Nonperturbative treatment of electron-impact ionization of Ar(3p)

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Phys. Rev. A **85**, 032708 — Published 15 March 2012

DOI: 10.1103/PhysRevA.85.032708

Nonperturbative Treatment of Electron-Impact Ionization of Ar(3p)

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We present triple-differential cross sections for electron-impact ionization of a $3p$ electron in Ar. Results from a fully nonperturbative close-coupling formalism using our B-Spline R-matrix approach are compared with those from a hybrid distorted-wave plus R-matrix (close-coupling) expansion as well as recent experimental data of Ren *et al.* (Phys. Rev. A **83** (2011) 052714). We find overall good agreement between the two sets of entirely independent theoretical predictions, but serious discrepancies with the published experimental data regarding the drop of the cross section with increasing detection angle of "scattered projectile", i.e., the faster of the two outgoing electrons. A detailed investigation of the dependence of the results on this angle suggests that obtaining reliable data, both experimentally and theoretically, is highly challenging in the regime where the largest discrepancies occur.

PACS numbers: 34.80.Dp
Keywords: argon, electron impact, ionization, B-spline R-matrix

I. INTRODUCTION

In a recent publication [1], we presented a fully nonperturbative treatment based on the close-coupling plus pseudostates expansion for the highly correlated ionization with excitation problem in helium. Excellent agreement with available experimental data [2–4] for the ratio of the triple-differential cross section (TDCS) for ionization without excitation (i.e., leaving the residual He^+ ion in its $1s$ ground state) or simultaneous ionization to the $n = 2$ $(2s, 2p)$ states was achieved. Our treatment was based upon the B-spline R-matrix with pseudostates (BSRMPS) method. It is a close-coupling approach similar to the standard Belfast RMPS method [5–9], except for the fact that the excellent numerical properties of B-splines as the primitive basis are taken full advantage of and that it is possible to use nonorthogonal sets of orbitals to describe the target and the projectile electrons. Details can be found in [10]. The method is also closely related to the convergent close-coupling (CCC) approach [11, 12], which is formulated in momentum rather than coordinate space and has been widely used to produce numerical benchmark results for ionization without excitation in H, He, and other quasi-one and quasi-two electron targets.

Given the generality of our method, we are not restricted to systems where the ionized electron originates from a subshell with a one-electron orbital angular momentum $\ell = 0$ and the final ion remains in a state with orbital angular momentum $L_{\rm ion} = 0$ as well. Hence, we can use the approach developed in [1] to investigate electron-impact ionization of more complex systems such as the heavy noble gases. Of particular interest in this respect is the ionization of a $3p$ electron in Ar, for which *absolute* TDCS values have been determined experimentally [13] and extensive data for emission of the ionized electron in and out of the collision plane were published by Ren *et al.* [14].

In the latter paper [14], the experimental data were compared with predictions from a hybrid approach [15], in which the interaction of a "fast" projectile electron with the target is described by a first-order or second-order distorted-wave approach, while the initial bound state and the scattering of a "slow" ejected electron from the residual ion is treated by an R-matrix (close-coupling) expansion. While one might have expected some disagreement between experiment and theory for the case studied, describing the direct ionization of a $3p$ electron by a projectile with incident energy of 195 eV for relatively small scattering angles of 20° or less and very asymmetric energy sharing between the two outgoing electrons, the discrepancies were surprisingly large and, interestingly, seemed to be even more pronounced in the predicted magnitude of the TDCS than in the angular dependence.

Being able to employ an entirely different, and in principle superior, theoretical method to this problem provided the main motivation for the present work. Below we will briefly summarize the basic features of both the previous hybrid and our new BSRMPS approach. Results obtained by the two methods are then compared with each other and with the recent experimental data of Ren *et al.* [14]. In particular, we will analyze the sensitivity of the results to small variations in the fixed detection angle of the faster of the two outgoing electrons. We finish with a summary and a few conclusions.

