# Time-dependent calculations of double photoionization of the aligned $H_2$ molecule

I. A. Ivanov<sup>\*</sup> and A. S. Kheifets<sup>†</sup>

Research School of Physical Sciences,

The Australian National University, Canberra ACT 0200, Australia

(Dated: November 1, 2011)

# Abstract

We perform time-dependent calculations of single-photon two-electron ionization of the aligned  $H_2$  molecule by an XUV pulse. Solution of the time-dependent Schröding equation is sought in spherical coordinates on a radial grid by time propagation using the Arnoldi-Lanczos method. From these calculations, we derive the total integrated as well as fully differential ionization crosssections for equal energy sharing and various orientations of the internuclear axis relative to the polarization vector of light. Satisfactory agreement with available literature data validates the present theoretical model. We supplement our numerical computations by amplitude analysis of differential cross-sections using atomic-like formalism introduced by Feagin [J. Phys. B **31**, L729 (1998)]. This analysis provides some additional insight into mechanisms of double photoionization of the aligned  $H_2$  molecule.

<sup>\*</sup>Electronic address: Igor.Ivanov@anu.edu.au

<sup>&</sup>lt;sup>†</sup>Electronic address: A.Kheifets@anu.edu.au

### I. INTRODUCTION

Single-photon two-electron ionization (double photoionization or DPI) of the H<sub>2</sub> molecule became a subject of renewed interest after experimental data resolved with respect to the molecular axis orientation became available [1–3]. In these kinematically complete four-body fragmentation experiments, a strong dependence of the electron angular distribution on the orientation of the molecular axis was demonstrated. This observation was not possible in earlier measurements on randomly oriented  $H_2$  or  $D_2$  molecules [4–7] which could be described rather adequately by atomic-like models [8] or central field numerical computations [9, 10]. The new set of molecular orientation specific DPI measurements gave an impetus to rapid advancement of theory. First, *ab initio* non-perturbative calculations of the total integrated cross-section (TICS) were reported using the time-dependent close-coupling (TDCC) [11] and the exterior complex scaling (ECS) [12] methods. These integrated cross-section data were found in a much better agreement with experiment [13, 14] than the earlier perturbative calculations [15, 16]. Next, triply differential cross-sections (TDCS) resolved with photoelectron momenta and specific to molecular orientation were evaluated within the ECS [17] and TDCC [18] methods. The two sets of TDCS calculations were found in good agreement with each other and, after convolution with the instrumental function, fit the experimental data rather well. These initial reports were followed by two subsequent calculations performed in prolate spheroidal coordinates using grid-based [19] and time-dependent [20] methods. The TDCC data were also reevaluated by using a bigger box size and achieving better convergence [21]. Detailed comparison of the latest TDCS results [20] showed some model dependence which could not be unambiguously resolved by experiment because of its uncertainties in the molecular alignment and the emission angles of the photoelectrons. Nevertheless, the two calculations [20, 21] were found particularly close and could serve as a practical benchmark for further development of theory.

Apart from various numerical models, valuable insight into molecular DPI can be gained from qualitative analysis based on quantizing rotations of the momentum plane of the electron pair about its relative momentum [22]. In this analysis, the molecular DPI in the laboratory frame is represented by a pair of amplitudes  $g_{\Sigma}$  and  $g_{\Pi}$ . These amplitudes are defined in the molecular frame and correspond to the parallel  $\boldsymbol{e} \| \boldsymbol{R}_N$  and perpendicular  $\boldsymbol{e} \perp \hat{\boldsymbol{R}}_N$  orientations of the internuclear axis and polarization vector of light, respectively. This technique was very efficient in description of DPI of randomly oriented H<sub>2</sub> molecules [4–6]. It was successfully extended to account for recent observations of noncoplanar electron-pair, molecular-axis angular distributions [28], where the molecular orientation effects were particularly stark.

This state of numerical modelling and analytical analysis of DPI process in H<sub>2</sub> gives a starting point to the present work which has a dual purpose. First, we want to extend our time-dependent calculations of strong field ionization of atoms (hydrogen [23], helium [24], lithium [25]) to molecular targets. Our approach is based on numerical solution of the timedependent Schrödinger equation (TDSE) in spherical coordinates on a radial grid by time propagation using the Arnoldi-Lanczos method. By projecting this solution onto the fieldfree states of the molecular  $H_2^+$  ion, we obtain probabilities and cross-sections for various ionization channels. This approach is similar to that taken in Ref. [20], except that instead of prolate spheroidal coordinates we employ spherical coordinates. We test our calculations of TICS of DPI of H<sub>2</sub> across a wide range of photon energies against the most recent and consistent sets of experimental and theoretical data [11, 12, 14]. We also perform TDCS calculations for equal energy sharing at two fixed photon energies. The first photon energy of 75 eV is chosen to test the accuracy of the present model by making comparison with the benchmark data [20, 21]. Coincidentally, this photon energy falls close to the center of a broad Cooper-like minimum in the dipole channel of single photoionization of  $H_2$  for the parallel field orientation [26]. The second photon energy of 120 eV is selected well outside this minimum. By comparing TDCS at these two selected photon energies, we evaluate the influence of the Cooper minimum in the single-ionization channel on the DPI process.

Our second goal is to study underlying many-body dynamics behind the molecular DPI process. This is achieved by analyzing TDCS of DPI on the aligned H<sub>2</sub> molecule in terms of the amplitudes  $g_{\Sigma}$  and  $g_{\Pi}$  introduced in the formalism of Feagin [22]. We perform this analysis using the parallel  $\boldsymbol{e} \parallel \hat{\boldsymbol{R}}_N$  and perpendicular  $\boldsymbol{e} \perp \hat{\boldsymbol{R}}_N$  coplanar TDCS at the equal energy sharing. We find that the case of perpendicular field orientation is described rather

well by a single amplitude  $g_{\Pi}$  for all mutual orientations of the reference photoelectron relative to the internuclear axis. This amplitude is well fitted by the Gaussian ansatz and is rather similar to the symmetric amplitude of DPI of He at the corresponding excess energy. The coplanar TDCS in the case of parallel field orientation can also be described by the corresponding amplitude  $g_{\Sigma}$ . However, this amplitude demonstrates some variation with the reference photoelectron fixed angle. Most strikingly, this amplitude shows very strong deviation from the Gaussian ansatz and can only be fitted by a di-Gaussian parametrization. This distortion of the amplitude is typical for DPI of various atomic targets containing an *L*-shell [27].

