show the harmonic spectra of the hydrogen molecular ion with $R = 1.4$ a.u., $I = 5 \times 10^{14}$ W/cm² and $R = 2$ a.u., $I = 3 \times 10^{14}$ W/cm². The positions of minima (arrows) arising from destructive interference can be seen clearly. With the fixed internuclear distance increasing, the positions of minima shift toward lower order harmonics, which is consistent with Eq. (1). In the case of $R = 1.4$ a.u., the positions of the minima do not shift with different ionization energy, while for the case of $R = 2$ a.u., the position of the minimum shifts. There are two factors which contribute to this shift, ionization energy and electron kinetic energy, corresponding to the destructive interference in the recombination matrix element. As the soft-core parameter increases, the ionization energy becomes small, i.e., the parent ion has a lower ability to attract the continuum electron. Furthermore, the soft-core parameter also changes the ground state and the exact continuum wavefunction in the recombination matrix element, thus affecting the position of destructive interference.
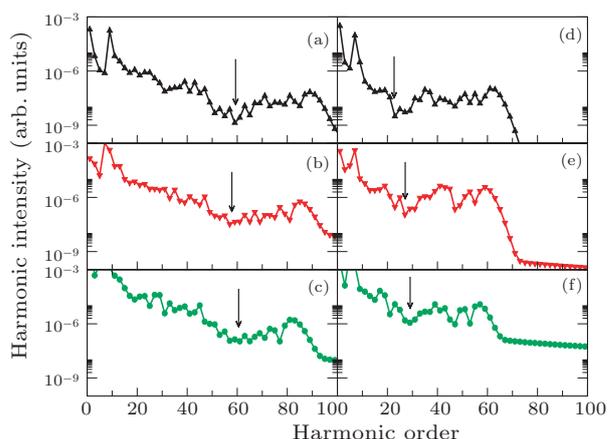

Fig. 1. The harmonic spectra of the hydrogen molecular ion with $R = 1.4$ a.u., $I = 5 \times 10^{14}$ W/cm² [(a), (b), (c)] and $R = 2$ a.u., $I = 3 \times 10^{14}$ W/cm² [(d), (e), (f)]. The soft-core parameters are 1.0 [(a), (d)], 1.44 [(b), (e)] and 2.0 [(c), (f)].

In the following the recollision process which dominantly determines the interference effect is studied. The recombination amplitude is expressed by the dipole moment

$$d_{rec}(k, R) = \langle \psi(k)|x|\psi_g(R)\rangle, \qquad (6)$$

or dipole acceleration

$$d_{rec}(k, R) = \langle \psi(k)|\frac{d}{dx}V_c(R, x)|\psi_g(R)\rangle. \qquad (7)$$

It represents the simple interpretation of the electron transition amplitude from the continuum state $|\psi(k)\rangle$ with asymptotic momentum k to the ground state. The plane wave approximation has an advantage in the reconstruction of molecular orbitals[22] because of the simplicity of the inversion algorithm,

and it is widely used to explain the interference effect qualitatively. However, it gives quantitatively different results by choosing different dipole expressions. The exact continuum state $|\psi(k)\rangle$ is obtained by numerically diagonalizing the field-free Hamiltonian $H_0 = P^2/2 + V_c(R, x)$ with the two-center potential. With the plane wave approximation, the energy relation $\omega = E_k$ is more reasonable to predict the positions of minima in harmonic spectra, namely the ionization energy I_p is contained in the increase in the electron kinetic energy E_k upon entering the Coulomb potential well, while for the case of the exact continuum state, the energy relation $\omega = E_k + I_p$ means energy conservation when an electron with kinetic energy E_k transits from a continuum state to the ground state.
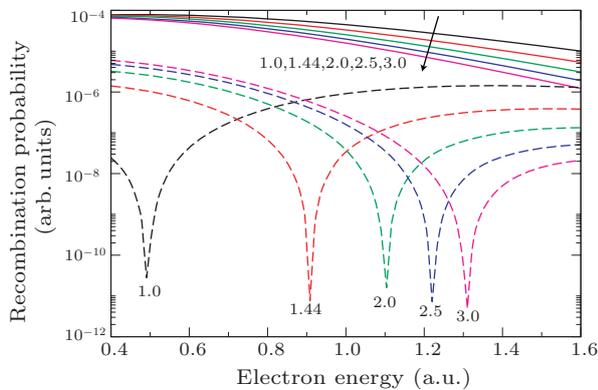

