A quantum simulation of dissociative ionization of $H_2^+$ in full dimensionality with time-dependent surface flux method

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The dissociative ionization of $H_2^+$ in a linearly polarized, 400 nm laser pulse is simulated by solving a three-particle time-dependent Schrödinger equation in full dimensionality without using any data from quantum chemistry computation. The joint energy spectrum (JES) is computed using a time-dependent surface flux (tSurff) method, the details of which are given. The calculated ground energy is -0.597 atomic units and internuclear distance is 1.997 atomic units if the kinetic energy term of protons is excluded, consistent with the reported precise values from quantum chemistry computation. If the kinetic term of the protons is included, the ground energy is -0.592 atomic units with an internuclear distance 2.05 atomic units. Energy sharing is observed in JES and we find peak of the JES with respect to nuclear kinetic energy release (KER) is within 2 ∼ 4 eV, which is different from the previous two dimensional computations (over 10 eV), but is close to the reported experimental values. The projected energy distribution on azimuth angles shows that the electron and the protons tend to dissociate in the direction of polarization of the laser pulse.

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I. INTRODUCTION

Understanding the three-body Coulomb interaction problem is an on-going challenge in attosecond physics. The typical candidates for investigation include Helium atom and $H_2^+$ molecule. In attosecond experiments, a short, intense laser pulse is introduced as a probe for the measurements. Various mechanisms were proposed in the recent decades to describe the dissociation and dissociative ionization of $H_2^+$, including bond softening [1], the charge-resonance enhanced ionization (CREI) [2], bond hardening [3], above threshold dissociation (ATD) [4, 5], high-order-harmonic generation (HHG) [6] and above threshold explosion [7]. One may find a summary of the above mechanisms in theoretical and experimental investigations of $H_2^+$ in literature [8, 9]. Experimental studies on the $H_2^+$ ion exposed to circular and linearly polarized lasers for angular and energy distributions of electrons were reported recently [10–13].

In theory, the joint energy spectra (JES) of the kinetic energy release (KER) for one electron and two protons of the $H_2^+$ ion are predominant observables that show how energy distributes around the fragments, where the JES is represented by the KER of two electrons for dissociative ionization of the $H_2^+$ ion [10, 20] in a two-dimensional (2D) model, where the energy sharing of the photons and electron is observed in JES.

The dissociative ionization of the $H_2^+$ ion has been simulated by many groups [10, 14, 21–26]. However, they are all in reduced dimensionality. Quantum simulation in full dimensionality is not available yet. Although the correlation among the fragments could be observed in the 2D model, the peaks of the JES with total nuclear KER are always above 10 eV. This is far from experimental observables [11, 13], which are usually below 5 eV. The tRecX code, which successfully implements the tSurff method in full dimensionality, has been applied successfully in the simulations of the double ionization of Helium [16] and the single ionization of polyelectron molecules [27–31]. The dissociative ionization of the $H_2^+$ ion has not been computed using the tRecX code from before, even in reduced dimensionality.

In this paper, we will introduce simulations of the dissociative ionization of the $H_2^+$ ion by solving the time-dependent Schrödinger equation (TDSE) in full dimensionality with the tRecX code. We will first present the computational method for scattering amplitudes with tSurff methods, from which the JES can be obtained. Then we will introduce the specific numerical recipes for the $H_2^+$ ion based on the existing discretization methods of tRecX code. With such numerical implementations, the ab initio calculation of field free ground energy of the Hamiltonian is available. Finally we will present results of dissociative ionization in a 400 nm laser pulse, the JES, and projected energy spectrum on the azimuth angle.

II. METHODS

In this paper, atomic units with specifying $\hbar = e^2 = m_e = 4\pi\epsilon_0 \equiv 1$ are used if not specified. Spherical coord-
ordinates with center of the two protons as the origin are applied. Instead of using the vector between two protons \( \vec{R} \) as an coordinate \([14 19 20]\), we specify the coordinates of the protons and electrons as \( \vec{r}_1, -\vec{r}_1^*, \) and \( \vec{r}_2, -\vec{r}_2^* \). We denote \( M = 1836 \) atomic units as the mass of the proton.