II. NUMERICAL APPROACHES

As mentioned above, a partially successful theory for electron-impact ionization has been a hybrid approach, in which the interaction of a "fast" projectile electron with the target is described by a first-order or second-order distorted-wave approach, while the initial bound state and the scattering of a "slow" ejected electron from the residual ion is treated by an R-matrix (RM) approach. These DWB1-RM [16, 17] and DWB2-RM [18] models were formulated for highly asymmetric kinematics and small energy losses compared to the incident energy. Ap-

plication to ionization of both the $3p$ and the $3s$ subshells of Ar [15] was indeed relatively successful for asymmetric kinematics and generally, albeit with many notable exceptions, the predictions agreed better with the available *relative* experimental data [19–21] than those from other theories. However, the picture became less clear when data were obtained over the entire angular range [22] and, finally, on an absolute scale [13]. In fact, a distorted-wave approach, sometimes also including the final-state post-collision interaction (see, for example, Prideaux *et al.* [23]), often did just as well and sometimes even better than the hybrid theory.

Details of the hybrid approach can be found in many of the references given above, e.g. [14, 15, 17], and hence will not be repeated here. Given that emission of the $3p$ electron is generally the dominant ionization process in the kinematical regime considered here, it is not surprising that using either a first-order or an approximate second-order treatment of the projectile produced very similar results, especially for $3p$ ionization. Also, coupling only the two final ionic states $(3s^2 3p^5)^2P^o$ and $(3s3p^6)^2S$, rather than employing a much larger RMPS expansion for the ejected-electron–residual-ion problem, was generally found to be sufficient. A key issue, on the other hand, is the description of the initial bound state and the final ionic states included in the close-coupling expansion for the electron scattering from the residual ion. In the hybrid method, we use the multi-configuration expansions developed by Burke and Taylor [24] for the corresponding photoionization problem.

The BSRMPS method is based upon an entirely different formulation. It basically contains two steps, namely: i) the treatment of electron collisions with neutral argon using an extensive close-coupling expansion that contains both physical and pseudostates, with the latter being used to approximate the effect of high-lying discrete Rydberg states as well as the coupling to various (depending on the final ionic states) ionization continua; and ii) the construction of the *ionization* amplitude by combining the scattering amplitudes for *excitation* of the pseudostates using coefficients obtained by direct projection of the wavefunction to the various scattering channels associated with a particular final ionic state.

For the case at hand, we performed a nonrelativistic RMPS calculation for e-Ar collisions with a total of 482 states in the close-coupling expansion. The atomic wave functions for neutral Ar were obtained by the B-spline box-based close-coupling method [25]. They were first expanded in terms of products of N-electron ionic states and radial functions for the outer electron. In the present model, we included the $(3s^2 3p^5)^2P^o$, $(3s3p^6)^2S$, and $(3s^2 3p^4 3d)^2S$ states of Ar^+, based on the experienced gained in related work by Guan *et al.* [26].

The radial functions for the outer electron were expanded in a B-spline basis. The expansion coefficients were obtained by diagonalizing the $(N+1)$-electron target hamiltonian matrix inside a box of radius $a = 28\,a_0$, where $a_0 = 0.529 \times 10^{-10}\,\mathrm{m}$ denotes the Bohr radius. These functions were forced to vanish at the edge of the box. Along with the physical states, this scheme provides a set of pseudostates that, as mentioned above, represent the Rydberg spectrum and the ionization continua. The number of physical bound states and the density of the continuum pseudostates depends upon the radius of the box and the number of B-splines. We used 69 B-splines of order 8 on a semiexponential grid of knots. This results in 482 physical and pseudo target states with coupled orbital angular momenta $L = 0 - 5$ and energies reaching up to 80 eV.

We then obtained the scattering amplitudes for excitation of all pseudostates using our suite of BSR codes [10] for electron collisions. Contributions from $(N + 2)$-electron symmetries with coupled orbital angular momenta up to 25 were included in the partial-wave expansion. The present model contained up to 1,445 scattering channels, leading to generalized eigenvalue problems with matrix dimensions up to 90,000 in the B-spline basis. The corresponding solutions were obtained with a newly developed parallelized version of the BSR complex.

