Dissociative ionization of $\text{H}_2^+$ using intense femtosecond XUV laser pulses

Lun Yue and Lars Bojer Madsen

Department of Physics and Astronomy,
Aarhus University, DK-8000 Aarhus C, Denmark

(Dated: October 9, 2014)

Abstract

The dissociative ionization of $\text{H}_2^+$ interacting with intense, femtosecond extreme-ultraviolet laser pulses is investigated theoretically. This is done by numerical propagation of the time-dependent Schrödinger equation for a colinear one-dimensional model of $\text{H}_2^+$, with electronic and nuclear motion treated exactly within the limitations of the model. The joint-energy spectra (JES) are extracted for the fragmented electron and nuclei by means of the t-SURFF method. The dynamic interference effect, which was first observed in one-electron atomic systems, is in the present work observed for $\text{H}_2^+$, emerging as interference patterns in the JES. The photoelectron spectrum and the nuclear energy spectrum is obtained by integration of the JES. Without the JES, the photoelectron spectrum itself is shown to be inadequate for the observation of the dynamic interference effect. The resulting JES are analyzed in terms of two models. In one model the wave function is expanded in terms of the "essential" states of the system, consisting of the ground state and the continuum states. In the second model the photoelectron spectra from fixed nuclei calculations are used to reproduce the JES using simple reflection arguments. The range of validity of these models is discussed and it is shown that the continuum-continuum couplings and the consideration of the population of excited vibrational states are crucial for understanding the structures of the JES.

PACS numbers: 33.20.Xx, 82.50.Kx, 33.80.Eh
I. INTRODUCTION

The rapid developments in laser technology have made it possible to produce extreme-ultraviolet (XUV) laser pulses in the femtosecond to sub-femtosecond time domains [1–3]. These new light sources have led to a range of novel attosecond time-resolved probing techniques, such as attosecond streaking spectroscopy [4, 5], time-resolved innershell spectroscopy [6], attosecond transient absorption spectroscopy [7] and attosecond interferometry [8]. Due to new focusing techniques, XUV pulses with very high peak intensities in the femtosecond time domain have been achieved [9, 10]. Projects such as the pan-European ELI [11] lead us to expect that even higher laser intensities will be realizable in the future.

There has recently been theoretical interest in the ionization of simple atomic systems using such intense XUV laser pulses [12–17]. Intensity modulations in the photoelectron spectra (PES) were observed and explained as follows. Due to the external field, the field-dressed ground state energy is shifted in time by the ac-Stark energy shift, which follows the laser field intensity envelope. There are two times during the pulse at which there is resonance conditions to the same continuum energy, once at the rising part and another at the falling part of the laser pulse [12, 14]. The two electronic wave packets ionized at the two different times pick up different phases during the duration of the pulse and interfere in the continuum, resulting in the interference structure observed in the PES. This ac-Stark shift induced effect is referred to as the dynamic interference [14].

Following the prediction of dynamic interference in atomic systems interacting with strong XUV laser pulses, it is natural to ask the question whether the same effect occurs in molecules. One work addressed this question by considering dissociative ionization of H$_2^+$ in a 1D model [18], where dynamic interference was reported to occur in the PES. In that work, the Born-Oppenheimer (BO) approximation was employed, and the wave function was expanded in terms of the BO electronic ground state and approximate continuum states represented by plane waves. Continuum-continuum couplings, which should play a role for the intense pulses considered, were neglected. In this work, we investigate dissociative ionization of H$_2^+$ by direct numerical propagation of the TDSE for a reduced dimensionality model of H$_2^+$, treating both the electronic and nuclear degrees of freedom exactly within the limitations of the reduced dimensions. We focus on the joint energy spectrum (JES), which provides the differential probability of measuring a given electronic and nuclear ki-
netic energy. For interaction with strong near-infrared light, the JES is known to contain much more physical information than the standard PES and nuclear energy spectrum (NES) [19–22]. The aim of the present work is to demonstrate that dynamic interference occurs in \( H_2^+ \), and that the JES is crucial for the detection of the effect. When the JES is integrated to obtain the PES and NES, the interference patterns will be severely or completely washed out, and important information will be lost.

Aside from the exact numerical propagation of the TDSE, we employ two models to analyze the JES. One model consists of making an ansatz for the wave function consisting of only the initial state and the final continuum states, making the BO approximation, the rotating-wave approximation (RWA) and neglecting continuum-continuum couplings. In the other model we construct the JES from fixed nuclei TDSE calculations by applying simple reflection arguments. Both models fail to work for certain laser parameters, and the range of applicability and the reasons for the failure will be discussed.

Obtaining spectra from numerical simulations is a challenge. Standard methods of obtaining PES from numerical calculations include the projection on plane waves [16, 23], the projection on scattering states [19, 24], and the usage of flux methods [25–28]. In the first method, huge simulation volumes are required, as it must be ensured that after the end of the pulse, the scattered parts of the wave packet are well-separated from its bound part and not reflected from the box boundaries. In the second method, the simulation volume can be reduced somewhat compared to the first method due to the orthogonality between the scattering and bound states, and the projection can be performed immediately at the end of the pulse. However, the construction of scattering states is tedious and constitutes a numerical challenge in itself. For the flux methods, absorbers are placed at the boundaries of the simulation volume to remove the outgoing flux, and spectra are obtained by monitoring the flux going through surfaces placed at distances smaller than the absorber regions. In this way the simulation volume can be reduced significantly. We calculate the JES of \( H_2^+ \) by employing a flux method, the time-dependent surface flux (t-SURFF) method [22] (see Refs. [28–31] for application to single atoms), which reduces the numerical effort significantly compared to other methods [19, 20].