A. Hamiltonian

The total Hamiltonian can be represented by sum of the electron-proton interaction \( H_{EP} \) and two tensor products, written as

\[
H = H_B = H^{(+)} \otimes 1 + 1 \otimes H^{(-)} - H_{EP},
\]

where the tensor products are formed by the identity operator \( 1 \) multiplied by the Hamiltonian for two protons \( (H^{(+)}) \), or that for the electron \( (H^{(-)}) \). \( H_B \) is called the Hamiltonian in the \( B \) region and will be detailed later. With the coordinate transformation used in Ref. \([32]\), which is also illustrated in Appendix \( A \) for our specific case, the single operator for the electron is

\[
H^{(-)} = -\frac{\Delta}{2m} - i\beta \vec{A}(t) \cdot \vec{\nabla},
\]

and the Hamiltonian for protons can be written as

\[
H^{(+)} = -\frac{\Delta}{4M} + \frac{1}{2r},
\]

where we introduce reduced mass \( m = \frac{2M}{2M+1} \approx 1 \) and \( \beta = \frac{1+M}{M} \approx 1 \) for the electron. The Hamiltonian of the electron-proton interaction can be written as

\[
H_{EP} = \frac{1}{|\vec{r}_1^* + \vec{r}_2^*|} + \frac{1}{|\vec{r}_1^* - \vec{r}_2^*|}.
\]

B. tSurf for dissociative ionization

The tSurf method is applied here for the dissociative ionizations, which was successfully applied to the polyelectron molecules and to the double emission of He atom \([15 28 31]\). In this section, we will follow a similar procedure as is done in Ref. \([16]\).

According to the approximations of tSurf method, beyond a sufficient large tSurf radius \( R_{c}^{(+/-)} \), the interactions of protons and electrons can be neglected, with the corresponding Hamiltonians being \( H^{(+)} = -\Delta/4M \) for each proton and \( H^{(-)} = -\Delta/2m - i\beta \vec{A}(t) \cdot \vec{\nabla} \) for the electron. The scattered states of the two protons, which satisfy \( i\partial_t \chi_{k_1^*}(\vec{r}_1^*) = H^{(+)}_{V^*} \chi_{k_1^*}(\vec{r}_1^*) \), are

\[
\chi_{k_1^*}(\vec{r}_1^*) = \frac{1}{(2\pi)^{3/2}} \exp(-i\int_{t_0}^{t} \frac{k_1^2}{4M} d\tau) \exp(-i\vec{k}_1 \vec{r}_1^*),
\]

and those of the electron, which satisfies \( i\partial_t \chi_{k_2}(\vec{r}_2^*) = H^{(-)}_{V} \chi_{k_2}(\vec{r}_2^*) \), are

\[
\chi_{k_2}(\vec{r}_2^*) = \frac{1}{(2\pi)^{3/2}} \exp(-i\int_{t_0}^{t} \frac{k_2^2}{2m} - i\beta \vec{A}(\tau) \cdot \vec{\nabla} d\tau) \exp(-i\vec{k}_2 \vec{r}_2),
\]

where we assume the laser field starts at \( t_0 \) and \( k_{1/2} \) denote the momenta of the protons or the electron.

Based on the tSurf radius \( R_{c}^{(+/-)} \), we may split the dissociative ionization into four regions namely \( B, I, D, DI \), shown in figure \( 1 \) where bound region \( B \) preserves the full Hamiltonian in Eq. \( 1 \). \( D, I \) are time propagations by single particles with the Hamiltonian

\[
H_D(\vec{r}_2^*, t) = H^{(-)}_{V} \chi_{k_2}(\vec{r}_2^*),
\]

and

\[
H_I(\vec{r}_1^*, t) = -\Delta/4M + \frac{1}{2\vec{r}_1},
\]

and \( DI \) is an integration process. The treatment was first introduced in the double ionization of Helium in Ref. \([15]\) and then applied in a 2D simulation of the \( H^{+} \) ion in Ref. \([19]\). Without considering the low-energy free electrons that stay inside the box after time propagation, we may write

