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Calculation of the multifold differential cross section of the electron-impact ionization of molecular hydrogen by prolate spheroidal external complex scaling method with second Born corrections

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We introduce the second Born dipole corrections in our recently developed *ab initio* procedure based on the driven Schrödinger equation formalism and the external scaling method for the determination of the multifold differential cross sections of the single and double ionization of molecular hydrogen by electron impact. To test our procedure, we first apply it to the excitation-ionization process of a He atom and compare the results to those of equivalent theoretical results, which are available. We then show that the introduction of the second Born correction including only dipole terms improves the agreement with the experimental results only in the case of the simple ionization. We think that the introduction of nondipole contributions in the second Born term which are not taken into account in the present work is necessary in the case of the double ionization process.

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I. INTRODUCTION

The so-called $(e,2e)$ [1–3] and $(e,3e)$ [4,5] experiments consisting in coincidence detection of the scattered and one and two ejected electrons, respectively, from atomic or molecular targets by electron impact represent fundamental processes, which can be considered as basic tools for probing the electronic structure of targets, electron-electron correlation, and the ionization mechanisms. They require an important theoretical effort for the determination of the multiply differential cross sections, which are directly related to the event counts performed by these complete experiments.

In the past, a huge amount of literature has been accumulated concerning semiclassical and quantum procedures for the study of the inelastic scattering processes (see [6–8] for the basic theory). In the $(e,2e)$ and $(e,3e)$ domain, progress in coincidence-detection techniques [9–11] and the development of computational facilities have encouraged the realization of more elaborate theoretical procedures. In the case of $(e,2e)$, the distorted wave [12], the convergent close coupling (CCC) [13], and more accurate fully numerical approaches [14] have been quite successful. In the case of $(e,3e)$, whose treatment is much more difficult than that of simple ionization, a first Born treatment with correlated double continuum wave function [15,16] seems to describe well the correlated state of the two slow ejected electrons. The CCC applied to the $(e,3e)$ also brings quite satisfactory results to this complex problem [17]. In spite of the progress realized and the multitude of new procedures, many experimental results are still not confirmed, especially for the sequential processes, for which higher (second)-order perturbation methods [18] seem to be needed and whose application entails important computational difficulties.

We have recently developed [19] for diatomic systems an *ab initio* procedure based on the completely numerical solution of the driven Schrödinger equation by the external complex scaling method treated by spheroidal coordinates which possess the natural symmetry of diatomic systems. The aim of the present article is to introduce the second Born corrections in the determination of the multifold differential cross section of the single and the double ionization of diatomic hydrogen for which existing theoretical calculations fail to reproduce the existing experimental results.

II. SECOND BORN TERM IMPLEMENTATION

Our method [19] is based on the solution of the driven Schrödinger equation [20],

$$(\hat{H} - E)\psi^{(+)} = -\hat{\mu}\psi_i \tag{1}$$

where $\psi^{(+)}$ represents the "first-order wave function," with the boundary conditions of an outgoing wave provided by the external complex scaling (ECS) [21]. Here $\hat{H}$ is the Hamiltonian of the target, E represents the final energy of the target electrons, and ψ_i is the initial state of the target. The excitation operator $\hat{\mu}$ takes into account the effect of the incoming electron. The details of the procedure named "prolate spheroidal external complex scaling" (PSECS) are presented in [19]. We refer to it just as ECS for briefness.

The potential energy of the interaction between the incoming electron and the H_2 target in atomic units is given by

$$V(\mathbf{r}_0,\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_0|} + \frac{1}{|\mathbf{r}_2 - \mathbf{r}_0|} - \frac{1}{|\mathbf{R}/2 - \mathbf{r}_0|} - \frac{1}{|\mathbf{R}/2 + \mathbf{r}_0|},$$

where $\mathbf{r}_0$ represents the radius vector of the incoming electron and $\mathbf{r}_{1,2}$ that of the molecular electrons. The vector $\mathbf{R}$ defines the internuclear distance and the orientation of the molecular axis. We consider the first-order Born term of the excitation operator by

$$\hat{\mu}_{1B} = -\frac{1}{2\pi}\langle \mathbf{k}_s|V|\mathbf{k}_i\rangle = -\frac{2}{K^2}[e^{i\mathbf{K}\cdot\mathbf{r}_1} + e^{i\mathbf{K}\cdot\mathbf{r}_2} - e^{i\mathbf{K}\cdot\mathbf{R}/2} - e^{-i\mathbf{K}\cdot\mathbf{R}/2}], \tag{2}$$

where $\mathbf{k}_i$ is the momentum of the incoming electron, $\mathbf{k}_s$ the momentum of the scattered electron, and $\mathbf{K}$ the momentum transfer. Here we have taken $|\mathbf{k}\rangle = |\exp(i\mathbf{k}\cdot\mathbf{r}_0)\rangle$.

