Electron impact double ionization of single oriented water molecules: evidence of the role of the two-step mechanism

C Dal Cappello¹, I Kada², A Mansouri² and C Champion¹

¹ Université Paul Verlaine-Metz, LPMC, Institut de Physique, 1 bd Arago, 57078 Metz Cedex 3, France
² Université Ferhat Abbas, LPQSD, Département de physique, 19000 Sétif, Algérie

E-mail : cappello@univ-metz.fr

Abstract. Double ionization of single oriented water molecules is here investigated within a theoretical approach based on the second Born approximation. The initial wave function describing the two active electrons is taken from a single-centre description previously used with success for describing the single ionization process whereas the final state wave function describing the two ejected electrons is the approximate BBK wave function. Secondary electron angular distributions for an incident energy close to 600 eV are then reported for particular kinematical conditions and compared to their first Born homologous. Strong similarities are observed in terms of maxima localization as well as identification of the main mechanisms involved in the double ionization. On the contrary, for particular kinematical conditions we demonstrate that the first-order treatment is unable to explain the observations contrary to the second-order approximation which points out pure TS2 contributions.

1. Introduction

Very recently Lahmam-Benanni et al. [1] have shown that the second Born approximation was needed for describing the experimental observations on double ionization of helium by 600-700 eV electron impact. In this kind of experiments - called \((e,3-1e)\) [1-2] - only the scattered electron and one of the bound ejected electrons are detected in coincidence contrary to the so-called \((e,3e)\) experiments [3-4] where the three “final” electrons are detected in coincidence both in direction and in energy, these latter being issued from the same ionizing event. However, due to their low cross sections, the \((e,3e)\) experiments remain up to now limited to noble gases [5-7] and helium atom, this latter being the ideal target for theoretical studies [4, 8-11].

In fact, similarly to the well-known \((e,2e)\) experiments for single ionization process, the \((e,3-1e)\) experiments permit the identification of the mechanisms of the double ionizing process, namely, the shake-off (SO), the two-step 1 (TS1) and the two-step 2 (TS2) [12]. Note that contrary to the SO process which consists in a single ionization of one of the target electrons - the other one being simply ejected due to the relaxation of the target - the TS1 and TS2 mechanisms imply two electrons: in the first one, the incident electron interacts with one target electron which is ejected and then collides another target electron whereas in the second one the incident electron successively ejects two target electrons itself. This last mechanism clearly involves two interactions between the incident electron...
and the target and then needs the use of the second Born approximation whose signature is an absence of symmetry around the momentum transfer [13].

In the present work, we treat the double ionization within the second Born approximation by using a 2CWG model previously used with success [14] for describing the big shift of the binary peak observed by Lahnum-Bennani et al. [1]. In this model, the two ejected electrons are described in terms of Coulomb waves together with a Gamow factor to take into account the repulsion between them whereas plane waves are used for treating the incident and the scattered electrons. The Gamow factor was first used by Brauner et al. [15] in their study on the ionization of atomic hydrogen. In fact, in its original version, the Gamow factor was seen as a normalization constant of the third Coulomb wave function (BBK model). A successful agreement in reproducing a great number of (e,2e) cross section measurements was then reported by many authors (see for example Röder et al. [16]) although this latter was unable to reproduce the Wannier law, what was corrected by Ward and Macek [17] who proposed in 1994 a “revised” Gamow factor (almost identical to the original Gamow factor in particular in shape). It was then shown that introducing the Gamow factor into the cross section calculations allowed reproducing the dominant angular behaviour of the differential cross sections although such a multiplicative factor annihilates the overall normalization of the theoretical differential cross sections. Under these conditions, our model appears as a valid approximation for predicting new experimental results and then exploring the possible mechanisms.

Despite its importance in many fields like astrophysics, plasma physics and especially in radiobiology where it is considered as the privileged molecule for modelling the biological medium, water has been only rarely approached in (e,3e) studies. Let us nevertheless cite the recent work of Champion et al. [18] where it has been clearly shown that the target orientation might play a major role in the secondary electron angular distributions for isolated water molecules impacted by 1 keV electrons. In their study, the authors have described the double ionization process within the 1st Born approximation. Kheifets [19] and El Mkhanter and Dal Cappello [20] have shown that the second Born approximation was especially important at 0.5 keV. In the present work we consider an incident energy close to 600 eV and use the second Born approximation in order to know if the TS2 mechanism can be identified when considering the orientation of the molecule.