\[
\psi_B(\vec{r}_1^*, \vec{r}_2^*, t) \approx 0, \quad r_1 \geq R_{c}^{(+)} \text{ or } r_2 \geq R_{c}^{(-)}
\]

\[
\psi_D(\vec{r}_1^*, \vec{r}_2^*, t) \approx 0, \quad r_1 < R_{c}^{(+)} \text{ or } r_2 \geq R_{c}^{(-)}
\]

\[
\psi_I(\vec{r}_1^*, \vec{r}_2^*, t) \approx 0, \quad r_1 \geq R_{c}^{(+)} \text{ or } r_2 < R_{c}^{(-)}
\]

\[
\psi_{DI}(\vec{r}_1^*, \vec{r}_2^*, t) \approx 0, \quad r_1 < R_{c}^{(+)} \text{ or } r_2 < R_{c}^{(-)}
\]
We assume that for a sufficiently long propagation time $T$, the scattering ansatz of electron and protons disentangle. By introducing the step function

$$
\Theta_{1/2}(R_e) = \begin{cases} 
0, & r_{1/2} < R_e^{(+/-)} \\
1, & r_{1/2} \geq R_e^{(+/-)} 
\end{cases},
$$

the unbound spectra can be written as

$$
P(\vec{k}_1, \vec{k}_2) = P(\phi_1, \theta_1, k_1, \phi_2, \theta_2, k_2) = |b(\vec{k}_1, \vec{k}_2, T)|^2. 
$$

$b(\vec{k}_1, \vec{k}_2, T)$ is the scattering amplitudes and can be written as

$$
b(\vec{k}_1, \vec{k}_2, T) = \langle \chi_{\vec{k}_1} \otimes \chi_{\vec{k}_2} | \Theta_1(R_e) \Theta_2(R_e) | \psi(r_1, r_2, t) \rangle 
= \int_{-\infty}^{T} [F(\vec{k}_1, \vec{k}_2, t) + \bar{F}(\vec{k}_1, \vec{k}_2, t)] dt 
$$

with two sources written as

$$
F(\vec{k}_1, \vec{k}_2, t) = \langle \chi_{\vec{k}_1} (r_2, t) | [H_{V}^{(-)}(r_2, t), \Theta_2(R_e)] | \varphi_{\vec{k}_1}(r_2, t) \rangle 
$$

and

$$
\bar{F}(\vec{k}_1, \vec{k}_2, t) = \langle \chi_{\vec{k}_1} (r_1, t) | [H_{V}^{(+)}(r_1, t), \Theta_1(R_e)] | \varphi_{\vec{k}_2}(r_1, t) \rangle. 
$$

The single particle wavefunctions $\varphi_{\vec{k}_1}(r_2, t)$ and $\varphi_{\vec{k}_2}(r_1, t)$ satisfy

$$
\frac{d}{dt} \varphi_{\vec{k}_1}(r_2, t) = H_D(r_2, t) \varphi_{\vec{k}_1}(r_2, t) - C_{\vec{k}_1}(r_2, t) 
$$

and

$$
\frac{d}{dt} \varphi_{\vec{k}_2}(r_1, t) = H_I(r_1, t) \varphi_{\vec{k}_2}(r_1, t) - C_{\vec{k}_2}(r_1, t). 
$$

The sources are the overlaps of the two-electron wavefunction on the Volkov solutions shown by

$$
C_{\vec{k}_1}(r_2, t) = \int d\vec{r}_1 \chi_{\vec{k}_1}(\vec{r}_1, t) |H_{V}^{(+)}(\vec{r}_1, t), \Theta_1(R_e)| \psi(\vec{r}_1, r_2, t) 
$$

and

$$
C_{\vec{k}_2}(r_1, t) = \int d\vec{r}_2 \chi_{\vec{k}_2}(\vec{r}_2, t) |H_{V}^{(-)}(\vec{r}_2, t), \Theta_2(R_e)| \psi(\vec{r}_1, \vec{r}_2, t),
$$