The second-order Born term in the transition amplitude is given by

$$f_{2\mathrm{B}} = -\frac{1}{2\pi}\sum_n \int \frac{d\mathbf{k}}{(2\pi)^3}\frac{\langle \mathbf{k}_s f|V|\mathbf{k}n\rangle\langle \mathbf{k}n|V|\mathbf{k}_i i\rangle}{k_i^2/2 + E_0 - k^2/2 - E_n + i\epsilon},$$

where $|\mathbf{k}_i i\rangle = |e^{i\mathbf{k}_i\cdot\mathbf{r}_0}\psi_i(\mathbf{r}_1,\mathbf{r}_2)\rangle$, $|\mathbf{k}_s f\rangle = |e^{i\mathbf{k}_s\cdot\mathbf{r}_0}\psi_f(\mathbf{r}_1,\mathbf{r}_2)\rangle$, and $|\mathbf{k}n\rangle = |e^{i\mathbf{k}\cdot\mathbf{r}_0}\psi_n(\mathbf{r}_1,\mathbf{r}_2)\rangle$ represent, respectively, the initial, the final, and the intermediate states of the system. The E_0 and E_n are the initial and intermediate target state energies. For simplification of the calculation we use the closure approximation (see [18] and references therein), which consists of replacing E_n in the denominator with some constant value E_t for all channels. This will make it possible to apply the completeness relation $\sum_n \psi_n^*(\mathbf{r})\psi_n(\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}')$ to obtain

$$f_{2\mathrm{B}} = -\frac{1}{2\pi}\langle\psi_f|\int \frac{d\mathbf{k}}{(2\pi)^3}\frac{\langle \mathbf{k}_s|V|\mathbf{k}\rangle\langle \mathbf{k}|V|\mathbf{k}_i\rangle}{k_i^2/2 + E_0 - k^2/2 - E_t + i\epsilon}|\psi_i\rangle,$$

which can be expressed in the terms of the second Born excitation operator,

$$\hat{\mu}_{2\mathrm{B}} = -\frac{1}{2\pi}\int \frac{d\mathbf{k}}{(2\pi)^3}\frac{\langle \mathbf{k}_s|V|\mathbf{k}\rangle\langle \mathbf{k}|V|\mathbf{k}_i\rangle}{k_i^2/2 + E_0 - k^2/2 - E_t + i\epsilon}, \tag{3}$$

such that $f_{2\mathrm{B}} = \langle\psi_f|\hat{\mu}_{2\mathrm{B}}|\psi_i\rangle$.

In the frame of the closure approximation the result must not be sensitive to the choice of E_t in the neighborhood of the energy of the dominating intermediate channel. We have checked this by calculating the multifold differential cross section (MDCS) for several values $E_t \in (E_0, E_f)$, where E_f is the final target state energy, and have found that the MDCS actually does not depend on E_t for all cases discussed in what follows. This justifies the use of the closure approximation. Following the choice in [22], we have displayed in what follows results only for $E_t = E_0 + k_i(k_i - k_s)/2 \simeq (E_0 + E_f)/2$.

Replacing $\langle\mathbf{k}|V|\mathbf{k}'\rangle$ with its analytical expression and rearranging, we can put the operator in Eq. (3) in the following form:

$$\begin{aligned}\hat{\mu}_{2\mathrm{B}} = {} & \mathcal{W}(\mathbf{r}_1,\mathbf{r}_1) + \mathcal{W}(\mathbf{r}_1,\mathbf{r}_2) - \mathcal{W}(\mathbf{r}_1,\mathbf{R}/2) - \mathcal{W}(\mathbf{r}_1,-\mathbf{R}/2)\\ & + \mathcal{W}(\mathbf{r}_2,\mathbf{r}_1) + \mathcal{W}(\mathbf{r}_2,\mathbf{r}_2) - \mathcal{W}(\mathbf{r}_2,\mathbf{R}/2)\\ & - \mathcal{W}(\mathbf{r}_2,-\mathbf{R}/2) - \mathcal{W}(\mathbf{R}/2,\mathbf{r}_1) + \mathcal{W}(\mathbf{R}/2,\mathbf{r}_2)\\ & + \mathcal{W}(\mathbf{R}/2,\mathbf{R}/2) + \mathcal{W}(\mathbf{R}/2,-\mathbf{R}/2) - \mathcal{W}(-\mathbf{R}/2,\mathbf{r}_1)\\ & + \mathcal{W}(-\mathbf{R}/2,\mathbf{r}_2) + \mathcal{W}(-\mathbf{R}/2,\mathbf{R}/2)\\ & + \mathcal{W}(-\mathbf{R}/2,-\mathbf{R}/2),\end{aligned}$$