Fig. 2. (Color online) Comparison of recombination probability between the hydrogen molecular ion (dashed line) and the helium ion (solid line). The black, red, green, blue and magenta correspond to soft-core parameter 1.0, 1.44, 2.0, 2.5 and 3.0, respectively.

Before we present a systematic survey of how the interference effect in HHG depends on the ionization energy, we first investigate the difference of the recombination probabilities between the helium ion and hydrogen molecular ion. We expect that the interference effect in HHG indeed originates from recombination interference. The comparison result is plotted in Fig. 2. It can be seen clearly that there are minima of recombination probabilities from H_2^+ at some given electron kinetic energy, while for He^+, the recombination probability goes down slowly without any extremum as the electron energy increases. For the hydrogen molecular ion, the curves represent the recombination probabilities with different soft-core parameter, i.e., ionization energy, with internuclear separation $R = 2.0$ a.u.. The black dashed line has the same soft-core parameters as in Fig. 1(d), the same for red and Fig. 1(e), green and Fig. 1(f). The electron kinetic energy with respect to the minimum of the recombination probability plus the ionization energy are exactly equal to the harmonic frequency of the minimum in Fig. 1. This suggests that positions of minima in harmonic spectra can be predicted accurately through the exact recombination matrix element.

Next we further investigate the recombination matrix element with different wavefunctions describing continuum electrons. In Fig. 3(a), the recombination probability versus the electron momentum is shown for the case of nuclear separation 2 a.u. It can be seen that the positions of the minima are different between the dipole moment and dipole acceleration when the plane wave approximation is applied, while the same positions of minima are obtained when the numerically calculated exact continuum wavefunction is used, which is consistent with previous work.[26] Comparing the predicted minima in harmonic spectra with different dipole expressions, we find that the predicted positions of minima with dipole acceleration give closer results to our numerical simulations in Fig. 1.
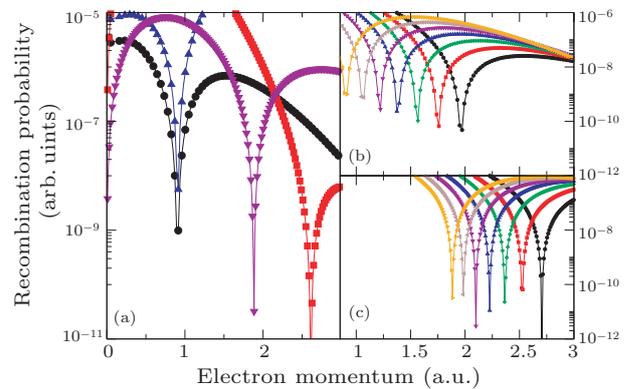

Fig. 3. (Color online) Electron momentum dependence of the recombination probability. Left panel (a) represents the result of the different simulation method. Square: plane wave in dipole moment. Down-triangle: plane wave in dipole acceleration. Dot: Exact continuum wavefunction model in dipole moment. Up-triangle: Exact continuum wavefunction model in dipole acceleration. (b) Internuclear separation dependence of recombination probability with two-center continuum wavefunction in dipole moment. (c) Internuclear separation dependence of recombination probability with plane wave approximation in dipole acceleration (see text for details).