with initial values being 0. The two tSurff radii could be set to equivalent $R_c^{(+)} = R_c^{(-)}$, because all Coulomb interactions are neglected when either the protons or electron is out of the tSurff radius. According to our previous researches, the spectrum computation is independent of the $R_e$ if all Coulomb terms are removed and the wavefunction is propagated long enough after the pulse [15] [16]. The tSurff for double emission of two particles was firstly introduced in Ref. [15]. The above derivations are very similar to what was reported in Ref. [16] of double emission of Helium, where the only differences are constants before different operators, say $\Delta, \mathcal{V}$ and $\frac{1}{2}$. Thus, detailed formulas are omitted here and the interested readers can refer to Ref. [15] [16].

The computation for photoelectron spectrum includes four steps, similar to the one used in Ref. [16], detailed as

1. Solve full 6D TDSE with the Hamiltonian in the $B$ region, given in Eq. (1), and write the time-dependent surface values in the disk.
2. Advance the single-particle wave packets in the $D$ region by Eq. (13) with surface values given in the $B$ region time propagation.
3. Advance the single-particle wave packets in $I$ region by Eq. (14) with the surface values given in the $B$ region time propagation.
4. Integrate the fluxes calculated from surface values written in the $D$ and $I$ regions’ time propagation by Eq. (12).

### III. Numerical Implementations

The numerical methods here are similar to what was detailed in Ref. [16] [18]. In fact, the code in this paper is developed based on the double ionization framework of the tRecX code used in the reference [16] [18]. Thus, we will focus on the electron-protons interaction which was not talked about before and only list relevant discretization methods in this paper.

#### A. Discretization and basis functions

The 6D wavefunction $\psi$ is represented by the product of spherical harmonics for angular momentum and radial functions as

$$
\psi(\vec{r}_1, \vec{r}_2, t) = \psi(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2, t) = \sum_{m_1, l_1, m_2, l_2} Y_{l_1m_1}^{m_1}(\theta_1, \phi_1) Y_{l_2m_2}^{m_2}(\theta_2, \phi_2) R_{m_1, m_2, l_1, l_2}(r_1, r_2, t),
$$

where $Y_{l_1m_1}^{m_1}(\theta_1, \phi_1)$ and $Y_{l_2m_2}^{m_2}(\theta_2, \phi_2)$ are the spherical harmonics of the two electrons and the radial function is represented by the finite-element discretization variable representation (FE-DVR) method as

$$
R_{m_1, m_2, l_1, l_2}(r_1, r_2, t) = \sum_{n_1, n_2} R_{n_1n_2,m_1,m_2,l_1,l_2}(r_1, r_2, t) \frac{1}{r_1r_2}
$$

$$
\frac{n_1}{c_{n_1n_2,m_1,m_2,l_1,l_2}(t)}
$$

and

$$
\bar{R}_{n_1n_2,m_1,m_2,l_1,l_2}(r_1, r_2, t) = \sum_{p_1, p_2} f_{n_1}(r_1) f_{n_2}(r_2) \frac{1}{r_1r_2}
$$

$$
\frac{m_1}{c_{m_1m_2,l_1,l_2}(t)}
$$
where \( f_{p1/2}^{(n_{1/2})}(r_{1/2}) \) are \( p_{1/2} \)th basis functions on \( n_{1/2} \)th element, and the time-dependency of the three particles are included in the radial functions and coefficients \( c_{m_{1},m_{2},l_{1},l_{2}}^{n_{1},n_{2}}(t) \), as is used in Ref. [15] [16]. The infinite-range exterior complex scaling (irECS) method is utilized as an absorber [33]. The tSurf expression for computing spectra of such discretization can be found in Ref. [10].