with

$$\begin{aligned}\mathcal{W}(\mathbf{k}_i,\mathbf{K};\mathbf{r}_1,\mathbf{r}_2) &= -\frac{1}{2\pi}\int\frac{d\mathbf{k}}{(2\pi)^3}\\ &\quad\times\frac{\frac{4\pi}{|\mathbf{q}_2|^2}\exp(i\mathbf{q}_2\cdot\mathbf{r}_2)\frac{4\pi}{|\mathbf{q}|^2}\exp(i\mathbf{q}\cdot\mathbf{r}_1)}{k_i^2/2 + E_0 - k^2/2 - E_t + i\epsilon}\\ &= -\frac{\exp(i\mathbf{K}\cdot\mathbf{r}_2)}{\pi^2 k_i}\mathcal{I}(\mathbf{k}_i,\mathbf{K};\mathbf{r}_1-\mathbf{r}_2).\end{aligned} \tag{4}$$

Here we have introduced the intermediate momentum transfer vectors $\mathbf{q} = \mathbf{k}_i - \mathbf{k}$ and $\mathbf{q}_2 = \mathbf{k} - \mathbf{k}_s = \mathbf{K} - \mathbf{q}$. The integral $\mathcal{I}(\mathbf{k}_i,\mathbf{K};\mathbf{r})$ is given by (A1). Some complementary details of the integration procedure are given in the Appendix.

Relation (4) gives the correct second Born term, but it is not convenient in the case of nonaligned molecules, because its application requires the solution of Eq. (1) for each orientation of $\mathbf{R}$. One way to avoid this problem is to use of the multipole expansion. In the present work, we take into account the leading dipole term only:

$$\hat{\mu}_{2\mathrm{BD}}(\mathbf{r}_1,\mathbf{r}_2) = \sum_{M_1,M_2=-1}^{1}\mathcal{M}^{M_1M_2}(x_{1M_1}+x_{2M_1})(x_{1M_2}+x_{2M_2}). \tag{5}$$

Here $x_{\alpha,\pm1} = \frac{1}{\sqrt{2}}(\mp x_\alpha - iy_\alpha)$, $x_{\alpha0} = z_\alpha$, and the second-rank tensor

$$\mathcal{M}^{M_1M_2} = \left.\frac{\partial^2\mathcal{W}(\mathbf{r}_1,\mathbf{r}_2)}{\partial x_{1M_1}\partial x_{2M_2}}\right|_{\mathbf{r}_1=0,\,\mathbf{r}_2=0}. \tag{6}$$

Equation (1) can then be put, using (5), in the form of a set of nine uncoupled equations,

$$\begin{aligned}(\hat{H}-E)\psi^{(+)}_{M_1M_2}(\mathbf{r}_1',\mathbf{r}_2') = {} & -\big(x'_{1M_1}+x'_{2M_1}\big)\\ & \times\big(x'_{1M_2}+x'_{2M_2}\big)\psi_i(\mathbf{r}_1',\mathbf{r}_2'),\end{aligned} \tag{7}$$

where $\mathbf{r}'_{1,2}$ are coordinates defined in the molecular frame, $Oz'||\mathbf{R}$. We can then get the component of the amplitude of transition to the state ψ_f of the target [19,20],

$$f_{M_1M_2} = \langle f'|\psi^{(+)}_{M_1M_2}\rangle,$$

where $|f'\rangle$ is the "testing function" [23] of the final state. In the case of double ionization, $|f'\rangle = \chi^{(-)}_{\mathbf{k}_1}(\mathbf{r}_1)\chi^{(-)}_{\mathbf{k}_2}(\mathbf{r}_2)$, while for single ionization, $|f'\rangle = \chi^{(-)}_{\mathbf{k}_e}(\mathbf{r}_1)\varphi_{nlm}(\mathbf{r}_2)$. $\chi^{(-)}_{\mathbf{k}}$ and φ_{nlm} represent, respectively, the continuum function and bound-state functions of the residual ion [19]. Finally, the dipole component of the second Born contribution can be represented by

$$f_{2\mathrm{B}} = \sum_{M_1,M_2=-1}^{1}\mathcal{M}'^{M_1M_2}(\mathbf{n}_R)f_{M_1M_2}, \tag{8}$$

where $\mathcal{M}'$ corresponds to the tensor defined in Eq. (6) transformed to the molecular frame for a given orientation of $\mathbf{R}$ by the formula for contravariant tensors [24],