The last, and most crucial, step in the process is the generation of the ionization amplitudes. This is done by summing up the amplitudes for excitation of all energetically accessible pseudostates, with the expansion factors given by the overlap of the pseudostates and the true continuum functions [1]. At this stage in the calculation, consistency between the models for the bound states (physical and pseudo) and the physical continuum scattering channels is critical. We ensure this consistency by employing the same expansions including the three ionic states $(3s^2 3p^5)^2P^o$, $(3s3p^6)^2S$, and $(3s^2 3p^4 3d)^2S$ mentioned above.

The key point of the BSR method is the use of B-splines as a universal and effectively complete basis to describe the projectile electron in the close-coupling expansion of the collision system. A distinctive feature of our BSR implementation is the possibility to employ individually optimized, and hence "nonorthogonal" orbitals to describe the target states, and we do not restrict the projectile orbitals to be orthogonal to the target orbitals either. Although the lack of these restrictions makes the setting up of the hamiltonian matrix significantly more complicated than in the standard R-matrix approach [5], the flexibility of the method has proven to be a critical advantage on many occasions. Since we can generate accurate descriptions of both the ionic and the neutral states with relatively compact multi-configuration expansions, the principal purpose of the pseudostates is to approximate the coupling to high-lying Rydberg states and the ionization continua.

III. RESULTS AND DISCUSSION

Figure 1 exhibits our results for the coplanar geometry. Overall, there is very satisfactory agreement between the two sets of theoretical predictions, and hence there re-

mains sometimes severe disagreement with the experimental data, as discussed by Ren *et al.* [14]. Note, however, that these experimental data were effectively obtained in a single run of the apparatus, recording all events for different scattering and emissions angles (in and out of the scattering plane) as well as different energy distributions between the two outgoing electrons *simultaneously* in a reaction microscope. Hence, the results are cross-normalized to each other to produce, in principle, consistent *relative* TDCS results. Finally, these relative data were put on an *absolute* scale by determining a single overall normalization factor through comparison with the data of Hargreaves *et al.* [13]. The latter were determined for an incident projectile energy of 200 eV, a nominal scattering angle of $\theta_1 = -15°$, and an energy $E_2 = 10$ eV of the slow outgoing electron.

Figures 2 and 3 show the corresponding results for detection of the slow outgoing electron in two planes perpendicular to the scattering plane. Here the agreement between the two sets of theoretical results is even better than for the coplanar arrangement. Given the many ongoing discussions about theory potentially facing special challenges for out-of-plane geometries, this agreement is noteworthy in its own right.

Another point worth mentioning concerns the overall good agreement in the predicted shape, and sometimes even the magnitude, between experiment and theory when the TDCS values are relatively large. The most striking discrepancies occur when the magnitude of the TDCS is small, i.e., generally at the largest scattering angle of $\theta_1 = -20°$. This may not be too surprising, however, as it is well known that the difficulties of calculating – and measuring – a signal accurately will generally increase with decreasing signal strength and, consequently, usually increasing signal-to-noise ratio.

Figure 4 shows a detailed analysis of the BSRMPS results for the coplanar situation depicted in the left column of Fig. 1, i.e. for $E_2 = 10$ eV. Two items are worth pointing out in some detail, namely: i) The largest predicted TDCS value for $\theta_1 = -5°$ is about a factor 100 (or two orders of magnitude) larger than the predicted maximum at $\theta_1 = -20°$. ii) The predicted angular dependence of the maximum TDCS in the binary region near $\theta_1 = -15°$ is very significant; specifically, the BSRMPS results for $\theta_1 = -14°$ in this angular regime are about three times larger than the corresponding results for $\theta_1 = -16°$. On the other hand, the relative angular dependence of the results does not change very much.