**B. Electron-protons interaction**

The first part of electron-protons interaction can be written in a multi-pole expansion as

\[
\frac{1}{|r_{1} - r_{2}|} = \frac{1}{\sqrt{r_{1}^{2} + r_{2}^{2} - 2r_{1}r_{2}\cos \gamma}} = \frac{1}{r_{2} > \sqrt{1 + h^{2} - 2h\cos \gamma}} = \sum_{l=0}^{\infty} \frac{h^{l}}{r_{2} >} P_{l}(\cos \gamma),
\]

where \( r_{2} = \max(r_{1}, r_{2}), r_{2}^{\prime} = \min(r_{1}, r_{2}), h = \frac{r_{2}}{r_{2}^{\prime}}, \gamma \) is the angle between \( r_{1}^{\prime}, r_{2}^{\prime} \) and \( P_{l}(\cos \gamma) \) are Legendre polynomials. Similarly, we have

\[
\frac{1}{|r_{1} + r_{2}|} = \frac{1}{r_{2} > \sqrt{1 + h^{2} + 2h\cos \gamma}} = \sum_{l=0}^{\infty} \frac{(-1)^{l}}{r_{2} >} P_{l}(\cos \gamma).
\]

And the summation goes as

\[
\frac{1}{|r_{1} + r_{2}|} + \frac{1}{|r_{1} - r_{2}|} = 2 \sum_{l=0}^{\infty} \frac{h^{l}}{r_{2} >} P_{l}(\cos \gamma) \quad l\%2 = 0.
\]

With the Legendre polynomials expanded by spherical harmonics \( Y_{1}^{m}(\theta_{2}, \phi_{2}) \) and \( Y_{m}^{n*}(\theta_{1}, \phi_{1}) \), we have

\[
H_{EP} = 2 \sum_{l=0}^{\infty} \sum_{m_{1}, m_{2} = -l}^{l} \frac{(-1)^{l}}{r_{2} >} Y_{l}^{m}(\theta_{2}, \phi_{2}) Y_{m}^{n*}(\theta_{1}, \phi_{1})
\]

\[
l\%2 = 0.
\]

The matrix elements of electron-protons are

\[
\left\langle \psi_{m_{1}, m_{2}, l_{1}, l_{2}}^{n_{1}, n_{2}} \right| \frac{1}{|r_{1} - r_{2}|} \left| \psi_{m_{1}, m_{2}, l_{1}, l_{2}}^{n_{1}, n_{2}} \right\rangle = \frac{2}{2\lambda + 1} \sum_{l_{1}, l_{2}} \frac{4\pi}{\lambda \mu} \left( Y_{l_{1}}^{m_{1}} Y_{l_{2}}^{m_{2}} Y_{l_{1}}^{m_{1}} \right) \left( Y_{l_{2}}^{m_{2}} \right) Y_{m_{2}}^{n_{2}}
\]

\[
\left\langle R_{m_{1}, m_{2}, l_{1}, l_{2}}^{n_{1}, n_{2}} \right| \frac{r_{2}^{\lambda}}{r_{2}^{\lambda+1}} \left| R_{m_{1}, m_{2}, l_{1}, l_{2}}^{n_{1}, n_{2}} \right\rangle , \lambda \%2 = 0,
\]

which could be obtained by dropping the odd \( \lambda \) terms and doubling the even \( \lambda \) terms in the standard multi-pole expansion for electron electron interactions from Ref. [10] as

\[
\left\langle \psi_{m_{1}, m_{2}, l_{1}, l_{2}}^{n_{1}, n_{2}} \right| \frac{1}{|r_{1} - r_{2}|} \left| \psi_{m_{1}, m_{2}, l_{1}, l_{2}}^{n_{1}, n_{2}} \right\rangle = \sum_{l_{1}, l_{2}} \frac{4\pi}{\lambda \mu} \left( Y_{l_{1}}^{m_{1}} Y_{l_{2}}^{m_{2}} Y_{l_{1}}^{m_{1}} \right) \left( Y_{l_{2}}^{m_{2}} \right) Y_{m_{2}}^{n_{2}}
\]

\[
\left\langle R_{m_{1}, m_{2}, l_{1}, l_{2}}^{n_{1}, n_{2}} \right| \frac{r_{2}^{\lambda}}{r_{2}^{\lambda+1}} \left| R_{m_{1}, m_{2}, l_{1}, l_{2}}^{n_{1}, n_{2}} \right\rangle , \lambda \%2 = 0,
\]

Here

\[
\psi_{m_{1}, m_{2}, l_{1}, l_{2}}^{n_{1}, n_{2}} = Y_{l_{1}}^{m_{1}}(\theta_{1}, \phi_{1}) Y_{l_{2}}^{m_{2}}(\theta_{2}, \phi_{2}) R_{m_{1}, m_{2}, l_{1}, l_{2}}^{n_{1}, n_{2}}(r_{1}, r_{2}, t).
\]

Therein, the matrix for electron-protons interaction could be obtained by the numerical recipes used in Ref. [10] [34] with limited changes. Numerically, we find \( \lambda \) does not need to go to infinity and a maximum value of 8 already suffices our simulations.

