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# Attosecond streaking of molecules in the low-energy region studied by a wavefunction splitting scheme

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## Abstract

We present a theoretical study of the low-energy photoelectron spectra of hydrogen molecular ion generated by a single attosecond pulse in the presence of an infrared (IR) laser field. In order to investigate this type of attosecond streaking of molecules, we developed a very efficient grid-based numerical method to solve the two-centre time-dependent Schrödinger equation (TDSE) in the prolate spheroidal coordinates. Specifically, the radial coordinate is discretized with the finite-element discrete variable representation (FE-DVR) for easy parallel computation and the angular coordinate with the usual DVR. A wavefunction splitting scheme is utilized to reduce the demanding requirement of the computational resource to solve the corresponding TDSE when an IR field is present. After verification of the accuracy and efficiency of our method, we then apply it to investigate the attosecond streaking spectra of  $H_2^+$ in the low-energy region. In contrast to the usual attosecond streaking in the high-energy region, part of the low-energy electrons may be driven back to rescatter with the residual two-centre core. Very interesting interference structures are present in the low-energy region. When the internuclear distance is small, they are very similar to what we have recently observed in the atomic case.

(Some figures may appear in colour only in the online journal)

# 1. Introduction

The production of single attosecond pulses (SAPs) [1–3] has enabled a new kind of experiment, in which an electron wavepacket is created in the continuum by a SAP and then steered by a synchronized infrared (IR) field with a stabilized carrier-envelope phase [4]. The decoupling of the creation and acceleration of the electrons provides a convenient means of controlling the electron motion in the continuum. For photoelectrons with high initial momenta, the interaction with the parent ion can be neglected. The photoelectron momenta is simply shifted by the vector potential of the IR pulse at the time of ionization by the SAP [5]. Attosecond streaking, based on this principle, has enabled measurements of electron dynamics with a time resolution approaching the atomic unit [6].

However, due to the broadband of the SAP, there may exist a significant amount of low-energy electrons, which may be driven back by the IR field to rescatter with the core [7]. These rescattered electrons can interfere with those directly ionized electrons with higher initial momenta. Recently, we pointed out that the resultant interference patterns may serve as a holography image by the electrons, which contains the important structural and dynamical information of the parent core [8]. This may open the way to image the atomic and molecular dynamics using the low-energy electrons in the above context. In contrast to the imaging using high-order harmonic generation [9] or high-order abovethreshold ionization [10] in the cutoff region, the imaging in the low-energy region is much more challenging for both experimentalists and theoreticians because of the simple reasons that the low-energy electrons are difficult to collect experimentally and the complete theoretical treatment needs

to deal with the external laser interaction and the core potential collisions on an equal footing. On the other hand, intense laser pulses in the mid-IR region or even longer wavelengths have brought many surprises to the strong field community. Specifically, a series of unexpected peaks in the low-energy spectra of electrons were observed [11, 12] and electron hologram by a single long-wavelength laser pulse was demonstrated for the first time [13]. In the viewpoint of these new findings, the electron spectra in the low-energy region represents another arena of the strong field physics. For the molecular case, there may be many more new interesting phenomena because of multiple Coulomb centres. At the same time, the theoretical treatment becomes even more challenging than the atomic case as multiple forward and backward scattering among the multiple Coulomb centres may occur for the low-energy electrons.

The main purpose of this work is to introduce a stable and efficient numerical method for the simplest diatomic molecule  $H_2^+$ , which can facilitate quantitatively accurate investigations of the differential distributions of the lowenergy electrons ionized by strong laser pulses. For the ab initio calculations without the soft-core approximation, the difficulties in the time-dependent calculations of diatomic molecules are twofold. The first lies in the singularities of the two Coulomb centres. The second is related to the accurate computation of the molecular scattering states, especially at large electron momenta. In the previous studies, most of the work for the differential momentum distributions of the ionized electrons concentrated on the relatively simpler case where short XUV laser pulses are used; see a very recent work by Guan et al [14] and references therein. For the more challenging cases of molecular ionization by intense IR pulses, only a very few attempts have been made to attack the differential electron distributions. To our best knowledge, only very recently, several works by Madsen and co-workers [15–17] have made great effort to provide a completely differential analysis of the electrons ionized by an intense 800 nm laser. However, their method is based on an expansion of the two-centre wavefunction in the spherical coordinates, which brings challenges for the convergence against the number of the angular momentum for high-energy electrons. Moreover, the convergence is extremely difficult when the internuclear distance becomes large. There were some other calculations which made attempts in providing the differential momentum distributions of ionized electrons based on 2D model molecules or 3D soft-Coulomb potentials. References [18, 19] represent very recent effort in such kinds of calculations on model molecules.

