Electron impact single ionization of the water molecule in the second Born approximation

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Abstract

A general formalism is presented to calculate the triple-differential cross section for the ionization of neutral atoms and simple molecules with the chemical form XH_n in the frame of the second Born approximation using the closure approximation. The first Born term and a part of the second term are calculated analytically and the remainder is calculated semi-analytically. A new method is given to eliminate analytically the singularities occurring in the second Born term. The post-collision interaction between the scattered and ejected electrons is considered approximately using the Gamow factor. To check the accuracy of the present formalism, the ionization of the atomic hydrogen by electron impact is considered. The present formalism is developed to investigate the single ionization of the water molecule by electron impact. The comparison of our results with the experiments and previous theoretical findings shows good agreement and contrary to the previous theoretical calculations, our results predict two peaks in the recoil region.

(Some figures may appear in colour only in the online journal)

1. Introduction

Many theoretical models and experimental methods have been developed to study the ionization of atomic and molecular targets by electron impact. Understanding this process is of great importance to many areas, such as plasma physics, astrophysics and radiobiology. Moreover, the investigation of atomic or molecular targets with more than two electrons is a problem. Then it is necessary to find the approximation that allows us to extract precise data without complicated calculations. The chosen approximation must be constructed to give accurate results and an identification of mechanisms occurring during the collision process. The Born method is one of these approximations. This model is flexible in the analytical and numerical calculations and remains a preferable model to investigate the collision processes when the incident particle energy is large. Some mechanisms can be identified by the Born method as, for example, the multiple collision process in the single ionization and the shake-off (SO), the two-step 1 (TS1) and two-step 2 (TS2) mechanisms in double ionization [1–4].

Water constitutes the major component of the biological material, which makes the water molecule very interesting to investigate the particle track structure processes. Several numerical simulations of these processes need accurate sets of ionization cross sections for the water molecule [5–9]. For this reason, several theoretical and experimental activities are focused on the evaluation of the cross sections for the ionization of the water molecule by charged particles. In this work, we investigate the single ionization of the water molecule by electron impact. A general formalism is given, in the frame of the second Born approximation, to calculate the triple-differential cross section (TDCS) for the ionization of this molecule. This formalism can also be used in neutral atoms and molecules with the chemical form XH_n, with X a heavy atom compared to the hydrogen atom H. In the present formalism, the first term of the Born approximation is calculated analytically [10, 11] and the second Born term is divided into two parts, one calculated analytically and the other calculated semi-analytically using the closure approximation. The singularities in the second Born term are eliminated analytically and only continued two- and three-dimensional

integrals are calculated numerically. To treat the post-collision interaction (PCI) between the scattered and ejected electrons, the Gamow factor is introduced in the TDCS. This PCI has been achieved in the so-called three Coulomb wave (3C) model given by Brauner *et al* [12], where the final state is described asymptotically by a product of three Coulomb functions. However, the use of the 3C functions complicates the analytical and numerical calculations. The Gamow factor is the normalization factor of the third Coulomb wave which describes the PCI between the scattered and ejected electrons. Kheifets *et al* [13] have shown that the largest effect of the PCI is contained in this factor alone. This factor has been used by Dal Cappello *et al* [4, 14] to describe the PCI between the ejected electrons in the double ionization of the helium atom and the water molecule by electrons and positrons, where good correction to the cross sections has been observed and the big shift of the binary peak found experimentally by Lahmam-Bennani *et al* [1] has well been reproduced showing that the second Born approximation is needed to describe the TS2 mechanism. The PCI between the ejected electrons is always considered because the energies are comparable. However, this interaction is often neglected between the scattered and ejected electrons in the Born approximation because the scattered particle is considered faster than the ejected one. So we show in this paper that this interaction must always be considered.

To check the accuracy of our formalism and to analyse the correction given by the Gamow factor to the first and second Born approximations, the ionization of the atomic hydrogen by electron impact is first considered. Significant improvement has been observed in the first Born approximation and good agreement of the second Born approximation with the 3C model and the experiment is found. The same remarks are observed when we analyse the results of the water molecule where good agreement is found with the experimental data of Milne-Brownlie *et al* [15] and with the previous theoretical results of Champion *et al* [16] extracted in the frame of the 3C model and the so-called dynamic screening of the three-body Coulomb interaction (DS3C) model [17]. Furthermore, contrary to the previous calculations, our formalism predicts two peaks in the recoil region.

The paper is organized as follows. In section 2, the electron impact ionization TDCS of neutral atomic and molecular targets are presented. In section 3, the results of ionization of the atomic hydrogen and water molecule are discussed. We conclude in section 3.2. Atomic units are used throughout unless otherwise stated.

2. Theory

In the ionization of the atomic target by electron impact, the non-relativistic TDCS is given by

$$\frac{d^3\sigma}{dE_e \, d\hat{\mathbf{k}}_e \, d\hat{\mathbf{k}}_s} = \frac{1}{(2\pi)^2} \frac{k_e k_s}{k_i} |T|^2, \tag{1}$$

where $\hat{\mathbf{k}}_s \equiv (\theta_s, \varphi_s)$ and $\hat{\mathbf{k}}_e \equiv (\theta_e, \varphi_e)$ are the solid angles of the scattering and ejection directions, respectively, and E_e is the energy of the ejected electron. T is a matrix element

describing the transition of the system projectile–target from the initial state $|\Psi_i\rangle$ to the final state $|\Psi_f\rangle$, defined as

$$T = \langle \Psi_f | (V + V G_0^+ V) | \Psi_i \rangle, \tag{2}$$

where G_0^+ is the Green operator and V is the interaction energy between the incident particle and the atomic target

$$V = -\frac{Z}{r_0} + \sum_{i=1}^{N} \frac{1}{|\mathbf{r}_0 - \mathbf{r}_i|}, \tag{3}$$

where $\mathbf{r}_0$ is the position vector of the incident electron, $\mathbf{r}_i$ is the position vector of the ith electron of the target, Z is the atomic number and N is the number of electrons of the target. The initial state which corresponds to an incident particle and N bound electrons is described as the product

$$|\Psi_i\rangle = \varphi_{\mathbf{k}_i}(\mathbf{r}_0)\, \Phi_i(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N), \tag{4}$$

where $\mathbf{k}_i$ is the kinetic momentum of the incident particle. The final state is characterized by

$$|\Psi_f\rangle = \varphi_{\mathbf{k}_s}(\mathbf{r}_0)\, \Phi_f(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N), \tag{5}$$

where $\mathbf{k}_s$ is the momentum of the scattered particle.

We work in the second Born approximation, where the functions $|\varphi_{\mathbf{k}}\rangle$ are plane waves, $\exp(i\mathbf{k} \cdot \mathbf{r})$. The problem of N electrons can be reduced to one active electron problem using the so-called frozen-core approximation. So the matrix element T can be reduced to the sum of the following two terms:

$$T^{B1} = \langle \varphi_{\mathbf{k}_s} \psi_{\mathbf{k}_e} | V | \varphi_{\mathbf{k}_i} \phi_{\text{AO}} \rangle \tag{6}$$

$$T^{B2} = -\frac{1}{4\pi^3} \sum_n \int \frac{d\mathbf{k}}{k^2 - k_n^2 - i\eta}$$
$$\times \langle \varphi_{\mathbf{k}_s} \psi_{\mathbf{k}_e} | V | \varphi_{\mathbf{k}} \phi_n \rangle \langle \varphi_{\mathbf{k}} \phi_n | V | \varphi_{\mathbf{k}_i} \phi_{\text{AO}} \rangle, \tag{7}$$

where $\eta \to 0^+$, $|\Phi_{\text{AO}}\rangle$ is the ionized atomic orbital (AO) and V is reduced now to