**IV. NUMERICAL RESULTS**

A numerical convergence study shows, unlike the 6D double emission of He, where \( m_{1/2} = 0, \quad 0 \leq l_{1/2} \leq 2 \) already gives convergent ground eigenenergy [10], here the angular quantum number \( 0 \leq m_{1/2} \leq 2 \) and \( 0 \leq l_{1/2} \leq 8 \) starts to give convergent calculations, due to the lower symmetric property of the \( H_{2}^{+} \) ion. The \( R_{c}^{(+)}, R_{c}^{(-)} = 12.5 \) atomic units is chosen for computation, as we find \( R_{c}^{(-)} \) does not change the quality of the spectrum but introduces longer propagation time for low-energy particles to fly out. \( R_{c}^{(+)} = 12.5 \) atomic units gives the internuclear distance \( R = 25 \) as is used in Ref. [19]. The wavefunction is propagated long enough after the pulse for to include the unbound states low kinetic energies.

If the kinetic energy of protons is included, the field free ground energy value is \( E_{0} = -0.592 \) atomic units and the internuclear distance is 2.05 atomic units. With the kinetic energy of protons excluded, the ground eigenenergy is -0.597 atomic units, three digits exact to ground energy from quantum chemistry calculations in Ref. [35], where the internuclear distance is fixed. The internuclear distance is 1.997 atomic units, three digits exact to from the precise computations in Ref. [36].

**A. Laser pulses**

The dipole field of a laser pulse with peak intensity \( I = E_{0}^{2} / \omega \) (atomic units) and linear polarization in \( z \)-direction is defined as \( E_{z}(t) = \partial_{t}A_{z}(t) \) with

\[
A_{z}(t) = \frac{E_{0}}{\omega} a(t) \sin(\omega t + \phi_{CEP}).
\]

A pulse with \( \lambda = 400 \text{ nm} \) is given with intensities \( 8.3 \times 10^{13} \text{ W/cm}^{2} \) close to 2D computation in reference [19].
and $5.9 \times 10^{13} \text{ W/cm}^2$ close to experimental conditions in Ref. [12]. We choose $a(t) = [\cos(t/T)]^8$ as a realistic envelope. Pulse durations are specified as FWHM=5 opt. cyc. w.r.t. intensity.

### B. Joint energy spectra

The JES of the two dissociative protons and the electron is obtained by integrating Eq. (11) over angular coordinates as

$$
\sigma(E_N, E_e) = \int d\phi_1 \int d\phi_2 \int d\theta_1 \sin \theta_1 \int d\theta_2 \sin \theta_2 \left(4M \times E_N, \phi_2, \theta_2, \sqrt{2m \times E_e}\right),
$$

(29)