It is well known that the natural coordinates for the two-centre Coulomb problem are the prolate spheroidal coordinates. In this work, we develop a numerical method to accurately calculate the differential momentum distributions of the ionized electrons in intense laser fields in such coordinates. When solving the corresponding time-dependent Schödinger equation (TDSE), for the spatial coordinates discretization, we use a two-dimensional DVR, following the prescription of Tao *et al* [20]. The time evolution of the wavefunction is achieved by the well-known Arnoldi propagator in the Krylov subspace,

which has been routinely used in our previous work [21–24]. For the stability and efficiency of solving the TDSE, we adopt a wavefunction splitting technique, in which the outer part of the wavefunction is projected onto the molecular scattering states and then analytically propagated in the momentum space. The accurate computation of the scattering states are based on our previous work, in which the angular part is solved using a DVR basis method [25] and the radial part is stably integrated using the Killingbeck–Miller approach [26]. As an example, we apply our current methods to deal with the attosecond streaking of  $H_2^+$  in the low-energy region.

The rest of the paper is organized as follows. In section 2, we briefly formulate the problem and describe our numerical methods. In section 3, we present some results which verify the accuracy and efficiency of the developed code. In particular, we carry out comparison studies in both the length and the velocity gauge and illustrate the advantages of our splitting technique. The robustness of the splitting scheme is further tested against the change of the spatial box size and the splitting parameters. In section 4, we draw a short conclusion.

# 2. Theoretical methods

In this section, we briefly describe our numerical method for solving the TDSE of the simplest diatomic molecule in a linearly polarized laser field, whose polarization is aligned with the molecular axis. In the prolate spheroidal coordinates, we discretize the spatial coordinates of the TDSE with the combination of the finite-element DVR (FE-DVR) for the radial coordinate and the usual DVR for the angular coordinate. The temporal evolution of the wavefunction is carried out with the Arnoldi propagator. The differential energy or momentum distribution of the ionized electrons is then extracted by projecting the final wavefunction onto the scattering states of the field-free system. When an IR pulse is present, it is well known that the computation is quite demanding and the convergence in the angular coordinates is very slow; we thus employed a wavefunction splitting technique to improve the capability and efficiency. Details of our scheme are presented in the following subsections.

#### 2.1. The TDSE discretization scheme

The TDSE of a one-electron diatomic system has the following form:

$$i\frac{\partial}{\partial t}\psi(\mathbf{r},t) = H(\mathbf{r},t)\psi(\mathbf{r},t), \qquad (1)$$

with the Hamiltonian operator H being

$$H(\mathbf{r},t) = -\frac{1}{2}\nabla^2 - \frac{Z_1}{r_1} - \frac{Z_2}{r_2} + V^{\text{int}}(\mathbf{r},t), \qquad (2)$$

where  $r_1$  and  $r_2$  are the distances of the electron from the two nuclei, respectively, and  $Z_1$  and  $Z_2$  are the charges on each nucleus. For two-centre problems, it is convenient to adopt the prolate spheroidal coordinates [27], in which the dimensionless coordinates  $\xi$  and  $\eta$  are defined as

$$\xi = \frac{r_1 + r_2}{2a} \quad (1 \le \xi < \infty), \tag{3}$$

$$\eta = \frac{r_1 - r_2}{2a} \quad (-1 \leqslant \eta \leqslant 1), \tag{4}$$

where a is half of the internuclear distance R. So the Hamiltonian operator in these coordinates can be rewritten as

$$H(\xi, \eta, \phi, t) = \left\{ -\frac{1}{2a^2 \left(\xi^2 - \eta^2\right)} \left[ \frac{\partial}{\partial \xi} \left(\xi^2 - 1\right) \frac{\partial}{\partial \xi} + \frac{\partial}{\partial \eta} \left(1 - \eta^2\right) \frac{\partial}{\partial \eta} + \frac{1}{\left(\xi^2 - 1\right)} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\left(1 - \eta^2\right)} \frac{\partial^2}{\partial \phi^2} \right] - \frac{(Z_1 + Z_2)\xi + (Z_2 - Z_1)\eta}{a(\xi^2 - \eta^2)} + V^{\text{int}}(\xi, \eta, \phi, t), \quad (5)$$

where  $\phi$  is the azimuthal angle around the molecular axis.