The paper is organized as follows. In Sec. II, the reduced-dimensionality model for \( H_2^+ \) is described, and the extraction of JES using the t-SURFF method is outlined. In Sec. III, exact numerical results for the dissociative ionization of \( H_2^+ \) are presented for different pulse
parameters. In Sec. IV, the JES is analyzed in terms of two models. Section V concludes
the work. Atomic units are used throughout, unless indicated otherwise.

II. THEORY

A. Model for H$_2^+$

We consider a simplified model for H$_2^+$ with reduced dimensionality that includes only
the dimension that is aligned with a linearly polarized laser pulse [32–34]. Within this model,
electronic and nuclear degrees of freedom are treated exactly. The center-of-mass motion of
the molecule can be separated, such that the TDSE for the relative motion in the dipole
approximation and velocity gauge reads

$$i\partial_t |\Psi(t)\rangle = H(t) |\Psi(t)\rangle$$

(1)

with the Hamiltonian

$$H(t) = T_e + T_N + V_{eN} + V_N + V_I(t),$$

(2)

where $|\Psi(t)\rangle$ in coordinate space depends on the internuclear distance $R$ and the electronic
coordinate $x$ measured with respect to the center-of-mass of the nuclei. The components of
the Hamiltonian in Eq. (2) are $T_e = -(1/2\mu)\partial^2/\partial x^2$, $T_N = -(1/m_p)\partial^2/\partial R^2$, $V_{eN}(x,R) =
-1/\sqrt{(x - R/2)^2 + a(R)} - 1/\sqrt{(x + R/2)^2 + a(R)}$, $V_N(R) = 1/R$ and $V_I(t) = -i\beta A(t)\partial/\partial x$,
where $m_p = 1.836 \times 10^3$ a.u. is the proton mass, $\mu = 2m_p/(2m_p + 1)$ is the reduced electron
mass, $\beta = (m_p + 1)/m_p$, and the softening parameter $a(R)$ for the Coulomb singularity is
chosen to produce the exact three-dimensional 1$s\sigma_g$ BO potential energy curve [19, 22].

We use vector potentials of the form

$$A(t) = A_0 g(t) \cos(\omega t),$$

(3)

where $\omega$ is the carrier angular frequency and $A_0$ is the amplitude chosen such that $\omega^2 A_0^2 = I$,
with $I$ the intensity. The field envelope is taken to be of Gaussian form

$$g(t) = \exp \left( -4 \ln 2 \frac{t^2}{\tau^2} \right)$$

(4)

where $\tau$ is the full width half maximum of the field envelope.
Equation (1) is solved exactly on a two-dimensional spatial grid using the split-operator, fast fourier transform (FFT) method [35], with a time-step of $\Delta t = 0.005$ in the time-propagation. The grid size is defined by $|x| \leq 200$ and $R \leq 60$, with grid spacings $\Delta x = 0.391$ and $\Delta R = 0.059$. These parameters ensured converged results.

B. Extraction of JES

The JES gives the differential probability for observing a nuclear kinetic energy of $E_N = \frac{k^2}{m_p}$ and an electron with kinetic energy $E_e = \frac{p^2}{2\mu}$, and can be calculated using the expression

$$\frac{\partial^2 P}{\partial E_e \partial E_N} = \sum_{\text{sgn}(p)} \frac{m_p\mu}{2|p|k} |b_{p,k}(T)|^2,$$

(5)

where the summation over sgn($p$) refers to the summation of $\pm p$ corresponding to the same $E_e$, and $T$ is a sufficient large time after the end of the laser pulse when the flux corresponding to dissociative ionization has moved into the asymptotic regions. As the Gaussian pulses used have asymptotic tails that extend to infinity, we take $T$ to be the smallest time at which the JES has converged numerically. The JES is obtained from the TDSE calculations by using the molecular t-SURFF method described in Ref. [22]. In this method, the coordinate space is partitioned into spatial regions corresponding to different reaction channels. The amplitudes $b_{p,k}(T)$ in Eq. (5) are written as

$$b_{p,k}(T) = \langle \phi_p(T)\chi_k(T)|\Psi_{DI}(T)\rangle,$$

(6)

where $\phi_p(x,T)$ and $\chi_k(R,T)$ are plane waves for the electron and nuclei, respectively, and $\Psi_{DI}(x,R,T)$ is the wave packet corresponding to dissociative ionization at large $x$ and $R$. We denote the positions of the electronic and nuclear boundaries of the spatial region corresponding to dissociative ionization as $x_s$ and $R_s$, respectively. Equation (6) is then evaluated by the method of Ref. [22], where the amplitudes $b_{p,k}(T)$ are rewritten into time-integrals over the flux going through surfaces placed at $x = x_s$ and $R = R_s$. Evaluation of the time integrals require the usage of Volkov waves instead of the plane waves $\phi_p(x,T)$. In the present calculations we choose $x_s = 100$, $R_s = 20$ and $T = 4\tau + 800$.