As theorists we will refrain from speculations regarding experimental details. Nevertheless, it seems appropriate to draw attention to the fact that using $\theta_1 = -15°$ in order to put the data on an absolute scale will require confidence in knowing the actual value of θ_1 to an accuracy of most likely better than $\pm 0.5°$. Furthermore, having to distinguish signal sizes that differ by two orders of magnitude in a single run might pose significant challenges to the detector electronics. It is also important to keep in mind that the experimental data were obtained with a certain energy and angular resolution by "binning" the results. Specifically, the angular resolutions were $\pm 1°$ for $\theta_1 = 5°$, $\pm 1.5°$ for $\theta_1 = 10°$, and $\pm 2°$ for $\theta_1 = 15°$ and $20°$. Similarly, the energy resolution was ± 1.5 eV for $E_2 = 10$ eV and ± 2.5 eV for $E_2 = 15$ eV and 20 eV, respectively [27]. While it might seem desirable to convolute the theoretical predictions with these angular and energy resolutions, this is impractical due to the large number of additional calculations that would be required.

Finally, it seems appropriate to summarize, once again, the approximations made in our theoretical treatment. Although we used an extensive "convergent" RMPS expansion for electron scattering from neutral Ar, the continuum was discretized, and we also limited the maximum orbital angular momentum in the target states. For consistency, we then only used a three-state expansion for e-Ar^+ collisions in order to obtain the final continuum states for direct projection, and we neglected the exchange amplitude in this projection. Furthermore, although the BSR method is known to provide excellent (compared to other collision models) structure descriptions for both neutral Ar and singly ionized Ar^+, using even more extensive configuration-interaction expansions would improve what we employed in the current work. And, finally, we used a nonrelativistic model. Unfortunately, the size of our calculation was at the very limit of our computational resources. Hence we could only perform limited tests by reducing the size of the respective expansions, and even a semirelativistic model based on the Breit-Pauli approximation was entirely out of reach. Nevertheless, based on these limited tests and extensive experience in the past, it seems unlikely to us that these approximations would explain the remaining discrepancies between the observed and the predicted drop in the TDCS with increasing detection angle of the projectile.

IV. SUMMARY AND CONCLUSIONS

We have presented triple-differential cross sections for electron-impact ionization of a $3p$ electron in Ar. While the agreement between the predictions from two independent theoretical models is generally good, there remain serious discrepancies with recent experimental data. However, obtaining accurate results in the kinematical regimes associated with the largest disagreements seems to be a significant challenge, as is the procedure for putting the experimental data on an absolute scale. Consequently, we believe that great care should be taken before much weight is put on the remaining deviations between experiment and theory. It seems very important to study this process further before definite conclusions can be drawn regarding the ability of theory to describe this process accurately. Joint experimental and theoretical work in this direction is currently in progress.

ACKNOWLEDGMENTS

We thank Drs. X. Ren and A. Dorn for stimulating discussions and providing some details about the experimental angular and energy resolutions. This work was supported by the United States National Science Foundation under grants #PHY-1068140 and #PHY-0903818, and by supercomputer resources through the TeraGrid/XSEDE allocation TG-PHY090031 (Ranger and Lonestar at the Texas Advanced Computing Center). We are also grateful for additional support from Drake University through a Troyer Research Fellowship.