As usual, one can separate the  $\phi$  dependence from the equation by writing

$$\psi(\xi,\eta,\phi,t) = \sum_{m} \psi^{m}(\xi,\eta,t) \frac{\mathrm{e}^{\mathrm{i}m\phi}}{\sqrt{2\pi}},$$
  
$$m = 0, \pm 1, \pm 2, \dots, \qquad (6)$$

and  $\psi^{m}(\xi, \eta, t)$  satisfies

$$i\frac{\partial}{\partial t}\psi^{m}(\xi,\eta,t) = H^{m}(\xi,\eta,t)\psi^{m}(\xi,\eta,t),$$
(7)

where

$$H^{m}(\xi,\eta,\phi,t) = -\frac{1}{2a^{2}(\xi^{2}-\eta^{2})} \left[ \frac{\partial}{\partial\xi}(\xi^{2}-1) \frac{\partial}{\partial\xi} + \frac{\partial}{\partial\eta}(1-\eta^{2}) \frac{\partial}{\partial\eta} - \frac{m^{2}}{\xi^{2}-1} - \frac{m^{2}}{1-\eta^{2}} + 2a(Z_{1}+Z_{2})\xi + 2a(Z_{2}-Z_{1})\eta \right] + V_{m}^{\text{int}}(\xi,\eta,\phi,t).$$
(8)

Equation (7) in prolate spheroidal coordinates can be solved using different grid-based methods [20, 28–31]. We follow the method proposed by Tao *et al* [20] for the advantages discussed in detail by these authors. In this scheme, the radial coordinate  $\xi$  is discretized by a FE-DVR for easy parallel computation and the angular coordinate  $\eta$  is dealt with the usual Gaussian–Legendre DVR. Specifically, the time-dependent wavefunction is expanded as

$$\psi^{m}(\xi,\eta,t) = \sum_{i=1}^{N_{\xi}} \sum_{j=1}^{N_{\eta}} C_{ij}(t) \chi_{i}(\xi) K_{j}(\eta), \qquad (9)$$

where  $\chi_i(\xi)$  and  $K_j(\eta)$  are the DVR basis functions [20]. In this work, we only solve the TDSE for a linearly polarized laser pulse along the molecular axis, in which the azimuthal symmetry is preserved. Therefore, starting from the ground  $1\sigma_g$  state, one always has m = 0. After discretization, the resultant Hamiltonian matrix elements are given by

$$H_{ij,kl}(\xi,\eta,t) = \frac{1}{2a^2\sqrt{\xi_i^2 - \eta_j^2}\sqrt{\xi_k^2 - \eta_l^2}} \\ \times \left\{ \delta_{jl} \int (\xi^2 - 1) \frac{d\chi_i(\xi)}{d\xi} \frac{d\chi_k(\xi)}{d\xi} d\xi \\ + \delta_{ik} \int (1 - \eta^2) \frac{dK_j(\eta)}{d\eta} \frac{dK_l(\eta)}{d\eta} d\eta \\ + \delta_{ik}\delta_{jl}[-2a(Z_1 + Z_2)\xi_i - 2a(Z_2 - Z_1)\eta_j] \right\} \\ + V_{ij,kl}^{int}(\xi,\eta,t),$$
(10)

where the overlap terms are transformed out by reconstructing the Hamiltonian matrix elements using equation (14) in [20]. In this case, the matrix elements of the interaction Hamiltonian are given by

$$V_{ij,kl}^{\text{int,L}}(\xi,\eta,t) = \delta_{ik}\delta_{jl}E(t)a\xi_i\eta_j,$$
(11)

in the length gauge, and

$$V_{ij,kl}^{\text{int},\mathbf{V}}(\xi,\eta,t) = \frac{-iA(t)}{a\sqrt{\xi_i^2 - \eta_j^2}\sqrt{\xi_k^2 - \eta_l^2}} \\ \times \left(\delta_{jl}\eta_j \int \chi_i(\xi^2 - 1)\frac{\partial\chi_k}{\partial\xi}\,\mathrm{d}\xi + \delta_{ik}\xi_i \int K_j(1-\eta^2)\frac{\partial K_l}{\partial\eta}\,\mathrm{d}\eta\right),$$
(12)

in the velocity gauge, where E(t) and A(t) is the electric field and the vector potential of the external laser pulse, respectively.

For the time evolution of the wavefunction, we use the Arnoldi propagator, which has been widely used in the numerical solution of TDSE [21–24]. We first propagate an arbitrary trial wavefunction with the field-free Hamiltonian in an imaginary time to obtain the initial state of the molecule and then perform the real-time propagation till the end of the laser pulse  $t_f$ .