The t-SURFF method allows the use of absorbers to remove the outgoing flux, avoiding unphysical reflections at the boundaries of the simulation volume and thus severely reducing
the size of the simulation volume. We make use of complex absorbing potentials (CAPs) with the form [36]

\[ V_{\text{CAP}}(r) = \begin{cases} 
- \imath \eta (|r| - r_{\text{CAP}})^n, & |r| \geq r_{\text{CAP}} \\
0, & \text{elsewhere,} \end{cases} \]  

(7)

with \( r \) being either the electronic coordinate \( x \) or the nuclear coordinate \( R \). We choose \( \eta_e = 0.001, x_{\text{CAP}} = 110 \) and \( n_e = 2 \) for the electronic CAP, and \( \eta_N = 0.001, R_{\text{CAP}} = 25 \) and \( n_N = 2 \) for the nuclear CAP.

### III. NUMERICAL RESULTS

In order to investigate the JES, we first prepare \( \text{H}_2^+ \) in its ground state \( |\Psi_0\rangle \), obtained by imaginary propagation of Eq. (1). The ground state energy is found to be \( E_0 = -0.597 \). Convergence of all results are checked with respect to different box parameters, CAP parameters and placement of t-SURFF surfaces. The carrier frequency of the laser pulse is chosen as \( \omega = 2.278 \), allowing for dissociative ionization by one-photon absorption, and the intensities are in the range from \( I = 3 \times 10^{17} \text{ W/cm}^2 \) to \( I = 24 \times 10^{17} \text{ W/cm}^2 \). In this work, we are specifically interested in the first JES peak corresponding to one-photon absorption, located close along the diagonal line \( E_N + E_e \approx E_0 + \omega \) in the JES [see Fig. 1]. Note that although the pulses considered in this work are ultra-intense, we are still in the non-relativistic regime. Indeed, if the cycle-averaged quiver energy of a free electron (the ponderomotive energy) \( U_p = A_0^2 / 4 \) is much less than its rest energy \( m_e c^2 = 137^2 \), we are in the non-relativistic regime [37–39]. This condition is certainly satisfied here, as even for the most intense pulse \( I = 24 \times 10^{17} \text{ W/cm}^2 \) the ponderomotive energy is only \( U_p \approx 3.29 \).

Figure 1 shows the JES, NES and PES for dissociative ionization of \( \text{H}_2^+ \) for laser pulses with \( \tau = 1.1 \text{ fs} \) and two different intensities. In the JES panels, we define the Stark energy shift \( \Delta \) of the ground state \( |\Psi_0\rangle \) to be the shift at the field maximum, \( t = 0 \), [see Eqs. (3) and (4)]

\[ \Delta = \dot{\phi}(0) - E_0, \]  

(8)

where \( \phi(t) \) is the phase of the ground state amplitude \( \langle \Psi_0 | \Psi(t) \rangle \approx | \langle \Psi_0 | \Psi(t) \rangle | e^{-\imath \phi(t)} \), which is directly extracted from the TDSE calculations [15]. In the side subpanels of Fig. 1, the NES from the TDSE calculations and the reflection principle are shown. The reflection principle [40–42] amounts to the approximation where the electron is emitted into the continuum.
FIG. 1. (Color online). Spectra of H$_2^+$ exposed to pulses with $\omega = 2.278$, $\tau = 1.1$ fs and two different intensities $I$. Main panels show the JES [Eq. (5)]. The two dashed diagonal lines indicate the energy conservations $E_e + E_N = E_0 + \omega$ and $E_e + E'_N = E_0 + \omega + \Delta$, respectively, with $\Delta$ the Stark shift [Eq. (8)]. In the upper subpanels, thick, black curves show the PES obtained by integration of the JES, while the thin, grey curves show the PES for nuclei fixed at the equilibrium distance $R_0 = 2.06$. The fixed nuclei PES are scaled for better comparability with the moving nuclei PES. The dashed grey vertical lines show the energy conservations and Stark shifted energies for the fixed nuclei calculations. In the side subpanels, thick, black curves show the NES obtained by integration of the JES, while the thin, grey curves show the scaled reflection principle results [Eq. (9)]. The horizontal dashed grey lines indicate the position $E_N = 1/R_0$.

by the laser at the internuclear distance $R$, leaving behind two bare protons that Coulomb explode, gaining the kinetic energy $E_N = 1/R$. The NES is then obtained by reflecting the probability density of the initial vibrational state $\chi_0(R)$, and weighting with $-dR/dE_N = 1/E_N^2$:

$$\frac{dP}{dE_N} \propto \left| \chi_0(1/E_N) \right|^2.$$  \hspace{1cm} (9)
In the upper subpanels of Fig. 1, the PES are shown for the moving nuclei and fixed nuclei TDSE calculations. For the fixed nuclei calculations, we fix the internuclear distance at the equilibrium $R_0 \equiv \langle \Psi_0 | R | \Psi_0 \rangle = 2.06$.

For the intensity $I = 3 \times 10^{17}$ W/cm$^2$ in Fig. 1(a), the JES displays a single peak centered at $(E_e, E_N) = (1.23, 0.46)$, with a region of zero density along the line $E_N = 0.6$ (perhaps more discernible in the NES). In the NES panel, the result for the reflection approximation peaks at $E_N = 1/R_0 = 0.484$, a clear shift with respect to the correct NES peak located at 0.455. Furthermore, the minima at $E_N = 0.6$ is absent in the reflection principle result. This is to be expected, as the reflection principle is a crude approximation, and can only be used for qualitative analysis. In the PES panel, there is a shift of the peak of the fixed nuclei result compared to the moving nuclei result. This shift is due to the fact that the fixed nuclei result does not take into account the probability density of the initial vibrational state $|\chi_0(1/E_N)|^2$.