Atomic units are used throughout unless otherwise stated.

2. Theory

In the second Born approximation, the fivefold differential cross section (FDCS) is given by

\[ \sigma^{(5)}(\alpha, \beta, \gamma) = \frac{d^3 \sigma(\alpha, \beta, \gamma)}{d\Omega_a d\Omega_b d\Omega_a dE_a dE_b} = \frac{k_i k_s k_b}{k_i} \left| f_{B1} + f_{B2} \right|^2, \]

where \(d\Omega_a, d\Omega_b\) and \(d\Omega_b\) denote the elements of solid angles for the scattered and the 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, scattered, and ejected electrons are denoted by \(\vec{k}_i\), \(\vec{k}_s\), \(\vec{k}_a\), and \(\vec{k}_b\), respectively. Furthermore, note that the FDCS depends here on the Euler angles \((\alpha, \beta, \gamma)\).

The first Born term \(f_{B1}\) is written as

\[ f_{B1} = -\frac{1}{2\pi} \left\langle \exp\left( i \vec{k}_s \cdot \vec{r}_0 \right) \Psi_f \left( \vec{k}_a, \vec{k}_b, \vec{r}_1, ..., \vec{r}_{10} \right) \right| \left[ \exp\left( i \vec{k}_s \cdot \vec{r}_0 \right) \Phi_i \left( \vec{r}_1, \vec{r}_2, ..., \vec{r}_{10} \right) \right], \]

where \(\Phi_i(\vec{r}_1, ..., \vec{r}_{10})\) is the wave function of the initial state of the water molecule and \(\Psi_f(\vec{k}_a, \vec{k}_b, \vec{r}_1, ..., \vec{r}_{10})\) is the wave function for the double continuum state of the water molecule. The potential \(V\) represents the Coulomb interaction between the incoming electron and the target and is given by...
\[ V = -\frac{8}{r_0} - \frac{1}{|\vec{r}_0 - \vec{R}_1|} - \frac{1}{|\vec{r}_0 - \vec{R}_2|} + \sum_{i=1}^{10} \frac{1}{r_{0,i}}, \]  

with \( R_1 = R_2 = R_{0ff} = 1.814 \) a.u. while \( \vec{r}_i \) is the position vector of the \( i^{th} \) bound electron of the target with respect to the centre of the oxygen nucleus and \( r_0 \) denotes the coordinate of the incident particle with \( \vec{r}_{0i} = \vec{r}_0 - \vec{r}_i \). Furthermore, note that we have used in this work the well-known frozen-core approximation in order to reduce the 10-electron target problem to a two-active electron target \cite{21} i.e. those which will be ejected after the collision, what is coherent with the fact that we are here essentially interested by the ejection of electrons from valence shells. In these conditions, it is reasonable to assume that the remaining electrons of the doubly charged ion core are unaffected by the ionization process itself \cite{21-22}.

The initial wave function describing the two active electrons is \( \Phi_i(\vec{r}_1, \vec{r}_2) \) and is taken from the single centre description reported by Moccia \cite{23} whereas the final state wave function describing the two ejected electrons is the approximate BBK wave function (often called 2CWG model) \cite{24} such as

\[ \Psi_f(\vec{k}_a, \vec{r}_1, \vec{k}_b, \vec{r}_2) = \frac{1}{\sqrt{2}} \left[ \Psi^c_c(\vec{k}_a, \vec{r}_1) \Psi^c_c(\vec{k}_b, \vec{r}_2) + \Psi^c_c(\vec{k}_a, \vec{r}_2) \Psi^c_c(\vec{k}_b, \vec{r}_1) \right] \varphi(\vec{k}_a - \vec{k}_b) \]  

and

\[ \Psi^c_c(\vec{k}, \vec{r}_i) = \frac{1}{(2\pi)^{3/2}} \exp(i\vec{k} \cdot \vec{r}_i) \Gamma(1-i\alpha) \exp(-\frac{\pi}{2} \alpha I) F_i(\alpha, \omega, \gamma) \]  

with \( \alpha = Z/k_e \), \( Z = 2 \). The Gamow factor is \( \varphi(\vec{k}_a - \vec{k}_b) = \exp(-\frac{\pi \chi_{ab}}{2}) \Gamma(1-i\chi_{ab}) \) and \( \chi_{ab} = \frac{1}{|\vec{k}_a - \vec{k}_b|} \).