$$V = -\frac{1}{r_0} + \frac{1}{|\mathbf{r}_0 - \mathbf{r}_1|}, \tag{8}$$

where $\mathbf{r}_1$ is the position vector of the active electron which is ejected after the collision with the momentum $\mathbf{k}_e$. We note that a spectral resolution to the Green operator has been used in equation (7), where the sum is over all bound and continuum states $|\phi_n\rangle$ of the atomic target and k_n is defined by $k_n^2 = k_i^2 - 2(E_n - E_{\text{AO}})$, with E_n being the eigenvalue of the atomic Hamiltonian corresponding to the eigenfunction $|\phi_n\rangle$. Using now the so-called Bethe's integral [18]

$$\int \frac{e^{i\mathbf{q} \cdot \mathbf{r}_0}}{|\mathbf{r}_0 - \mathbf{r}_1|} d\mathbf{r}_0 = \frac{4\pi}{q^2} e^{i\mathbf{q} \cdot \mathbf{r}_1}, \tag{9}$$

and the closure approximation where the difference $E_n - E_{\text{AO}}$ is replaced by the averaged excitation energy $\bar{w}$ to make use of the closure relation $\sum_n |\phi_n\rangle\langle\phi_n| = 1$, we obtain

$$T^{B1} = \frac{4\pi}{q^2} [F(\mathbf{q}) - P] \tag{10}$$

$$T^{B2} = -\frac{4}{\pi} \int d\mathbf{k} \frac{F(\mathbf{q}) + P - H(\mathbf{q}_s, \mathbf{q}_i)}{q_s^2 q_i^2 (k^2 - \bar{k}^2 - i\eta)}, \tag{11}$$

where $F(\mathbf{q}) = \langle \psi_{\mathbf{k}_e} | \exp(\mathbf{q} \cdot \mathbf{r}_1) | \phi_{AO} \rangle$, $H(\mathbf{q}_s, \mathbf{q}_i) = F(\mathbf{q}_s) - F(\mathbf{q}_i)$ and $P = \langle \psi_{\mathbf{k}_e} | \phi_{AO} \rangle . \mathbf{q} = \mathbf{k}_i - \mathbf{k}_s$ is the momentum transfer, $\mathbf{q}_i = \mathbf{k}_i - \mathbf{k}$ and $\mathbf{q}_s = \mathbf{k} - \mathbf{k}_s$.

To perform analytically the triple-dimensional integrals in $F(\mathbf{q})$, $H(\mathbf{q}_s, \mathbf{q}_i)$ and P, the continuum state of the ejected electron is described here by the Coulomb wavefunction which satisfies the outgoing boundary condition

$$\psi_{\mathbf{k}_e}^{(-)}(\mathbf{r}_1) = \frac{e^{i\mathbf{k}_e \cdot \mathbf{r}_1}}{(2\pi)^{3/2}} D_{\xi_e}^{(-)} C_{\mathbf{k}_e}^{\xi_e}(\mathbf{r}_1), \tag{12}$$

with $D_{\xi_e}^{(-)} = e^{-\frac{\pi \xi_e}{2}} \Gamma(1 - i\xi_e)$, $\xi_e = -Z_{eff}/k_e$ is the Sommerfeld parameter where Z_{eff} is the effective ionic charge and

$$C_{\mathbf{k}_e}^{\xi_e}(\mathbf{r}_1) = {}_1F_1[i\xi_e; 1; -i(k_e r_1 + \mathbf{k}_e \cdot \mathbf{r}_1)]. \tag{13}$$

The radial part of the bound-state wavefunction is expanded on Slater-type basis functions which have the following analytical form:

$$R_n^\alpha(r_1) = \frac{(2\alpha)^{n+1/2}}{\sqrt{(2n)!}} r_1^{n-1} e^{-\alpha r_1}, \tag{14}$$

where α is a variational parameter and n is a positive integer. The analytical form of the initial and final wavefunctions chosen here to describe the active electron allows us to perform analytically the three-dimensional integral in $F(\mathbf{q})$, $H(\mathbf{q}_s, \mathbf{q}_i)$ and P [10].

The term $T^{B2} = T_1^{B2} + T_2^{B2}$ contains a singular three-dimensional integral often difficult to resolve numerically. This term, in the form given in equation (11), can be performed numerically using the method of Marchalant *et al* [19] where the singularities arising at $\mathbf{k} = \mathbf{k}_i$ and $\mathbf{k} = \mathbf{k}_s$ can be overcome using prolate spheroidal coordinates. However, the term

$$T_1^{B2} = -\frac{4}{\pi} \int d\mathbf{k} \frac{F(\mathbf{q}) + P}{q_s^2 q_i^2 (k^2 - \bar{k}^2 - i\eta)} \tag{15}$$

can be performed analytically where we have the same integrals $F(\mathbf{q})$ and P as in equation (10). The singular three-dimensional integral in equation (15) can be deduced following Byron *et al* [20]. Moreover, the method of Marchalant *et al* [19] is very time consuming before reaching the good accuracy of the numerical calculation. To calculate the second term

$$T_2^{B2} = \frac{4}{\pi} \int d\mathbf{k} \frac{H(\mathbf{q}_s, \mathbf{q}_i)}{q_s^2 q_i^2 (k^2 - \bar{k}^2 - i\eta)}, \tag{16}$$

a new semi-analytical method, given in the appendix, is used in this work, where the singularities are eliminated analytically.

We need now to include in the TDCS the PCI between the scattered and ejected particles. This interaction has been achieved within the so-called 3C model given by Brauner *et al* [12] where the final state has been described asymptotically by a product of three Coulomb wavefunctions, two describing the scattered and ejected electrons and one describing the PCI between these electrons. Therefore, choosing the 3C wavefunctions complicates the analytical and numerical calculations. However, Kheifets *et al* [13] have demonstrated that the largest effect of the PCI is contained in the normalization factor of the Coulomb wavefunction, the so-called Gamow factor

$$\left| D_{\xi_{se}}^{(-)} \right|^2 = \frac{2\pi \xi_{se}}{e^{\frac{\pi \xi_{se}}{2}} - 1}, \tag{17}$$

where $\xi_{se} = 1/q_{se}$ and $\mathbf{q}_{se} = \mathbf{k}_s - \mathbf{k}_e$. So to include in the TDCS the PCI, approximately, between the outgoing electrons, equation (1) must be multiplied by the Gamow factor

$$\frac{d^3\sigma}{dE_e \, d\hat{\mathbf{k}}_e \, d\hat{\mathbf{k}}_s} = \frac{1}{(2\pi)^2} \frac{k_e k_s}{k_i} \left| D_{\xi_{se}}^{(-)} T \right|^2. \tag{18}$$

Until now a formalism to calculate the TDCS of atomic targets is given. However, this formalism can also be used to study the ionization of molecular targets with the chemical form XH_n where X is a heavy atom compared to the hydrogen atom H. In these types of molecules, the centre of the system is very close to the heaviest nucleus. Then each molecular orbital (MO) can be expanded on a set of basis $\{\phi_{n_\nu l_\nu m_\nu}^{\alpha_\nu}(\mathbf{r}_1)\}$ centred on the heavy atom [21–23]

$$\Phi_{MO}(\mathbf{r}_1) = \sum_{\nu=1}^{N_{MO}} w_\nu \phi_{n_\nu l_\nu m_\nu}^{\alpha_\nu}(\mathbf{r}_1), \tag{19}$$

where w_ν are the coefficients indicating the magnitude of contribution of each element of the basis $\phi_{n_\nu l_\nu m_\nu}^{\alpha_\nu}(\mathbf{r}_1)$ and N_{MO} is the number of basis elements. The general form of an element of this basis set is

$$\phi_{n_\nu l_\nu m_\nu}^{\alpha_\nu}(\mathbf{r}_1) = R_{n_\nu}^{\alpha_\nu}(r_1) Y_{l_\nu}^{m_\nu}(\hat{\mathbf{r}}_1), \tag{20}$$

where $R_{n_\nu}^{\alpha_\nu}(r_1)$ is the radial part defined in equation (14) and $Y_{l_\nu}^{m_\nu}(\hat{\mathbf{r}}_1)$ is the normalized spherical harmonic.

