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Double ionization of single oriented water molecules by electron impact: Second-order Born description

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The double ionization of isolated water molecules fixed in space is investigated within a theoretical approach based on the second-order Born approximation. Electron angular distributions have been studied for specific kinematical conditions. The three usual mechanisms, the shake-off and the two two-step mechanisms, have been identified. A significant contribution of the two-step mechanism is clearly visible for some particular kinematics.

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I. INTRODUCTION

Multiple ionization of atoms and molecules by charged particles is of considerable interest in many branches of physics as well as in life science. In this paper we propose a theoretical approach for studying the electron-induced double-ionization process of an oriented water molecule. In double-ionization experiments, usually referred as (e,3e) measurements, the scattered and the two ejected electrons are detected in coincidence. These experiments are very sensitive to the finest details of the dynamic process. However, due to their low cross sections, these (e,3e) experiments remain limited, up to now, to noble gases [1–4] and more particularly to the helium atom, which is an ideal target for theoretical studies [5–9]. When the scattered electron and one of the ejected electrons are detected in coincidence, these experiments are usually referred as (e,3-1e) measurements [10] and provide results that look like the well-known (e,2e) experiments corresponding to the single-ionization process. They are nevertheless able to identify the mechanisms of the double ionization.

Double ionization by electron impact can be generally envisaged either as a first-order or as a second-order process [11,12]. In the first case the incident electron interacts with one of the target electrons leading to its ejection. Afterwards, a second electron leaves the target because of the resulting change of the Coulomb potential. This first-order process is called shake-off (SO) [13]. For the other processes, Carlson and Krause [13] have proposed two other mechanisms usually referred to as two-step mechanisms, namely, the two-step 1 (TS1) and the two-step 2 (TS2) processes. The TS1 mechanism consists of a first interaction between the incoming projectile and one of the target electrons. Note that this first step is the same as that observed in the SO process. Once ejected, this target electron interacts with another one that is finally ejected. In the TS2 mechanism an incident electron interacts successively with two different target electrons ejecting them one by one. Other mechanisms can be found (see, for instance, Ref. [14]), but it is generally well accepted that these three mechanisms (SO, TS1, and TS2) are the main ones involved in the electron-induced double ionization of atoms or molecules [15].

On the theoretical side, very few models have been developed within the second-order Born approximation for describing the electron-induced double ionization of atoms. Thus, Popov *et al.* [12] have used a simple plane-wave model for describing the three electrons (incident, scattered, and ejected) in order to point out the relevance of each mechanism at high impact energies. Later, El Mkhanter and Dal Cappello [16] and Dal Cappello *et al.* [17] have introduced the TS2 process by assuming that the first step was an intermediate ionization and by describing the ejected electrons by Coulomb waves. Grin *et al.* [18] and Choubisa *et al.* [19] have considered all the possibilities (such as an elastic collision as a first step or a collision without ionization but with an excitation as a first step) by using the closure approximation. Finally, let us mention another calculation performed in the second-order Born approximation (with the closure approximation) by using the sophisticated Brauner, Briggs and Klar (BBK) model [20–22] (see Ancarani *et al.* [23]), which remains nevertheless very time consuming. Kheifets has also used the second-order Born approximation (with the closure approximation) [24] *coupled* to the sophisticated convergent close coupling (CCC) model [25]. This CCC model consists of solving the Lippmann-Schwinger equation for the three-body problem. However, due to a strong computationally intensive CCC part, Kheifets was obliged to restrict the applicability of his model to the kinematics including only *small momentum transfer* from the projectile to the target. All these models have been applied to the double ionization of helium.

Considering now the case of molecular target double ionization, to the best of our knowledge there are only two available models in the literature that use the second-order Born approximation for describing the double ionization of H_2. Thus, Mansouri *et al.* [26] have included the closure approximation with or without taking into account the contributions of some intermediate states and have used two Coulomb waves for describing the two ejected electrons. Alternatively, Serov and Joulakian have applied the external scaling method with the closure approximation but without the nondipole second-order Born terms [27].

Recently Lahmam-Bennani *et al.* [28,29] have shown that the second-order Born approximation was needed to describe the (e, 3-1e) data on double ionization of helium at the incident energy of about 600–700 eV, in particular for explaining the big shift of the binary peak experimentally observed. In these experiments, the symmetry around the momentum transfer is destroyed. This result can be explained only by the TS2 mechanism because the TS2 involves two successive collisions of the incoming particle with the target.

In the case of the double ionization of molecules, the target orientation may play an important role as reported by Champion *et al.* [30] in their recent study on double ionization of water by electron impact described within the first-order Born approximation.

In the present work, we consider the second-order Born approximation in order to understand the role of the TS2 mechanism in the double ionization of single-oriented water molecules. For this task, we have applied a second-order Born approximation, which is referred to as the 2CWG model, in which the two ejected electrons are described by Coulomb waves with a Gamow factor to take into account the repulsion between them, the incident and the scattered particles being described by plane waves.

Atomic units (a.u.) are used throughout unless otherwise stated.

II. THEORY

We here consider the following $(e,3e)$ reaction:

$$\mathrm{e}^- + \mathrm{H_2O} \rightarrow 3\mathrm{e}^- + \mathrm{H_2O}^{++}.$$

This reaction can be regarded as a pure electronic transition, since the closure relation over all possible rotational and vibrational states of the residual ion can be applied [31].