where $E_N, E_e$ are kinetic energies of two protons and an electron, respectively. $\sigma(E_N, E_e)$ is presented in Fig. 2(a, b). The tilt lines with formula $E_N + E_e = N\omega + E_0 - U_p$ with $U_p = \frac{A^2}{2m}$ specify the energy sharing of $N$ protons for both the computations from $8.3 \times 10^{13} \text{ W/cm}^2$ and $5.9 \times 10^{13} \text{ W/cm}^2$, indicating correlated emissions of the electron and protons, which is also observed in the 2D computations [14, 19]. The yields are intense around nuclear KER from 2 eV to 4 eV in the cos$^8$ envelope pulse, consistent with the experimental values reported in Ref. [12] [13]. The peak of JES for dissociative ionization is for lower nuclear KER than that (3-4 eV) of Coulomb explosion from ground eigenstate of the $H_2^+$ ion, which property is also close to experimental observables [37]. The Coulomb explosion JES is obtained with the same method as dissociative ionization except that $H_{EP}$ is removed from $B$ region Hamiltonian as $H_{\text{EP}}^{(CS)} = H^{(+)} + 1 + 1 \otimes H^{(-)}$, but the initial state is still obtained from Hamiltonian $H_B$ in Eq. (1). We find that the contribution from time-propagation in sub-region $D \rightarrow DI$ (see Eq. (13)) is small, as the numerical error of JES $\delta(\sigma)$ of $\sigma$ computed from $S \rightarrow DI$, and $\sigma'$ computed from two subregions $(S \rightarrow DI$ and $D \rightarrow DI)$, is always below 1% the main contribution of the JES ($2 < E_N < 4 \text{eV}$), see Fig. 2(d). This numerical property is also observed in two-dimensional (2D) simulations [19]. This is because the electrons are much faster than protons and the $H_2^+$ ion tends to release first.

One may find that the JES is most considerable around $2 \sim 4 \text{eV}$ nuclear KER, different from $\approx 0.5 \text{a.u.} > 10 \text{eV}$ obtained in the 2D simulations. The difference can also be observed from the Coulomb explosion computation shown in shown in Fig. 2(c). In experiments, the distribution of emitted protons peaks at nuclear KER=4 eV for a 780 nm laser pulse $6 \times 10^{14} \text{ W/cm}^2$ [11], Ref. [37] reported the Coulomb explosion peak is around 3eV nuclear KER for a 791 nm, $9.3 \times 10^{13} \text{ W/cm}^2$ laser pulse and Ref. [12, 13] reported the nuclear KER is most probable around 3 eV for two protons for 400 nm laser pulses. These observables at different experimental conditions show nuclear KERs are around $2 \sim 4 \text{eV}$, which are close to our computations but far from the computations in the 2D simulations [14, 19]. The deviation of the 2D simulation may arise from its limitations for obtaining the ground states of protons, because their rotational kinetic energy around the molecular center is not included, both for electrons and protons. The existing 2D simulations for the dissociative ionization put corrections to the electron-proton interaction with a smooth factor to give the correct ground energy of electrons $H_2^+$ [14, 19]. However, the pure Coulomb repulsion of the two protons 1/R (R is the internuclear distance) is included without a smooth factor. The ground eigenenergy from 2D simulation including the nuclear KER is -0.597 atomic units, identical to the quantum chemistry computations, where the nuclear KER is excluded. We would like to point out that, for the 2D simulation, for consistency of the correction of Coulomb interaction of the electron, the Coulomb repulsion term of the two protons may also need a smooth factor, which needs further investigations.
C. Angular distribution

The projected energy distribution on the azimuth angle of the electron and the protons is calculated by integrating the 6D scattering amplitudes as

\[
p_N(\theta_1, E_1) = \int d\vec{k}_1 \int d\phi_1 (|\vec{k}_1, \vec{k}_2, T)|^2, \tag{30}
\]

for protons, and

\[
p_e(\theta_2, E_2) = \int d\vec{k}_2 \int d\phi_2 (|\vec{k}_1, \vec{k}_2, T)|^2, \tag{31}
\]

for electron, where \(E_1\) and \(E_2\) are kinetic energies for an individual proton and electron.

As is observed in Fig. 3, the probability distributions of electron and protons reach the highest value in the polarization direction, which is consistent with the experimental observations for linearly polarized laser pulses \[11\] \[37\]. The probability of the dissociative protons is most considerable with \(1 \leq E_1 \leq 2\) eV, higher than the \(E_1 < 1\) eV for dissociative channels reported in Ref. \[11\] \[37\], but in the range of their Coulomb explosion channel, where the laser wavelength is 800 nm. For higher intensity \(8.3 \times 10^{13} \text{ W/cm}^2\), the angular distribution of released protons and electron extends more in the polarization direction. For distribution of protons, tiny yields around 3 eV in radial coordinates indicates the Coulomb explosion channel, close to what is observed in experiments, however, for different laser pulses \[37\].

