

## Nonsequential double ionization of the hydrogen molecule in a few-cycle laser pulse

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We present *ab initio* calculations of the interaction of the hydrogen molecule with an intense few-cycle near-infrared laser pulse beyond the one-dimensional approximation. The results show that the two pathways to nonsequential double ionization of the molecule, namely, the emission of a correlated electron pair near the zeros of the field and the electron emission from the previously excited molecular ion near the maxima of the field, are linked to the return of the initially singly ionized electron wave packet to the residual ion. Patterns in the double ionization probability distributions arise due to interference effects between different quantum paths.

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It is a major goal of photochemistry to monitor and control the dynamics of electrons and nuclei in a molecular reaction by a laser pulse. Thus, it is essential to explore the routes to ionization and fragmentation of a molecule induced by the external field. The hydrogen molecule has attracted a lot of interest, since it is one of the simplest molecules and easily accessible in experiments [1]. A number of fragmentation pathways of H<sub>2</sub> in a strong near-infrared laser field have been identified, namely, the dissociation of the hydrogen molecular ion via bond softening [2], bond hardening [3], or zero-photon mechanism [4], charge resonance enhanced ionization (CREI) of the ion [5–7], sequential double ionization (SDI) [8,9], and nonsequential double ionization (NSDI) of the neutral molecule [8,10,11].

In all but one of these processes (dissociation, SDI, and CREI) the electrons interact independently of each other with the field. These mechanisms can be essentially understood from the dynamics in the ion, which is a single-active-electron problem. The nonsequential double ionization constitutes an exception, since it is a prototype of a two-electron problem, in which both electrons are highly correlated via the electron-electron interaction. In atoms, the underlying mechanism has been identified as laser-induced recollision [12–16]. According to this picture, an electron, emitted due to the interaction with the linearly polarized laser field, can be driven afterwards back to the parent ion where it interacts and exchanges energy with the second electron. Depending on the amount of energy exchanged in the recollision, either both electrons directly leave the atom together or only one is detached, leaving the ion in an excited state, which is subsequently ionized by the field interaction [17–20]. Recent experimental observations using nitrogen and oxygen molecules as targets suggest that the rescattering mechanism is active in diatomics, too [21,22].

Below we will consider the molecular double ionization problem by exactly solving the time-dependent Schrödinger equation (TDSE) within a multidimensional model. Until recently, the conventional strategy to investigate the two-

electron problem was a one-dimensional (1D) approach, in which the motion of both electrons is restricted to the axis of the linearly polarized field [23]. We have recently introduced an alternative model, in which the center-of-mass motion of the electrons is restricted to the field direction but the electron relative coordinate, and therefore the electron-electron interaction, is left unchanged [24]. Its application to the helium atom has unveiled an intense dynamics of the two electrons transversal to the field direction, which cannot be resolved in the traditional 1D approach. Our aim is, therefore, to take advantage of this new source of information to unveil the relevant processes leading to double ionization of a diatomic molecule.

In our approach, the Hamiltonian of the hydrogen molecule interacting with an intense linearly polarized laser pulse, given by its vector potential  $A(t)$ , is approximated as (Hartree atomic units,  $e=m=\hbar=1$ , are used)

$$\begin{aligned}
 H = & \frac{P_Z^2}{4} + \mathbf{p}^2 - \frac{P_Z A(t)}{c} + \frac{1}{r} - \frac{1}{\sqrt{\left[\frac{(2Z+R)\mathbf{e}_z + \mathbf{r}}{2}\right]^2 + a^2}} \\
 & - \frac{1}{\sqrt{\left[\frac{(2Z+R)\mathbf{e}_z - \mathbf{r}}{2}\right]^2 + a^2}} \\
 & - \frac{1}{\sqrt{\left[\frac{(2Z-R)\mathbf{e}_z + \mathbf{r}}{2}\right]^2 + a^2}} \\
 & - \frac{1}{\sqrt{\left[\frac{(2Z-R)\mathbf{e}_z - \mathbf{r}}{2}\right]^2 + a^2}}, \quad (1)
 \end{aligned}$$