In the experiment, the molecular target is considered randomly oriented in the space. Therefore, the theoretical TDCS must be averaged over all the molecular orientations,

$$\frac{d^3\sigma}{dE_e \, d\hat{\mathbf{k}}_e \, d\hat{\mathbf{k}}_s} = \frac{1}{(2\pi)^2} \frac{k_e k_s}{k_i} \int \frac{d\omega}{8\pi^2} \left| D_{\xi_{se}}^{(-)} T \right|^2, \tag{21}$$

where the molecular orientation in the laboratory frame is defined by $d\omega = \sin\beta \, d\beta \, d\alpha \, d\gamma$ with (α, β, γ) the Euler angles. To perform analytically the integral over $d\omega$ in equation (21), we use the following transformation of the molecular orientation from the molecular frame to the laboratory frame:

$$Y_l^m(\hat{\mathbf{r}}) = \sum_{\mu=-l}^{l} D_{m\mu}^{(l)}(\alpha, \beta, \gamma) Y_l^\mu(\hat{\mathbf{r}}), \tag{22}$$

where $D_{m\mu}^{(l)}(\alpha, \beta, \gamma)$ is a rotation matrix element. So the following orthonormalization property

$$\int D_{m_1\mu_1}^{(l_1)} D_{m_2\mu_2}^{(l_2)} \, d\omega = \frac{8\pi^2}{2l_1 + 1} \delta_{l_1 l_2} \delta_{m_1 m_2} \delta_{\mu_1 \mu_2} \tag{23}$$

can used to perform the integral in equation (21), to find the result

$$\frac{d^3\sigma}{dE_e \, d\hat{\mathbf{k}}_e \, d\hat{\mathbf{k}}_s} = \frac{1}{(2\pi)^2} \frac{k_e k_s}{k_i} \sum_{\nu=1}^{N_{MO}} \sum_{\mu=-l_\nu}^{l_\nu} \frac{\left| w_\nu D_{\xi_{se}}^{(-)} T_\nu \right|^2}{2l_\nu + 1}, \tag{24}$$

where $T_\nu = T_\nu^{B1} + T_\nu^{B2}$, with

$$T_\nu^{B1} = \frac{4\pi}{q^2} [F_\nu(\mathbf{q}) - P_\nu] \tag{25}$$

$$T_\nu^{B2} = -\frac{4}{\pi} \int d\mathbf{k} \frac{F_\nu(\mathbf{q}) + P_\nu - H_\nu(\mathbf{q}_s, \mathbf{q}_i)}{q_s^2 q_i^2 (k^2 - \bar{k}^2 - i\eta)}, \tag{26}$$

where $F_\nu(\mathbf{q}) = \langle \psi_{\mathbf{k}_e} | \exp(\mathbf{q} \cdot \mathbf{r}_1) | \phi_{n_\nu l_\nu \mu}^{\alpha_\nu} \rangle$ and $P_\nu = \langle \psi_{\mathbf{k}_e} | \phi_{n_\nu l_\nu \mu}^{\alpha_\nu} \rangle$.
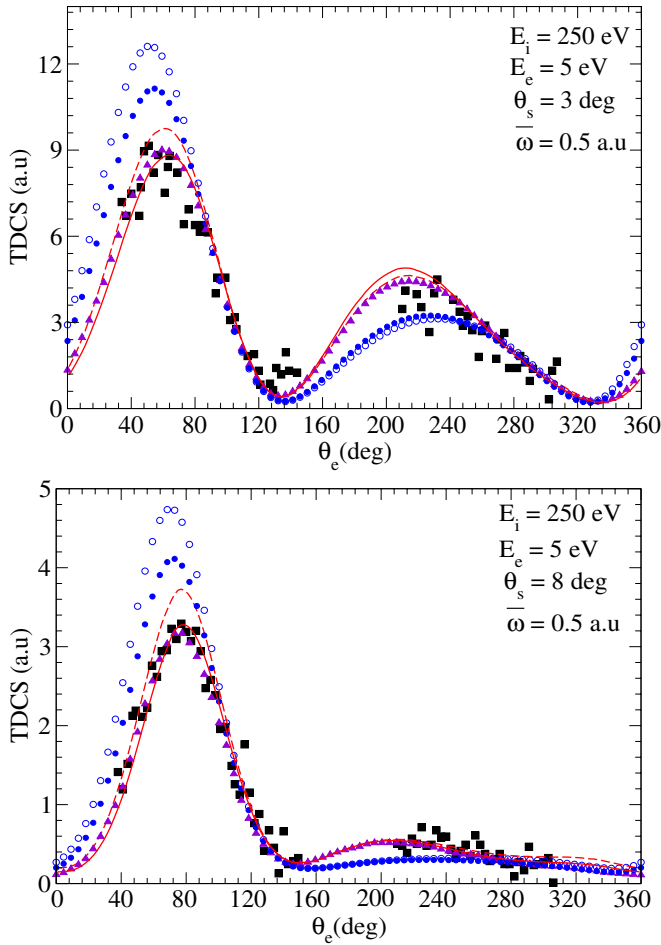
Figure 1. TDCS for the electron impact ionization of the atomic hydrogen. Our results: the open circles for the first Born approximation without the Gamow factor, the solid circles for the first Born approximation corrected by the Gamow factor, the dashed line for the second Born approximation without the Gamow factor and the solid line for the second Born approximation corrected by the Gamow factor. The solid triangles for the 3C model [12]. The solid squares for the experiment [26, 27].

3. Results and discussion

3.1. Ionization of the atomic hydrogen

Recently, Dal Cappello *et al* [4] have investigated in detail the application of the second Born approximation to the single and double ionization processes. To check the accuracy of this approximation, simple atomic systems, namely the hydrogen and helium atoms, have been considered. For the hydrogen atom, 100 exact discrete intermediate states corresponding to the principal quantum numbers $n = 1$–10 have been used, and the authors find that the convergence is reached at the intermediate state $n = 6$. The results of Byron *et al* [20] have also been confirmed, where they find that the contribution of the intermediate state $n = 2$ is the most important. The contribution of the continuum states has been checked using the closure approximation and the pseudo-states of Callaway [24, 25], and from the comparisons of the theoretical results with the experimental data of Ehrhardt *et al* [26, 27], they conclude that the contribution of discrete states is insufficient
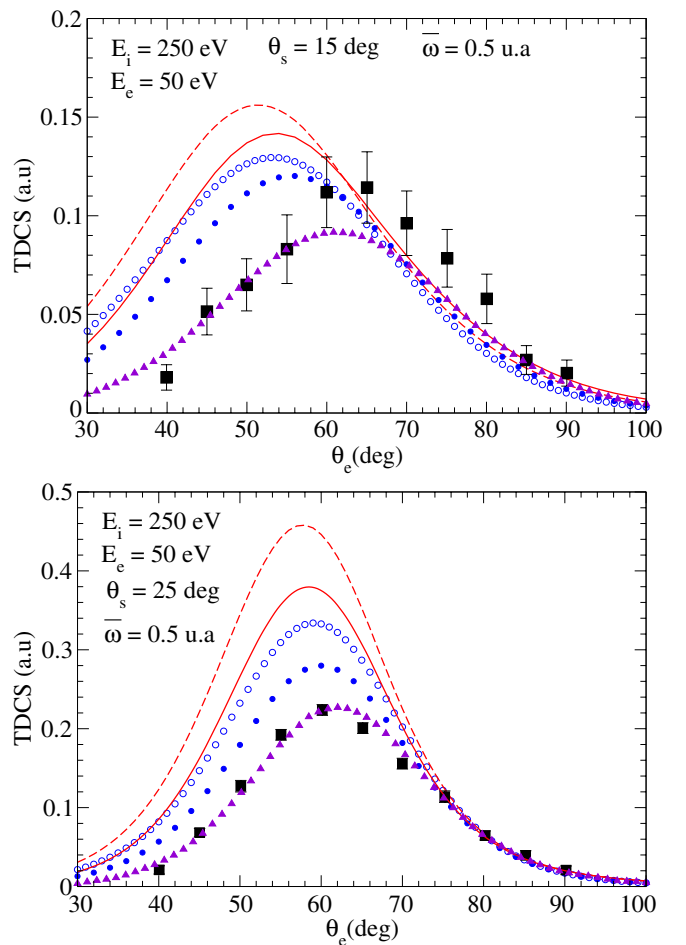