In the second-order Born approximation, the sixfold differential cross section (6DCS) is written, for a given molecular orientation defined by the Euler angles $(\alpha;\beta;\gamma)$, as [32]

$$\sigma^{(6)}(\alpha;\beta;\gamma) = \frac{d^6\sigma(\alpha;\beta;\gamma)}{d\Omega_{\mathrm{Euler}}d\Omega_a d\Omega_b d\Omega_s dE_a dE_b} = \frac{k_s k_a k_b}{k_i}|f_{B1} + f_{B2}|^2, \qquad (1)$$

where $d\Omega_{\mathrm{Euler}} = \sin\beta d\beta d\alpha d\gamma$ and $d\Omega_s$, $d\Omega_a$, and $d\Omega_b$ denote the elements of solid angles for the scattered and the two ejected electrons a and b, respectively, whereas the energy intervals of the ejected electrons are represented by dE_a and dE_b. The momenta of the incident, the scattered, and the two ejected electrons are denoted by $\vec{k}_i$, $\vec{k}_s$, $\vec{k}_a$, and $\vec{k}_b$, respectively.

In a $(e,3e)$ reaction the conservation of energy imposes $\frac{k_i^2}{2} = \frac{k_s^2}{2} + \frac{k_a^2}{2} + \frac{k_b^2}{2} + I^{2+}$, where I^{2+} represents the energy needed to eject two electrons from the water molecule.

The first-order Born term f_{B1} is written as

$$f_{B1} = -\frac{1}{2\pi}\langle \exp(i\vec{k}_s\cdot\vec{r}_0)\Psi_f(\vec{k}_a,\vec{k}_b,\vec{r}_1,\ldots,\vec{r}_{10}) \times |V|\exp(i\vec{k}_i\cdot\vec{r}_0)\Phi_i(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_{10})\rangle, \qquad (2)$$

where $\Phi_i(\vec{r}_1,\ldots,\vec{r}_{10})$ is the wave function of the initial state of the water molecule and $\Psi_f(\vec{k}_a,\vec{k}_b,\vec{r}_1,\ldots,\vec{r}_{10})$ is the wave function for the double continuum state of the water molecule. Note that we here neglect the exchange effects between the incoming particle and the ejected electrons because both the incident and the scattered electrons are faster than any ejected one.

In Eq. (2), the potential V represents the Coulomb interaction between the incoming electron and the target and is written as

$$V = -\frac{8}{r_0} - \frac{1}{|\vec{r}_0 - \vec{R}_1|} - \frac{1}{|\vec{r}_0 - \vec{R}_2|} + \sum_{i=1}^{10}\frac{1}{r_{0i}}, \qquad (3)$$

with $R_1 = R_2 = R_{\mathrm{OH}} = 1.814$ a.u., and $\vec{r}_i$ is the position vector of the ith bound electron of the target with respect to the center of the oxygen nucleus and $\vec{r}_0$ denotes the coordinate of the incident particle with $\vec{r}_{0i} = \vec{r}_0 - \vec{r}_i$.

Furthermore, the reduction of this 10-electron target problem to a two-electron target [33] may be done within the well-known frozen-core approximation. In this case the two target electrons are those that will be ejected during the double-ionization process. Moreover, it is worthwhile to note that the electrons in the doubly charged ion core are assumed to remain unaffected by the ionization process. This is a reasonable approximation provided that our study is limited to the ejection of valence shell electrons [33,34]. Then the initial wave function describing the two active electrons is $|\Phi_i(\vec{r}_1,\vec{r}_2)\rangle$ and is given by the single center wave function of Moccia [35] where the symmetry of the molecule is included. The final state wave function describing the two ejected electrons is the approximate BBK wave function (often called 2CWG model) [36] such as

$$\Psi_f(\vec{k}_a,\vec{r}_1,\vec{k}_b,\vec{r}_2) = \frac{1}{\sqrt{2}}[\Psi_C^-(\vec{k}_a,\vec{r}_1)\Psi_C^-(\vec{k}_b,\vec{r}_2) + \Psi_C^-(\vec{k}_a,\vec{r}_2)\Psi_C^-(\vec{k}_b,\vec{r}_1)]\varphi(|\vec{k}_a - \vec{k}_b|) \qquad (4)$$

with

$$\Psi_C^-(\vec{k}_e,\vec{r}_1) = \frac{1}{(2\pi)^{3/2}}\exp(i\vec{k}_e.\vec{r}_1)\Gamma(1 - i\alpha) \times \exp\left(-\frac{\pi}{2}\alpha\right){}_1F_1\,(i\alpha,1,-i(\vec{k}_e.\vec{r}_1 + k_e r_1)), \qquad (5)$$

where $\alpha = -Z/k_e$ and $Z = 2$, while the Gamow factor present in Eq. (4) is $\varphi(|\vec{k}_a - \vec{k}_b|) = \exp(-\frac{\pi\chi_{ab}}{2})\Gamma(1 - i\chi_{ab})$ with $\chi_{ab} = \frac{1}{|\vec{k}_a - \vec{k}_b|}$.

Note that the wave function (and then the symmetry) of the ionized $\mathrm{H_2O}^{++}$ molecule is not included in our model since a frozen-core approximation is used.