$$\begin{aligned}\mathcal{M}'^{M_1M_2}(\mathbf{n}_R) = {} & \sum_{M_1',M_2'=-1}^{1}\mathcal{M}^{M_1'M_2'}D^{1*}_{M_1'M_1}(\varphi_R,\theta_R,0)\\ & \times D^{1*}_{M_2'M_2}(\varphi_R,\theta_R,0),\end{aligned}$$

where $D^l_{mm'}(\alpha,\beta,\gamma)$ is the Wigner D function. Note that one must solve Eq. (7) only for four (M_1,M_2) combinations: (0,0), (−1,1), (1,1), and (1,0). All the other $\psi^{(+)}_{M_1M_2}$ can be deduced from these four values by using electron exchange symmetry $\psi^{(+)}_{M_2M_1}(\mathbf{r}_1,\mathbf{r}_2) = \psi^{(+)}_{M_1M_2}(\mathbf{r}_1,\mathbf{r}_2)$ and axial symmetry $\langle\ell_1 m_1\ell_2 m_2|\psi^{(+)}_{-M_1,-M_2}\rangle = \langle\ell_1,-m_1,\ell_2,-m_2|\psi^{(+)}_{M_1,M_2}\rangle$.

As demonstrated in [22], the dipole approximation for the second Born term in the usual form gives strongly overestimated results, because of the fact that the original second Born term (4) deviates widely from the double linear dependence of the radius on the size of the atom. The method of correction, proposed in [22], is inconsistent with our present procedure. We thus correct the dipole approximation in the following alternative way. Let us introduce

$$\mathcal{W}^{M_1M_2}(r_1,r_2) = \oint \oint Y^*_{1M_1}(\Omega_1)Y^*_{1M_2}(\Omega_2)\mathcal{W}(\mathbf{r}_1,\mathbf{r}_2)d\Omega_1 d\Omega_2. \tag{9}$$

As the dipole approximation (5) is equivalent to applying the double linear approximation $\mathcal{W}^{M_1M_2}(r_1,r_2) \simeq \frac{4\pi}{3}\mathcal{M}^{M_1M_2}r_1r_2$, the general idea is to use a double linear approximation $\frac{4\pi}{3}\widetilde{\mathcal{M}}^{M_1M_2}r_1r_2$ that coincides exactly with $\mathcal{W}^{M_1M_2}(r_1,r_2)$ for some radius r_{mol}. So from the relation $\mathcal{W}^{M_1M_2}(r_{\text{mol}},r_{\text{mol}}) = \frac{4\pi}{3}\widetilde{\mathcal{M}}^{M_1M_2}r^2_{\text{mol}}$ we get

$$\widetilde{\mathcal{M}}^{M_1M_2} = \frac{3}{4\pi}\frac{\mathcal{W}^{M_1M_2}(r_{\text{mol}},r_{\text{mol}})}{r^2_{\text{mol}}}. \tag{10}$$

For $r_{\text{mol}} \to 0$ expression (10) converges to (6). It is thus reasonable to choose r_{mol} equal to the radius of the highest electron density in the expression of the right-hand side of Eq. (7) corresponding to the position of the maximum of $|[\text{right-hand side of (7)}]|^2 r_1^2 r_2^2$. Now using the uncorrelated initial function $\psi_i(\mathbf{r}_1,\mathbf{r}_2) = \varphi_1(\mathbf{r}_1)\varphi_1(\mathbf{r}_2)$ and averaging over the angles, we get r_{mol} from

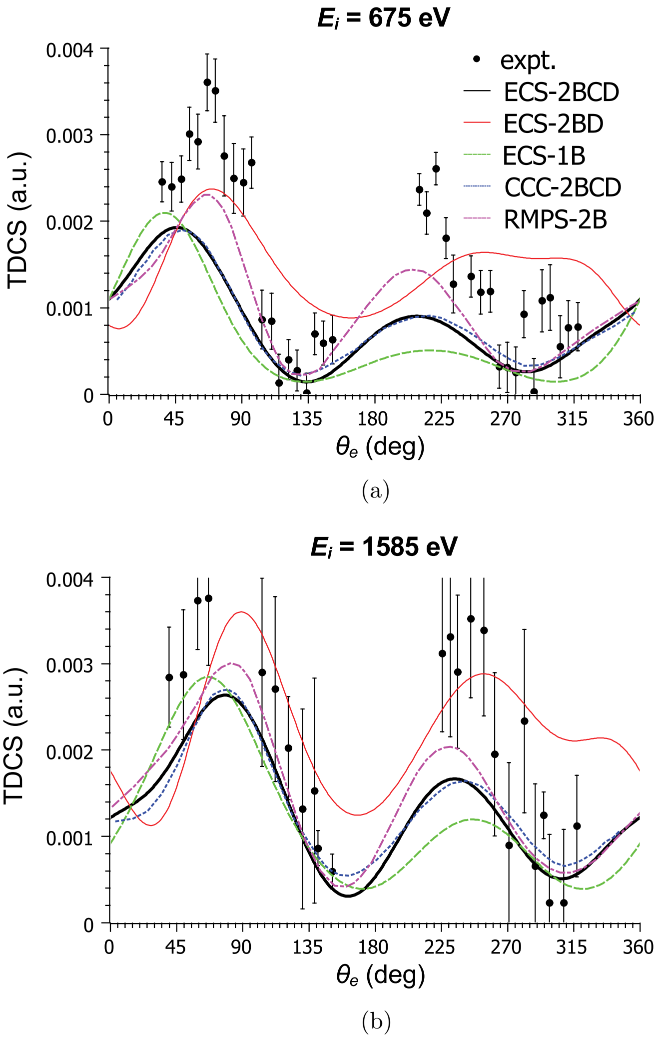
$$\frac{\partial}{\partial r}\left[r^4 \oint |\varphi_1(\mathbf{r})|^2 d\Omega\right]\Bigg|_{r_{\text{mol}}} = 0.$$