where  $Z=(z_1+z_2)/2$ ,  $P_Z=p_{1,z}+p_{2,z}$  and  $\mathbf{r}=\mathbf{r}_1-\mathbf{r}_2$ ,  $\mathbf{p}=(\mathbf{p}_1-\mathbf{p}_2)/2$  are the one-dimensional center-of-mass and three-dimensional relative coordinates and momenta of the two electrons, respectively. The nuclei are assumed to be fixed at  $\pm R/2$  along the direction of the field. In this geometry the system has azimuthal symmetry about the direction of polarization and the final model Hamiltonian has three degrees of

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freedom, which we have chosen as  $\{Z, \rho, z\}$ , where  $\rho$  and  $z$  are the radius of the transversal and the longitudinal relative coordinate, respectively. The parameter  $a^2$  is used to soften the electron-nucleus potential in the computations.

The initial ground state wave function of  $H_2$  at the equilibrium distance is obtained via imaginary time propagation. With  $a^2=0.415$  the equilibrium distance is  $R=2.042$  a.u. and the ground state energies of the molecule and its ion are  $-1.1745$  a.u. and  $-0.6235$  a.u., respectively. We have considered a three-cycle sinelike laser pulse with a pulse envelope  $f(t)=\sin^2(\omega t/6)$ . The carrier frequency of  $\omega=0.0570$  a.u. ( $\lambda=800$  nm) and the peak intensity of  $2.9 \times 10^{14}$  W/cm<sup>2</sup> are typical parameters of a Ti:sapphire laser system. Equation (1) was solved on a grid with spatial steps  $\Delta\rho=\Delta z=\Delta Z=0.5$  a.u., time step  $\Delta t=0.05$  a.u., and 150 grid points in the  $\rho$  direction, 500 in the  $z$  and 250 in the  $Z$  direction. A  $\cos^{1/2}$ -like absorbing mask function is used to avoid reflections at the boundaries. The results are analyzed with respect to single and double ionization by partition the coordinate space as [25]

$$H_2: r_1 < 17.3 \text{ a.u. and } r_2 < 17.3 \text{ a.u.},$$

$$H_2^+: \text{either } r_1 < 14.0 \text{ a.u. and } r_2 > 17.3 \text{ a.u.},$$

$$\text{or } r_1 > 17.3 \text{ a.u. and } r_2 < 14.0 \text{ a.u.},$$

$$H_2^{2+}: \text{rest of the space,}$$

with  $r_1 = \sqrt{(Z + \frac{z}{2})^2 + \frac{\rho^2}{4}}$  and  $r_2 = \sqrt{(Z - \frac{z}{2})^2 + \frac{\rho^2}{4}}$ . The choice of two different distances in the partition ensures that probability density is transferred directly from the  $H_2$  region to the  $H_2^{2+}$  region (without passing the  $H_2^+$  region), when two electrons are emitted at the same time. Note that during the calculation the positions of the nuclei are fixed, which suppresses processes that appear at large internuclear separations, such as dissociation or charge resonant enhanced ionization. This is justified by recent observations [26,27] that have shown that nonsequential double ionization is the dominant process in a few-cycle pulse [28].

Figure 1 shows the temporal evolution of the single and double ionization probabilities during the interaction with the field. As can be noticed, the probability for single ionization rises quickly during short time intervals near the maxima of the field in agreement with the expectations of the tunnel ionization picture. The short delay with respect to the field maxima is due to the partition of the coordinate space (i.e., the corresponding part of the probability density has to reach the  $H_2^+$  region). The dips, followed by small increases, before the steep rises at  $t=140$  a.u. and  $t=210$  a.u. arise from the part of the ionized wave packet which returns to and passes the bound region. On the other hand, the curve for double ionization shows a more complex structure: it starts to rise quickly in a time interval after the first major field maximum through after the next zero of the field. A small increase near the second main maximum of the field (marked with an arrow) is followed by another rapid increase which extends again through after the zero of the field.