Additionally, let us note that the present work describes only the double ionization of doubly occupied molecular orbitals of the water molecule target [see Eq. (4)], but it is worthwhile to note that our model is not limited to this particular case and may be extrapolated to the double ionization of mixed target orbitals. In this context, let us mention the study of Elazzouzi *et al.* [37] dedicated to the double ionization of noble gases within the second-order Born approximation where the six electrons of the last shell (np^6) as well as the three final states of the ion (^3P, ^1D, and ^1S) were considered. More recently, such singlet and triplet state contributions into the double ionization of water molecule were also considered by Oubaziz *et al.* [38] within the first-order Born approximation.

Finally, note that the integration over the projectile coordinates (r_0) can be performed analytically so that the first-order

Born term f_{B1} now becomes

$$f_{B1} = -\frac{2\sqrt{2}}{K^2}\langle \Psi_C^-(\vec{k}_a,\vec{r}_1)\Psi_C^-(\vec{k}_b,\vec{r}_2)|\exp(i\vec{K}\cdot\vec{r}_1) + \exp(i\vec{K}\cdot\vec{r}_2) - 2|\Phi_i(\vec{r}_1,\vec{r}_2)\rangle\phi(|\vec{k}_a - \vec{k}_b|) \quad (6)$$

with $\vec{K} = \vec{k}_i - \vec{k}_s$ being the momentum transfer. The term due to the nucleus in Eq. (6) can be removed if orthogonalized wave functions are used to describe the initial state and the final state. In fact, many authors have shown that only the differential cross sections are a little bit affected by the above-cited nuclear interaction term (see, for instance, Ref. [39]).

Finally, let us also mention that we can consider the Eq. (6) as including the SO mechanism since there is only one interaction between the incoming particle and the target. Nevertheless, the TS1 mechanism is also included in a partial way since the interaction between the two ejected electrons is taken into account via the Gamow factor [12].

The second-order Born term f_{B2} is given by

$$f_{B2} = \frac{1}{8\pi^4}\sum_n\int\frac{d\vec{q}}{q^2 - k_n^2 - i\varepsilon}\langle\exp(i\vec{k}_s\cdot\vec{r}_0)\Psi_f(\vec{k}_a,\vec{r}_1,\vec{k}_b,\vec{r}_2)| \times V|\exp(i\vec{q}\cdot\vec{r}_0)\Phi_n(\vec{r}_1,\vec{r}_2)\rangle\langle\exp(i\vec{q}\cdot\vec{r}_0)\Phi_n(\vec{r}_1,\vec{r}_2)| \times V|\exp(i\vec{k}_i\cdot\vec{r}_0)\Phi_i(\vec{r}_1,\vec{r}_2)\rangle, \quad (7)$$

where the summation over n means that we take into account all the contributions of the n discrete and continuum states of the water molecule. It means that the incident electron collides two times with the target. This corresponds to the well-known TS2 mechanism. Performing the integration over $\vec{r}_0$ in Eq. (7) and applying the closure approximation we get [18]

$$\bar{f}_{B2} = \frac{2}{\pi^2}\int\frac{d\vec{q}}{q^2 - p^2 - i\varepsilon}\frac{1}{K_i^2K_f^2} \times \langle\Psi_f(\vec{k}_a,\vec{r}_1,\vec{k}_b,\vec{r}_2)|\exp(i\vec{K}_f\cdot\vec{r}_1)+\exp(i\vec{K}_f\cdot\vec{r}_2) - 2| \times |\exp(i\vec{K}_i\cdot\vec{r}_1) + \exp(i\vec{K}_i\cdot\vec{r}_2) - 2|\Phi_i(\vec{r}_1,\vec{r}_2)\rangle, \quad (8)$$

where $\vec{K}_i = \vec{k}_i - \vec{q}$ and $\vec{K}_f = \vec{q} - \vec{k}_s$, $\vec{K} = \vec{K}_i + \vec{K}_f = \vec{k}_i - \vec{k}_s$ being the momentum transfer.

We have also

$$\frac{p^2}{2} = \frac{k_i^2}{2} - \bar{w}, \quad (9)$$

where $\bar{w}$ refers to the average excitation energy.

Finally, it is important to note that the integrals over $d\vec{q}$ must be performed numerically with great care [40].

III. RESULTS AND DISCUSSION

Here we investigate the double ionization of the four outer molecular subshells of an oriented water molecule, hereafter referred to as $1b_1$, $3a_1$, $1b_2$, and $2a_1$. The kinematics corresponds to a scattered electron of 250 eV, i.e., a case where a relatively important second-order Born contribution already has been reported by several authors for the single-ionization process [40–42].

We first study the case $(\alpha;\beta;\gamma) = (0;0;0)$ and consider the 6DCSs for a $(e,3e)$ experiment as a function of the ejected angles θ_a and θ_b in a coplanar geometry, i.e., with $\varphi_s = \varphi_a = \varphi_b = 0$ like in Refs. [30,41].

