Nonsequential double ionization of molecules

Jakub S. Prauzner-Bechcicki, 1 Krzysztof Sacha, 1 Bruno Eckhardt, 2 and Jakub Zakrzewski 1

1Instytut Fizyki imienia Mariana Smoluchowskiego, Uniwersytet Jagielloński, ulica Reymonta 4, PL-30-059 Kraków, Poland
2Fachbereich Physik, Philipps-Universität Marburg, D-35032 Marburg, Germany

(Received 25 May 2004; published 15 March 2005)

Double ionization of diatomic molecules by short linearly polarized laser pulses is analyzed. We consider the final stage of the ionization process, that is the decay of a highly excited two electron molecule, which is formed after rescattering. The saddles of the effective adiabatic potential energy close to which simultaneous escape of electrons takes place are identified. Numerical simulations of the ionization of molecules show that the process can be dominated by either sequential or nonsequential events. In order to increase the ratio of nonsequential to sequential ionizations very short laser pulses should be applied.

I. INTRODUCTION

High intensity ultrashort-pulse lasers allow experimental studies of such effects as a non-sequential double ionization, high order harmonic generation or above threshold ionization [1,2]. While the single ionization of atoms or molecules, as well as the high order harmonic generation can be described within a single active electron model, such an approximation in the case of double ionization and laser intensity below the saturation value gives ionization rates that are much smaller than experimentally observed, indicating that interactions between electrons are important [1–4]. In this paper we consider the double ionization of molecules within a classical model for electrons in a combined Coulomb and external field applying the approach developed in [5–9] for the multiple ionization of atoms.

Multiphoton double ionization of atoms in strong laser fields can be regarded as a three step process [1,2]. In the first step one electron tunnels out through the Stark saddle and then is returned back to the nucleus [10,11]. Thereafter, in the second step, a highly excited state of an atom or molecule is formed at the expense of the energy brought back by the returning electron (up to 3.17U_p, where U_p is a ponderomotive energy). Finally, in the third step, such a highly excited compound state decays in one of several ways, through a single, double or multiple ionization. The starting point in our classical analysis of the double ionization of molecules is the excited complex, i.e., we assume that we have an initial state of two highly excited electrons close to the molecular core. We shall focus on double ionization events that can then appear as a possible channel of decay.

We would like to stress that sometimes all the double ionization events that happen after the rescattering process are referred to as being nonsequential. The classical analysis, as evidenced in [5], clearly suggests to distinguish events where both electrons escape during the same half-cycle of the electric field after the formation of the highly excited state and those where there is a time delay of one or several half-cycles between escaping electrons. In the following the term “nonsequential” will be reserved for the simultaneous escape of both electrons during the same half-cycle of the external field exclusively.

Experimental investigations of double ionization of diatomic molecules [12–15] showed that there are differences between molecular species. For example, the nitrogen molecule, N_2, clearly exhibits a “knee structure” in a double-to-single ionization yields ratio, like atoms do, while for the oxygen molecule, O_2, such a structure is not visible [13,14]. Moreover, in the case of N_2 it seems that electrons escape with similar momenta along field polarization axis more often than in the case of O_2 [15]. We will here consider this problem from the point of view of the classical analysis, which starts after the formation of the highly excited compound state, and discuss possible reasons for such different experimental observations. In our discourse we will approximate the molecule by two electrons and two charged nuclei, what is standard procedure in a case of highly excited states (internal structure is neglected). On the other hand, the Coulomb potentials are taken to describe all particle interactions, not the δ potentials as often assumed (see, e.g. [15]). In a consequence, what is considered here is a hydrogenlike molecule with different internuclear spacing. Internuclear distance, d=2.067 a.u., is referred to as N_2 molecule and internuclear distance, d=2.28 a.u., as O_2 molecule, respectively.

The paper is structured as follows. In Sec. II we introduce a theoretical model on which we base our analysis. Section III consists of the identification and description of the saddles in the potential. Then in Sec. IV we present results of the numerical simulations. And finally, in Sec. V we conclude.