These results suggest, as in helium [24], two different

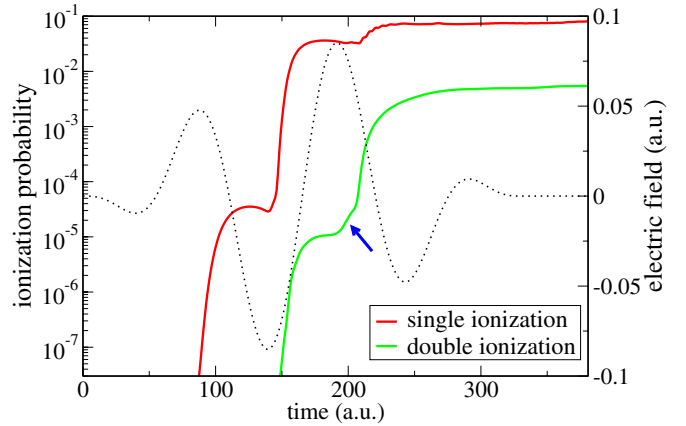


FIG. 1. (Color online) Single (red line) and double ionization (green line) probabilities as a function of time. The dotted line represents the amplitude of the electric field. The enhancement of the double ionization near the field maximum is marked by an arrow.

pathways to double ionization of the hydrogen molecule. They can be indeed confirmed by the snapshots of the probability distribution  $|\Psi(Z, z, \rho; t)|^2$  in Fig. 2, taken at two time instants during the pulse, namely, shortly after the maximum of the field at  $t=201$  a.u. [panels (a) and (b)] and shortly after the next zero of the field at  $t=230$  a.u. [panels (c) and (d)]. While the panels on the left-hand side show the  $(Z-z)$  distributions, integrated over  $\rho$ , the panels on the right offer the complementary view of the  $(\rho-z)$  distributions, integrated over  $Z$ . The diagonals in the  $(Z-z)$  distributions represent the  $z_1$  and  $z_2$  axes and correspond to single ionization of the molecule. The double ionized population is found in between the  $z_1$  and  $z_2$  axes.

In the  $(Z-z)$  distribution at  $t=201$  a.u. [Fig. 2(a)] one sees an elongated structure which is detached parallel to the  $z_1$

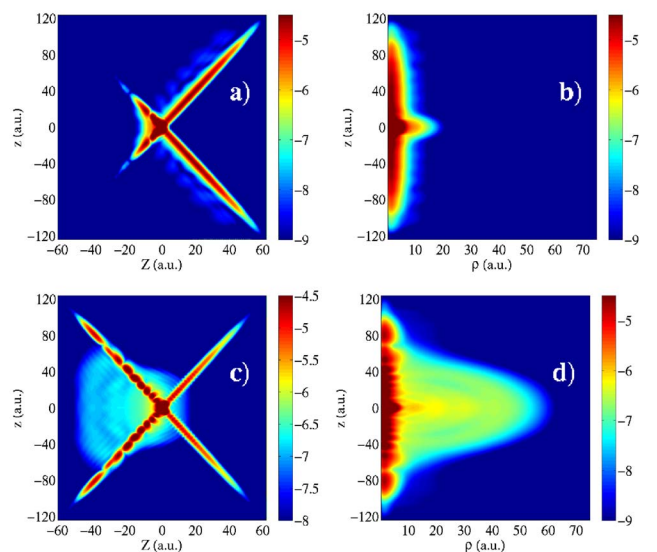


FIG. 2. (Color online) Spatial probability distributions integrated over  $\rho$  (left column) and  $Z$  (right column) at  $t=201$  a.u. (upper panels) and  $t=230$  a.u. (lower panels).