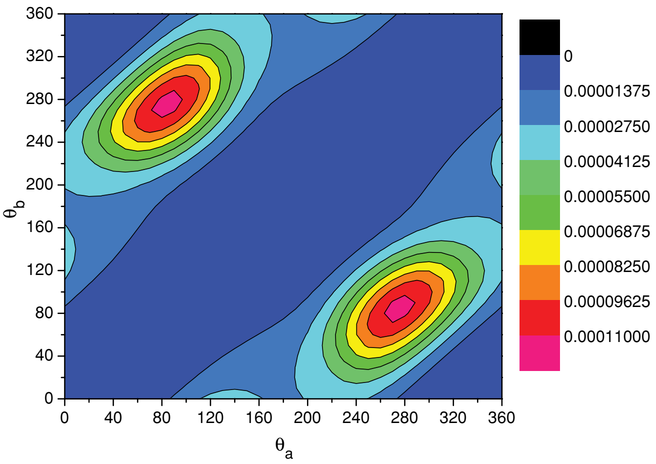

FIG. 1. (Color online) Sixfold differential cross sections (expressed in a.u.) for the double ionization of the water molecule ($1b_2$) oriented in the direction $\alpha = \beta = \gamma = 0$ for $\theta_s = 0$ and $\varphi_s = \varphi_a = \varphi_b = 0$ as a function of the ejected angles θ_a and θ_b relative to the incident electron. The ejected energies are $E_a = E_b = 10$ eV and $E_s = 250$ eV. The 6DCSs have been calculated in the second-order Born approximation.

In the case of the $1b_2$ molecular state, we observe nonnegligible 6DCSs (see Fig. 1) as opposed to Champion *et al.*, who have described the double-ionization process within the first-order Born description [30], whereas we reveal a "genuine" contribution of the TS2 mechanism.

Thus, for $\theta_s = 0$ and a particular target orientation defined by $(\alpha;\beta;\gamma) = (0;0;0)$, it appears necessary to consider, for the $1b_2$ molecular state, two successive collisions of the projectile: a first one characterized by a scattered angle close to 0 such as $\theta_{s1} \cong 0^\circ_+$ and a second one where the scattered angle is also close to 0 ($\theta_{s2} \cong 0^\circ_-$)in order to verify the relation $\theta_{s1} + \theta_{s2} = \theta_s = 0$ (see Fig. 2). Then the positions of the maxima, namely, ($\theta_a = 90^\circ$,$\theta_b = 270^\circ$) and ($\theta_a = 270^\circ$,$\theta_b = 90^\circ$), can be easily explained. Indeed, during a fast collision a first target electron is ejected along the direction $\theta_a = 90^\circ$, while a second one is ejected along the direction $\theta_b = 270^\circ$ during a second collision.

In Figs. 3(a) and 3(b), we report the results predicted by the first- and the second-order Born approximation, respectively, for the double ionization of the molecular state $2a_1$. It is

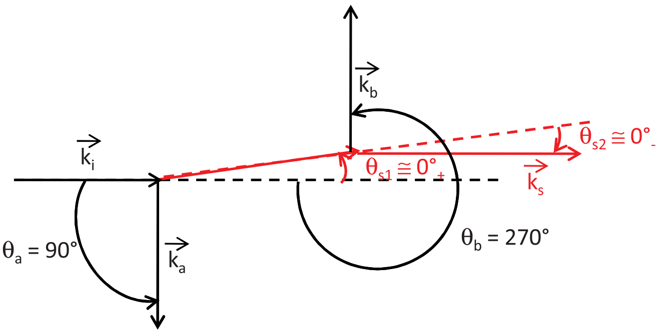

FIG. 2. (Color online) Sketch of the kinematics for the two-step 2 (TS2) process observed for the $1b_2$ molecular state oriented in the direction $\alpha = \beta = \gamma = 0$ for $\theta_s = 0$ and $\varphi_s = \varphi_a = \varphi_b = 0$. The ejected energies are $E_a = E_b = 10$ eV and $E_s = 250$ eV.