### 2.2. Extraction of energy and momentum distribution

At the end of the real-time propagation of the TDSE, the differential energy and momentum distribution of the ionized electrons have to be extracted. The direct and accurate way to achieve this is to project the final wavefunction onto the exact scattering states of the field-free two-centre system. However, due to the difficulty in computation of the two-centre scattering states, several alternative methods have been developed, such as the Fourier transformation of the autocorrelation function [32], asymptotic projection onto plane waves or one-centre Coulomb scattering states [33], or the application of the exterior complex scaling (ECS) [20].

In this work, we directly project the final wavefunction onto the two-centre scattering states with an incoming wave boundary conditions. In practice, the angular part of the continuum wavefunction is calculated using a DVR method [25]. For the radial part, we use the extended Killingbeck– Miller approach [26] which can propagate the radial equation of continuum wavefunction stably and accurately.

The normalized scattering state with momentum  $\mathbf{k} = (k, \theta_e, \phi_e)$  can be expressed as

$$\psi_{\mathbf{k}}^{(-)}(\xi,\eta,\phi) = \frac{2\pi}{k} \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} i^{l} e^{-i\delta_{lm}} S_{lm}^{*}(\cos\theta_{e},k)$$
$$\times X_{lm}(\xi,k) S_{lm}(\eta,k) \frac{e^{im(\phi-\phi_{e})}}{2\pi}, \qquad (13)$$

where  $S_{lm}$  and  $X_{lm}$  is the angular and radial part of the continuum wavefunction respectively, and  $\delta_{lm}$  is the corresponding phase shift.

The momentum distribution of the ionized electrons can then be extracted by the following projection:

$$P(k, \theta_{\rm e}, \phi_{\rm e}) = \left| \left\langle \psi_{\mathbf{k}}^{(-)}(\xi, \eta, \phi) | \psi(\xi, \eta, \phi, t_f) \right\rangle \right|^2.$$
(14)

For the case of a linearly polarized laser along the molecular axis, due to the azimuthal symmetry, one can define the following  $\phi_{e}$ -integrated energy distribution:

$$P(E, \theta_{\rm e}) = 2\pi k P(k, \theta_{\rm e}, \phi_{\rm e} = 0).$$
(15)

#### 2.3. Wavefunction splitting technique

In order to eliminate the reflection at the boundary and to save the computation resources, at different instances during the real-time propagation, we split the wavefunction into two parts. The inner part is propagated under the full molecular and interaction Hamiltonian. At the time of splitting  $t_i$ , the wavefunction in the outer region is first projected onto the scattering states and is then analytically propagated in the momentum space to a common time  $t_f$ . In practice, the splitting process is performed every half-cycle when the vector potential of the external laser field is zero. All pieces of the momentum space wavefunction, which have been propagated to the common time  $t_f$ , are coherently added up with a proper Volkov phase factor to give the final momentum distributions of the ionized electrons.

The splitting technique [34-36] is implemented by a splitting function *M* which equals unity near the nuclei and goes asymptotically to zero very smoothly at large distances. The wavefunction is split into the following two parts:

$$\psi = \psi_{\text{inner}} + \psi_{\text{outer}} = M\psi + (1 - M)\psi, \qquad (16)$$

where the mask function M is taken to be

$$M = \frac{1}{1 + e^{-(\xi - \xi_s)/\xi_d}}.$$
(17)

Here,  $\xi_s$  is related to the central position of the splitting function and  $\xi_d$  is the steepness. The Volkov phase factor associated with the piece of the outer part split at time  $t_i$  is given by

$$U^{\rm V}(t_f, t_i) = e^{-i \int_{t_i}^{t_f} dt' [\mathbf{k} + \mathbf{A}(t')]^2 / 2},$$
(18)

which ignores the Coulomb potential in the asymptotic region. After all the propagation and splitting procedures are completed, one can reconstruct the total momentum distribution of the ionized electrons by

$$P(k, \theta_{e}, \phi_{e}) = \left| \sum_{i} U^{\mathrm{V}}(t_{f}, t_{i}) \langle \psi_{\mathbf{k}}^{(-)}(\xi, \eta, \phi) | \psi_{\mathrm{outer}}(\xi, \eta, \phi, t_{i}) \rangle \right|^{2}.$$
(19)

Please note that, after the end of the real-time propagation in the laser fields, the inner part of the wavefunction should also be projected onto the molecular scattering states and be coherently added up to the above formula.

With the above splitting technique, one can deal with the challenging case where an intense and long IR laser pulse is applied, preventing one from using a huge box and thus saving a lot of computation time. As can be seen in the following section, the splitting technique can also allow one to use much fewer points in the angular coordinate.