It is well documented that the dipole approximation fails most strongly for non-coplanar DPI of H<sub>2</sub> [3, 28]. This failure can be attributed to a strong Cooper-like minimum in the dipole channel of single photoionization of H<sub>2</sub> for the  $\Sigma$  orientation at the photon energy close to 75 eV [26]. It may also be for the same reason that the Gaussian ansatz fails for the coplanar TDCS in the parallel field orientation. To test this hypothesis, we repeated our TDCS calculations at a much higher photon energy of 120 eV, well away from the Cooper minimum in the dipole channel. Much to our surprise, the same pattern of the coplanar TDCS was observed. The perpendicular field orientation was very well fitted by the Gaussian ansatz to the amplitude  $g_{\Pi}$  but the parallel field orientation required strongly non-Gaussian amplitude  $g_{\Sigma}$ .

The paper is organized as follows. In Section II we give details of our computational method implementing numerical solution of TDSE (IIA) and extraction of various DPI cross-sections (IIB). We conclude by projecting possible extensions of the present work.

## **II. COMPUTATIONAL DETAILS**

## A. Solution of TDSE

We consider evolution of the  $H_2$  molecule in presence of an XUV pulse

$$\boldsymbol{E}(t) = \boldsymbol{E}_0 f(t) \cos \omega t , \qquad (1)$$

with the carrier frequency  $\omega = 75.5$  eV and the peak field strength  $E_0 = 0.1$  a.u (corresponding to the intensity of  $3.5 \times 10^{14}$  W/cm<sup>2</sup>). The pulse is switched off outside the time interval (0, 10T), where  $T = 2\pi/\omega$  is an optical cycle of the carrier frequency. The envelope function f(t) is chosen in such a way that the amplitude of the XUV field is ramped on and off smoothly during one optical cycle T, and is constant in between. In the following, we consider cases of parallel and perpendicular mutual orientations of the XUV field and the H<sub>2</sub> molecule which is assumed to be oriented along the quantization axis  $\hat{\mathbf{R}}_N \parallel z$ . The field is linearly polarized along the z or x axes for parallel or perpendicular orientations, respectively.

We solve numerically the TDSE for the H<sub>2</sub> molecule interacting with the XUV field

$$i \ \partial \Psi / \partial t = \left[ \hat{H}_{\text{mol}} + \hat{H}_{\text{int}}(t) \right] \Psi$$
, (2)

where  $\hat{H}_{\text{mol}}$  is the Hamiltonian of a field-free hydrogen molecule, the operator  $\hat{H}_{\text{int}}(t)$  describes molecule-field interaction. We choose the velocity form for this operator:

$$\hat{H}_{\text{int}}(t) = \boldsymbol{A}(t) \cdot (\hat{\boldsymbol{p}}_1 + \hat{\boldsymbol{p}}_2), \tag{3}$$

with the vector potential  $\boldsymbol{A}(t) = -\int_{0}^{t} \boldsymbol{E}(\tau) d\tau$ .

The Hamiltonian operator is discretized on a spatial grid  $\{r_i\}$  composed of several intervals with a progressively increasing stepsize. The wave function at the grid points is represented as a partial wave expansion

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \sum_{l_1, l_2, J} f^J_{l_1 l_2}(r_1, r_2) |l_1(1) l_2(2) J\rangle .$$
(4)

Here the notation  $|l_1(1)l_2(2) J\rangle$  is used for bipolar harmonics [29], and summation is restricted to  $l_1, l_2 = 0 - 6$  with the total angular momenta J = 0 - 5.

The initial  ${}^{1}\Sigma_{g}$  state was prepared by using imaginary time propagation of the fieldfree H<sub>2</sub> molecule (relaxation procedure) starting from some trial wave-function. Using this procedure, we obtained the ground state energy of -1.167 a.u. at the equilibrium internuclear distance R = 1.401 a.u. This value corresponds to the Coulomb interaction of nuclei included into the Hamiltonian, i.e., it represents the total energy of the hydrogen molecule. More useful characteristics of the initial state in our problem, where the nuclei are kept fixed, and their repulsion energy in initial and final states cancels out, is the value obtained if the term 1/R is subtracted from the Hamiltonian. This subtraction gives us the value of -1.8807 a.u. for the double ionization potential in good agreement with the literature data.

With this initial state, the solution of the TDSE was propagated in time over the interval (0, 20T) using the Arnoldi-Lanczos method [30, 31]. After the field pulse is off for t > 10T, the system evolves freely. Information obtained using this field-free evolution after the end of the pulse can be used to assess the accuracy of the TDSE solution.

## B. Final states and extraction of DPI cross-sections

To extract information about the DPI cross-sections from the solution of the TDSE, we project this solution after the end of the pulse on the set of the doubly ionized states of the  $H_2$  molecule  $\Psi_{\mathbf{k}_1,\mathbf{k}_2}^-(\mathbf{r}_1,\mathbf{r}_2)$  with ingoing boundary conditions. These state are constructed from ingoing scattering states of the  $H_2^+$  molecular ion with asymptotic momenta  $\mathbf{k}_1$  and  $\mathbf{k}_2$ . The latter are found as follows.