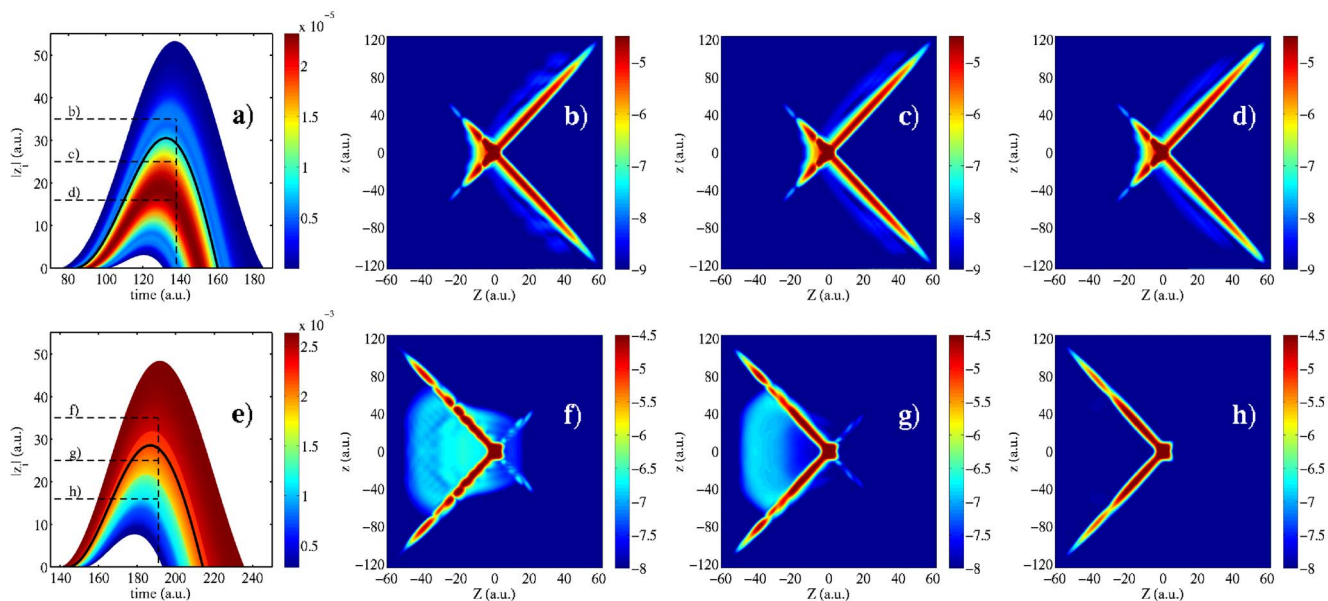


FIG. 3. (Color online) Panels (a) and (e): Classical electron trajectories leading to excitation of the ion around  $t=160$  a.u. [panel (a)] and to its ionization around  $t=220$  a.u. [panel (e)]. The color coding displays the  $S$ -matrix estimates for each trajectory. Note the solid black line which indicates the trajectory with the largest return energy. Other panels: Spatial probability distributions, integrated over  $\rho$ , at  $t=201$  a.u. [(b)–(d)] and at  $t=230$  a.u. [(f)–(h)]. Additional absorbing boundaries, indicated by the dashed lines in (a) and (e), are introduced for  $t \leq 138$  a.u. in the upper and for  $t \leq 191$  a.u. in the lower row.

and  $z_2$  axes in the upper and lower triangle of the double ionization region. This contribution corresponds to the small increase in the double ionization probability near the field maximum in Fig. 1 and is obviously due to the field ionization of the singly ionized  $\text{H}_2^+$  molecular ion. Since both electrons are released in opposite sides of the molecule at rather large interelectron distances along the polarization axis ( $z$  coordinate), the correlation between the electrons is small, as can be seen from the confinement of the distribution to low  $\rho$  [Fig. 2(b)]. In order to further analyze the origin of this contribution, we have performed test calculations, in which we removed the interelectron repulsion term  $\frac{1}{r}$  from Eq. (1). The resulting Hamiltonian is equivalent to two independent electrons in a  $\text{H}_2^+$  model potential. Starting from the ground state of this system and using the same laser pulse we obtained an ionization probability which is one order of magnitude smaller than the contribution corresponding to the small increase in Fig. 1. Thus, we concluded the latter one has to arise predominantly from the excited states of the ion. This excitation may be produced either by the rescattering of the first electron, i.e., the indirect excitation-tunnel mechanism of nonsequential double ionization [17–20], or by an alternative excitation mechanism, e.g., shake-up process [29].