For the more intense pulse in Fig. 1(b), additional structures appear in the JES and the Stark shift is larger as indicated by the dashed energy conservation lines in the JES. At least four peaks are now clearly visible in the JES, with the largest one centered at $(E_e, E_N) = (1.28, 0.44)$. The three most visible peaks are more or less along energy conservation lines $E_e + E_N = 1.62, 1.72, 1.85$ (lines not drawn in Fig. 1(b)). In the NES, the TDSE result is shifted towards lower $E_N$, with the magnitude of the shift similar to the case for the lower laser intensity in Fig. 1(a). In the PES for moving nuclei, only two peaks are visible, with the highest energy peak in the JES being weighted out from the integration of the JES. We therefore stress the importance of the JES: if only the PES and the NES were at our disposal, no information on the third peak in the JES could be obtained. This extends the conclusion of Refs. [19–21] to the XUV regime that the JES is a very useful observable.

It should be noted that in Ref. [16], it was suggested that the combination of using small simulation volumes and CAPs placed at the box boundaries would make it impossible to produce the dynamic interference in the PES, and enormously large simulation volumes (radial coordinate up to $r_{\text{max}} = 10000$) were used in their calculations to obtain the PES for hydrogen. However, as shown in Fig. 1(b), it is indeed possible to observe interference effects in the JES and PES by using t-SURFF in a small simulation volume $|x| \leq 200$.

Figure 2 shows the JES for longer laser pulses $\tau = 5.6$ fs, 11.1 fs, with intensity $I = 15 \times 10^{17}$ W/cm$^2$. The increase of the pulse duration has several effects on the JES. Firstly,
due to the smaller bandwidth of the laser pulse, the JES in Fig. 2 are now narrower compared to the results for the shorter pulses in Fig. 1. Secondly, the increase of pulse duration from 5.6 fs in Fig. 2(a) to 11.1 fs in Fig. 2(b) leads to more interference peaks emerging, similar to the case of dynamic interference in hydrogen [14–17], but now visible along the diagonal in the JES. In addition, the JES and NES for the 5.6 fs pulse in Fig. 2(a) are shifted toward smaller $E_N$ values compared to the shorter pulses used in Fig. 1, with the peak now located around $E_N = 0.4$ in the NES. For the 11.1 fs pulse in Fig. 2(b), a peak is observed around $E_N = 0.36$ in the NES, while a "shoulder" structure is seen around $E_N = 0.42$. When we compare the PES results for moving nuclei to the corresponding fixed nuclei results in Fig. 2, the PES for moving nuclei has its dynamic interference peaks completely smeared out, with no interference patterns visible. Furthermore, the PES for moving nuclei in Fig. 2(b) peaks at $E_e = 1.31$, a clear shift with respect to the fixed nuclei peaks around $E_e = 1.21$. Thus, due to the inclusion of nuclear motion, the fixed nuclei results for the PES are completely

FIG. 2. (Color online). As Fig. 1, but for pulses with parameters $\omega = 2.278$, $I = 15 \times 10^{17}$ W/cm$^2$ and two different pulse durations.
wrong. This again stresses the importance of using the JES for the detection of dynamic interference in molecules.

IV. ANALYSIS OF THE JES

We will now analyze the structures in the spectra of Figs. 1 and 2, using two methods.

A. Essential states expansion

In the first analysis we follow Ref. [14] and extend it to the molecular case of $H_2^+$ by including nuclear motion. The molecule-laser interaction is now chosen in the length gauge, where the interaction potential in Eq. (2) is given by $V_{1}^{\text{LG}} = \beta_{\text{LG}} x F(t)$, with $\beta_{\text{LG}} = 1 + 1/(2m_p + 1)$. The electric field is chosen on the form $F(t) = F_0 g(t) \cos(\omega t)$, with $g(t)$ given by Eq. (4) and $F_0 = \omega A_0$. For the many-cycle pulses considered in this work, the carrier-envelope phase difference between the fields in the length and velocity gauges is unimportant for the resulting spectrum [43]. We also verified this in fixed nuclei TDSE calculations where we checked that the usage of length and velocity gauge Hamiltonians produce identical spectra.

The wave function is first expanded in terms of the "essential" states consisting of the initial state and the continuum eigenstates of the field-free Hamiltonian

$$|\Psi(t)\rangle = c_0(t)|\Psi_0\rangle + \sum_P \int dE_e \int dE_N c_{E_e,E_N}^P(t)|u_{E_e,E_N}^P\rangle e^{-i\omega t}, \quad (10)$$

where $|u_{E_e,E_N}^P\rangle$ is a field-free continuum state of $H_2^+$ with parity $P$ ("e" for even, "o" for odd), electronic continuum energy $E_e$ and nuclear continuum energy $E_N$. The latter states are obtained in the BO approximation by the method outlined in the Appendix. Inserting Eq. (10) into the TDSE (1) and projecting onto the "essential" states, we arrive at the coupled differential equations:

$$i\dot{c}_0(t) = E_0 c_0(t) + \int dE_e \int dE_N \left[ \frac{1}{2} d_{E_e,E_N}^{\text{res}} F_0 \right] g(t) c_{E_e,E_N}^0(t) \quad (11a)$$

$$i\dot{c}_{E_e,E_N}^P(t) = \left[ \frac{1}{2} d_{E_e,E_N}^P F_0 \right] g(t) c_0(t) + (E_e + E_N - \omega) c_{E_e,E_N}^P(t), \quad (11b)$$

where $d_{E_e,E_N}^P = \langle u_{E_e,E_N}^P | x | \Psi_0 \rangle$ is the transition dipole matrix element. In obtaining Eq. (11), we have used the RWA and the fact that the initial state $|\Psi_0\rangle$ has even parity.
we have neglected the continuum-continuum couplings. The solution to Eq. (11b) is given by

$$c_{E_e,E_N}(t) = -i \left[ \frac{1}{2} d_{E_e,E_N}^0 F_0 \right] e^{-i\delta t} \int_{-\infty}^{t} c_0(t') g(t') e^{i\delta t'} dt',$$