First, we prepare a one-electron basis set  $\Psi_{k l_0 M}(\mathbf{r})$  of the continuum spectrum of the  $\mathrm{H}_2^+$  ion. These states are obtained as eigenfunctions of the  $\mathrm{H}_2^+$  Hamiltonian corresponding to a given value of the angular momentum projection M on the internuclear axis  $\hat{\mathbf{R}}_N$ , and a given positive energy  $E = k^2/2$ . We represent these states as

$$\Psi_{k \, l_0 M}(\boldsymbol{r}) = \sum_{l \ge |M|} r^l g_{k \, l l_0 M}(r) Y_{l M}(\hat{\boldsymbol{r}}) , \qquad (5)$$

with the boundary conditions at the origin  $g_{k l l_0 M}(0) = \delta_{l l_0}$ . Substituting this expansion into the Schrödinger equation for the positive energy eigenstates of the H<sub>2</sub><sup>+</sup> ion gives a set of equations for the functions  $g_{k l l_0 M}(r)$ .

Now we can represent the ingoing scattering states of the  $H_2^+$  ion as

$$\Psi_{\boldsymbol{k}}^{-}(\boldsymbol{r}) = \sum_{l_0 M} a_{l_0 M} \Psi_{k \, l_0 M}(\boldsymbol{r}) \ . \tag{6}$$

Substituting expression (5) for  $\Psi_{k l_0 M}(\mathbf{r})$  into Eq. (6) gives us a partial wave expansion for the ingoing scattering states of the  $H_2^+$  ion. Coefficients  $a_{l_0 M}$  can now be found from the requirement that, in each partial wave, the terms containing outgoing exponentials  $e^{ikr}$  coincide for  $r \to \infty$  with those of the ingoing scattering state for the hydrogen-like ion with the nuclear charge Z = 2.

Differential probability of DPI can now be found as

$$P(\boldsymbol{k}_1, \boldsymbol{k}_2) = |\langle \Psi_{\boldsymbol{k}_1, \boldsymbol{k}_2}^- | \Psi(t) \rangle|^2 , \qquad (7)$$

where  $\Psi(t)$  is the solution of TDSE at the moment of time after the end of the XUV pulse. When computing this overlap, we use the recipe proposed in Ref. [32] to extract contributions of the bound and singly ionized states. This procedure suggests that all the radial integrals entering the overlap (7) should be computed starting from some value  $r = R_0$  or, equivalently,  $\Psi(t)$  should be put to zero if either  $r_1 < R_0$  or  $r_2 < R_0$ . The rationale behind this recipe is the following. If we wait long enough, the wavepacket describing doubly ionized states leaves the region where either  $r_1 < R_0$  or  $r_2 < R_0$ . Outside this region, the part of the wave function describing contributions of bound and singly ionized states is heavily dumped due to bound character of at least one of the electrons. We can expect that if we choose  $R_0$  and the moment of time t after the end of the pulse appropriately, then we can avoid contamination of the DPI process by singly ionized or bound channels.

The differential probability (7) is converted into the cross-section in a usual way. First, we should take into account the fact that TDCS is defined on the energy shell which corresponds to the strict energy conservation. For the pulse of a finite duration (1), the energy is conserved only approximately. Therefore, we have to employ a procedure [20, 33] which corrects for this fact, effectively reducing differential probabilities to energy shell only. For the case of equal energy sharing between the two photoelectrons, the corresponding formula reads:

$$P^{\rm av}(E_1, \hat{k}_1, \hat{k}_2) = \frac{1}{E_1} \int_0^\infty P(u\hat{k}_1, u\hat{k}_2)u \ du , \qquad (8)$$

where  $E_1 = E_2$  is the energy of an escaping electron. Physically, this procedure corresponds to averaging the differential probability over the whole region of electron momenta, keeping the ratio of electron energies constant. Finally, we have to convert the averaged probability  $P^{\rm av}$  into the differential cross section as

$$\frac{d^3\sigma}{dEd\hat{\boldsymbol{k}}_1d\hat{\boldsymbol{k}}_2} = \frac{8\pi\omega}{c} \frac{P^{\rm av}(E,\hat{\boldsymbol{k}}_1,\hat{\boldsymbol{k}}_2)}{W} , \qquad (9)$$

where  $W = 2 \int_0^{10T} E^2(t) dt$ , and  $c \approx 137$  is the speed of light in atomic units.

# III. NUMERICAL RESULTS

#### A. Total integrated cross-sections

The total integrated cross-section (TICS) of DPI of  $H_2$  as a function of the photon energy is shown on the left panel of Figure 1. The present TDSE results are compared with the TDCC calculation [11], the ECS theory [12] and experiment [14]. The ECS result is shown in the velocity gauge. The corresponding length gauge result is only marginally different. The theoretical data are the sum of cross-sections for parallel and perpendicular orientations of the internuclear axis relative to the field. The experimental data are taken at random orientation of the internuclear axis.



FIG. 1: Left: Total integrated cross-section of DPI of randomly oriented H<sub>2</sub> as a function of photon energy. Present TDSE results, exhibited with filled red circles, are plotted along with the TDCC calculation (blue filled squares) [11], the ECS calculation (black solid line) [12] and the experiment [14]. Right: Cross-section ratios for perpendicular and parallel filed orientations. The DPI ratio  $\sigma_{\Pi}^{2+}/\sigma_{\Sigma}^{2+}$  from the ECS calculation [12] is shown by a thin black line whereas the single photoionization ratio  $\sigma_{\Pi}^{+}/\sigma_{\Sigma}^{+}$  from the RPA calculation [26] is displayed with a thick blue line.

Some information on the molecular orientation dependence of TICS can be gained from

the right panel of Figure 1 where we compare the cross-section ratios for perpendicular versus parallel filed orientations. The DPI ratio  $\sigma_{\Pi}^{2+}/\sigma_{\Sigma}^{2+}$  from the ECS calculation [12] is shown by a thin black line whereas the single photoionization ratio  $\sigma_{\Pi}^{+}/\sigma_{\Sigma}^{+}$  from the RPA calculation [26] is displayed with a thick blue line. The single photoionization ratio peaks at the photon energy of about 75 eV which corresponds to a Cooper-like minimum in the dipole channel for the parallel field orientation. This maximum is replicated in the DPI cross-section ratio at a slightly lower photon energy. Generally, the  $\Pi/\Sigma$  ratios are similar in the single and double photoionization channels. This allows one to speculate that the two-step mechanism of DPI of H<sub>2</sub> is dominant in this photon energy range. In other words, DPI proceeds via single photoionization of H<sub>2</sub> and subsequent electron impact ionization of the H<sub>2</sub><sup>+</sup> ion. This second stage of DPI process is also dependent on the molecular orientation but its angular anisotropy is much weaker than that of the single photoionization.