The second Born term \( f_{B2} \) is given by

\[ f_{B2} = \frac{1}{8 \pi^4} \sum_n \int \frac{d\vec{q}}{q^2 - k_n^2 - i\epsilon} \left\langle \Phi_n(\vec{r}_1, \vec{r}_2) \right| V \left| \Phi_i(\vec{r}_1, \vec{r}_2) \right\rangle \left( \exp(i\vec{q} \cdot \vec{r}_0) \right) \]  

\[ \left( \exp(i\vec{q} \cdot \vec{r}_0) \right) \left| \Phi_n(\vec{r}_1, \vec{r}_2) \right\rangle, \]  

where the summation over \( n \) means that we take into account all the contributions of the \( n \) discrete states and those of the continuum states of the water molecule. Eq.5 means that the incident electron collides two times with the target and corresponds to the well-known two-step 2 mechanism (TS2) \cite{12}. Then, by performing the integration over \( \vec{r}_0 \) in Eq.(5) and by applying the closure approximation, we get

\[ \bar{f}_{B2} = \frac{2}{\pi^2} \int \frac{d\vec{q}}{q^2 - p^2 - i\epsilon} \frac{1}{K^2} \]  

\[ \left\langle \Psi_f(\vec{k}_a, \vec{r}_1, \vec{k}_b, \vec{r}_2) \left| \exp(i\vec{K} \cdot \vec{r}_1) + \exp(i\vec{K} \cdot \vec{r}_2) - 2 \right| \Phi_i(\vec{r}_1, \vec{r}_2) \right\rangle, \]  

where \( \vec{K} = \vec{k} - \vec{q} \) and \( \vec{K}_f = \vec{q} - \vec{k}_1 \), \( \vec{K} = \vec{k}_i + \vec{K}_f = \vec{k}_i - \vec{k}_i \) being the momentum transfer. Here we have
\[ p^2 = \frac{k^2}{2} - \overline{W}, \]  

(7)

where \( \overline{W} \) refers to the average excitation energy.

Finally, note that the integrals on \( dq \) must be performed numerically with a great care.

3. Results and discussion

We here investigate the double ionization of the four molecular states of the water molecule hereafter referred as \( 1b_1, 3a_1, 1b_2 \) and \( 2a_1 \). The incident and ejected electron energies have been selected in order to have a scattering energy of 500 eV, what corresponds to the experimental conditions reported by Lahmam-Bennani et al. [1]. Furthermore, we only consider the target orientation given by \( \alpha = \beta = \gamma = 0 \) and report in the following \((e, 3e)\) FDCS as a function of the ejected angles \( \theta_a \) and \( \theta_b \) in a coplanar geometry \( (\varphi_a = \varphi_a = \varphi_b = 0) \). Note that this kinematics is similar to that studied by Champion et al. in Ref. [18].

In Figure 1, fivefold differential cross sections (FDCS) for the double ionization of the water molecular orbital \( 1b_2 \) oriented in the direction \( \alpha = \beta = \gamma = 0 \) are reported as a function of the ejected angles \( \theta_a \) and \( \theta_b \) for the kinematical conditions above detailed \( (E_a = E_b = 10 \text{ eV} \text{ and } E_s = 500 \text{ eV}) \). For the first time we observe the signature of the TS2 mechanism which here appears without any interference effects due to other double ionization mechanisms in particular the SO process. Thus, contrary to Champion et al. who reported negligible cross sections within the 1\textsuperscript{st} Born approximation for the \( 1b_2 \) molecular orbital in this particular target orientation \( (\alpha = \beta = \gamma = 0) \) [18] we here show that the \((e,3-1e)\) FDCS are not null. For these particular conditions, it is clear that the double ionization process has to be described as a double collision between an incoming electron and two target ones. However, note that two successive collisions with a scattering angle \( \theta_{s1} \) and \( \theta_{s2} \), respectively) different from 0 are needed such as the sum \( \theta_{s1} + \theta_{s2} = \theta_s = 0 \). Furthermore, note that the positions of the maxima here obtained, namely, \( (\theta_a = 90^0, \theta_b = 270^0) \) and \( (\theta_a = 270^0, \theta_b = 90^0) \) are easily interpretable. Indeed, in a fast collision between an incident electron and a molecular target, a pure elastic collision occurs during which a target electron is ejected along a \( \theta_a \) direction defined by \( \theta_{s1} + \theta_a = 90^0 \) (with \( \theta_{s1} \equiv 0 \)) whereas a second target electron is ejected during a second elastic collision for which \( \theta_{s2} + \theta_b = 270^0 \).
Figure 1. Fivefold differential cross sections (FDCS) for the double ionization of the water molecular orbital $1b_2$ oriented in the direction $\alpha = \beta = \gamma = 0$ for $\theta_z = 0$ and $\varphi_z = \varphi_a = \varphi_b = 0$ as a function of the ejected angles $\theta_a$ and $\theta_b$ relative to the incident electron. The ejected energies are $E_a = E_b = 10$ eV and $E_f = 500$ eV. The FDCS have been calculated within the second Born approximation.