II. MODEL

As we mentioned above, we start from a configuration that forms as a result of the re-scattering: it has two highly excited electrons close to the molecular core in the presence of linearly polarized laser field. The motion of the molecular core is frozen due to the fact that for short laser pulses molecules have not enough time to change their orientation [15,16]. Thus the Hamiltonian reads (in atomic units, which are used throughout)

\[ H = \frac{p^2}{2} + V, \]

where the potential
\[ V = V_1 + V_2 + V_{12} + V_F \]  

(2) 

consists of the potential energies associated with interactions of the electrons with the nuclei (the entire structure of the molecular core is approximated by two positively charge nuclei), 

\[ V_i = -\frac{1}{|\mathbf{r}_i - \mathbf{R}_1|} - \frac{1}{|\mathbf{r}_i - \mathbf{R}_2|}, \]  

(3) 

for \((i = 1, 2)\), where \(\mathbf{R}_i\) and \(\mathbf{r}_i\) indicate position of the nuclei and the electrons, respectively, the repulsion between electrons, 

\[ V_{12} = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}, \]  

(4) 

and the term describing interaction with the field (polarized along the \(z\) axis), 

\[ V_F = F(t)(z_1 + z_2). \]  

(5) 

The electric field strength \(F(t)\) has an oscillatory component times the envelope from the pulse, namely 

\[ F(t) = F_f(t)\cos(\omega t + \phi), \]  

(6) 

with \(F, \omega\) and \(\phi\) the peak amplitude, frequency, and initial phase of the filed, respectively, and with 

\[ f(t) = \sin^2(\pi t/T_d), \]  

(7) 

the pulse envelope of duration 

\[ T_d = n \frac{2\pi}{\omega}, \]  

(8) 

where \(n\) is number of cycles in the pulse.

For convenience, we place the origin of our coordinate system in the center of mass of the nuclei. Then two parameters appear, namely \(d\), the distance between nuclei, and \(\theta\), the angle between the molecular axis and the \(z\) axis (the polarization axis). Without loss of generality we assume that the molecule lies in the \(x\)-\(z\) plane, so that the potential energies for each electron become 

\[ V_i = -\frac{1}{\sqrt{\left(x_i + \frac{d}{2}\sin\theta\right)^2 + y_i^2 + \left(z_i + \frac{d}{2}\cos\theta\right)^2}} \]  

\[ -\frac{1}{\sqrt{\left(x_i - \frac{d}{2}\sin\theta\right)^2 + y_i^2 + \left(z_i - \frac{d}{2}\cos\theta\right)^2}}. \]  

(9) 

Within this model the only difference between different diatomic species lies in the distance, \(d\), between the nuclei. As mentioned in Sec. I, what is considered here is a hydrogen-like molecule with different internuclear spacing. Internuclear distance, \(d = 2.067\) a.u., is referred to as \(\text{N}_2\) molecule and internuclear distance, \(d = 2.28\) a.u., as \(\text{O}_2\) molecule, respectively.

**III. LOCAL ANALYSIS**

We consider here the evolution of electrons in combined Coulomb and external fields after a rescattering event once the highly excited compound state has formed. For one electron in the Coulomb potential, a superimposed external field opens a Stark saddle over which electrons can ionize. In our case we have two electrons and if there were no interaction between them they could escape simultaneously through the same saddle on top of each other. But with repulsion between electrons taken into account, the Stark saddle splits into two saddles that lie on opposite sides of the field polarization axis. In the case of atoms the two saddles lie symmetrically with respect to the polarization axis and the motion of the electrons can be analyzed in some symmetry subspace [6, 7]. For diatomic molecules (such as \(\text{N}_2\) or \(\text{O}_2\)) that does not generally occur since they possess their own symmetry axis which can be oriented at any angle with respect to the polarization axis, thus destroying the global symmetry. Nevertheless, an external field will introduce saddles over which electrons can escape, and the arguments presented in [6–9] again suggest that electrons that escape simultaneously during one half-cycle of the field have to pass close to the interacting electron saddles.

Before the double ionization escape both electrons pass close to the nuclei where they interact strongly with each other and with the nuclei. For that reason we may assume that all memory of the previous motion is lost. Then it is possible to assume that the compound state which decays to a doubly charged molecule can be modeled classically by a statistical distribution for two electrons close to the nuclei. Furthermore, the classical motion of the electrons is fast compared to the field oscillations and an adiabatic approximation, keeping the field fixed, becomes useful in the analysis of the ionization channels. Using this adiabatic assumption we will identify and describe saddle points near which the electrons can escape nonsequentially.