FIG. 2: Coplanar TDCS of DPI of H<sub>2</sub> at photon energy of 75 eV and equal energy sharing. The angle of the internuclear axis  $\theta_N = 0$  and the fixed reference photoelectron angle  $\theta_1 = 0$ . Left panel: Results obtained for t = 16T, and  $R_0 = 5$  a.u. (red) solid line, 10 a.u. (green) crosses, 15 a.u. (blue) boxes, and 25 a.u. (magenta) dots. Right panel: Results obtained for  $R_0 = 10$  a.u., and t = 10T (red) solid line, t = 14T (green) dashed line, t = 16T (blue) dots.

#### B. Differential cross-sections

## 1. Stability test

Firstly, before presenting a complete set of TDCS calculations, we show some results of the stability test. Our numerical procedure is based on the expectation that there exists a range of distances  $R_0$  and the time interval t where projection of the solution of TDSE on the field-free molecular states produce stable results. Figure 2 illustrates that these expectations are well founded. In this figure, we present a coplanar TDCS of DPI of H<sub>2</sub> at the photon energy of 75 eV and equal excess energy sharing between the two photoelectrons. The angle of the internuclear axis  $\theta_N = 90^\circ$  and the fixed reference photoelectron angle  $\theta_1 = 0^\circ$ , both angles are measured relative to the polarization vector of light. One can see from the Figure that varying parameter  $R_0$  between 5 and 15 a.u. produces virtually no effect on the TDCS. For larger values of  $R_0$  results start changing fast. By using  $R_0 = 25$  a.u. and t = 16T we simply do not give doubly ionized wavepacket enough time to leave the region where either  $r_1 < R_0$  or  $r_2 < R_0$ . Figure 2 shows, that computing projection at t = 16T gives us a comfortably large interval of  $R_0$  to implement the recipe of Ref. [32] . All results presented below have been obtained for  $R_0 = 10$  a.u.

Similarly, the right panel of the Figure 2 shows that if we let the system to evolve sufficiently far in time using the fixed value of  $R_0$  for the cutting parameter of the projection operation, we obtain results which become very stable in time. Computing projection at t = 10T cannot give accurate results with the chosen value  $R_0 = 10$  a.u. as we cut away too large a part of the doubly ionized wavepacket. For the results reported below, we used t = 16T.

#### 2. Photon energy $75 \ eV$

The TDCS of DPI of H<sub>2</sub> at photon energy of 75.5 eV is shown in Figure 2. The excess energy is shared equally between the photoelectrons. The top row displays the  $\Pi$  molecular orientation with the internuclear axis at the angle  $\theta_N = 90^\circ$  to the linearly polarized XUV field. The bottom row displays TDCS corresponding to the  $\Sigma$  orientation with  $\theta_N = 0^\circ$ . On



FIG. 3: Coplanar TDCS of DPI of H<sub>2</sub> at photon energy of 75 eV and equal energy sharing. The angle of the internuclear axis  $\theta_N$  and the fixed reference photoelectron angle  $\theta_1$ , both measured relative to the polarization vector of light, are indicated on each panel. The present spherical TDSE results are plotted with red filled circles, the prolate TDSE results [20] are shown with the thin green line, the TDCC results [21] are exhibited by the thick blue line.

the left and right columns, the reference photoelectron angle is fixed at  $\theta_1 = 0^\circ$  and  $90^\circ$ , respectively. For each combination of angles  $\theta_N$  and  $\theta_1$ , comparison is made with another two sets of time dependent calculations: one is seeking solution of TDSE in prolate spheroidal coordinates [20], another employing the TDCC method [21].

In Figure 2, comparison is made on the absolute scale. Given quite a different shape, duration and intensity of the field pulse assumed in these three models, agreement between the TDCS is rather satisfactory. The literature values [20, 21] tend to converge better except for the parallel field orientation at  $\theta_1 = 90^\circ$  where the present calculation and that of Ref. [20] agree between themselves but deviate somewhat from Ref. [21]. Generally, we may conclude that the present model is sufficiently accurate to capture essential dynamics of the DPI process in H<sub>2</sub> and its orientation dependence.

In the atomic-like description of DPI of  $H_2$  introduced by Feagin [22], the coplanar TDCS

at the equal energy sharing can be represented by the following expression:

$$\frac{d^{3}\sigma}{dEd\theta_{1}d\theta_{2}} = \left| (g_{\Sigma}\cos^{2}\theta_{N} + g_{\Pi}\sin^{2}\theta_{N})(\cos\theta_{1} + \cos\theta_{2}) + (g_{\Sigma} - g_{\Pi})\cos\theta_{N}\sin\theta_{N}(\sin\theta_{1} + \sin\theta_{2}) \right|^{2}.$$
(10)

Here the molecular orientation angle  $\theta_N$  and the photoelectron escape angles  $\theta_1$ ,  $\theta_2$  are counted from the direction of the polarization vector of light. The pair of amplitudes  $g_{\Sigma}$ and  $g_{\Pi}$ , which both depend on the mutual photoelectron angle  $\theta_{12} = |\theta_1 - \theta_2|$ , correspond to the parallel  $\boldsymbol{e} \parallel \hat{\boldsymbol{R}}_N$  and perpendicular  $\boldsymbol{e} \perp \hat{\boldsymbol{R}}_N$  molecular orientations, respectively. The TDCS formula (10) can be inverted to yield the moduli of the amplitudes:

$$|g_{\Sigma/\Pi}(\theta_{12})| = \left[\frac{d^3\sigma(\theta_N = 0^\circ/90^\circ)}{dEd\theta_1 d\theta_2}\right]^{1/2} \frac{1}{\cos\theta_1 + \cos\theta_2}$$
(11)

In Figures (3) and (4), we use this expression to obtain the amplitudes  $g_{\Sigma}$  and  $g_{\Pi}$  from the corresponding TDCS exhibited in Figure 2. Thus, we obtain the amplitudes for all values of  $\theta_{12}$  except of a small interval around  $\theta_{12} = 180^{\circ}$  where the kinematic factor  $\cos \theta_1 + \cos \theta_2$  tends to zero.