In Figs.2a and 2b we successively report the FDCS for the molecular state $2a_1$ within the first and the second Born approximations. As previously reported by Champion et al. [18] for an incident energy of 1 keV, Fig.2a clearly shows that the TS1 mechanism is the main mechanism involved in the double ionization process when the first Born approximation is considered. In this case, the maxima are located at $|\theta_a - \theta_b| = 140^\circ$: the incoming electron collides one target electron which is ejected along the direction of the momentum transfer $\vec{K}$, this latter colliding - in a second step - another molecular electron during a not-pure collision [10] leading to a $|\theta_a - \theta_b|$ angle greater than $90^\circ$ due to the electronic repulsion. On the other hand, when the collision is treated within the second Born approximation, the observations differ (see Fig.2b). Indeed, the maxima are in this case given by $|\theta_a - \theta_b| = 180^\circ$ what means that the SO mechanism becomes now the main mechanism of the double ionization. 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 of a second electron in the opposite direction. We nevertheless observe a secondary (smaller) maximum for
\(|\theta_a - \theta_s| = 140^0\). In fact, in this particular case we may assess that the TS2 and TS1 mechanisms destructively interfere together.

Figure 3a reports the first Born FDCS for the molecular state 1b_1. Like previously, the observations are similar to those reported by Champion et al. [18] for an incident energy of 1 keV. We here observe four hills: a first one extending from \(\theta_a = 15^0\) to \(\theta_a = 135^0\) (while \(\theta_b\) varying from \(\theta_b = 215^0\) to \(\theta_b = 345^0\)) and a second one (with a bigger maximum) extending from \(\theta_a = 75^0\) to \(\theta_a = 150^0\) (while \(\theta_b\) varying from \(\theta_b = 200^0\) to \(\theta_b = 280^0\)), the two other hills being obtained by symmetry. These two groups of maxima verify \(\approx -b a\theta_a\theta_s\) for the biggest and \(\approx -b a\theta_a\theta_s\) for the smallest, what indicates that the TS1 is the main mechanism, as already observed by Kada et al. [26] for the double ionization of a non-oriented 1b_1 molecular state.

![Figure 2a](image_url)  
**Figure 2a.** Fivefold differential cross sections for the double ionization of the water molecular orbital 2a_1 oriented in the direction \(\alpha = \beta = \gamma = 0\) for \(\theta_a = 0\) and \(\varphi_a = \varphi_s = \varphi_b = 0\) as a function of the ejected angles \(\theta_a\) and \(\theta_b\) relative to the incident electron. The ejected energies are \(E_a = E_b = 10\) eV and \(E_s = 500\) eV. The FDCS have been calculated within the first Born approximation.
When the second Born approximation is considered (see Fig. 3b) the amplitude of the forward scattering increases while that of the backscattering decreases. Thus, the TS2 mechanism plays here no important role except for the magnitudes of the maximum.

The FDCS of the molecular state $3a_1$ are reported in Figs. 4a and 4b within the 1st and 2nd Born predictions, respectively. In both cases we observe maxima given by $|\theta_a - \theta_b| = 180^0$ what corresponds to the signature of the SO mechanism with nevertheless a slight decreasing of the corresponding magnitudes when the second Born approximation is used.
Figure 3a. Fivefold differential cross sections for the double ionization of the water molecular orbital $1b_1$ 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 $\theta_a$ and $\theta_b$ relative to the incident electron. The ejected energies are $E_a = E_b = 10$ eV and $E_s = 500$ eV. The FDCS have been calculated within the first Born approximation.
Figure 3b. Same as in Fig.3a by using the second Born approximation.
Figure 4a. Fivefold differential cross sections for the double ionization of the water molecular orbital $3a_1$ 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 $\theta_a$ and $\theta_b$ relative to the incident electron. The ejected energies are $E_a = E_b = 10$ eV and $E_s = 500$ eV. The FDCS have been calculated within the first Born approximation.
Figure 4b. Same as in Fig.4a by using the second Born approximation.