Then we study the dependence of the recombination probability on internuclear separation with an exact continuum wavefunction in the dipole moment (Fig. 3(b)) and the plane wave in dipole acceleration (Fig. 3(c)). In both figures, the curves from right to left represent the recombination probability with nuclear separation from 1.4 a.u. to 2.0 a.u. with a step of 0.1 a.u. It is shown that the positions of minima of the recombination probability shift toward lower electron momentum as the internuclear separation increases, in agreement with Eq. (1). However, the difference of the positions of minima of electron kinetic energy between these two approaches is not equal to the ionization energy I_p strictly. That is to say, the positions of minima of harmonic intensity predicted by these two cases are different. Considering that the exact continuum wavefunction is more accurate to describe the propagated continuum electron, we demonstrate that the recombination matrix element with the exact continuum wavefunction agrees better with the nu-

merically obtained harmonic spectra in Fig. 1.

Regarding that the electron kinetic energy related to the minima of the exact recombination probability and ionization energy can be applied to predict the positions of minima in harmonic spectra accurately, we further investigate how the interference effect depends on the soft-core parameter.
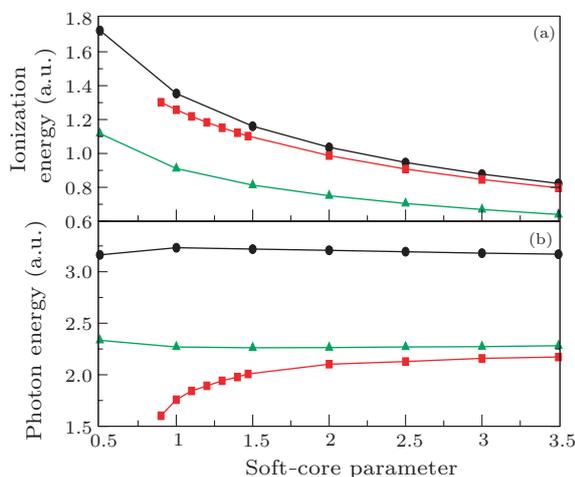

Fig. 4. (Color online) Ionization energy (a) and harmonic frequency corresponding to interference minima in harmonic spectra (b) as a function of soft-core parameter with internuclear distance 1.4 a.u.(black dot), 2 a.u. (red square) and 5 a.u. (green triangle).

As we all know, the soft-core parameter is applied to eliminate the singularity at $x = 0$. By changing the soft-core parameter, we can change the ionization energy, i.e. the ability to attract continuum electrons. First, we can see from Fig. 4(a) that the ionization energy goes forward to a lower value when the soft-core parameter becomes larger. Then we give the exact positions of minima in harmonic spectra as a function of soft-core parameter for three internuclear distances in Fig. 4(b). It is interesting to find that the positions of minima hardly shift for the case of internuclear distance $R = 2$ a.u. This can be explained by the exact recombination probability with the energy relation $\omega = E_k + I_p$. From Fig. 2 we can see that the difference between E_k with soft-core parameter $\sigma = 1.0$ (black dashed line)and $\sigma = 1.5$ (red dashed line) is 0.405 a.u., while the difference of the ionization energy is only 0.155 a.u., so the positions of minima in Figs. 1(d) and 1(e) are obviously different. The different trends among internuclear distances can be explained as follows. For the case of small nuclear separation ($R = 1.4$ a.u.), the electron has large kinetic energy corresponding to the destructive interference and the plane wave is a good approximation to describe it. For the case of large nuclear separation ($R = 5$ a.u.), the effects of the additional phase arising from the exact continuum wavefunction are negligible. Therefore the positions of minima in harmonic spectra in the two cases hardly shift, while for the case of equilibrium position ($R = 2$ a.u.), the soft-core parameter has the greatest effects on the recombination

interference and makes the position of minimum shift. Based on the above analysis, we can conclude that positions of extrema in harmonic spectra are mainly affected by the bounding potential dependence of the recombination interference.

In summary, we have investigated the ionization energy dependence of the interference effect in HHG. By comparing the recombination probability from helium ions and hydrogen molecular ions, we verify that the interference effect in HHG indeed originates from the recombination interference. The frequency of the emitted radiation related to the interference effect is given by the kinetic energy of the recolliding electron, where the recombination interference occurs, and the ionization energy. Through numerical study on recombination matrix elements in 1D, it is shown that the positions of extrema in harmonic spectra are mainly affected by the bounding potential dependence of the recombination interference.

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