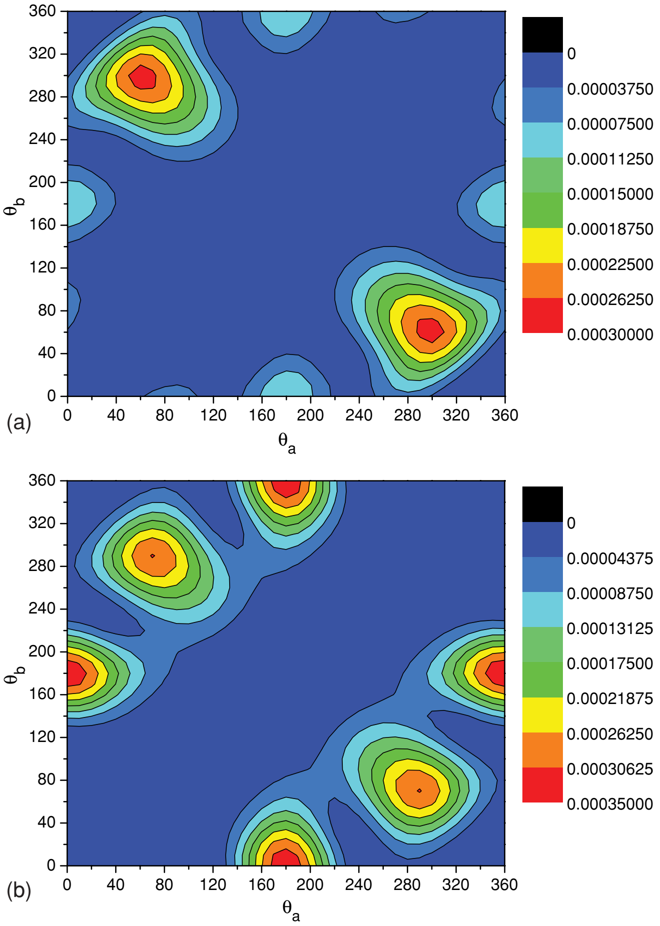

FIG. 3. (Color online) (a) Sixfold differential cross sections (expressed in a.u.) for the double ionization of the water molecule ($2a_1$) oriented in the direction $\alpha = \beta = \gamma = 0$ for $\theta_s = 0$ and $\varphi_s = \varphi_a = \varphi_b = 0$ as a function of the ejected angles θ_a and θ_b relative to the incident electron. The ejected energies are $E_a = E_b = 10$ eV and $E_s = 250$ eV. The 6DCSs have been calculated in the first-order Born approximation. (b) Sixfold differential cross sections (expressed in a.u.) for the double ionization of the water molecule ($2a_1$) oriented in the direction $\alpha = \beta = \gamma = 0$ for $\theta_s = 0$ and $\varphi_s = \varphi_a = \varphi_b = 0$ as a function of the ejected angles θ_a and θ_b relative to the incident electron. The ejected energies are $E_a = E_b = 10$ eV and $E_s = 250$ eV. The 6DCSs have been calculated in the second-order Born approximation.

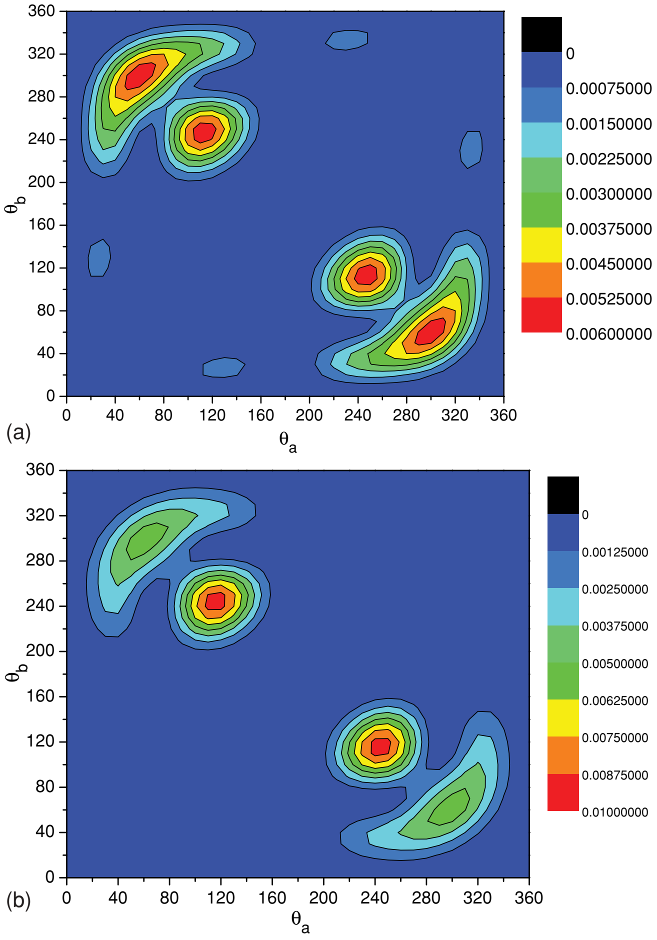

FIG. 4. (Color online) (a) Sixfold differential cross sections (expressed in a.u.) for the double ionization of the water molecule ($1b_1$) oriented in the direction $\alpha = \beta = \gamma = 0$ for $\theta_s = 0$ and $\varphi_s = \varphi_a = \varphi_b = 0$ as a function of the ejected angles θ_a and θ_b relative to the incident electron. The ejected energies are $E_a = E_b = 10$ eV and $E_s = 250$ eV. The 6DCSs have been calculated in the first-order Born approximation. (b) Sixfold differential cross sections (expressed in a.u.) for the double ionization of the water molecule ($1b_1$) oriented in the direction $\alpha = \beta = \gamma = 0$ for $\theta_s = 0$ and $\varphi_s = \varphi_a = \varphi_b = 0$ as a function of the ejected angles θ_a and θ_b relative to the incident electron. The ejected energies are $E_a = E_b = 10$ eV and $E_s = 250$ eV. The 6DCSs have been calculated in the second-order Born approximation.

evident from Fig. 3(a) that the TS1 mechanism is the main mechanism in view of the first-order Born approximation, as already reported by Champion *et al.* [30] for an incident energy of 1 keV and Dal Cappello *et al.* [41] for a scattered energy of 500 eV. In this case, the maxima are located at $|\theta_a - \theta_b| = 140°$. The incoming electron collides with one target electron, which is ejected along the direction of the momentum transfer $\vec{K}$. Then this target electron collides with another molecular electron. This second collision is not a pure elastic collision [8], and the two electrons are ejected with $|\theta_a - \theta_b|$ greater than 90° due to the repulsion between them. Furthermore, when the second term of the Born amplitude is added [see Fig. 3(b)], we clearly observe a dramatic change of the results. The maxima are now obtained for $|\theta_a - \theta_b| = 180°$. This means that the SO mechanism is the main mechanism involved in the double-ionization process. The signature of the SO mechanism is characterized by a first electron ejected along the momentum transfer leading to an electronic rearrangement of the target and to the ejection by a second electron in the opposite direction. Nevertheless, we also observe a secondary (smaller) maximum for $|\theta_a - \theta_b| = 140°$ as observed by Dal Cappello *et al.* [41] for a scattered energy of 500 eV. In this case, the TS1 and TS2 mechanisms destructively interfere.