Let us turn to the snapshots displayed in the lower panels of Fig. 2, which correspond to the wave function shortly after the next zero crossing of the field. In Fig. 2(c) one sees the correlated emission of two electrons at the same side of the core (in the  $-Z$  direction). This contribution corresponds to the second steep rise in the double ionization probability shown in Fig. 1. In comparison with Fig. 2(b), here the two electrons exhibit a strong transversal dynamics in the  $\rho$  direction [Fig. 2(d)]. Indeed, we observe that the smaller the

interelectron separation along the polarization direction (reflected by the  $z$  coordinate) the larger is the transversal distance ( $\rho$  coordinate) between the electrons, as expected for the direct NSDI emission of an electron pair.

To further identify the actual mechanisms we now attend to more subtle details. Following earlier suggestions [30,31] we will use an absorbing boundary to inhibit some return trajectories of the singly ionized wave packet to the ion. To illustrate our strategy we present in Figs. 3(a) and 3(e) the classical electron trajectories, which can lead to an excitation of the ion around  $t=160$  a.u. [Fig. 3(a)] and an ionization of the ion around  $t=220$  a.u. [Fig. 3(e)]. We note that an initial velocity  $v_0=0$  and the interaction with the field is taken into account only. The color coding represents the  $S$ -matrix estimates of ionization rates of  $\text{H}_2$  [32,33], evaluated for the field intensity at the starting time of the individual trajectories. We have performed a series of calculations with absorbers at different positions for  $t < t_0$ , as depicted by the dotted black lines in the Figs. 3(a) and 3(e).

The results of these additional calculations for the  $(Z, z)$  distributions are presented in the other panels of Fig. 3, where the panels in the upper and lower rows are taken at the same time instants as the corresponding ones in Fig. 2. In the panels from the left to the right the position of the additional absorber is moved towards the bound state region, therefore excluding the trajectories with longer excursions. It is clear that as the longer trajectories of the returning electron are gradually omitted, the patterns in the double ionization wave packets are altered. This is a clear evidence that the rescattering process is important for both mechanisms. It becomes particularly obvious from a specific detail of the results. According to the quantum theory of rescattering the firstly ion-

ized electron returns via a short and a long path with the same energy to the ion [34,35], and, hence, both contributions are expected to interfere. The comparison of the results in Figs. 3(c) and 3(g), where all but the short trajectories are omitted, with those of the full calculations [Figs. 2(a) and 2(c)] reveal indeed the disappearance of the characteristic interference patterns in the double ionization wave packets. Our analysis demonstrates, in particular, that the ionization process shown in Figs. 2(a) and 2(b) is indeed of the indirect nonsequential type, where the rescattering leads to an excitation of the ion. Note that in this case even the closest absorber does not lead to a suppression of the double ionization as drastic as in the direct case. This can be understood by inspection of Figs. 3(a) and 3(e), where it is clear that in the indirect case the shorter trajectories have associated higher ionization rates than in the direct one.

As pointed out above, the interference pattern in the double ionization distribution arise due to interferences between the different pathways. We did not detect any additional interference traces arising from the two nuclei. Indeed, due to the small internuclear distance in the equilibrium geometry the nonsequential double ionization dynamics of the

H<sub>2</sub> molecule, aligned along the polarization axis, appears to be very similar to that of the He atom [24]. This result is in agreement with recent observations on N<sub>2</sub> [22].

In conclusion, we have presented the *ab initio* calculations of the two-electron dynamics of H<sub>2</sub> in an intense few-cycle laser pulse beyond the one-dimensional approximation. Two pathways to double ionization have been identified, namely, the emission of a strongly correlated electron pair near the zeros of the field, and the ejection of an electron from the excited states of the molecular ion, and are shown to be linked to the return of the single ionized electron wave packet. Structures in the double ionization density have been interpreted as due to the interference of the contributions corresponding to the short and long quantum paths.

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