When inspecting Figure 3, we observe that the modulus of the amplitude  $g_{\Pi}$  can be fitted very well with the Gaussian ansatz

$$|g_{\Pi}(\theta_{12})| = A \exp\left[-2\ln 2\frac{(180^{\circ} - \theta_{12})^2}{\Delta\theta^2}\right] .$$
 (12)

The Gaussian magnitude A and width  $\Delta \theta$  parameters derived from TDCS for perpendicular field orientation  $\theta_N = 90^\circ$  and the reference photoelectron angles  $\theta_1 = 0^\circ$  and  $90^\circ$  are shown in Table I. In the same table, we present the analogous values derived from the TDCS produced by other methods [20, 21]. The difference between the pair of the Gaussian parameters derived from TDCS at  $\theta_1 = 0^\circ$  and  $90^\circ$  serves as an indication of the accuracy of the atomic-like expression (10). For an atomic target, these parameters should be identical. Surprisingly, these parameters are very close for the perpendicular orientation of the H<sub>2</sub> molecule as well, especially in the prolate TDSE calculation [21].

Similar extraction of the  $g_{\Sigma}$  amplitude from the TDCS at the parallel field  $\theta_N = 0^{\circ}$  is illustrated in Figure 4. In this case, in a stark contrast to the perpendicular orientation



FIG. 4: The TDCS of Figure 2 at  $\theta_N = 90^\circ$  (left column) and the corresponding amplitude  $g_{\Pi}$  (right column) (both shown by the red dots) are fitted with the Gaussian ansatz (shown as a dotted line). The top and bottom rows correspond to the reference photoelectron angle fixed at  $\theta_1 = 0^\circ$  and 90°, respectively.

at  $\theta_N = 90^\circ$ , the amplitude  $g_{\Sigma}$  is manifestly non-Gaussian. Similar shape of the amplitude was encountered when analyzing the TDCS of DPI of various atomic targets containing an *L*-shell [27]. It can be represented by a superposition of two Gaussians, each containing its own set of magnitude and width parameters:

$$|g_{\Sigma}(\theta_{12})| = \left| A_1 \exp\left[ -2\ln 2\left(\frac{180^\circ - \theta_{12}}{\Delta \theta_1}\right)^2 \right] + e^{i\phi} A_2 \exp\left[ -2\ln 2\left(\frac{180^\circ - \theta_{12}}{\Delta \theta_2}\right)^2 \right] \right| .$$
(13)

The phase shift  $\phi$  in Eq. (13) is usually close to  $\pi$ .

The amplitude  $g_{\Sigma}$  has two prominent features. Similarly to the amplitude  $g_{\Pi}$ , it shows a Gaussian-like peak at the back-to-back emission corresponding to  $\theta_{12} = 180^{\circ}$ . In addition, it has a shoulder at about 70°. In the atomic-like description of DPI process (10), the back-to-back emission with equal energy sharing is strongly forbidden by the dipole selection rule [34]. So the kinematic factor  $\cos \theta_1 + \cos \theta_2$  and the dynamic amplitude factor should "negotiate"



FIG. 5: The TDCS of Figure 2 at  $\theta_N = 0^\circ$  (left column) and the corresponding amplitude  $g_{\Sigma}$  (right column) (both shown by the red dots) are fitted with the di-Gaussian ansatz (shown as a dotted line). The top and bottom rows correspond to the reference photoelectron angle fixed at  $\theta_1 = 0^\circ$  and 90°, respectively.

a compromise angle where the TDCS reaches its maximum. With a simple Gaussian shape of the amplitude  $g_{\Sigma}$ , this maximum is reached at a mutual electron angle  $\theta_{12} \simeq 120^{\circ}$ , i.e. the photoelectrons escape predominantly in the opposite directions. With a non-Gaussian amplitude  $g_{\Sigma}$ , this situation changes dramatically. Indeed, at the fixed reference electron angle  $\theta_1 = 0^{\circ}$ , the TDCS reaches its maximum exactly where the amplitude  $g_{\Sigma}$  has its shoulder, i.e.  $\theta_{12} \simeq 70^{\circ}$ . This corresponds to the photoelectron escaping predominantly to the same direction. This behavior is exhibited clearly in Fig. 8 of Ref. [20], albeit without qualitative physical explanation. At another fixed reference electron angle of  $\theta_1 = 90^{\circ}$ , the maximum of the TDCS is moved away from the shoulder of  $g_{\Sigma}$ , which is not so prominent as in the case of  $\theta_1 = 0^{\circ}$ . The di-Gaussian parameters of the amplitude  $g_{\Sigma}$ , derived from the TDCS at the angles

 $\theta_N = \theta_1 = 0^\circ$ , are given in Table II for the present calculation in comparison with the

	Magnit	ude $A_{\Pi}$	Width $\Delta \theta_{\Pi}$		
	$(b^{1/2}/sr/ev^{1/2})$		(degree)		
	$\theta_1=0^\circ$	$\theta_1 = 90^\circ$	$\theta_1=0^\circ$	$\theta_1 = 90^\circ$	
Present	6.8	4.8	82	86	
TDSE [20]	6.7	6.0	81	82	
TDCC [21]	6.5	5.5	82	86	

TABLE I: Gaussian magnitude A and width  $\Delta \theta$  parameters of the symmetric amplitude  $g_{\Pi}$  derived from TDCS for perpendicular field orientation  $\theta_N = 90^\circ$  and the reference photoelectron angles  $\theta_1 = 0^\circ$  and  $90^\circ$ 