V. CONCLUSION AND DISCUSSIONS

We simulate the dissociative ionization of the \(\text{H}_2^+\) ion in full dimensionality and obtain the ground energy same as the quantum chemistry methods. Using tSurff methods, we obtained the JES where energy sharing is observed, which indicates a correlation between proton and electrons. The JES peaked at \(E_N\) from 2 eV to 4 eV, which is different from the previous 2D simulations, but is consistent with the experimental data. The projected energy distribution on angles shows that the electron and protons tend to dissociate in the direction of polarization of the laser pulse.

The simulation of the single emission spectrum showing dissociation channels, is however not possible yet. The difficulty lies mainly in constructing the internuclear-distance-dependent electronic ansatz of \(H\) with a given ionic state in a single emission TDSE on \(r_1\), which might be solved by reading the energy surfaces from quantum chemistry calculations or another tRecX calculation. We leave work for future studies.

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Appendix A: Coordinate transformation

We use sub-indices "a", "b" and "e" represent the two protons and the electron of an arbitrary coordinate. The sub-indices "0", "1" and "2" represent the center of the two protons, the relative position of an proton to the center and the electron in our transformed coordinate, respectively. Suppose originally the coordinates of the two protons and electrons are represented by vectors \(\vec{x}_a, \vec{x}_b\) and \(\vec{x}_e\) of an arbitrary origin, respectively. The new co-
ordinates \( r_1^0 \) and \( r_2^0 \) satisfies

\[
\begin{align*}
    r_0^2 &= \frac{x_a^2 + x_b^2}{2} \\
    r_1^2 &= \frac{x_a^2 - x_b^2}{2} \\
    r_2^2 &= \frac{x_a^2 + x_b^2}{2},
\end{align*}
\]

(A1)

where \( r^0_0 \) is the coordinate of the center of the two protons. The Laplacian of the two protons \( \nabla_a^2, \nabla_b^2 \) and electron \( \nabla_e^2 \) are

\[
\begin{align*}
    \nabla_a^2 &= \frac{\nabla_1^2}{4} + \frac{\nabla_2^2}{4} + \frac{1}{4} \nabla_0 \cdot \nabla_1 - \frac{1}{2} \nabla_1 \cdot \nabla_2 - \frac{1}{2} \nabla_2 \cdot \nabla_0 \\
    \nabla_b^2 &= \frac{\nabla_0^2}{4} + \frac{\nabla_2^2}{4} + \frac{1}{4} \nabla_0 \cdot \nabla_1 + \frac{1}{2} \nabla_1 \cdot \nabla_2 - \frac{1}{2} \nabla_2 \cdot \nabla_0 \\
    \nabla_e^2 &= \nabla_2^2,
\end{align*}
\]

(A2)

Thus the kinetic energy of the system can be represented by

\[
\frac{1}{2} \left( \frac{\nabla_a^2}{M} + \frac{\nabla_b^2}{M} + \frac{\nabla_e^2}{1} \right)
\]

\[
= -\frac{\nabla_0^2}{4M} - \frac{\nabla_1^2}{4M} - \frac{\nabla_2^2}{4M} + \frac{\nabla_0 \cdot \nabla_1}{M} + \frac{\nabla_2 \cdot \nabla_0}{2}
\]

(A3)

where \( m = \frac{2M}{\Delta + 2M} \), and \( \approx \) means the motion of the \( r^0_0 \) is neglected. The interaction of the two protons with the laser pulse can be written as

\[
\frac{i}{M} \vec{A} \cdot (\nabla_a^0 + \nabla_b^0) = i \vec{A} \cdot (\nabla_0^2 - \nabla_2^2) \approx -\frac{i}{M} \vec{A} \cdot \nabla_2^2,
\]

(A4)

with which the total interaction with the laser field can be written as

\[
-\frac{i}{M} \vec{A} \cdot \left( \frac{1}{M} \nabla_2^2 \right) = -i \beta \vec{A} \cdot \nabla_2^2,
\]

(A5)

where \( \beta = \frac{M + 1}{M} \).

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