Figure 2. The same as in figure 1, but the 3C model results are from [4] and the experience from [28].

to describe the ionization process and the continuum states must be added. They also find that the closure approximation works very well for small ejection energies but completely fails to describe the experiment for large ejection energies.

In this subsection, we check the accuracy of our formalism on the atomic hydrogen and analyse the correction given by the Gamow factor. This factor is always included in the cross section when the outgoing particles acquire comparable energies, but often neglected when the energies are very different. To analyse the correction given by the Gamow factor, we present in figures 1 and 2 the TDCS obtained with and without correction. The calculations have been performed for an averaged excitation energy $\bar{w} = 0.5$ au corresponding to the ionization energy. We note that the accuracy of our numerical calculations has been checked by the calculation of the singular integral in equation (15), which has an analytical solution, and by the comparison of our results with the theoretical results given by Dal Cappello *et al* [4], where identical curves have been obtained.

Figure 1 shows the corrected and non-corrected cross sections given in the first and second Born approximation compared to the results of Brauner *et al* [12] extracted in the frame of the 3C model and to the experimental data of Ehrhardt *et al* [26, 27]. The experiment has been performed in the coplanar asymmetry with an incident energy
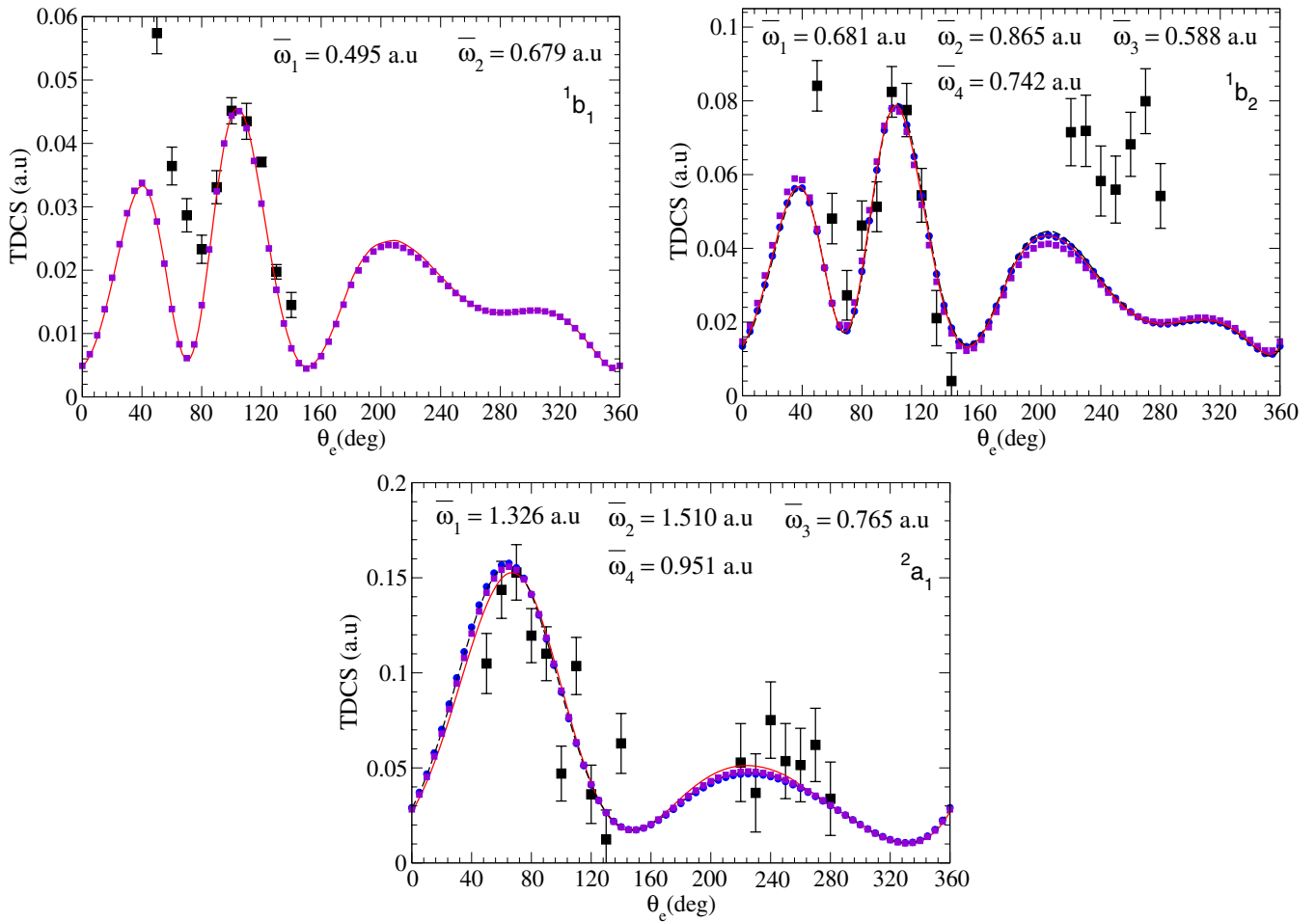
Figure 3. TDCS without the Gamow factor for the orbitals $^2a_1$, $^1b_1$ and $^1b_2$ to analyse the dependence of the second Born approximation on $\bar{w}$. Experiment [15]: black squares. The parameter $\bar{w}$ equals $\bar{w}_1$, the ionization energy by the solid line; $\bar{w}_2$, the average between the ionization and the excitation to the continuum energies by the solid circles; $\bar{w}_3$, the average between the ionization energies by the dashed line; and $\bar{w}_4$, the average between the ionization energies and the excitation to the continuum energy by the small solid squares.

$E_i = 250$ eV and ejection energy $E_e = 5$ eV for the scattering angles $\theta_s = 3°$ and $\theta_s = 8°$. We point out that the final state of the three-particle reaction is described in the 3C model by an exact solution of the Schrödinger equation in the asymptotic region (far from the centre of reaction) and the PCI between the two outgoing electrons is considered asymptotically of infinite order. For this reason, the 3C model gives a good description of the process of single ionization by electron impact. The experimental data and the 3C model results have been normalized in $\theta_e = 64°$ for $\theta_s = 3°$ and in $\theta_e = 78°$ for $\theta_s = 8°$ to our corrected results (with the Gamow factor) given in the second Born approximation.