(12)

where $\delta = E_e + E_N - \omega$. The JES is then

$$\frac{\partial^2 P}{\partial E_e \partial E_N} = \left| c_{E_e,E_N}(T) \right|^2$$

(13)

with $T \gg \tau$.

We see from Eqs. (12) and (13) that in the present model, the structure of $\left| d_{E_e,E_N}^0 \right|^2$ will determine the structure of the JES. The former is plotted in Fig. 3. The highest-density region is located along $E_N = 0.45$, immediately explaining the peaks in the JES and NES of Fig. 1(a). Furthermore, a valley of zero density is seen in Fig. 3, explaining the minima in Fig. 1(a) located around $(E_e, E_N) = (1.1, 0.6)$ in the JES. However, Fig. 3 does not explain the structures in Fig. 1(b), where the peak in the NES is still at $E_N = 0.45$, but instead of a minimum at $E_N = 0.60$, there is now a local maximum. As will be explained later, this is due to the continuum-continuum couplings that are neglected in the present model.

To calculate the JES using Eq. (13), we need to solve the coupled differential equations in Eq. (11). However, a closed form for the continuum amplitudes in $c_{E_e,E_N}^0(t)$ in Eq. (12) can be obtained if we approximate the ground state amplitude $c_0(t)$ as [14]

$$c_0(t) = e^{-iE_0 t - (i\Delta + \Gamma/2) J(t)},$$

(14)

where $\Delta$ is the Stark shift, $\Gamma$ the ionization rate, and $J(t) = \int_{-\infty}^{t} g(t')^2 dt'$. Note that for $\Delta = \Gamma = 0$, Eq. (12) reduces to the result of first-order time-dependent pertubation theory
for the amplitudes $c_{E_e,E_N}(t)$. As noted in Ref. [15], $\Delta$ is difficult to calculate and also depends on the "non-essential" states which were omitted in the present model. We therefore follow the procedure of Ref. [15] and extract $\Delta$ from the TDSE calculations employing Eq. (8) and use them in Eq. (14). The rate $\Gamma$ is calculated by noting that $c_0(t')g(t')$ in Eq. (12) varies slowly compared to the rest of the integrand, and can be taken out of the integral and evaluated at time $t$. This approximation will be referred to as the local approximation. By evaluating Eq. (12), plugging the result into Eq. (11a) and solving the resulting uncoupled differential equation, we get $c_0(t)$ on the form of Eq. (14), with $\Gamma$ given by

$$
\Gamma = 2\pi \int dE_e \int dE_N \left| \frac{dE_e E_N F_0}{2} \right|^2 \delta \left( E_0 + \omega - E_e - E_N \right).
$$

Note that Eq. (15) can also be obtained using Fermi’s golden rule. Compared with the previous work on atoms [14], $\Gamma$ now contains an extra integral over the nuclear kinetic energy, with the energies related by $E_N = E_0 + \omega - E_e$. For the laser pulse used in Fig. 1(a), the survival probability of the ground state in the present model is

$$
P_0^{\text{model}}(\infty) = |c_0(\infty)|^2 = e^{-\Gamma J(\infty)} = 0.978,
$$

which is comparable to the TDSE result $P_0^{\text{TDSE}} = 0.975$. This demonstrates that the approximation (15) is not too bad, at least for the intensity used in Fig. 1(a).

Now that we have an approximation to $c_0(t)$, we may insert it into Eq. (12) and calculate the JES from Eq. (13). Figure 4 shows PES and NES calculated from the JES [Eq. (13)], for four different intensities. For the lowest intensity $I = 10^{17}$ W/cm$^2$ in Figs. 4(a) and 4(b), the result matches that obtained from the exact TDSE calculation. For $I = 3 \times 10^{17}$ W/cm$^2$ in Figs. 4(c) and 4(d), the shapes of the spectra in the "essential" model are still similar to the TDSE results, albeit with difference in amplitudes. For the higher intensities in Figs. 4(e)-(h), there are qualitative differences, with more peaks emerging in the PES of the TDSE calculations compared to the essential model calculations. Such differences were also observed in the atomic case [16].