For He, we use the single exponential function $\varphi_1(\mathbf{r}) \sim \exp(-\zeta r)$, $\zeta = 27/16$, and get $r_{\text{mol}} = 1.19$. For H_2, we use the Coulson's function $\varphi_1(\mathbf{r}) \sim \exp(-\zeta|\mathbf{r}-\mathbf{R}/2|) + \exp(-\zeta|\mathbf{r}+\mathbf{R}/2|)$, $\zeta = 1.197$, and get $r_{\text{mol}} = 1.76$. Here, the uncorrelated functions are used only for the estimation of r_{mol}. In the solution of (7), we have used the fully correlated initial function (see [19] for details). In what follows, we refer to our second Born calculation as ECS-2BD when the tensor (6) is used in relation (8), and as ECS-2BCD when the corrected tensor (10) is used in relation (8). The curves, where second Born term is not taken into account, are referred to as ECS-1B.

The numerical scheme parameters are the same as in the double photoionization calculations presented in [19]. The first Born term was calculated by the expansion of (2) on prolate spheroidal partial waves [19] restricted to $L_{\max} = 4$, $M_{\max} = 3$ in all examples.

III. RESULTS

Before applying our procedure to the ionization of molecular hydrogen, we begin by testing our procedure by calculating the triply differential cross section (TDCS) of the electron impact ionization-excitation of He with the formation of the residual ion in the excited $n = 2$ state, using the parameters of the experiment given in [25]. In Fig. 1, we compare our results to those of the CCC method with corrected dipole second Born term (CCC-2BCD) performed by Kheifets [22] and those of the R-matrix method with pseudostates with full second Born term (RMPS-2B) [26]. It can be seen that our ECS-2BCD results are very close to the ones obtained by the CCC-2BCD in spite of the fact that we are treating the problem with a very different approach for the correction of the second Born dipole term. However, it is clear from the comparison with experimental data [25] and with RMPS-2B curve that the dipole approximation for the secondnd Born term is not enough to reproduce the position of the maxima of the variation of the TDCS and that account probably must be taken of the following terms of the multipole expansion.