When we analyse the results given in figure 1, we can clearly observe the improvement given by the Gamow factor to the first Born approximation, and we see that the second Born approximation becomes very close to the 3C model and the experiment. The improvement is small in the recoil region ($\theta_e > 180°$) but significant in the binary region ($\theta_e < 180°$) where the interaction between the two outgoing electrons is important. This confirms the results of Kheifets *et al* [13] that the largest effect of the PCI is contained in the Gamow factor. The results in figure 1 also show an angular shift of the forward and backward lobes, with respect to the momentum transfer

direction, in both the first and second Born approximations given by the introduction of the Gamow factor.

In figure 2, we compare our results with those of the 3C model taken from [4] and with the experimental data of Weigold *et al* [28] extracted in the coplanar asymmetry for an incident energy $E_i = 250$ eV and ejection energy $E_e = 50$ eV for the scattering angles $\theta_s = 15°$ and $\theta_s = 25°$. The experimental data and the results obtained in the 3C model are normalized, in $\theta_e = 85°$ for $\theta_s = 15°$ and in $\theta_e = 90°$ for $\theta_s = 25°$, to our corrected results obtained in the second Born approximation. Pathak and Srivastava [29], Byron *et al* [30] and Dal Cappello *et al* [4] have concluded that for higher ejection energies, the second Born approximation with the closure approximation fails to describe the experiment, and this is clearly shown in figure 2. However, the 3C model where the PCI between the ejected and scattered electrons is considered of infinite order is very close to describe the experiment. We note that the exchange effect has been verified by the 3C model [4] and has been found small and can be safely neglected. Considerable improvement is given by the Gamow factor to the first and second Born approximations and the TDCS have been shifted towards the experiment. However, contrary to the results given in figure 2 for small ejected energy, the
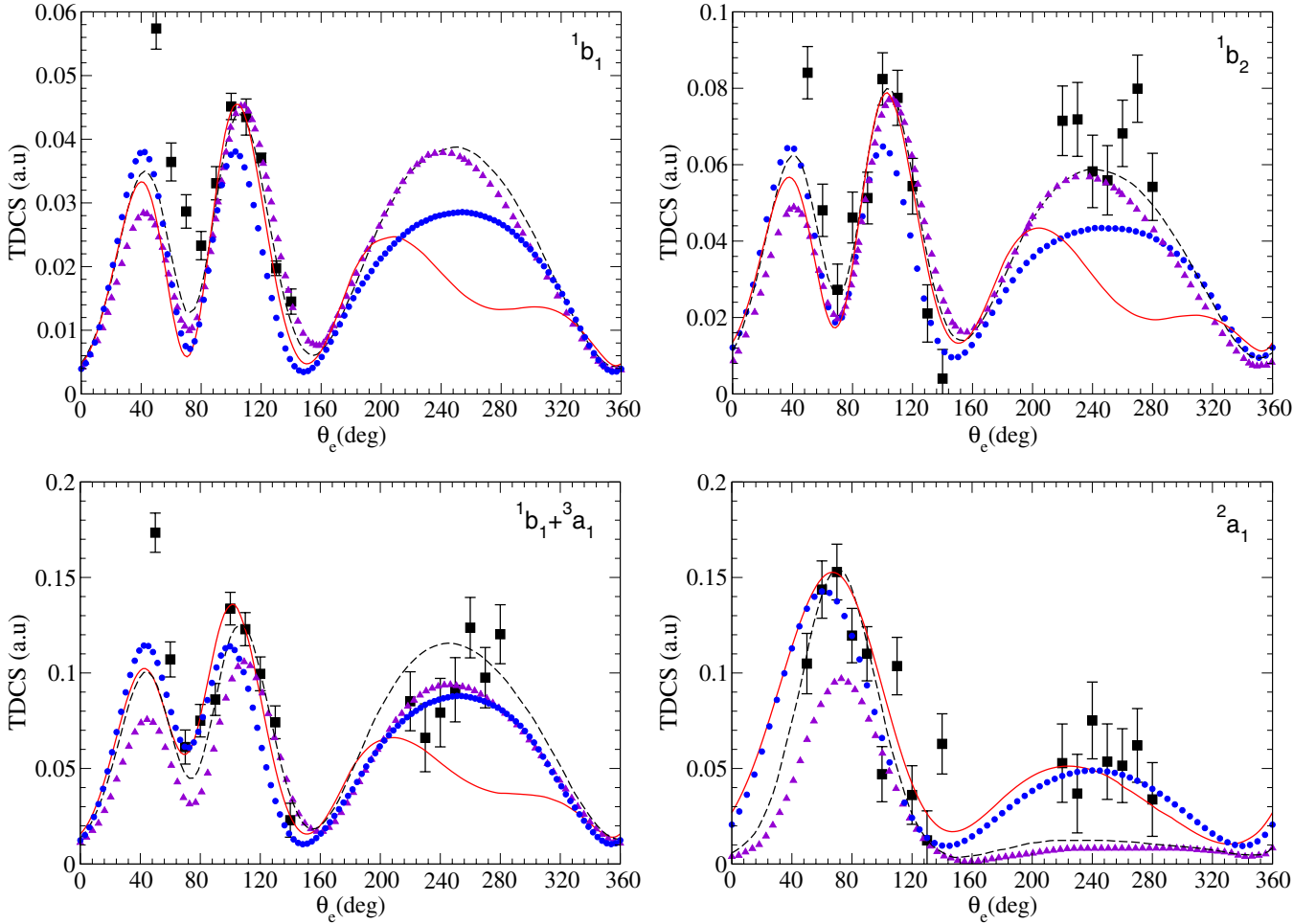
Figure 4. TDCS without the Gamow factor for the electron impact ionization of the molecular orbitals $^2b_1$, $^1b_1$, $^1b_2$, and the sum $^1b_1 + ^3b_1$ of the water molecule. Experiment [15]: black squares. Our results: the solid line for the second Born approximation and the solid circles for the first Born approximation. Results of Champion *et al* [16]: the dashed line for the DS3C model and the solid triangles for the 3C model.

second Born approximation still overestimates the experiment for higher ejection energies. This means that the larger the ejection energy, the more significant is the PCI between the outgoing particles, and the reaction in this case necessitates more rigorous theoretical description.

3.2. Ionization of the water molecule

Now we investigate the single ionization of the water molecule by electron impact. Our theoretical results extracted in the first and second Born approximations are compared to the experimental data of Milne-Brownlie *et al* [15] and to the previous theoretical results of Champion *et al* [16] extracted in the frame of the 3C model [12] and to the so-called dynamic screening of the three-body Coulomb interaction (DS3C) model [17]. The experimental data of the four outer molecular orbitals of the H_2O molecule have been measured in the coplanar asymmetric geometry where the conditions of the experiments are fixed to an incident energy $E_i = 250$ eV, an ejection energy $E_e = 10$ eV and the scattering angle $\theta_s = 15°$. In these kinematic conditions, the ejection energy is not large and the closure approximation can be safely used. This is confirmed by the comparison of our results, corrected by the

Gamow factor, with the 3C model results in the binary region. The ionization energies of the four outer molecular orbitals are 32.2 eV for the atomic-like orbital $^2a_1$, and 18.55, 14.73 and 12.63 eV for the molecular orbitals $^3a_1$, $^1b_2$ and $^1b_1$, respectively.