We now discuss the two main deficiencies in the present model that contribute to its failure at high intensities $I \gtrsim 3 \times 10^{17}$ W/cm$^2$. The first one is the neglect of the excited vibrational levels in the expansion of Eq. (10), which could have been populated during the pulse by impulsive Raman-type transitions from the ground vibrational state. However, as shown in Figs. 5(a)-5(b), for the short pulse with $\tau = 1.1$ fs, the excited vibrational populations...
FIG. 4. (Color online). Electronic (left panels) and nuclear (right panels) spectra from integration over the JES. The solid, black curves are the TDSE results and correspond to JES calculated from Eq. (5), while the dotted, orange curves correspond to the approximate JES evaluated using Eq. (13). Laser parameters are $\omega = 2.278$, $\tau = 1.1$ fs, and from top to bottom: $I = 10^{17}$ W/cm$^2$, $3 \times 10^{17}$ W/cm$^2$, $10 \times 10^{17}$ W/cm$^2$ and $24 \times 10^{17}$ W/cm$^2$.

where small compared to the ground state populations. For the most intense pulse with $I = 24 \times 10^{17}$ W/cm$^2$, the population of the excited vibrational states were about a third of the ground state population at the end of the pulse. We therefore expect that ionization from the ground state dominates the contribution to the JES. The second deficiency in the present model is the neglect of continuum-continuum couplings. As we have ruled out the population of excited states as the failure of the present model, we conclude that the primary reason for the failure of the model is due to the neglect of continuum-continuum couplings. The ponderomotive energy of the most intense pulse used is $U_p = 3.29$, larger than the photon energy $\omega = 2.278$. This indicates that multiphoton processes at these intensities cannot be neglected.

For the longer pulses used in Fig. 2, the pulse energy of the laser is much larger, meaning that much stronger Raman couplings and thus much greater population of excited vibrational states is observed, see Figs. 5(c) and 5(d). The present model will therefore fail for these laser pulses due to both the continuum-continuum couplings and the excited vibrational states. This is easily seen by comparing the transition dipole matrix element in Fig. 3 with
the JES in Fig. 2, e.g., by noticing that there is no peak at $E_N = 0.45$ in Fig. 2.

B. Reflection method for the JES

In situations where ionization from the initial state is dominant, the JES can be approximated by weighting the fixed nuclei results with the initial vibrational density:

$$\frac{\partial^2 P}{\partial E_e \partial E_N} \propto \frac{|\chi_0(1/E_N)|^2}{E_N^2} \frac{dP}{dE_e}(1/E_N),$$

(17)

where $dP/dE_e(R)$ is the PES calculated at the fixed internuclear distance $R$. We refer to this model as the reflection method for the JES. The JES calculated using Eq. (17) for the field parameters in Fig. 1(b) are shown in Fig. 6. There is indeed a good qualitative match, with all structures in the JES of Fig. 1(b) accounted for in Fig. 6. The reason for this is simple: all of the electron-laser couplings are included in $dP/dE_e(R)$ of Eq. (17), while there are minimal populations of higher excited vibrational states (see Fig. 5).

For the longer pulses considered in Fig. 2 there is significant vibrational excitation during the pulse, as shown in Figs. 5(c) and 5(d), and the approximation leading to Eq. (17) is not valid. This is indeed verified by comparing Fig. 7 with Fig. 2(a), where in Fig. 2(a) the JES is shifted towards lower $E_N$. Notice that we have solved the TDSE exactly at fixed internuclear distances in the present approximation, meaning that the electronic continuum-
FIG. 6. (Color online). JES calculated using Eq. (17) for the same laser parameters as in Fig. 1(b), \( \omega = 2.278 \), \( \tau = 1.1 \) fs and \( I = 24 \times 10^{17} \) W/cm\(^2\).

FIG. 7. (Color online). JES calculated using Eq. (17) for the same laser parameters as in Fig. 1(a), \( \omega = 2.278 \), \( \tau = 5.6 \) fs and \( I = 15 \times 10^{17} \) W/cm\(^2\).

The shift towards lower nuclear energies in the JES of Fig. 2 compared to Fig. 1 is due to the excited vibrational populations, which can be shown qualitatively using the simple reflection principle (9). In Fig. 8, results of Eq. (9) for the lowest four vibrational states are plotted. For the \( \tau = 5.6 \) fs pulse in Fig. 2(a), the most populated vibrational state at the end of the pulse is \( \nu = 1 \). In Fig. 8, reflection result for \( \nu = 1 \) has the large peak at \( E_N = 0.408 \), thus explaining the peak in the NES of Fig. 2(a) at around \( E_N = 0.408 \). Similarly, for the

continuum couplings neglected in the "essential states" model from Sec. IV A are included here.
\( \tau = 11.1 \, \text{fs} \) pulse in Fig. 2(b), the most populated vibrational state is \( \nu = 2 \), which in Fig. 8 has the largest peak located at \( E_N = 0.366 \), explaining the the peak in the NES of Fig. 2(b) at around \( E_N = 0.36 \). The shoulder structure in the NES of Fig. 2(b) at around \( E_N = 0.42 \) can be interpreted as resulting from the \( \nu = 1 \) state.

V. CONCLUSION

We investigated dissociative ionization of \( \text{H}_2^+ \) using intense, femtosecond XUV laser pulses by propagating the TDSE for a colinear model of \( \text{H}_2^+ \). The molecular t-SURFF method [22] was employed to obtain the JES and was shown to work well in the present high-frequency, high intensity regime. Using this method, we were able to severely reduce the simulation volume and thereby the computational effort. The dynamic interference effect, which was first observed in theoretical calculations for simple atomic systems [12, 14], was shown to be present in the case of \( \text{H}_2^+ \) as well, emerging as interference structures along the diagonal in the JES. The PES and NES were shown to be inadequate for the observation of the dynamic interference effect in \( \text{H}_2^+ \). For the longer pulses (11.1 fs) used, a clear shift of the NES and JES toward lower nuclear kinetic energies was observed.