In Fig. 4(a), the results of the first-order Born approximation have been reported for the double ionization of the molecular state $1b_1$. We find results close to those found by Champion *et al.* [30] and Dal Cappello *et al.* [41] for an higher incident energy. Thus, we observe four hills: a first one extending from $\theta_a = 10°$ to $\theta_a = 150°$ (while θ_b ranges from $\theta_b = 210°$ to $\theta_b = 350°$) and a second one extending

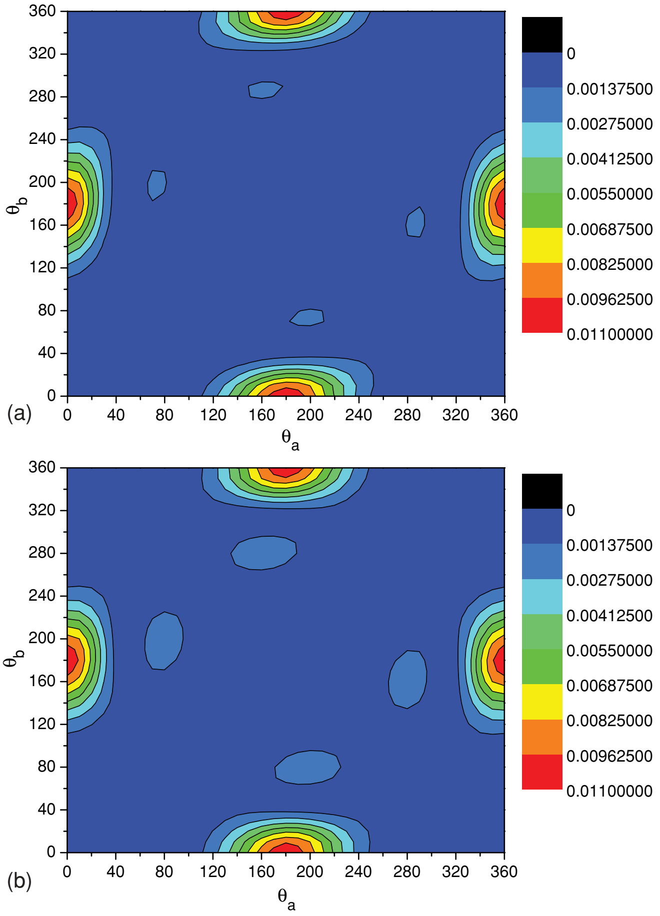

FIG. 5. (Color online) (a) Sixfold differential cross sections (expressed in a.u.) for the double ionization of the water molecule ($3a_1$) oriented in the direction $\alpha = \beta = \gamma = 0$ for $\theta_s = 0$ and $\varphi_s = \varphi_a = \varphi_b = 0$ as a function of the ejected angles θ_a and θ_b relative to the incident electron. The ejected energies are $E_a = E_b = 10$ eV and $E_s = 250$ eV. The 6DCSs have been calculated in the first-order Born approximation. (b) Sixfold differential cross sections (expressed in a.u.) for the double ionization of the water molecule ($3a_1$) oriented in the direction $\alpha = \beta = \gamma = 0$ for $\theta_s = 0$ and $\varphi_s = \varphi_a = \varphi_b = 0$ as a function of the ejected angles θ_a and θ_b relative to the incident electron. The ejected energies are $E_a = E_b = 10$ eV and $E_s = 250$ eV. The 6DCSs have been calculated in the second-order Born approximation.

from $\theta_a = 60^\circ$ to $\theta_a = 150^\circ$ (while θ_b ranges from $\theta_b = 200^\circ$ to $\theta_b = 290^\circ$), the two other hills being obtained by symmetry. These two groups of maxima verify $|\theta_a - \theta_b| \approx 120^\circ$ for the forward scattering and $|\theta_a - \theta_b| \approx 240^\circ$ for the backscattering. It means that the TS1 is the main mechanism, as already observed by Kada *et al.* [32] for the double ionization of a nonoriented molecular state $1b_1$. When the second-order Born approximation is considered [Fig. 4(b)], the amplitude obtained for describing the forward scattering is decreased, while that for the backscattering is increased. This may be explained by the presence of a destructive interference effect due to the TS2 mechanism for the forward scattering.

Figure 5(a) shows the results of the first-order Born approximation for the double ionization of the molecular state $3a_1$. We observe that the maxima are given by $|\theta_a - \theta_b| \approx 180^\circ$. This corresponds to the signature of the SO mechanism [30–39]. When the second term of the Born approximation is taken into account, the maxima remain still located at $|\theta_a - \theta_b| \approx 180^\circ$, but their magnitudes decrease a little bit [see Fig. 5(b)].