To describe the ground state of the water molecule, we have chosen the representation of Moccia [23] where each molecular orbital is described by means of the single-centre wavefunction expanded on the Slater-type basis as given in equation (19). The formalism given in section 2 is for an angular part of the initial state described by the normalized spherical harmonic. However, in the representation given by Moccia [23], the angular part of each basis element is described by the real spherical harmonic

$$S_{l_\nu m_\nu}(\hat{\mathbf{r}}) = \sqrt{\frac{\text{sgn}(m_\nu)}{2}}\{\text{sgn}(m_\nu) Y_{l_\nu |m_\nu|}(\hat{\mathbf{r}}) + (-1)^{m_\nu} Y_{l_\nu -|m_\nu|}(\hat{\mathbf{r}})\}, \quad (27)$$

where $S_{l_\nu 0}(\hat{\mathbf{r}}) = Y_{l_\nu 0}(\hat{\mathbf{r}})$ and $\text{sgn}(x) = x/|x|$ is the sign function, with $\text{sgn}(0) = 0$. This representation of the angular part does not change the result in equation (24) because when we carry out the spherical average given by the integral given in equation (21), we find the same expression.
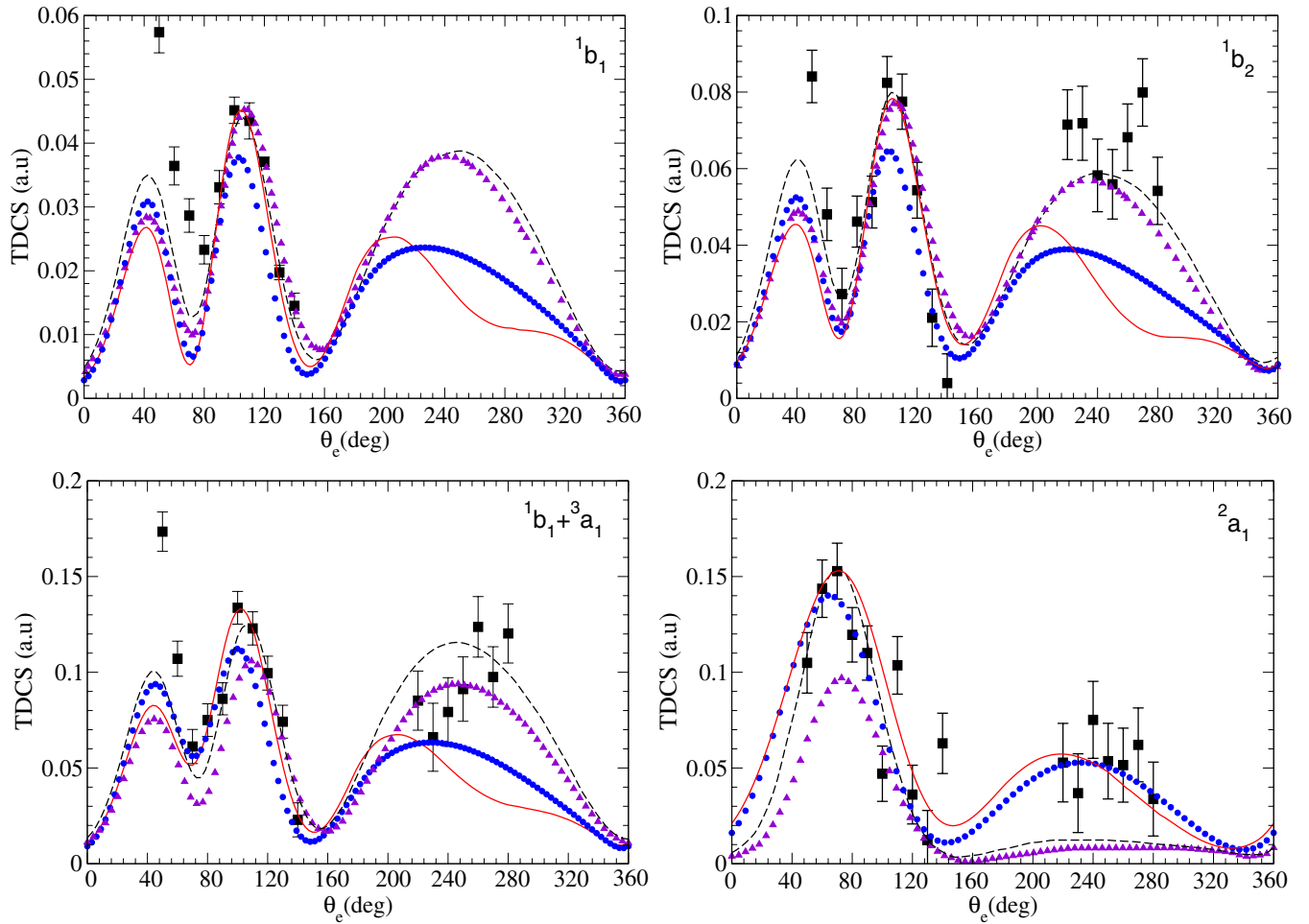
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Figure 5. The same as in figure 4, but with the Gamow factor.

Dal Cappello *et al* [4] find in the case of the ionization of the atomic hydrogen that the change of the value of the parameter $\bar{w}$, the averaged excitation energy, changes the results given by the second Born approximation. However, they find only small differences between the results in the case of the ionization of the helium atom. To make a good physical choice of the parameter $\bar{w}$ in the ionization reaction is a problem, and as indicated by Walters [31] a reasonable choice of $\bar{w}$ in this case is the ionization energy of the ionized orbital. To analyse the dependence of the second Born approximation on the value of the parameter $\bar{w}$ in the case of the water molecule, different values have been used to obtain the results given in figure 3. Four values of $\bar{w}$ have been used: the ionization energy $\bar{w}_1$, an average between the ionization and excitation to the continuum energies $\bar{w}_2$ where the continuum state of the ejected electron is considered as an intermediate state, an average between the ionization energies of the higher states of the ground state from the ionized orbital $\bar{w}_3$ and an average between the latter and the excitation to the continuum energy $\bar{w}_4$. Figure 3 shows that practically no difference exists between the curves for each orbital, and we can say that the ionization energies can be safely used as a value for the parameter $\bar{w}$.

In figure 4, our results extracted without the Gamow factor are compared to the experimental data of Milne-Brownlie *et al* [15] and to the theoretical results of Champion *et al* [16]

given by the 3C and DS3C models. The experimental and theoretical results are normalized to our findings, given in the second Born approximation, in the second binary peak. In figure 4, we observe from the results of the molecular orbitals $^1b_2$, $^1b_1$ and the sum $^1b_1 + ^3a_1$ that the second Born approximation, the 3C model and the DS3C model are in good agreement with the experiment in the second binary peak. However, our results underestimate the experimental data in the recoil region. Nevertheless, the present formalism describes the experimental data of the atomic-like orbital $^2a_1$ better than the 3C and DS3C models given by Champion *et al* [16]. We can also see that contrary to the other models, our calculations predict two peaks in the recoil region. From the analysis of the binary region, we can observe that the first Born approximation is not sufficient to describe the dynamic of ionization of the water molecule for the kinematic conditions $E_i = 250$ eV and $E_e = 10$ eV. So higher order effects are important especially for the molecular orbitals $^1b_2$, $^1b_1$ and $^3a_1$.

Figure 5 is similar to figure 4 but now the Gamow factor is introduced in the TDCS. In general, we have the same comments given previously in figure 4 when we compare the theoretical and experimental results. Nevertheless, we observe a significant improvement given by the Gamow factor to both the first and second Born approximations in

both the binary and recoil regions and an angular shift of the forward and backward lobes with respect to the momentum transfer direction. The second Born approximation became very close to the 3C model in the binary region, except for the atomic-like orbital $^2a_1$. These remarks have been observed in the investigation of the hydrogen atom and confirm that the closure approximation is safely used here. Although our calculations with the Gamow factor give a good description of the binary region, they still underestimate the experiment in the recoil region of the molecular orbitals $^1b_2$, $^1b_1$ and the sum $^1b_1 + ^3a_1$.