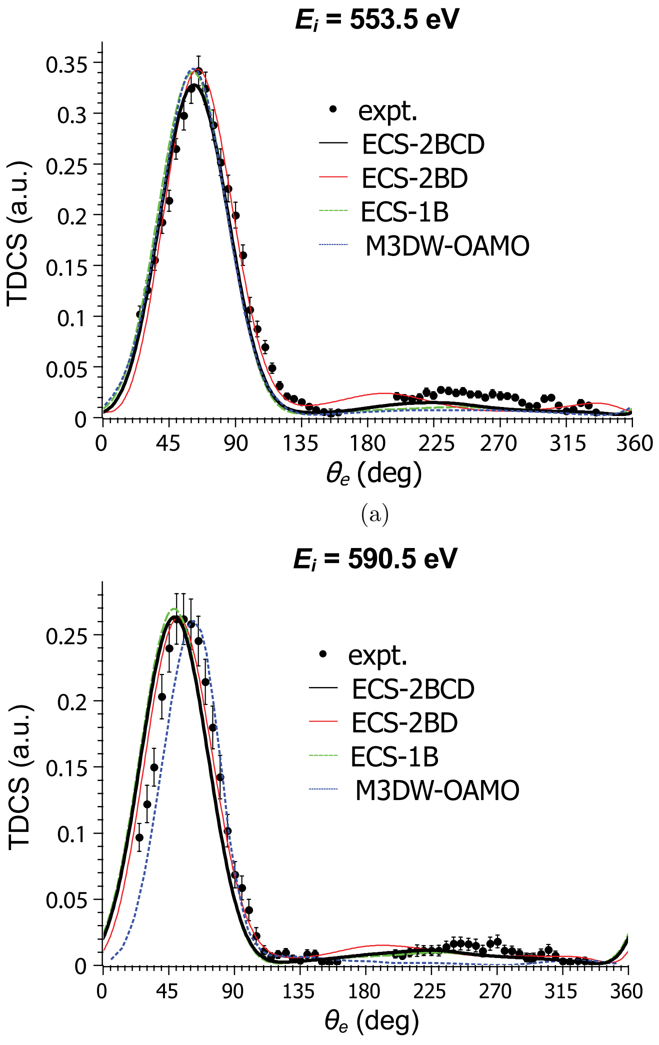


(a)

(b)

FIG. 1. (Color online) The variation of the TDCS of the impact ionization-excitation of He in terms of θ_e for (a) scattered electron energy $E_s = 570$ eV, scattering angle $\theta_s = -4^\circ$, ejected electron energy $E_e = 40$ eV and (b) $E_s = 1500$ eV, $\theta_s = -4^\circ$, $E_e = 20$ eV. Our ECS-2BD results are given by a thin solid line, the ECS-2BCD by a thick solid line, and ECS-1B by dashed lines. Also shown is the CCC-2BCD [22] by a dotted line and RMPS-2B [26] by a dash-dotted line. Experimental data [25] are shown by solid circles.

We then continue, in Fig. 2, to the comparison of the results concerning the variation of the TDCS of the electron impact ionization of H_2 for the experimental parameters given in [27]. We show our three results obtained by ECS-1B,



(a)

(b)

FIG. 2. (Color online) The variation of the TDCS of the impact ionization of nonaligned H_2 as a function of ejection angle θ_e for scattered electron energy $E_s = 500$ eV, scattering angle $\theta_s = -6°$, and ejected electron energy: (a) $E_e = 37$ eV; (b) $E_e = 74$ eV. Our ECS-2BD data are presented by a thin solid line, ECS-2BCD by a thick solid line, and ECS-1B by a dashed line. Also presented are the second Born M3DW-OAMO results [27] (dotted line) and the experimental data [27] (solid circles).

ECS-2BD, and ECS-2BCD together with those obtained using the "molecular three-body distorted wave with an orientation-averaged molecular orbital approximation" (M3DW-OAMO) second Born results [27]. We see that the ECS-2BD agrees best with experimental data, while ECS-2BCD underestimates the angular shift from the momentum transfer direction, while M3DW-OAMO overestimates it. The TDCS pattern in Fig. 2, where we observe that the binary peak (i.e., the peak near direction of the momentum transfer **K**) is much greater then the recoil peak (near $-\mathbf{K}$ direction), differs from TDCS pattern of He in Fig. 1. In Fig. 1 the two peaks have comparable magnitudes in spite of the fact that the value of K is large. The origin of this difference must be seen as a consequence of the difference of the processes: simple ionization in the H_2 case and ionization-excitation in the He case. For the simple ionization the target electron interacts directly with the incident electron, and most of the momentum is transferred to the ejected electron. On the other hand, in the case of ionization–excitation, the process is impossible without the interaction between target electrons, and very probably that ejected electron transfers part of its momentum to the other electrons and consequently to the residual ion.