We analyzed the resulting JES in terms of two different models. In the first model, we expanded the wave function in terms of the “essential” states of the system, consisting of the ground state and the continuum states. In the RWA and local approximation, and neglecting
the continuum-continuum couplings, the expression for the JES was expressed in terms of the Stark shift and the ionization rate. Following [15], the Stark shift was extracted from TDSE calculations to take into account effects of the ”non-essential” states. The model was shown to work for the shorter pulses with $\tau = 1.1$ fs and intensities $I \leq 3 \times 10^{17}$ W/cm$^2$, while failing at higher intensities and longer pulse durations. The failure of the model was attributed to the neglect of continuum-continuum couplings and neglect of excited vibrational states that were populated during the pulse.

In the second model, we calculated the PES of H$_2^+$ at fixed internuclear distances and obtained the JES from simple reflection arguments. Although this model included all the electronic continuum-continuum couplings, and was able to produce the correct JES for the short pulses used, it was unable to produce the correct JES for the longer pulses, due to the involvement of higher vibrational states excited during the pulse. However, by using the reflection principle on the excited nuclear vibrational states, we could qualitatively explain the shift of the JES towards lower nuclear kinetic energies.

ACKNOWLEDGMENTS

We thank J. Svensmark and J. E. Bækhøj for a careful reading of the manuscript. This work was supported by the Danish Center for Scientific Computing, an ERC-StG (Project No. 277767 - TDMET), and the VKR center of excellence, QUSCOPE.

Appendix: Field-free continuum eigenstates

In this Appendix, we describe the method used for obtaining the field-free continuum states of H$_2^+$ in the BO approximation.

The time-independent Schrödinger equation reads

$$[T_e + T_N + V_{eN}(x, R) + V_N(R)] u(x, R) = Eu(x, R).$$  \hspace{1cm} (A.1)

The continuum states $u(x, R)$ of Eq. (A.1) depend on the electronic energies $E_e$, the nuclear energies $E_N$, and the parity $P$. We make in Eq. (A.1) the ansatz

$$u_{E_eE_N}^P(x, R) = \xi_{E_e}^P(x; R) \chi_{EN}(R),$$  \hspace{1cm} (A.2)
and by neglecting the action of $T_N$ on $\xi_{E_e}^P (x, R)$ (BO approximation), the electronic and nuclear degrees of freedom decouple, resulting in the equations

$$
[T_e + V_{eN}(x, R)]\xi_{E_e}^P (x; R) = E_e\xi_{E_e}^P (x; R) \quad (A.3)
$$

$$
[T_N + V_N(R)]\chi_{E_N} (R) = E_N\chi_{E_N} (R) , \quad (A.4)
$$

with $E = E_e + E_N$. For a given $E_e$, Eq. (A.3) is solved for each internuclear distance $R$ to obtain $\xi_{E_e}^P (x; R)$. These approximate continuum solutions were used successfully in Ref. [19].

We find the solutions to Eq. (A.3) numerically as follows. Starting near the origin, we impose the parity conditions $\xi_{E_e}^P (-\delta x; R) = (-1)^P \xi_{E_e}^P (\delta x; R)$, with $\delta x$ being the integration step size. We then apply the Numerov algorithm to numerically integrate Eq. (A.3) outwards. The potential satisfies

$$
V_{eN}(x, R) \rightarrow -\frac{2}{|x|}, \quad \text{for } |x| \gg R/2, \quad (A.5)
$$

which implies that the energy-normalized continuum solution has the asymptotic behaviour

$$
\xi_{E_e}^P (x; R) \rightarrow \sqrt{\frac{\mu}{\pi p}} \left[ F_{E_e}(x; R, \alpha_0) \cos(\delta_P) + G_{E_e}(x; R, \alpha_0) \sin(\delta_P) \right], \quad (A.6)
$$

where $p = \sqrt{2\mu E_e}$, $\delta_P$ is the phaseshift, $F_{E_e}(x; R, \alpha_0)$ and $G_{E_e}(x; R, \alpha_0)$ are the regular and irregular Coulomb functions, respectively. The latter functions were obtained using the GNU Scientific Library. By matching our numerical solutions to the asymptotic form in Eq. (A.6), we can obtain the energy delta-normalized states satisfying $\langle \xi_{E_e}^P (R) | \xi_{E_e'}^P (R) \rangle = \delta (E_e - E_e')$.

[1] G. Sansone, L. Poletto, and M. Nisoli, Nat. Photonics 5, 655 (2011).
[2] W. Ackermann, G. Asova, V. Ayvazyan, A. Azima, N. Baboi, J. Bähr, V. Balandin, B. Beutner, A. Brandt, A. Bolzmann, R. Brinkmann, O. I. Brovko, M. Castellano, P. Castro, L. Catani, E. Chiadroni, S. Choroba, A. Cianchi, J. T. Costello, D. Cubaynes, et al., Nature Photonics 1, 336 (2007).
[3] B. W. J. McNeil and N. R. Thompson, Nat. Photonics 4, 814 (2010).
[4] R. Kienberger, M. Hentschel, M. Uiberacker, Ch. Spielmann, M. Kitzler, A. Scrinzi, M. Wieland, Th. Westerwalbesloh, U. Kleineberg, U. Heinzmann, M. Drescher, and F. Krausz, Science 297, 1144 (2002).
[5] M. Schultze, M. Fieß, N. Karpowicz, J. Gagnon, M. Korbman, M. Hofstetter, S. Neppl, A. L. Cavalieri, Y. Komninos, Th. Mercouris, C. A. Nicolaides, R. Pazourek, S. Nagele, J. Feist, J. Burgdörfer, A. M. Azzeer, R. Ermstorfer, R. Kienberger, U. Kleineberg, E. Goulielmakis, F. Krausz, and V. S. Yakovlev, Science 328, 1658 (2010).