For a molecule oriented along the field axis the problem possesses axial symmetry. Then switching to the cylindrical coordinates \((\rho, \varphi, z_i)\), for \(i\)th electron one can easily define a symmetry subspace of electron motion. Restricting the electrons to a plane (i.e., \(\varphi_1 - \varphi_2 = \pi\)) their coordinates in the \(C_{2v}\) symmetry subspace are \(\rho_1 = \rho_2 = R, z_1 = z_2 = Z\) and the potential energy reduces to 

\[ V = -\frac{2}{\sqrt{R^2 + \left(Z - \frac{d}{2}\right)^2}} - \frac{2}{\sqrt{R^2 + \left(Z + \frac{d}{2}\right)^2}} + \frac{1}{2|R|} + 2F(t)Z. \]  

(10) 

The saddle configuration in this plane then corresponds to a ring of saddles around the field axis in the full configuration space.

With a molecule oriented perpendicular to the field there are two \(C_{2v}\) symmetry subspaces. One subspace is defined in the \(xz\) plane, the other in the \(yz\) plane. In the former case, the
electron coordinates in the subspace are $x_1 = X, y_1 = 0, z_1 = Z$ and $x_2 = -X, y_2 = 0, z_2 = Z$ and the potential energy reads

$$V = -\frac{2}{\sqrt{(X - \frac{d}{2})^2 + Z^2}} - \frac{2}{\sqrt{(X + \frac{d}{2})^2 + Z^2}} + \frac{1}{2|F|} + 2F(t)Z.$$  \hspace{1cm} (11)

For saddles which are in the $yz$ plane coordinates are $x_1 = 0, y_1 = Y, z_1 = Z$ and $x_2 = 0, y_2 = -Y, z_2 = Z$ and the potential energy is

$$V = -\frac{4}{\sqrt{\frac{d^2}{4} + y^2 + z^2}} + \frac{1}{2|F|} + 2F(t)Z.$$ \hspace{1cm} (12)

The potential energies Eqs. (10)–(12) and are shown in Fig. 1 for a set of parameters corresponding to the nitrogen molecule with an internuclear distance of $d = 2.067$ a.u. and for the field $F(t) = 0.07$ a.u., corresponding to an intensity of $1.7 \times 10^{14}$ W/cm$^2$. The saddles are clearly visible.

The case of a general orientation of the molecule is similar to the one with a perpendicular orientation: there are in general two saddles for nonsequential ionization, one in the plane defined by the molecular axis and the field, and a pair of saddles outside this plane. These two channels become equivalent when the molecule is parallel to the field axis and the axial symmetry is restored.

For a fixed external field the local stability analysis of the saddles reveals a few stable and several unstable directions. One unstable direction corresponds to the “reaction coordinate” for double ionization. The other unstable directions reflect interactions that will push electrons away from the double ionization path; if successful, they will push one electron back to the molecular core. If only one electron escapes the remaining one will typically be in a highly excited state and will have a chance to singly ionize during another field cycle. But following the distinction introduced earlier, we would not call such an event nonsequential.

The cross section behavior for nonsequential double ionization events can be obtained from the Lyapunov exponents that characterize the different directions. As in the case of double ionization without a field, analyzed many years ago by Wannier [17–20], the competition between the various unstable directions gives rise to an algebraic variation of the cross section with energy close to the threshold, namely,

$$\sigma(E) \propto (E - V_s)^\alpha,$$ \hspace{1cm} (13)

where $V_s$ is the saddle energy and the exponent contains the Lyapunov exponents,

$$\alpha = \frac{\sum \lambda_i}{\lambda_1};$$ \hspace{1cm} (14)

$\lambda_i$ is the Lyapunov exponent of the unstable direction corresponding to the nonsequential double ionization path, and $\lambda_j$ are the Lyapunov exponents of all other unstable directions of the saddle [8,21].

FIG. 1. Section through equipotential surfaces of the adiabatic potential, $V = V_1 + V_2 + V_3 + V_F$, for fixed time $t$ and for two symmetric orientation of the molecule, namely parallel [$\theta = 0$, top panel corresponding to Eq. (10)] and perpendicular to the field polarization axis, $Z$ [$\theta = \pi/2$, middle and bottom panels corresponding to Eq. (11) and Eq. (12), respectively]; the molecular parameter $d = 2.067$ a.u. and the external field $F(t) = -0.07$ a.u.