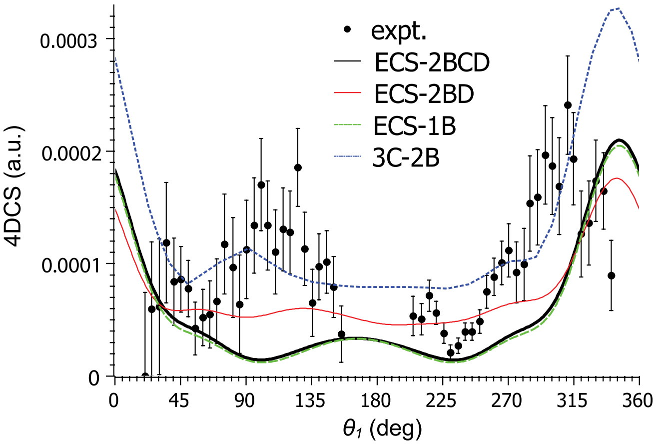
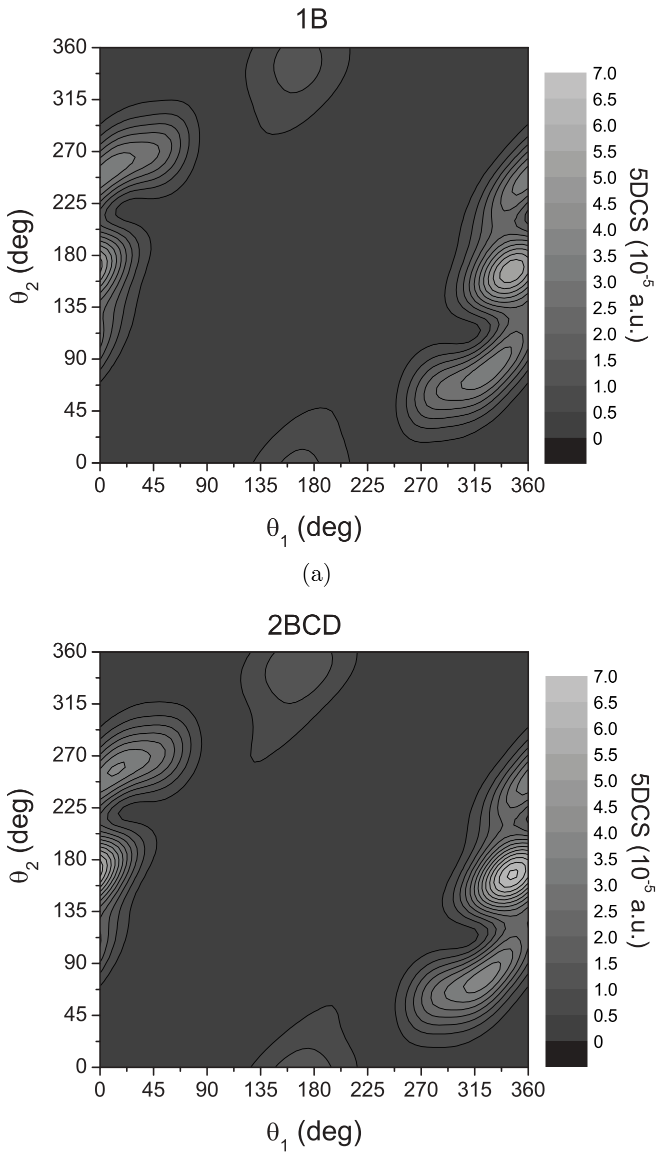


FIG. 3. (Color online) The variation of the 4DCS of the double ionization of nonaligned H_2 by electron impact in terms of ejection angle θ_1 for scattered electron energy $E_s = 500$ eV, scattering angle $\theta_s = 1.5°$, and ejected-electron energies $E_1 = 51$ eV and $E_2 = 10$ eV. Also shown are our ECS results with the dipole second Born term (thin solid line), the corrected dipole second Born term (thick solid line), and the first Born (dashed line). Also presented are 3C-2B [29] (dotted line) and experimental data [28] (solid circles).

We finally try to reproduce in Fig. 3 the fourfold differential cross section (4DCS) of the $(e,3\text{-}1e)$ process on H_2, where only one of the two ejected electrons is detected in coincidence with the scattered electron for the parameters of the experiment presented in [28]. Comparison of our results obtained by ECS-1B, ECS-2BD, and ECS-2BCD and 3C second Born (3C-2B) [29] is done with the experimental data [28] rescaled to our curves' binary maximum magnitude. This shows that, surprisingly, ECS-2BCD results are indistinguishable from the first Born results. On the other hand, we see in Fig. 4 that such compensation of the second Born contribution comes from averaging by the ejection direction of the slow $E_2 = 10$ eV electron. The ECS-2BD curve differs noticeably from the ECS-1B one, but the position of the major peak is less shifted from one of the first Born curves than the experimental data. We can suppose that, as in the case of electron impact ionization-excitation of He (Fig. 1), angular shift of the maximum is mainly induced by nondipole contributions in the second Born multipole expansion.

The fivefold differential cross section (5DCS) of the $(e,3e)$ process on H_2 for the parameters of [28], but without integration by ejection directions of the second electron, is demonstrated in Fig. 4. One can see that the 5DCS angular distribution has a rather sophisticated structure. The introduction of the dipole second Born contribution leads to the increase of the magnitudes of the maxima but actually does not change their positions.



(a)

(b)

FIG. 4. Gray-scale map of the 5DCS of the double ionization of the nonaligned H_2 by electron impact as a function of ejection angles θ_1 and θ_2 for the same parameters as in Fig. 3: (a) ECS-1B; (b) ECS-2BCD.