4. Conclusion

A new formalism is presented to calculate the triple-differential cross section for the single ionization of atomic and molecular targets with the chemical form XH_n. In this formalism, the calculation of the transition amplitude has been performed in the second Born approximation using the closure approximation. The first Born term and a part of the second Born term are determined analytically and the obtained results have been used to calculate semi-analytically the other part of the second Born term. The singularities that appear in the second Born term have been eliminated analytically. The post-collision interaction (PCI) between the scattered and ejected electrons was considered approximately using the Gamow factor. The present formalism was developed to study the single ionization of the water molecule by electron impact. The accuracy of the formalism was checked first by considering the ionization of the hydrogen atom.

From the good agreement of our results with the experiments and with the previous theoretical findings, we found that the present formalism is well adapted to study the single ionization process for neutral atomic and molecular targets with the chemical form XH_n when the ejection energies are not large. Our results show that the PCI must be considered even when the outgoing particles are of very different energies, because the interaction between two electrons is a strong long-range force. The present approach can be extended to describe the ionization of atoms and molecules by other charged particles such as protons, positrons and bare ions.

From the investigation of the water molecule, we find that the first-order approximation is not sufficient to describe the dynamic of ionization for the kinematic conditions $E_i = 250$ eV and $E_e = 10$ eV, and the second-order perturbation needs some corrections to give improved results as it describes the ejected particle by a distorted wavefunction and describes the scattered particle by a more precise wavefunction than the plane wave.

Appendix

In this section, a new semi-analytical method is given to treat the following singular integral:

$$I = \lim_{\eta \to 0^+} \int d\mathbf{k} \frac{H(\mathbf{q}_s, \mathbf{q}_i)}{(k^2 - \bar{k}^2 - i\eta) q_s^2 q_i^2}, \quad (A.1)$$

where $H(\mathbf{q}_s, \mathbf{q}_i) = F(\mathbf{q}_s) + F(\mathbf{q}_i)$. Using the Cauchy identity

$$\lim_{\eta \to 0^+} \frac{1}{k^2 - \bar{k}^2 - i\eta} = P\left(\frac{1}{k^2 - \bar{k}^2}\right) + i\pi\delta(k^2 - \bar{k}^2), \quad (A.2)$$

where P stands for the principal value, the integral in equation (A.1) can be written in the form

$$I = P \int d\mathbf{k} \frac{H(\mathbf{q}_s, \mathbf{q}_i)}{(k^2 - \bar{k}^2) q_s^2 q_i^2} + \frac{i\pi\bar{k}}{2} \int_0^{4\pi} d\hat{\mathbf{k}} \frac{H(\bar{\mathbf{q}}_s, \bar{\mathbf{q}}_i)}{\bar{q}_s^2 \bar{q}_i^2}, \quad (A.3)$$

where $\bar{\mathbf{q}}_i = \mathbf{k}_i - \bar{k}\hat{\mathbf{k}}$ and $\bar{\mathbf{q}}_s = \bar{k}\hat{\mathbf{k}} - \mathbf{k}_s$. The first term of this integral contains two three-dimensional singularities at $\mathbf{k} = \mathbf{k}_i$ and $\mathbf{k} = \mathbf{k}_s$ and one uni-dimensional singularity at $k = \bar{k}$. This term can be split into two integrals J_1 and J_2 by using the following identity:

$$\frac{1}{ab} = \frac{1}{(a+b)}\left(\frac{1}{a} + \frac{1}{b}\right), \quad (A.4)$$

with

$$J_1 = P \int d\mathbf{k} \frac{H(\mathbf{q}_s, \mathbf{q}_i)}{(k^2 - \bar{k}^2)(q_i^2 + q_s^2) q_s^2} \quad (A.5)$$

$$J_2 = P \int d\mathbf{k} \frac{H(\mathbf{q}_s, \mathbf{q}_i)}{(k^2 - \bar{k}^2)(q_i^2 + q_s^2) q_i^2}. \quad (A.6)$$

The singularity at $k = \bar{k}$ in the integrals J_1 and J_2 can be transferred to an other integral of a simple form using a subtraction procedure like that used in the method of Marchalant *et al* [19]. In this case, these integrals take the forms $J_1 = I_1 + K_1$ and $J_2 = I_2 + K_2$, where

$$I_1 = \int \frac{d\mathbf{k}}{q_s^2(k^2 - \bar{k}^2)} \left[\frac{H(\mathbf{q}_s, \mathbf{q}_i)}{(q_i^2 + q_s^2)} \right.$$
$$\left. - \frac{q_s^2 H(\bar{\mathbf{q}}_s, \bar{\mathbf{q}}_i)}{\bar{q}_s^2(\bar{q}_i^2 + \bar{q}_s^2)} \exp(-\gamma(k - \bar{k})^2) \right] \quad (A.7)$$

$$K_1 = P \int d\mathbf{k} \frac{H(\bar{\mathbf{q}}_s, \bar{\mathbf{q}}_i) \exp(-\gamma(k - \bar{k})^2)}{(k^2 - \bar{k}^2)\bar{q}_s^2(\bar{q}_i^2 + \bar{q}_s^2)} \quad (A.8)$$

and

$$I_2 = \int \frac{d\mathbf{k}}{q_i^2(k^2 - \bar{k}^2)} \left[\frac{H(\mathbf{q}_s, \mathbf{q}_i)}{(q_i^2 + q_s^2)} \right.$$
$$\left. - \frac{q_i^2 H(\bar{\mathbf{q}}_s, \bar{\mathbf{q}}_i)}{\bar{q}_i^2(\bar{q}_i^2 + \bar{q}_s^2)} \exp(-\gamma(k - \bar{k})^2) \right] \quad (A.9)$$

$$K_2 = P \int d\mathbf{k} \frac{H(\bar{\mathbf{q}}_s, \bar{\mathbf{q}}_i) \exp(-\gamma(k - \bar{k})^2)}{\bar{q}_i^2(\bar{q}_i^2 + \bar{q}_s^2)(k^2 - \bar{k}^2)}, \quad (A.10)$$

which allows us to rewrite the integral I in the form

$$I = I_1 + I_2 + \int_0^{4\pi} d\hat{\mathbf{k}} \frac{H(\bar{\mathbf{q}}_s, \bar{\mathbf{q}}_i)}{\bar{q}_s^2 \bar{q}_i^2}$$
$$\times \left(P \int_0^\infty dk \frac{k^2 \exp(-\gamma(k - \bar{k})^2)}{(k^2 - \bar{k}^2)} + \frac{i\pi\bar{k}}{2} \right). \quad (A.11)$$

The third term in this equation can be easily calculated numerically. In both the integrals I_1 and I_2, we have only

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one three-dimensional singularity that can be eliminated by the following variable change:

$$I_1 = \int \frac{d\mathbf{q}_s}{q_s^2 \left(K_s^2 - \bar{k}^2\right)} \left[\frac{H\left(\mathbf{q}_s, \mathbf{q} - \mathbf{q}_s\right)}{\left(q_s^2 + |\mathbf{q} - \mathbf{q}_s|^2\right)} \right.$$
$$\left. - \frac{q_s^2 H\left(\bar{\mathbf{q}}_s, \bar{\mathbf{q}}_i\right) \exp(-\gamma (K_s - \bar{k})^2)}{\bar{q}_s^2 \left(\bar{q}_i^2 + \bar{q}_s^2\right)} \right], \tag{A.12}$$

where $\bar{\mathbf{q}}_s = \bar{k}\hat{\mathbf{K}}_s - \mathbf{k}_s$, $\bar{\mathbf{q}}_i = \mathbf{k}_i - \bar{k}\hat{\mathbf{K}}_s$ and $\mathbf{K}_s = \mathbf{q}_s + \mathbf{k}_s$, and

$$I_2 = \int \frac{d\mathbf{q}_i}{q_i^2 \left(K_i^2 - \bar{k}^2\right)} \left[\frac{H\left(\mathbf{q} - \mathbf{q}_i, \mathbf{q}_i\right)}{\left(q_i^2 + |\mathbf{q} - \mathbf{q}_i|^2\right)} \right.$$
$$\left. - \frac{q_i^2 H\left(\bar{\mathbf{q}}_s, \bar{\mathbf{q}}_i\right) \exp(-\gamma (K_i - \bar{k})^2)}{\bar{q}_i^2 \left(\bar{q}_i^2 + \bar{q}_s^2\right)} \right], \tag{A.13}$$

where $\bar{\mathbf{q}}_s = \bar{k}\hat{\mathbf{K}}_i - \mathbf{k}_s$, $\bar{\mathbf{q}}_i = \mathbf{k}_i - \bar{k}\hat{\mathbf{K}}_i$ and $\mathbf{K}_i = \mathbf{k}_i - \mathbf{q}_i$.