	Magnitude		Width		Phase
	$(b^{1/2}/sr/ev^{1/2})$		(degree)		(rad)
	$A_1$	$A_2$	$\Delta \theta_1$	$\Delta \theta_2$	$\phi$
Present	7.6	6.6	96	107	-3.02
TDSE $[20]$	4.9	3.9	93	108	-2.95
TDCC [21]	4.9	4.2	102	116	-2.97

TABLE II: Di-Gaussian magnitude  $A_1$ ,  $A_2$ , width  $\Delta \theta_1$ ,  $\Delta \theta_2$  and phase shift  $\phi$  parameters of the symmetric amplitude  $g_{\Sigma}$  derived from TDCS for parallel field orientation  $\theta_N = 0^\circ$  and the reference photoelectron angle  $\theta_1 = 0^\circ$ 

other two sets of data [20, 21]. The width parameters of  $g_{\Sigma}$  are larger than that of  $g_{\Pi}$ . In atomic DPI, the width parameter is determined by the size of the ionic core left behind by the primary photoelectron. A tighter core corresponds to a larger Gaussian width and, conversely, a sparse core, extended in coordinate space, defines a narrow Gaussian [27, 35]. An explanation of this empirical rule can be traced to the two-step mechanism of atomic DPI which is dominant at the photon energies not far away from the threshold. In this mechanism, DPI proceeds via single photoionization and subsequent electron impact ionization of the singly charged positive ion. On this second stage, a larger number of partial waves can reach an extended ionic orbital. As the angular width and the angular momentum are the conjugate variables, more partial waves is needed to make a narrow Gaussian.



FIG. 6: Equal energy sharing coplanar TDCS of DPI of H<sub>2</sub> at various angles of the internuclear axis  $\theta_N = 90^\circ$ ,  $60^\circ$ ,  $30^\circ$  and  $0^\circ$  relative to polarization vector of light. The reference photoelectron angle is fixed at  $\theta_1 = 0$ . The red solid line represent the prolate TDSE calculation of Ref. [20]. The dotted line represents Eq. (10) with the amplitudes  $g_{\Pi}$  and  $g_{\Sigma}$  parametrized using the corresponding entries in Table I and Table II.

Deviation from a simple Gaussian shape of the symmetric amplitude in atomic DPI can be related to an extra node of the *L*-shell target orbital [27]. Similar arguments can be applied to the present case of DPI of the aligned H<sub>2</sub> molecule. As is shown in Figs. 4 and 5 of Ref. [26], at photon energy of 75 eV, the photoelectrons are aligned strongly with the field polarization vector. This means that they impinge on the molecular H<sub>2</sub><sup>+</sup> ion parallel and perpendicular to the internuclear axis in the  $\Sigma$  and  $\Pi$  orientations, respectively. The properties of the H<sub>2</sub><sup>+</sup> wave function in these two directions are manifestly different [36]. Going from the center of the molecular ion in the perpendicular direction, the projectile encounters a smooth wave function which has neither nodes nor singularities. In the parallel direction, the same route crosses a strong Coulomb singularity on the nucleus.

Up to now, we applied Eq. (10) to the two "pure" cases of parallel and perpendicular molecular orientation when only one of the amplitudes  $g_{\Pi}$  and  $g_{\Sigma}$  define the TDCS. To



FIG. 7: Noncoplanar TDCS of the aligned hydrogen molecule for equal energy sharing. The present spherical TDSE results (red solid dots) are compared with prolate TDSE (gren thin line) [20] and TDCC [21] predictions (blue thick line). The dotted line indicates the results obtained by using the amplitudes  $g_{\Pi}$  (left and middle panels) and  $g_{\Sigma}$  (right panel) with the Gaussian parameters tabulated in Table I and Table II, respectively.

test this atomic-like expression for mixed cases, we use the complete set of TDCS reported in Ref. [20]. We generate the amplitudes  $g_{\Pi}$  and  $g_{\Sigma}$  from the corresponding parameters tabulated in Table I and Table II. Then we feed these amplitudes into Eq. (10) for various field orientations corresponding to  $\theta_N = 90^\circ$ ,  $60^\circ$ ,  $30^\circ$  and  $0^\circ$  and the reference photoelectron angle  $\theta_1 = 0$ . We compare thus generated results with *ab initio* calculations presented in Fig 5 of Ref. [20]. This comparison is illustrated in Figure 5. In principle, the amplitudes  $g_{\Pi}$  and  $g_{\Sigma}$  should be treated as complex variables. However, the phase information cannot be retrieved from the TDCS analysis. So we ignore the phase difference between  $g_{\Pi}$  and  $g_{\Sigma}$ . Nevertheless, thus obtained "synthetic" TDCS match their *ab initio* counterparts rather well. This indicates that the atomic-like description of the co-planar TDCS is generally valid for H<sub>2</sub>.

Finally, in Figure 6 we present the TDCS for the perpendicular geometry when one of the two photoelectrons is detected out of the plane made by the internuclear axis  $\hat{\mathbf{R}}_N$  and the polarization vector  $\mathbf{e}$ . Generally, agreement with two other time dependent calculations [20, 21] is satisfactory.

For this perpendicular geometry, the atomic-like formula (10) reads:

$$\frac{d^3\sigma_{\Pi/\Sigma}}{dEd\theta_1 d\theta_2} = |g_{\Sigma/\Pi}(\theta_{12} = 90^\circ)|^2 \cos^2 \theta_2$$
(14)

where the amplitudes  $g_{\Pi}$  or  $g_{\Sigma}$  are chosen for the angles  $\theta_N = 90^{\circ}$  and  $\theta_N = 0^{\circ}$ , respectively. The pure  $\cos^2 \theta_2$  dependence is clearly observed on the left panel of Figure 7 but it is decisively broken on the right panel. Feagin et al. [28] suggested that the atomic-like description (10) can still be applied in the case of perpendicular geometry. However, the dipole kinematic factor  $(\cos \theta_1 + \cos \theta_2)^2$  should be replaced by a more general expression which accounts for higher multipoles of the molecular DPI. On the left panel of Figure 7, we use the amplitude  $g_{\Pi}$  generated from the Gaussian parameters of Table I to represent the TDCS according to Eq. (14). Agreement with *ab initio* results is indeed very good in this case. On the central and right panels of Figure 7, we repeat this procedure. However, we modify the kinematic factor  $\cos^2 \theta_2$  by additional multipliers  $0.5(1 + 0.4 \sin^2 \theta_2)^2$  (middle panel) and  $(1 + 0.23 \sin^2 \theta_2)^2$  (right panel) as prescribed in Ref. [28]. This procedure gives us very satisfactory results thus demonstrating utility of the amplitude analysis in a rather general case.