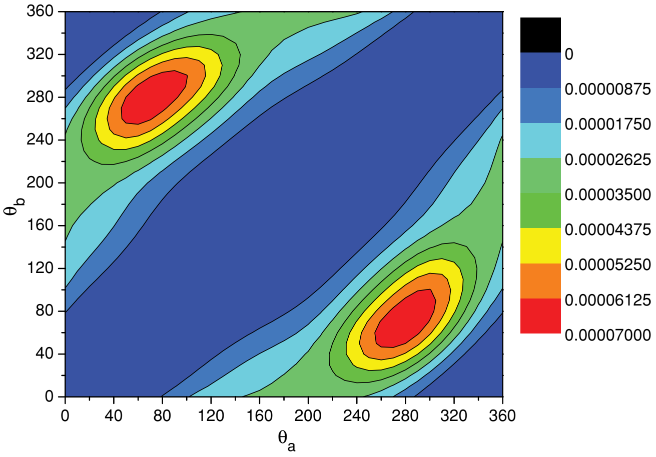

FIG. 6. (Color online) Sixfold differential cross sections (expressed in a.u.) for the double ionization of the water molecule ($1b_1$) oriented in the direction $\alpha = 0$, $\beta = \gamma = \pi/2$, for $\theta_s = 0$ and $\varphi_s = \varphi_a = \varphi_b = 0$ as a function of the ejected angles θ_a and θ_b relative to the incident electron. The ejected energies are $E_a = E_b = 10$ eV and $E_s = 250$ eV. The 6DCSs have been calculated in the second-order Born approximation.

When molecular target rotations such as $(\alpha;\beta;\gamma) = (0;\pi/2;0)$ and $(\alpha;\beta;\gamma) = (0;\pi/2;\pi/2)$ are applied, we obtain the following rules [30]:

$$R_0(0;\pi/2;0):\begin{cases}P_X \to P_Z\\ P_Y \to P_Y\\ P_Z \to P_X\end{cases}\quad \text{and}$$

$$R_0(0;\pi/2;\pi/2):\begin{cases}P_X \to P_Y\\ P_Y \to P_Z\\ P_Z \to P_X\end{cases},$$

where P_X corresponds to a $2p_{+1}$ orbital, which is collinear to the X molecular axis, P_Y to a $2p_{-1}$ orbital, which is collinear to the Y molecular axis, and P_Z to a $2p_0$ orbital, which is collinear to the Z molecular axis. The water molecule is situated in the YZ plane with its bisecting line along the Z axis.

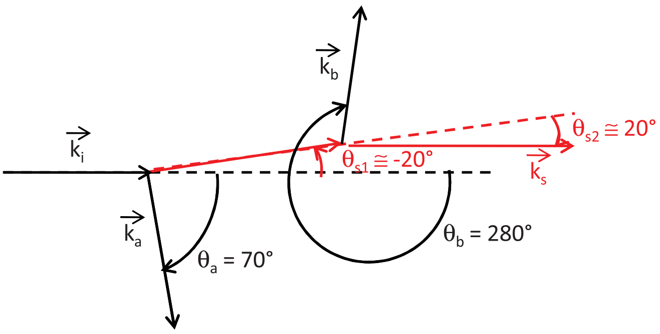

FIG. 7. (Color online) Sketch of the kinematics for the two-step 2 (TS2) process observed for the $1b_2$ molecular state oriented in the direction $\alpha = 0$, $\beta = \gamma = \pi/2$, for $\theta_s = 0$ and $\varphi_s = \varphi_a = \varphi_b = 0$. The ejected energies are $E_a = E_b = 10$ eV and $E_s = 250$ eV.

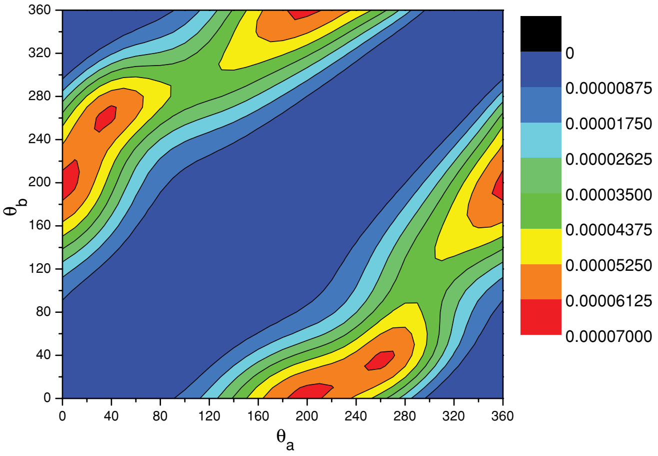

FIG. 8. (Color online) Sixfold differential cross sections (expressed in a.u.) for the double ionization of the water molecule ($1b_2$) oriented in the direction $\alpha = \gamma = 0$, $\beta = \pi/2$, for $\theta_s = 0$ and $\varphi_s = \varphi_a = \varphi_b = 0$ as a function of the ejected angles θ_a and θ_b relative to the incident electron. The ejected energies are $E_a = E_b = 10$ eV and $E_s = 250$ eV. The 6DCSs have been calculated in the second-order Born approximation.