[6] M. Drescher, M. Hentschel, R. Kienberger, M. Uiberacker, V. Yakovlev, A. Scrinzi, Th. Westerwalbesloh, U. Kleineberg, U. Heinzmann, and F. Krausz, Nature 419, 803 (2002).

[7] H. Wang, M. Chini, S. Chen, C.-H. Zhang, F. He, Y. Cheng, Y. Wu, U. Thumm, and Z. Chang, Phys. Rev. Lett. 105, 143002 (2010).

[8] T. Remetter, P. Johnsson, J. Mauritsson, K. Varjú, Y. Ni, F. Lépine, E. Gustafsson, M. Kling, J. Khan, R. López-Martens, K. J. Schafer, M. J. J. Vrakking, and A. L’Huillier, Nature Phys. 2, 323 (2006).

[9] H. Mashiko, A. Suda, and K. Midorikawa, Opt. Lett. 29, 1927 (2004).

[10] A. A. Sorokin, S. V. Bobashev, T. Feigl, K. Tiedtke, H. Wabnitz, and M. Richter, Phys. Rev. Lett. 99, 213002 (2007).

[11] http://www.eli-laser.eu.

[12] K. Toyota, O. I. Tolstikhin, T. Morishita, and S. Watanabe, Phys. Rev. A 76, 043418 (2007).

[13] K. Toyota, O. I. Tolstikhin, T. Morishita, and S. Watanabe, Phys. Rev. A 78, 033432 (2008).

[14] P. V. Demekhin and L. S. Cederbaum, Phys. Rev. Lett. 108, 253001 (2012).

[15] P. V. Demekhin and L. S. Cederbaum, Phys. Rev. A 88, 043414 (2013).

[16] P. V. Demekhin, D. Hochstuhl, and L. S. Cederbaum, Phys. Rev. A 88, 023422 (2013).

[17] C. Yu, N. Fu, G. Zhang, and J. Yao, Phys. Rev. A 87, 043405 (2013).

[18] C. Yu, N. Fu, T. Hu, G. Zhang, and J. Yao, Phys. Rev. A 88, 043408 (2013).

[19] C. B. Madsen, F. Anis, L. B. Madsen, and B. D. Esry, Phys. Rev. Lett. 109, 163003 (2012).

[20] R. E. F. Silva, F. Catoire, P. Rivière, H. Bachau, and F. Martín, Phys. Rev. Lett. 110, 113001 (2013).

[21] J. Wu, M. Kunitski, M. Pitzer, F. Trinten, L. Ph. Schmidt, T. Jahnke, M. Magrakvelidze, C. B. Madsen, L. B. Madsen, U. Thumm, and R. Dörner, Phys. Rev. Lett. 111, 023002 (2013).

[22] L. Yue and L. B. Madsen, Phys. Rev. A 88, 063420 (2013).

[23] L. B. Madsen, L. A. A. Nikolopoulos, T. K. Kjeldsen, and J. Fernández, Phys. Rev. A 76, 063407 (2007).
[24] J. Fernández and L. B. Madsen, J. Phys. B 42, 085602 (2009).
[25] B. Feuerstein and U. Thumm, J. Phys. B 36, 707 (2003).
[26] A. Keller, Phys. Rev. A 52, 1450 (1995).
[27] S. Chelkowski, C. Foisy, and A. D. Bandrauk, Phys. Rev. A 57, 1176 (1998).
[28] L. Tao and A. Scrinzi, New J. Phys. 14, 013021 (2012).
[29] A. Scrinzi, New J. Phys. 14, 085008 (2012).
[30] V. V. Serov, V. L. Derbov, T. A. Sergeeva, and S. I. Vinitsky, Phys. Rev. A 88, 043403 (2013).
[31] A. Karamatskou, S. Pabst, Y.-J. Chen, and R. Santra, Phys. Rev. A 89, 033415 (2014).
[32] K. C. Kulander, F. H. Mies, and K. J. Schafer, Phys. Rev. A 53, 2562 (1996).
[33] G. L. Ver. Steeg, K. Bartschat, and I. Bray, J. Phys. B 36, 3325 (2003).
[34] W. Qu, Z. Chen, Z. Xu, and C. H. Keitel, Phys. Rev. A 65, 013402 (2001).
[35] M. D. Feit, J. A. Fleck Jr., and A. Steiger, J. Comput. Phys. 47, 412 (1982).
[36] J. G. Muga, J. P. Palao, B. Navarro, and I. L. Egusquiza, Phys. Rep. 395, 357 (2004).
[37] E. S. Sarachik and G. T. Schappert, Phys. Rev. D 1, 2738 (1970).
[38] G. A. Mourou, T. Tajima, and S. V. Bulanov, Rev. Mod. Phys. 78, 309 (2006).
[39] R. W. Boyd, Nonlinear Optics (Academic, New York, 2008).
[40] S. Chelkowski, P. B. Corkum, and A. D. Bandrauk, Phys. Rev. Lett. 82, 3416 (1999).
[41] S. Barmaki and H. Bachau, J. Phys. B 40, 463 (2007).
[42] L. Ph. H. Schmidt, T. Jahnke, A. Czasch, M. Schöffler, H. Schmidt-Böcking, and R. Dörner, Phys. Rev. Lett. 108, 073202 (2012).
[43] L. B. Madsen, Phys. Rev. A 65, 053417 (2002).