<b>Table 1.</b> Energies of the first few bound states of $H_2^+$ at the
internuclear distance $R = 2$ au from the present calculations
(denoted by the superscript a), compared with those from [29]
(denoted by the superscript b).

State	Energy (au)
$1\sigma_{\rm g}$	-1.1026 3421 4494 951ª
	-1.1026 3421 4494 946 <sup>b</sup>
$1\sigma_{\rm u}$	-0.6675 3439 2202 376ª
	-0.6675 3439 2202 383 <sup>b</sup>
$2\sigma_{g}$	-0.3608 6487 5339 500 <sup>a</sup>
0	-0.3608 6487 5339 504 <sup>b</sup>
$2\sigma_{\rm u}$	-0.2554 1316 5086 485 <sup>a</sup>
	-0.2554 1316 5086 485 <sup>b</sup>

# 3. Results and discussion

In this section, we first verify the reliability and accuracy of our numerical scheme and computer codes. These test calculations include the comparisons of the energies of the first few bound states, the total and the differential cross sections of the single-photon ionization, with previous results available in the literature calculated by other different methods. After these verifications, we turn our attention to the convergence of the ionization dynamics by an attosecond pulse in the presence of an additional IR field, in both the length and the velocity gauge description of the interaction Hamiltonian. We find that the velocity gauge converges much faster than the length gauge against the increase of the grid points in the angular coordinate. However, we employ a wavefunction splitting scheme in the length gauge and find that the computation can be even faster than the velocity gauge. Finally, we apply our method to investigate the attosecond streaking in the low-energy region. Detailed analysis of these interesting interferences and their dependence on the internuclear distance R is underway and will be published elsewhere.

# 3.1. Bound states energies and single-photon ionization cross sections

For the illustration that our chosen grid scheme can accurately describe the field-free states of the molecule, we calculate the first few bound states by the imaginary time propagation method. The ground state is simply reached by propagating an arbitrary trial wavefunction for a sufficiently long time. The excited states are calculated by projecting out all the lower states during a recursive propagation of a trial wavefunction in the imaginary time. In our case, since the axial symmetry along the molecular axis is utilized, only  $\sigma$  states (m = 0) can be characterized in the calculations. In table 1, we compare the energies of the first few bound states from this study with those in [29] calculated by the generalized pseudospectral method. One can see excellent agreement between both results. The corresponding bound-state wavefunctions can be simultaneously obtained accurately but are not shown here.

Let us now turn to the total single-photon ionization cross section at R = 2 au, which can be calculated using the formula [37]

$$\sigma = \frac{\omega}{I_0} \frac{P_{\text{total}}}{T_{\text{eff}}},\tag{20}$$



**Figure 1.** Total cross section of single-photon ionization of  $H_2^+$  for laser polarization parallel to the molecular axis. Points: results of Bates and Öpik [38]; red solid line: the present LOPT results; and blue dashed line: the present TDSE results.

where  $\omega$  is the central frequency of the laser pulse and  $P_{\text{total}}$  is the total ionization probability of the molecule by the laser pulse. The effective interaction time  $T_{\text{eff}}$  is given by

$$T_{\rm eff} = \int \frac{I(t)}{I_0} \,\mathrm{d}t,\tag{21}$$

with I(t) being the laser intensity profile and  $I_0$  the peak intensity. For a better evaluation of the cross section, we use a trapezoidal shape laser pulse with one-cycle ramp on and off and 20 cycle flattop, at the intensity of  $5 \times 10^{12}$  W cm<sup>-2</sup>. A series of calculations are performed for the ejected electron energy up to 8 au. As shown in figure 1, the present TDSE results (we note that both the length and the velocity gauge give identical results) are in excellent agreement with the well-known accurate calculations by Bates and Öpik [38], which were reproduced by Plummer and McCann [39] using Floquet theory.

Actually, the single-photon total ionization cross section can also been evaluated by the lowest order perturbation theory (LOPT), provided that accurate initial and scattering states are available. Denoting the laser polarization vector as  $\hat{\varepsilon}$ , it is easy to show that the differential cross section of single-photon ionization is given by

$$\sigma^{(1)}(k,\theta_{e},\phi_{e},\Theta) = 4\pi^{2}\alpha\omega k \left| \left\langle \psi_{\mathbf{k}}^{(-)}(\xi,\eta,\phi) \left| \hat{\boldsymbol{\varepsilon}} \cdot \mathbf{r} \right| \psi_{0}(\xi,\eta,\phi) \right\rangle \right|^{2}, \quad (22)$$