Grossly speaking, the $1b_1$ molecular state is mainly governed by a $2p_{+1}$ orbital, the $1b_2$ by a $2p_{-1}$ orbital, the $3a_1$ by a $2p_0$ orbital, and the $2a_1$ by a $2s$ component. It means that, if we consider for instance the rotation $(\alpha;\beta;\gamma) = (0;\pi/2;\pi/2)$ for the $1b_1$ molecular state, we are in the same situation as that reported for the $1b_2$ molecular orbital for a target oriented in the $(\alpha;\beta;\gamma) = (0;0;0)$ direction [see the rotation rules reported above according to which $P_X \xrightarrow{R_0(0;\pi/2;\pi/2)} P_Y$. In this particular case, the first-order Born approximation gives no contribution (see Ref. [30]). When we take into account the second-order Born approximation we get two maxima located at ($\theta_a = 70°,\theta_b = 280°$) and ($\theta_a = 280°,\theta_b = 70°$) (Fig. 6) as in Fig. 1.

Here again we observe a situation of "pure" TS2 mechanism with nevertheless some minor changes for the location of the maxima. To explain them, we may propose a scheme according to which two successive collisions occur: a first one characterized by a scattered angle $\theta_{s1} = -20°$ and a second one where the scattered angle $\theta_{s2} = 20°$ in order to verify the relation $\theta_{s1} + \theta_{s2} = \theta_s = 0$ (Fig. 7).

Under these conditions, positions of the maxima, namely, ($\theta_a = 70°,\theta_b = 280°$) and ($\theta_a = 280°,\theta_b = 70°$) may easily be explained. Indeed, during a first fast collision one target electron is ejected along the direction $\theta_a = 70°$ such as $|\theta_a - \theta_{s1}| = 90°$(elastic collision) while a quasielastic collision such as $|\theta_b - \theta_s| = 280°$ occurs in a second step.

Another interesting case is that reported in Fig. 8 where the rotation $(\alpha;\beta;\gamma) = (0;\pi/2;0)$ is applied to the $1b_2$ molecular orbital.

Once again, no first-order Born contribution was reported by Champion *et al.* [30], where the authors relied to the relative position of the impacted orbital (here perpendicular) with respect to the chosen *XZ* collision plane ($\varphi_s = \varphi_a = \varphi_b = 0$). When the second-order Born approximation is used, we still get two maxima located at ($\theta_a = 40°$, $\theta_b = 260°$) and ($\theta_a = 260°$, $\theta_b = 40°$), these latter being easily explained by two successive collisions due to a "pure" TS2 mechanism. In this scheme, we would have a first collision characterized by a scattered angle such $\theta_{s1} = -60°$ and a second one with a scattered angle $\theta_{s2} = 60°$ in order to verify the relation $\theta_{s1} + \theta_{s2} = \theta_s = 0$. Thus, during a first fast collision one target electron is ejected along the direction $\theta_a = 40°$ such as $|\theta_a - \theta_{s1}| = 100°$ (quasielastic collision), while a quasielastic collision such as $|\theta_b - \theta_s| = 260°$ occurs in a second step (Fig. 9).

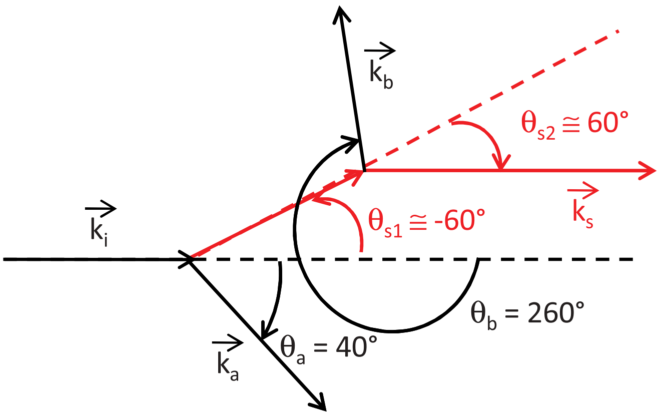

FIG. 9. (Color online) Sketch of the kinematics for the two-step 2 (TS2) process observed for the $1b_2$ molecular state oriented in the direction $\alpha = \gamma = 0$, $\beta = \pi/2$, for $\theta_s = 0$ and $\varphi_s = \varphi_a = \varphi_b = 0$. The ejected energies are $E_a = E_b = 10$ eV and $E_s = 250$ eV.

IV. CONCLUSION

In this work we have carried out a theoretical analysis of the sixfold differential cross sections for the double ionization of oriented water molecules by electron impact. The second-order Born approximation was used with a single-center molecular wave function for describing the initial state. Then, for the first time, we here clearly identify the three mechanisms involved in the double-ionization process and point out particular situations where the TS2 mechanism is the only one possible mechanism (where the contribution of the first-order Born approximation is zero). In the other cases investigated here, the TS2 mechanism does not appear as the main mechanism, but its contribution may slightly change the shape of the sixfold differential cross sections. It is clear that the differences between the first-order Born approximation and the second-order Born approximation are generally very important, particularly when the first-order Born approximation gives no contribution, and could be investigated in future experiments.

Finally, note that at this stage, no direct comparison with experiment is possible, and we hope that, in the near future, these current predictions will be confirmed by experimental observations.

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