IV. CONCLUSION

We have calculated the MDCS of the single and double ionization of helium and molecular hydrogen by fast electrons. We took into account up to the second term in the Born series for the scattered electron and used our *ab initio* scheme for the treatment of the ejected electrons. We suppose that the observed differences of our results from experimental angular distribution induced by nondipole contributions in the second Born term multipole expansion, which was not taken into account in present calculations. In the next works we plan to account for the nondipole second Born terms.

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APPENDIX: THE DETAILS OF THE INTEGRATION PROCEDURE IN THE CALCULATION OF THE SECOND BORN EXCITATION OPERATOR

In the laboratory frame with $Oz||\mathbf{k}_i$, we can write

$$\mathcal{I}(\mathbf{k}_i,\mathbf{K};\mathbf{r}) = \int_0^\infty \frac{dq}{q}\oint d\Omega_q \frac{\frac{1}{|\mathbf{K}-\mathbf{q}|^2}\exp(i\mathbf{q}\cdot\mathbf{r})}{\cos\theta_q - \frac{q^2/2+E_t-E_0}{k_i q}+i\epsilon}. \tag{A1}$$

We changed the variable in the integration from $\mathbf{k}$ to $\mathbf{q}$ because, in this case, the angular dependence in $1/|\mathbf{q}|^2$ disappears. We first reduce this integral to a sum of more simple integrals by using the two following well-known expansions:

$$\exp(i\mathbf{q}\cdot\mathbf{r}) \simeq \sum_{\ell=0}^{\ell_{\max}} i^\ell j_\ell(qr)(2\ell+1)P_\ell[\cos\angle(\mathbf{q},\mathbf{r})] \tag{A2}$$

and

$$\frac{1}{|\mathbf{K}-\mathbf{q}|^2} \simeq \frac{1}{2Kq}\sum_{l=0}^{l_{\max}} Q_l\left(\frac{K^2+q^2}{2Kq}\right)P_l[\cos\angle(\mathbf{K},\mathbf{q})] \tag{A3}$$

[24], with

$$P_l[\cos\angle(\mathbf{n},\mathbf{n}')] = \frac{4\pi}{2l+1}\sum_{m=-l}^{l} Y_{lm}^*(\theta,\phi)Y_{lm}(\theta',\phi'). \tag{A4}$$

The integration over the azimuthal angle ϕ_q is trivial. The integration over θ_q is then performed by using the identity which takes care of the products of the spherical harmonics [24], which results in

$$\int_{-1}^{1}\frac{P_l(x')}{x'-x+i\epsilon}dx = \begin{cases} -2Q_l(x) - i\pi P_l(x), & x\in[-1,1],\\ -2Q_l(x), & x>1, \end{cases} \tag{A5}$$

where $P_l(x)$ represents the Legendre polynomial and $Q_l(x)$ the Legendre function of the second kind, extended on the interval $x\in[-1,\infty)$ and satisfying the relation $Q_0(x)=\frac{1}{2}\ln\left|\frac{x+1}{x-1}\right|$, $Q_1(x)=xQ_0(x)-1$, $Q_l(x)=\frac{2l-1}{l}xQ_{l-1}(x)-\frac{l-1}{l}Q_{l-2}(x)$. The integration over q is then performed using a numerical quadrature method, which takes into account the fact that the integrand has logarithmic singularities in points $q_{a,b}=k_i\mp\sqrt{k_i^2-2(E_t-E_i)}$. For $q>q_b$ the integrand tends rapidly to zero. This permits us to fix the upper limit of integration $q_{\max}=2k_i$.

The direct application of the expansion (A3) presents a supplementary difficulty because it does not assure the convergence of off-shell part of the integral $\mathcal{I}$ with increasing $l_{\max}$, because the expansion (A3) has singularities on the $q=K$ sphere for any finite number $l_{\max}$. To avoid this difficulty, we have used the expansion

$$\frac{1}{|\mathbf{K}-\mathbf{q}|^2} = \frac{1}{K^2+q^2-2(\mathbf{K}\cdot\mathbf{q})} \simeq \frac{1}{K^2+q^2}\sum_{s=0}^{l_{\max}}\left[\frac{2(\mathbf{K}\cdot\mathbf{q})}{K^2+q^2}\right]^s,$$

which has no singularities for $K > 0$. This is equivalent to replacing $Q_l(x)$ in (A3) by its finite series expansion:

$$Q_l^{[l_{\max}]}(x) = \frac{1}{x}\sum_{n=0}^{\lfloor(l_{\max}-l)/2\rfloor}\frac{(2n+l)!}{(2n)!!(2n+2l+1)!!}\frac{1}{x^{2n+l}}. \quad \text{(A6)}$$

With this approach the calculated value of (A1) converges monotonously with increasing $l_{\max}$. In all calculations here we used $l_{\max} = 99$ and $\ell_{\max} = 3$.

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