#### 3. Photon energy $120 \ eV$

This photon energy is chosen to be well outside the Cooper-like minimum in the dipole channel of single photoionization of H<sub>2</sub> for the  $\Sigma$  orientation. By analyzing the TDCS at this photon energy and extracting the amplitudes via Eq. (10) we can check if the strongly non-Gaussian shape of the amplitude  $g_{\Sigma}$  is somehow related to this minimum. This analysis is presented in Figure 7. From this figure, we can see that, very similarly to the previous case of the photon energy of 75 eV, the amplitude  $g_{\Pi}$  is Gaussian whereas the amplitude  $g_{\Sigma}$  is not. This observation makes us believe that it is a general wave function structure of the H<sub>2</sub><sup>+</sup> ion that is responsible for this behavior rather than the Cooper-like minimum in the dipole  $\Pi$  channel at a specific photon energy of 75 eV



FIG. 8: Left: Coplanar TDCS of DPI of H<sub>2</sub> at photon energy of 120 eV and equal energy sharing. The angle of the internuclear axis  $\theta_N = 90^\circ$  (top) and  $0^\circ$  (bottom) and the fixed reference photoelectron angle  $\theta_1 = 0$ . Right: corresponding amplitude  $g_{\Pi}$  (top) and  $g_{\Sigma}$  (bottom) (both shown by the red dots) are fitted with the Gaussian ansatz (12) and di-Gaussian ansatz (13), respectively.

# IV. CONCLUSIONS

In the present work, we solve the time-dependent Schrödinger equation for the  $H_2$  molecule exposed to an XUV pulse. By propagating this solution in time outside the pulse interval and projecting it on the field-free continuum states of the  $H_2^+$  molecular ion, we derive the fully integrated as well as triply differential cross-sections (TDCS) of double photoionization of  $H_2$  with a given orientation of the internuclear axis relative to the polarization vector of light. We test thus found cross-sections against the most recent and consistent literature values and find generally good agreement. This validates our numerical model.

We use the coplanar TDCS at the parallel and perpendicular molecular-field mutual orientation to derive the symmetric amplitudes  $g_{\Pi}$  and  $g_{\Sigma}$ , which contain the most essential dynamical information of DPI process at the equal energy sharing. These amplitudes are fitted with a simple Gaussian and di-Gaussian ansatz, respectively. This shape of the amplitudes explains peculiarities of the coplanar TDCS, in particular, the prevalence of the same direction of escape of photoelectrons at parallel molecular-field orientation.

The amplitude information, obtained from the TDCS, is incomplete as the mutual phase of the amplitudes  $g_{\Pi}$  and  $g_{\Sigma}$  is missing. It would be more instructive to derive these amplitudes fully *ab initio* as can done in the atomic case (see e.g. Ref. [37]). With a complete amplitude information, the tests of the orientation dependence of the coplanar TDCS can be made more convincing. Also, it would be interesting to perform this amplitude analysis at various inter-nuclear distances. By increasing this distance from equilibrium, we can make the  $\Pi/\Sigma$  anisotropy stronger.

Finally, it would be very instructive to perform explicit calculations of electron impact ionization of the  $H_2^+$  molecular ion and to compare the angular correlation pattern in the  $(\gamma, 2e)$  reaction on  $H_2$  and the (e,2e) reaction on  $H_2^+$  at the corresponding incident energies. In the atomic case, these patterns are found to be very similar [27].

## V. ACKNOWLEDGMENTS

We are grateful to James Colgan, Klaus Bartschat and Xiaoxu Guan for communicating their data in numerical form. The authors acknowledge support of the Australian Research Council in the form of Discovery grant DP0985136. Facilities of the National Computational Infrastructure National Facility were used.

- T. Weber, A. Czasch, O. Jagutzki, A. Müller, V. Mergel, A. Kheifets, E. Rothenberg, G. Meigs, M. Prior, S. Daveau, et al., *Complete photo-fragmentation of the deuterium molecule*, Nature 431(7007), 437 (2004).
- [2] T. Weber, A. Czasch, O. Jagutzki, A. Müller, V. Mergel, A. Kheifets, J. Feagin, E. Rotenberg, G. Meigs, M. H. Prior, et al., *Fully differential cross sections for photo-double-ionization of D*<sub>2</sub>, Phys. Rev. Lett. **92**(16), 163001 (2004).
- M. Gisselbrecht, M. Lavollée, A. Huetz, P. Bolognesi, L. Avaldi, D. P. Seccombe, and T. J. Reddish, *Photodouble ionization dynamics for fixed-in-space H*<sub>2</sub>, Phys. Rev. Lett. 96(15), 153002 (2006).
- [4] T. J. Reddish, J. P. Wightman, M. A. MacDonald, and S. Cvejanović, Triple differential cross section measurements for double photoionization of D<sub>2</sub>, Phys. Rev. Lett. **79**, 2438 (1997).
- [5] J. P. Wightman, S. Cvejanovic, and T. J. Reddish, (γ, 2e) cross section measurements of H<sub>2</sub> and He, J. Phys. B **31**(8), 1753 (1998).
- [6] N. Scherer, H. Lörch, and V. Schmidt, Triple differential cross section measurements in H<sub>2</sub> and D<sub>2</sub>, J. Phys. B **31**(19), L817 (1998).
- [7] D. P. Seccombe, S. A. Collins, T. J. Reddish, P. Selles, L. Malegat, A. K. Kazansky, and A. Huetz, *Photodouble ionization differential cross sections for D<sub>2</sub> with various electron energy sharing conditions*, J. Phys. B **35**(17), 3767 (2002).
- [8] T. J. Reddish and J. M. Feagin, Photo double ionization of molecular deuterium, J. Phys. B 32(11), 2473 (1999).
- [9] A. S. Kheifets, Single-center model for double photoionization of the H<sub>2</sub> molecule, Phys. Rev. A 71(2), 022704 (2005).
- [10] A. S. Kheifets and I. Bray, Double photoionization of He and H<sub>2</sub> at unequal energy sharing, Phys. Rev. A 72, 022703 (2005).
- [11] J. Colgan, M. S. Pindzola, and F. Robicheaux, Time-dependent close-coupling calculations for the double photoionization of He and H<sub>2</sub>, J. Phys. B **37**(23), L377 (2004).
- [12] W. Vanroose, F. Martín, T. N. Rescigno, and C. W. McCurdy, Nonperturbative theory of double photoionization of the hydrogen molecule, Phys. Rev. A 70(5), 050703 (2004).
- [13] G. Dujardin, M. J. Besnard, L. Hellner, and Y. Malinovitch, Double photoionization of  $H_2$ :