in the length gauge, and

$$\sigma^{(\mathbf{v})}(k,\theta_{e},\phi_{e},\Theta) = \frac{4\pi^{2}\alpha k}{\omega} |\langle \psi_{\mathbf{k}}^{(-)}(\xi,\eta,\phi) | \hat{\varepsilon} \cdot \nabla | \psi_{0}(\xi,\eta,\phi) \rangle|^{2}, \qquad (23)$$

in the velocity gauge, respectively, where  $\Theta$  is the laser polarization direction with respect to the molecular axis. In all the calculations using the LOPT, we find that the above length and velocity gauge formula give identical differential and total ionization cross sections. Therefore, we only present the results from the velocity gauge for clarity. In figure 1, we also show the total single-photon ionization cross section from the LOPT, which is calculated by

$$\sigma = \int_0^{2\pi} d\phi_e \int_0^{\pi} \sin\theta_e \, d\theta_e \sigma \, (k, \theta_e, \phi_e, \Theta = 0).$$
(24)

To further confirm the accuracy of the computed scattering states, we calculate the differential single-photon ionization cross section using the LOPT at different photon energies and different laser polarization  $\Theta$ . Note that, as recently clarified by Guan *et al* [14], the differential cross section was defined to be 'unweighted' (given in equations (22) or (23)) or 'weighted' in the literature.

We first look at the differential cross section for the electron energy of 10 eV and R = 2 au at different laser polarization angles with respect to the molecular axis. In figure 2, one can see that excellent agreements are achieved between our 'weighted' differential cross sections with those of Rescigno *et al* [40]. The 'unweighted' ones from Picca *et al* [41] are also shown. Actually, our 'unweighted' differential cross sections (for clarity, they are not shown) are in reasonable agreement with those of Picca *et al* [41].

Then, we turn to compare our 'unweighted' differential cross section (cf, equations (22) or (23)) with those of Picca et al from another publication [42] at different electron energies for the laser polarization angle  $\Theta = 10^{\circ}$ . Surprisingly, the absolute values from both results cannot agree with each other but the shapes are almost the same for each photon energy considered. In figure 3, we present our 'unweighted' differential cross section together with the scaled data from [42]. Note that the absolute values of their data are scaled with a different factor in each frame. The sources of these discrepancies are unknown, but may be related to the computation and normalization of the scattering states. It is well known that computation of the scattering states at large energy is challenging. But we have carefully checked the convergence of the calculations and no differences or gauge dependence is identified.

### *3.2. Convergence against* $N_{\eta}$ *in the length gauge*

It is well known that, when solving the atomic TDSE in intense laser fields, the convergence against the number of the angular momentum is very slow in the length gauge. However, the good side of using the length gauge is that the interaction Hamiltonian is diagonal, and thus, the operation is fast. If one chooses the velocity gauge, the convergence against the number of the angular momentum is much faster but the interaction Hamiltonian is dense, and thus, it is time consuming to operate.

In this section, we will first make a comparison of calculations in the velocity and length gauge. Similar to the atomic case, we find that the velocity gauge converges much faster due to the increase of the number of the points in the  $\eta$  direction than the length gauge. Nevertheless, our algorithm in the length gauge is stable and is able to converge eventually to the result in the velocity gauge as one increases  $N_{\eta}$ .

We can see this clearly if we look at the electron density after the end of the laser pulse in the prolate spheroidal coordinates. As an example, the molecule is ionized by a



**Figure 2.** Differential cross section (DCS)  $\sigma$  ( $k, \theta_e, \phi_e = 0, \Theta$ ) of single-photon ionization of H<sub>2</sub><sup>+</sup> for the electron energy of 10 eV and R = 2 au at different laser polarization angle with respect to the molecular axis: (a)  $\Theta = 0^{\circ}$ , (b)  $\Theta = 30^{\circ}$ , (c)  $\Theta = 60^{\circ}$  and (d)  $\Theta = 90^{\circ}$ . Red solid line: the present calculations; blue dashed line: results of Rescigno *et al* [40]; black dash–dotted line: results of Picca *et al* [41]. Note that all sets of data in (a) are multiplied by a factor of 3 for better vision.



**Figure 3.** The 'unweighted' differential cross section of single-photon ionization for  $H_2^+$  at the laser polarization angle  $\Theta = 10^\circ$  and electron energy of (a) 10, (b) 50, (c) 150 and (d) 250 eV. Green dashed line: the present calculations; red solid line: scaled Picca's data. Note that the scale factor for each electron energy is different, as indicated in each panel.