The following singular integral

$$K = P \int_0^\infty dk \frac{k^2 \exp(-\gamma (k - \bar{k})^2)}{(k^2 - \bar{k}^2)} \tag{A.14}$$

can be easily performed numerically. However, the singularity in this integral can be eliminated analytically. Let the following variable change $z = k - \bar{k}$; then we obtain

$$K = P \int_{-\bar{k}}^\infty dz \frac{(z + \bar{k})^2 \exp(-\gamma z^2)}{z(z + 2\bar{k})} \tag{A.15}$$

which can be written as

$$K = \int_{-\bar{k}}^\infty dz \exp(-\gamma z^2) + \bar{k}^2 P \int_{-\bar{k}}^\infty dz \frac{\exp(-\gamma z^2)}{z(z + 2\bar{k})}. \tag{A.16}$$

In this last equation, the first integral is not singular and can be easily evaluated analytically to find the following result:

$$\int_{-\bar{k}}^\infty dz \exp(-\gamma z^2) = \sqrt{\frac{\pi}{4\gamma}}[1 + \text{erf}(\sqrt{\gamma}\bar{k})]. \tag{A.17}$$

The second integral in equation (A.16) contains the singularity. However, this singularity can be eliminated by splitting this integral into two terms as follows:

$$P \int_{-\bar{k}}^\infty dz \frac{\exp(-\gamma z^2)}{z(z + 2\bar{k})} = \frac{1}{2\bar{k}} P \int_{-\bar{k}}^\infty dz \frac{\exp(-\gamma z^2)}{z}$$
$$- \frac{1}{2\bar{k}} \int_{-\bar{k}}^\infty dz \frac{\exp(-\gamma z^2)}{(z + 2\bar{k})}. \tag{A.18}$$

Writing the first term in the form

$$P \int_{-\bar{k}}^\infty dz \frac{\exp(-\gamma z^2)}{z} = P \int_{-\bar{k}}^{+\bar{k}} dz \frac{\exp(-\gamma z^2)}{z}$$
$$+ \int_{\bar{k}}^\infty dz \frac{\exp(-\gamma z^2)}{z}, \tag{A.19}$$

we note that the first integral in this equation is equal to zero and by a succession of variables changes, the second integral can be identified as the exponential integral function

$$\int_{\bar{k}}^\infty dz \frac{\exp(-\gamma z^2)}{z} = \frac{1}{2} E_1(\gamma \bar{k}^2). \tag{A.20}$$

These analytical calculations enabled us to write the integral K given in equation (A.14) in the analytical form

$$K = \sqrt{\frac{\pi}{4\gamma}}[1 + \text{erf}(\sqrt{\gamma}\bar{k})] + \frac{\bar{k}}{4} E_1(\gamma \bar{k}^2)$$
$$- \frac{\bar{k}}{2} \int_{-\bar{k}}^\infty dz \frac{\exp(-\gamma z^2)}{(z + 2\bar{k})}. \tag{A.21}$$

The function in the integral of the last term is continuous over the domain of integration and decreases very quickly and can be easily performed numerically.

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] Staicu-Casagrande E M, Li C, Lahmam-Bennani A, Dal Cappello C, Schultz M and Ciappina M 2011 *J. Phys. B: At. Mol. Opt. Phys.* **44** 055201
[3] Li C, Lahmam-Bennani A, Staicu-Casagrande E M and Dal Cappello C 2011 *J. Phys. B: At. Mol. Opt. Phys.* **44** 115201
[4] Dal Cappello C, Haddadou A, Menas F and Roy A C 2011 *J. Phys. B: At. Mol. Opt. Phys.* **44** 015204
[5] Bigildeev E A and Michalik V 1996 *Radiat. Phys. Chem.* **47** 197–207
[6] Champion C, L'Hoir A, Politis M F, Chetioui A, Fayard B and Touati A 1998 *Nucl. Instrum. Methods* B **146** 533–40
[7] Champion C 2003 *Nucl. Instrum. Methods* B **205** 671–6
[8] Munoz A, Blanco F, Garcia G, Thorn P A, Brunger M J, Sullivan J P and Buckman S J 2008 *Int. J. Mass Spectrom.* **277** 175–9
[9] Lekadir H, Abbas I, Champion C and Hanssen J 2009 *Nucl. Instrum. Methods* B **267** 1011–4
[10] Sahlaoui M and Bouamoud M 2010 *Can. J. Phys.* **88** 905–10
[11] Sahlaoui M and Bouamoud M 2011 *Can. J. Phys.* **89** 723–7
[12] Brauner M, Briggs J S and Klar H 1989 *J. Phys. B: At. Mol. Opt. Phys.* **22** 2265–87
[13] Kheifets A S, Naja A, Staicu Casagrande E M and Lahmam-Bennani A 2008 *J. Phys. B: At. Mol. Opt. Phys.* **41** 145201
[14] Dal Cappello C, Kada I, Mansouri A and Champion C 2011 *J. Phys: Conf. Ser.* **288** 012004
[15] Milne-Brownlie D S, Cavanagh S J, Lohmann B, Champion C, Hervieux P A and Hanssen J 2004 *Phys. Rev.* A **69** 032701
[16] Champion C, Dal Cappello C, Houamer S and Mansouri A 2006 *Phys. Rev.* A **73** 012717
[17] Zhang S 2000 *J. Phys. B: At. Mol. Opt. Phys.* **33** 3545–53
[18] Bethe H A 1930 *Ann. Phys.* **5** 325
[19] Marchalant J P, Whelan C T and Walters H R J 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** 1141–78
[20] Byron F W Jr, Joachain C J and Piraux B 1985 *J. Phys. B: At. Mol. Phys.* **18** 3203
[21] Moccia R 1964 *J. Chem. Phys.* **40** 2164–76
[22] Moccia R 1964 *J. Chem. Phys.* **40** 2176–85
[23] Moccia R 1964 *J. Chem. Phys.* **40** 2186–92
[24] Callaway J 1978 *Phys. Rep.* **45** 89
[25] Callaway J and Unnikrishnan K 1993 *Phys. Rev.* A **48** 4292
[26] Ehrhardt H, Knoth G, Schlemmer P and Jung K 1985 *Phys. Lett.* **110** 92
[27] Ehrhardt H, Jung K, Knoth G and Schlemmer P 1986 *Z. Phys.* D **1** 3
[28] Weigold E, Noble C J, Hood S T and Fuss I 1979 *J. Phys. B: At. Mol. Phys.* **12** 291
[29] Pathak A and Srivastava M K 1981 *J. Phys. B: At. Mol. Phys.* **14** L773
[30] Byron F W Jr, Joachain C J and Piraux B 1982 *J. Phys. B: At. Mol. Phys.* **15** L293
[31] Walters H R J 1984 *Phys. Rep.* **116** 1