The properties of the saddles depend on the internuclear distance, $d$, as shown in Fig. 2. Starting with $d = 0$ (in which case the orientation angle $\theta$ is meaningless since a molecule reduces to an atom) and increasing $d$ the energy $V_s$ of the saddle corresponding to the parallel orientation ($\theta = 0$) is always the lowest and it decreases. For the other extremal orientation, i.e., $\theta = \pi/2$, the energies of the saddles (there are two saddles because of the axial symmetry breaking) increase and their values are the highest. Analyzing the dependence of $\alpha$ on the internuclear distance we see that increasing $d$ the cross section exponent of one of the saddles (corresponding to $\theta = \pi/2$) goes up while the other goes down. The exponent for $\theta = 0$ increases only slightly.
Variations of the parameters of the saddles with the orientation are shown in Fig. 3 for the internuclear distances corresponding to nitrogen, N₂, with \( d = 2.067 \) a.u., and oxygen, O₂, with \( d = 2.28 \) a.u. The energy \( V_S \) of all saddles increases and the exponent \( \alpha \) of one member of the saddle pairs increases while the other decreases. Figure 3 shows that the energies and exponents for the N₂ and O₂ molecules are quite similar—the largest differences between the species are of the order of few percent. Taking into account that the experimental results \([15,16]\) are for a statistical mixtures of different molecular orientations, we may conclude that from the point of view of our local analysis of the nonsequential decay channels one should not expect differences between N₂ and O₂.

IV. NUMERICAL SIMULATIONS

So far we have discussed the local analysis of the potential within the adiabatic assumption. Now we go one step further and perform numerical simulations of the dynamics of the ionization process.

Basic model of the rescattering process \([10,11]\) assumes that the electron, after tunneling, interacts only with the external field and is returned, by this field, back to the nucleus. From that model follows that the electron returns to the nucleus most probably when the field is zero. On the other hand, our local analysis implements that in order to have double nonsequential ionization event the saddle point in potential, through which electrons may escape simultaneously, is needed. From that fact it is evident that events when electron is returned back to the nucleus while the field is nonzero seem to dominate nonsequential ionization process. Similar conclusion is obtained from the analysis of experimental data for atoms; see Ref. [22]. In the following we perform numerical simulations starting with random initial phases of the field.

To avoid numerical divergences in the integration of the equations of motion, we introduce a smoothing factor \( e \) in the Coulomb potentials between the electrons and nuclei, Eq. (9) \([23,24]\). Then the potential terms read

\[
V_z = -\frac{1}{\sqrt{(x_i + \frac{d}{2} \sin \theta)^2 + y_i^2 + (z_i + \frac{d}{2} \cos \theta)^2 + e}}.
\]

We choose \( e = 0.01 \); it introduces negligible changes of the saddle energies \( V_S \) and exponents \( \alpha \) compared to the pure Coulomb values shown in Figs. 2 and 3.

During the final stages of a rescattering event both electrons are highly excited and they pass close to the nuclei where they interact strongly with them and with each other. Therefore, it is reasonable to assume, as mentioned in Sec. III, that all the memory of the earlier motion is lost. Then the initial state of the final stage for double ionization is a statistical distribution of two electrons close to the nuclei.
Hence we choose initial values of positions and momenta with respect to the microcanonical distribution for a given initial energy $E$. The energy should be in the range between $-I$ and $-I+3.17U_p$, where $I$ is the ionization energy. The positions are chosen microcanonically, but (for convenience) with the additional constraints that $z_i=0$ and $\sqrt{x_i^2+y_i^2} < 85$ a.u. (see discussion in [6]) and we start all simulations at the peak of the laser pulse with the phase of the field chosen randomly. In all simulations an ensemble of $10^5$ trajectories is used.

To simulate a real experiment one should consider a distribution of different initial energy of the complex and also different moments in a pulse when the complex is created. Within our model a fully quantitative description of the ionization process is not possible. We restrict ourselves to analysis how final distributions of electron momenta change with a change of the initial energy and pulse duration. We start all simulation at the peak of the pulse—starting at different moments changes the range but not the structure of the distributions [6,7].

Distributions of the final electron momenta parallel to the field axis for different initial energy $E$ and for different pulse durations are presented in Fig. 4. All data in the figure correspond to the $N_2$ molecule oriented along the field axis. For very short laser pulses ($n=2$ cycles) signatures of simultaneous electron escape are clearly visible—the distributions are localized along the diagonals indicating that the electrons escape predominately by passing close to the saddles analyzed in Sec. III. For longer pulses the distributions change their character. The first and fourth quadrants of the panels become strongly populated implying that a number of sequential decays significantly increases. The reason for that is quite obvious. After rescattering when a highly excited two
The electron complex is created, both a nonsequential double escape or a single ionization are possible. During the next cycles, a singly ionized molecule can emit their second electron, thus also contributing to double ionization. As the pulse becomes longer, the number of such sequential ionization events increases, even to the point of overwhelming the number of direct, nonsequential double ionization events.