**Figure 4.** The density of electrons on the logarithm scale in prolate spheroidal coordinates after the substraction of the initial-state component. (a) The colour flood plot of the density calculated in velocity gauge; (b)–(f) the contour plot of the density calculated in the length gauge with  $N_{\eta} = 48, 60, 72, 84$ , and 120, respectively (blue line in each frame), compared with that calculated in the velocity gauge (red line in each frame). Note that the differences are only visible in the electronic version. See the text for the laser parameters of the attosecond and IR pulses.

3 cycle sin<sup>2</sup>-shape attosecond pulse with the photon energy of 1.6 au at the peak intensity of  $5 \times 10^{12}$  W cm<sup>-2</sup>, in the presence of an additional 4 cycle trapezoidal IR pulse of wavelength 750 nm at the peak intensity of  $2 \times 10^{13}$  W cm<sup>-2</sup> [8]. The attosecond pulse is put at the peak of IR pulse vector potential so that a maximum streaking momentum shift is obtained. In the calculations, the maximum of  $\xi$  is taken to be 800 to absolutely make sure that there is no reflection. The time step of the Arnoldi propagator is taken to be quite small, about 0.004 au.

In order to examine the details of the excitation and ionized part of the electron density, we have projected and subtracted the initial-state component. We first carry out a series of calculations in the velocity gauge for different  $N_{\eta}$  and find that when  $N_{\eta} = 48$  it is completely converged. In figure 4(a), we show the colour flood plot for the electron density for  $N_{\eta} = 48$  in the velocity gauge.

One can see from figure 4(a) that the wavepackets extend beyond 500 and the wavepackets are stretched in the forward direction ( $\eta = -1$ ) and compressed in the backward direction ( $\eta = 1$ ). One also notices many interesting interferences in the region  $\xi < 100$ . The interference structures will be clearly seen when one analyses the electron energy and momentum distributions, as will be shown below.

We have also carried out the same calculation using the length gauge, as shown by the contour plots with the blue lines in figures 4(b)–(f). The red line contour plot in each of these five frames is the contour plot of figure 4(a), which represents the converged result from the velocity gauge calculation. As can be seen in figure 4(b), when  $N_{\eta} = 48$  for the length gauge, only the electron density below  $\xi = 150$  overlaps the converged result from the velocity. But as the number of points in  $\eta$  is increased, the length gauge result agrees better and better with that of the velocity gauge. For example, when  $N_{\eta} = 84$  in figure 4(e), the electron density below  $\xi = 280$  becomes

identical for the results from both gauges. The agreement will become even better as one increases  $N_{\eta}$ . As shown in figure 4(f), when  $N_{\eta} = 120$ , the two sets of results are almost not differentiable, except a very small discrepancy around the point ( $\xi \approx 380$ ,  $\eta \approx 0$ ). Actually, as one glances through (b)–(f), one notices an interesting phenomenon: for the length gauge, the convergence against  $N_{\eta}$  is always slower around  $\eta = 0$  than the two ends  $\eta = \pm 1$ . This is probably related to the fact that the Gaussian–Legendre quadrature points are denser at both ends.

# *3.3. The wavefunction splitting technique: application to the attosecond streaking of molecules*

The above observations tell us that, in the length gauge, one needs much denser grids in  $\eta$  to achieve a fully converged result than the velocity gauge. One notices the great property that the results are always fully converged below a certain value of  $\xi$  even for a relatively small number of points in the  $\eta$  direction. This property allows us to develop a very efficient method based on the wavefunction splitting technique. It is well known that the ionizing electron wavepackets will gradually evolve into the asymptotic regions where the Coulomb interactions become less important. Therefore, these outer region wavefunction can be split and projected into the momentum space and be analytically propagated till the end of the pulse or beyond. This wavefunction splitting technique has been adopted in many circumstances such as atomic ionization [34, 35] and molecular ionization [36].

We apply a wavefunction splitting technique to the molecular ionization problem in the combined fields of an attosecond and IR pulse. Different from most of the previous works, after the wavefunction splitting, we project the outer region wavefunction onto the molecular scattering states, instead of the plane waves or atomic scattering states. After the



**Figure 5.** (a) The colour flood plot of the electron momentum distributions calculated by the velocity gauge using a larger box. (b) The contour plot of the electron momentum distributions that are extracted from (a) (red solid line) and that are calculated by the splitting technique in the length gauge using a much smaller box (blue dashed line).



**Figure 6.** Comparisons of the electron energy distributions  $P(E, \theta_e)$  along the laser polarization lines: (a)  $\theta_e = 0^\circ$  and (b)  $\theta_e = 180^\circ$ , calculated by the velocity gauge (black solid line), by the length gauge splitting technique at  $\xi_s = 200$  with  $\xi_{max} = 400$  (red dashed line), and by the length gauge splitting technique at  $\xi_s = 100$  with  $\xi_{max} = 300$  (blue dash-dotted line). (c), (d) The logarithm scale plot of (a) and (b), respectively.

projection, this portion of the wave packet is then propagated analytically in the momentum space with a proper Volkov phase factor (cf, equation (19)).