4. Conclusion
In this work, we have carried out a theoretical analysis of the double ionization of single oriented water molecules within the second Born approximation. Fivefold differential cross sections were then reported and compared to their 1st Born homologous recently provided by Champion et al. [18]. Strong similarities were then reported in terms of maxima localization as well as identification of the main mechanisms involved in the double ionization whereas for particular kinematical conditions, it has been clearly shown that the first-order treatment was unable to explain the observations contrary to the second-order approximation which highlighted pure TS2 contributions.

Acknowledgments
We would like to thank the PMMS (Pôle Messin de Modélisation et de Simulation) for computer time.

References
[1] Lahmam-Bennani A, Staicu-Casagrande E M, Naja A, Dal Cappello C and Bolognesi P 2010 J. Phys. B: At. Mol. Opt. Phys. 43 105201
[2] El Marji B, Duguet A, Lahmam-Bennani A, Lecas M and Wellenstein H F 1995 J. Phys. B: At. Mol. Opt. Phys. 28 L733
[3] Lahmam-Bennani A, Dupré C and Duguet A 1989 Phys. Rev. Lett. 63 1582
[4] Taouil I, Lahmam-Bennani A, Duguet A and Avaldi L 1998 Phys. Rev. Lett. 81 4600
[5] El Marji B, Schröter C, Duguet A, Lahmam-Bennani A, Lecas M and Spielberger L 1997 J. Phys. B: At. Mol. Opt. Phys. 30 3677
[6] Schröter C, El Marji B, Lahmam-Bennani A, Duguet A, Lecas M and Spielberger L 1998 J. Phys. B: At. Mol. Opt. Phys. 31 131
[7] Jha L K, Santosh K, Roy O P and Kumar P 2008 Phys. Scr. 77 015304
[8] Dorn A, Moshammer R, Schröter C D, Zouros T J M, Schmitt W, Kollmus H, Mann R and Ullrich J 1999 Phys. Rev. Lett. 82 2496
[9] Dorn A, Kheifets A, Schröter C D, Najjari B, Höhr C, Moshammer R and Ullrich J 2001 Phys. Rev. Lett. 86 3755
[10] Dorn A, Kheifets A, Schröter C D, Najjari B, Höhr C, Moshammer R and Ullrich J 2002 Phys. Rev. A 65 032709
[11] Dürr M, Dorn A, Ullrich J, Cao S P, Kheifets A, Götz J R and Briggs J S 2007 Phys. Rev. Lett. 98 193201
[12] Carlson T A and Krause M O 1965 Phys.Rev. 140 1057
[13] Dal Cappello C and Le Rouzo H 1991 Phys.Rev. A 43 1395
[14] Dal Cappello C, Haddadou A, Menas F and Roy A C submitted to J. Phys. B: At. Mol. Opt. Phys.
[15] Brauner M, Briggs J S and Klar H 1989 J. Phys. B: At. Mol. Opt. Phys 22 2265
[16] Röder J, Rasch J, Jung K, Whelan C T, Ehrhardt H, Allan R J and Walters H R J 1996 Phys. Rev. A 53 225
[17] Ward S J and Macek J H 1994 Phys. Rev. A 49 1049
[18] Champion C, Oubaziz D, Aouchiche H, Popov Yu V and Dal Cappello C 2010 Phys. Rev. A 81 032704
[19] Kheifets A 2004 Phys. Rev. A 69 032712
[20] El Mkhanter R and Dal Cappello C 1998 J. Phys. B: At. Mol. Opt. Phys. 31 301
[21] Hda H, Dal Cappello C and Langlois J 1994 Z. Phys. D 29 25
[22] Cooper J W and Van Boeyen R W 2004 J. Phys. B: At. Mol. Opt. Phys. 37 L77
[23] Moccia R 1964 J. Chem. Phys. A 40 2186
[24] Dal Cappello C, Joulakian B and Langlois J 1993 J. Physique 3 125
[25] Grin M, Dal Cappello C, El Mkhanter R and Rasch J 2000 J. Phys. B: At. Mol. Opt. Phys. 33 131
[26] Kada I, Mansouri A, Dal Cappello C, Hervieux P A and Roy A C 2009 J. Phys. B: At. Mol. Opt. Phys. 42 025201