Thus for sufficiently long pulses, even though the rescattering scenario is involved in the double ionization process, the momentum distributions will also show signatures of the sequential electron escape. If the initial energy $E$ is much higher than the minimal energy of a saddle $V_{S} < -1.2 \text{ a.u.}$ then the probability of nonsequential ionization is bigger and even if the pulse duration is quite long e.g., $n=26$ in panel (b) of Fig. 4 the signatures of nonsequential process remain noticeable [contrary to panel (d) where for $E=-0.6 \text{ a.u.}$ such signatures are not visible].

Figure 5 shows the distributions of ion momenta parallel to the field that correspond to the data presented in Fig. 4. As expected, the distributions are much narrower in the case when sequential ionization dominates than in the case when nonsequential processes dominate.

When we change the orientation of the molecule the distributions do not change significantly as one can see by comparing Fig. 6 and Fig. 4. For the field amplitude used in the simulations (which corresponds also to the experiment [15])

the saddles for nonsequential process are far away from the nuclei and the positions and other parameters of the saddles change only slightly with the angle of orientation $\theta$—compare Fig. 3.

Finally, in Fig. 7 we show data for the O$_2$ molecule. As expected, from the local analysis presented in Sec. III for the same initial energies $E$ and pulse durations as in the case of the N$_2$ molecule, the observed momentum distributions are very similar, Fig. 4. In the experiment of Eremina et al. [15], the results for O$_2$ differ considerably from those for N$_2$. The latter shows signatures of simultaneous electron escape while for O$_2$ it seems that sequential processes dominate. Our analysis indicates that there is practically no difference between N$_2$ and O$_2$ if similar initial conditions for the highly excited complex are used. It thus strongly suggests that the differences between the observations in for the two molecules are due to differences in the early stages of the excitation process and the nature of the compound state before the final decay towards multiple ionization.

This conclusion agrees well with results of [25,26]. The latter indicate that the symmetry of the valence orbital (N$_2$ has $\sigma_v$ bonding symmetry and O$_2$ has $\pi_v$, antibonding symmetry) has an influence on the above-threshold ionization spectra. Thus it may affect also the excitation process and, in particular, the initial conditions for decay of highly exited complex for different molecular species. That, in turn, may
modify the final parallel momenta distributions.

Our analysis also indicates that very short laser pulses should increase the ratio of non-sequential to sequential ionizations. It opens a possibility for observation of clear signatures of simultaneous electron escape both for N₂ and O₂ molecules, but in particular for oxygen, where the sequential events seem to dominate the nonsequential one.

V. SUMMARY

To summarize, we have performed a purely classical analysis of the final stage of the nonsequential double ionization of molecules in the strong laser field. It is based on the fact that all trajectories leading to the nonsequential escape of electrons have to pass close to the saddles in the potential that is formed when the laser pulse arrives [6–9].

We have started with the local analysis of the potential within the adiabatic approximation, and we have identified and described the saddles. Thereafter, we have shown results of numerical simulations. The later allow us to draw two conclusions. (i) From the point of view of classical analysis, within the considered model, there is no difference between nitrogen and oxygen molecules in the sense that both of them can show signatures of simultaneous double escape. (ii) Orientation of the molecule with respect to the field axis does not influence significantly the final momentum distribution for the initial energy range considered in the model. These conclusions are based on classical analysis of decay of highly excited two electron complex (that is formed in a rescattering event) where a molecular core is approximated by two positively charged nuclei.

The numerical results and their interpretation suggests strongly that shorter laser pulses should lead to an increase of the ratio of nonsequential to sequential ionizations. That suggestion could be tested experimentally. Higher relative efficiency of nonsequential process would be visible in the momentum distributions as a more pronounced symmetrical escape of the electrons.

ACKNOWLEDGMENTS

We are grateful to E. Eremina for making the experimental results accessible before publication. This work was partly supported by the Polish Ministry of Scientific Research Grant PBZ-MIN-008/P03/2003 and by the Deutsche Forschungsgemeinschaft.