We want to emphasize that the utilization of the present wavefunction splitting technique has the following advantages. First, the velocity gauge, although converged faster in  $N_{\eta}$ , needs much more time and resources than the length gauge due to the fact that the interaction Hamiltonian is a full matrix in the DVR discretization scheme and has to be treated in the same way as the kinetic energy matrix. However, in length gauge, the interaction Hamiltonian can be simply multiplied to the wavefunction just like the Coulomb potential term, which is diagonal as a main performance improvement of the DVR method. If we use the splitting method, one can prevent the slow convergence of the length gauge against  $N_{\eta}$  and improve the computation speed by five times or more, depending on the laser parameters. Second, with this method, we can fix the box at a reasonable size for laser pulses of any length as long as one ensures that the wavepackets in the inner region will not reach the box boundary between two adjacent splitting times. Third, since we project the split wavefunction onto the the scattering states instead of the plane waves, one does not need to propagate the split portions beyond the end of the laser pulse, because at the end of the pulse, the whole wavefunction

in the inner region will be projected directly to the scattering states and be added up coherently to the split portions at early times. Compared to the usual projection onto plane waves, our method saves great time since there is no need to propagate the low energy electrons into the asymptotic region. In this way, the low energy part of the electrons can be precisely preserved without any loss.

Now we apply our method to the attosecond streaking spectra of the molecules in the low-energy region. In figure 5, we present the electron momentum distributions ionized by the same XUV and IR pulses as those in figure 4. In figure 5(a), we show the results from the velocity gauge by projecting the whole wavefunction at the end of the laser pulse onto the molecular scattering states. (The final electron density subtracted the initial state component is shown in figure 4(a).) In figure 5(b), we show the same electron momentum distributions using the contour plot as a red solid line. Also, in figure 5(b), as the blue dashed line, the resultant electron momentum distributions calculated by the splitting technique in the length gauge are shown (cf, equation (19)). One observes that the two sets of results agree completely with each other. For the length gauge calculations, we take  $\xi_{\text{max}} = 400, N_{\eta} = 96$  and  $\xi_{\text{s}} = 200$ . The wavefunction is split twice per IR cycle at the zero of the IR vector potential.

For the sake of quantitative comparison, we turn to examine the electron energy distributions along the laser polarization direction, i.e.  $P(E, \theta_e)$  for  $\theta_e = 0^\circ$  in figure 6(a) and  $\theta_e = 180^\circ$  in figure 6(b). For details, also shown are their logarithm scale plot in figures 6(c) and (d), respectively. In each of these frames, three different lines are shown. The black solid line represents the results from the velocity gauge (cf, figure 5(a)). To test the robustness of the splitting technique in the length gauge, we actually decrease  $N_n$  from 96 in figure 5(b) to 48 in figure 6. The red dashed line shows the results when  $\xi_{\text{max}} = 400$  and  $\xi_{\text{s}} = 200$ , while the blue dash-dotted line represents the results at a even smaller box at  $\xi_{\text{max}} = 300$  and  $\xi_{\text{s}} = 100$ . We note that, in each of these frames, the three results agree with each other very well, which confirms the accuracy and efficiency of our splitting method in the length gauge.

Note that the interference structures in the momentum and energy distributions of ionized electrons shown in figures 5 and 6 are very similar to what we have observed in atoms [7, 8]. Basically, these interferences are caused by the rescattering of the low-energy electrons with the core potential. Not surprisingly, at small internuclear distances, the interferences along the laser polarization are similar to those in the atomic case. However, one expects that, due to the multiple Coulomb centres in molecules, one may observe drastically different patterns from atoms. This kind of attosecond streaking of molecules in the low-energy regions is currently under an elaborate analysis and will be published elsewhere.

### 4. Conclusions

In summary, we have developed an efficient and accurate splitting technique combined FE-DVR for solving the TDSE

problem in intense laser fields. By using this method, the momentum spectra is accumulated by a recursive splitting technique, in which the wavefunction in the outer region is projected onto the scattering states of the two-centre system and then analytically propagated to the end of the laser pulse in the momentum space. By applying our method to the attosecond streaking of molecules in the low-energy region, we confirm the robustness and accuracy of our scheme. In principle, our method is applicable to the laser pulses of any length and can greatly save the CPU time and the memory resources.

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