An experimental test of electronic-correlation models in molecules, Phys. Rev. A **35**(12), 5012 (1987).

- [14] H. Kossmann, O. Schwarzkopf, B. Kämmerling, and V. Schmidt, Unexpected behaviour of double photoionization in H<sub>2</sub>, Phys. Rev. Lett. **63**(19), 2040 (1989).
- [15] H. L. Rouzo, A theoretical study of the double photoionisation of molecular hydrogen, J. Phys. B 19(19), L677 (1986).
- [16] H. Le Rouzo, Double photoionization of molecular hydrogen: A theoretical study including the nuclear dissociation, Phys. Rev. A 37(5), 1512 (1988).
- [17] W. Vanroose, F. Martín, T. N. Rescigno, and C. W. McCurdy, Complete photo-induced breakup of the H<sub>2</sub> molecule as a probe of molecular electron correlation, Science **310**(5755), 1787 (2005).
- [18] J. Colgan, M. S. Pindzola, and F. Robicheaux, Triple differential cross sections for the double photoionization of H<sub>2</sub>, Phys. Rev. Lett. **98**(15), 153001 (2007).
- [19] L. Tao, C. W. McCurdy, and T. N. Rescigno, Grid-based methods for diatomic quantum scattering problems. III. Double photoionization of molecular hydrogen in prolate spheroidal coordinates, Phys. Rev. A 82(2), 023423 (2010).
- [20] X. Guan, K. Bartschat, and B. I. Schneider, Breakup of the aligned H<sub>2</sub> molecule by xuv laser pulses: A time-dependent treatment in prolate spheroidal coordinates, Phys. Rev. A 83(4), 043403 (2011).
- [21] J. Colgan (2011), private communication.
- [22] J. M. Feagin, A helium-like description of molecular hydrogen photo-double ionization,
   J. Phys. B 31(18), L729 (1998).
- [23] M. G. Pullen, W. C. Wallace, D. E. Laban, A. J. Palmer, G. F. Hanne, A. N. Grum-Grzhimailo,
  B. Abeln, K. Bartschat, D. Weflen, I. Ivanov, et al., *Experimental ionization of atomic hydro*gen with few-cycle pulses, Opt. Lett. 36(18), 3660 (2011).
- [24] I. A. Ivanov and A. S. Kheifets, Two-photon double ionization of helium in the region of photon energies 42–50 eV, Phys. Rev. A 75(3), 033411 (2007).
- [25] M. Schuricke, G. Zhu, J. Steinmann, K. Simeonidis, I. Ivanov, A. Kheifets, A. N. Grum-Grzhimailo, K. Bartschat, A. Dorn, and J. Ullrich, *Strong-field ionization of lithium*, Phys. Rev. A 83(2), 023413 (2011).
- [26] S. K. Semenov and N. A. Cherepkov, Photoionization of the  $H_2$  molecule in the random phase

approximation, J. Phys. B **36**(7), 1409 (2003).

- [27] A. S. Kheifets, I. Bray, J. Colgan, and M. S. Pindzola, Interference effects in L-shell atomic double photoionization, J. Phys. B 44(1), 011002 (2011).
- [28] J. M. Feagin, J. Colgan, A. Huetz, and T. J. Reddish, *Electron-pair excitations and the molecular Coulomb continuum*, Phys. Rev. Lett. **103**(3), 033002 (2009).
- [29] D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskii, Quantum theory of angular momentum (World Scientific, Singapore, 1988).
- [30] T. J. Park and J. C. Light, Unitary quantum time evolution by iterative Lanczos reduction, J. Chem. Phys. 85, 5870 (1986).
- [31] D. Dundas, Efficient grid treatment of the ionization dynamics of laser-driven H<sup>+</sup><sub>2</sub>, Phys. Rev. A 65(2), 023408 (2002).
- [32] L. B. Madsen, L. A. A. Nikolopoulos, T. K. Kjeldsen, and J. Fernández, Extracting continuum information from ψ(t) in time-dependent wave-packet calculations, Phys. Rev. A 76(6), 063407 (2007).
- [33] J. Colgan and M. S. Pindzola, Core-excited resonance enhancement in the two-photon complete fragmentation of helium, Phys. Rev. Lett. 88, 173002 (2002).
- [34] F. Maulbetsch and J. S. Briggs, Selection rules for transitions to two-electron continuum states, J. Phys. B 28(4), 551 (1995).
- [35] A. S. Kheifets and I. Bray, Angular correlation in the two-electron continuum, Phys. Rev. A 73, 020708 (2006).
- [36] D. R. Bates, K. Ledsham, and A. L. Stewart, Wave functions of the hydrogen molecular ion, Phil. Trans. Roy. Soc. (London) A246(911), pp. 215 (1953).
- [37] A. S. Kheifets and I. Bray, Equal energy-sharing double photoionization of helium from nearthreshold to high energies, Phys. Rev. A 62(6), 065402 (2000).