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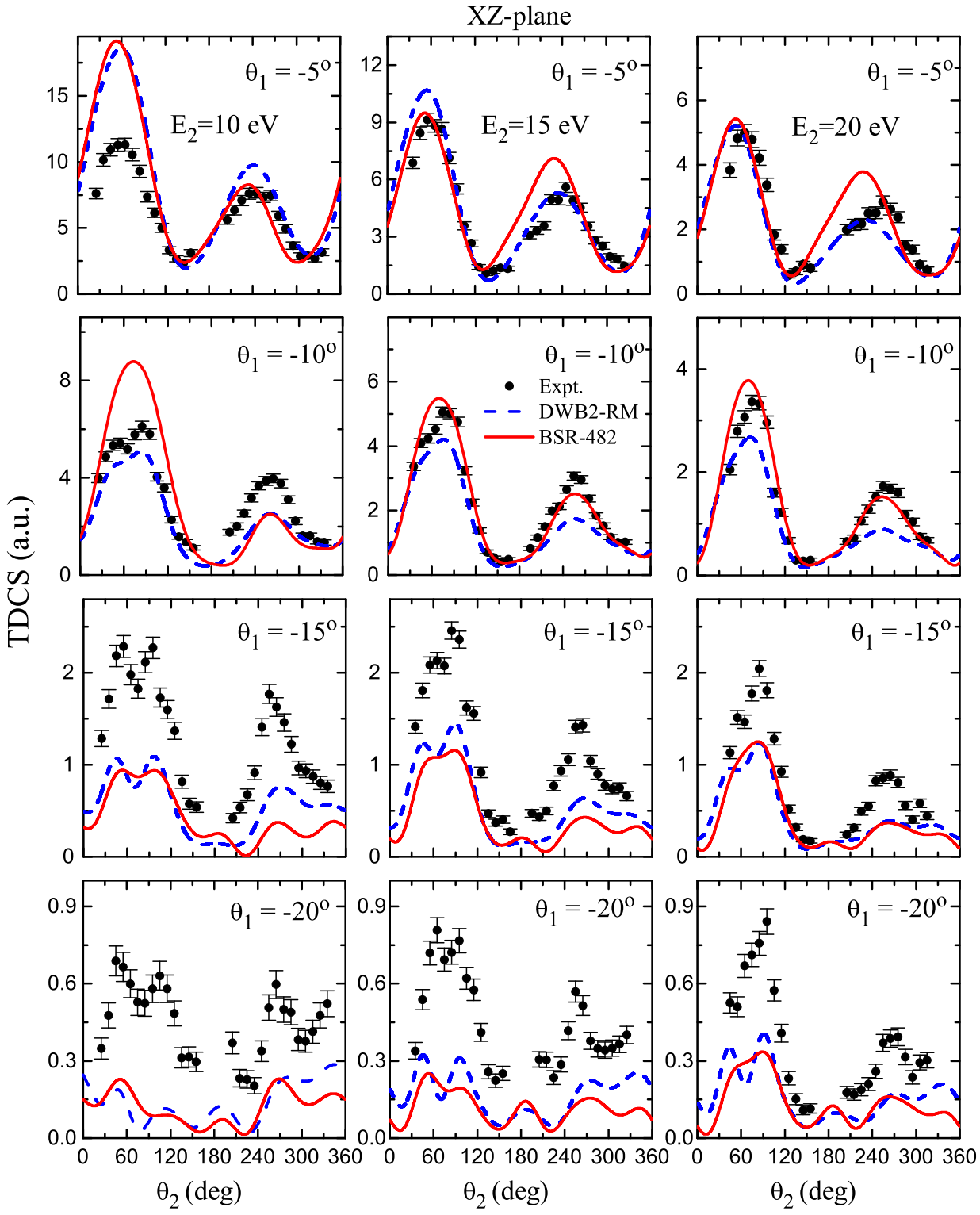

FIG. 1. (Color online) TDCS for electron impact ionization of Ar($3p$) for an incident electron energy of $E_0 = 195$ eV. The faster of the outgoing electrons is detected at fixed scattering angles (θ_1) of $-5°$, $-10°$, $-15°$, and $-20°$, respectively. The two linear momenta $\boldsymbol{k}_0$ and $\boldsymbol{k}_1$ define the XZ "collision plane", with the incident beam direction taken as the Z axis of the coordinate system. The slower of the two outgoing electrons with energy $E_2 = 10$ eV is also detected in the collision plane at variable angles $0° \leq \theta_2 \leq 360°$. The second-order hybrid (DWB2-RM) and the 482-state BSRMPS (BSR-482) results are compared with the experimental data of Ren *et al.* [14].

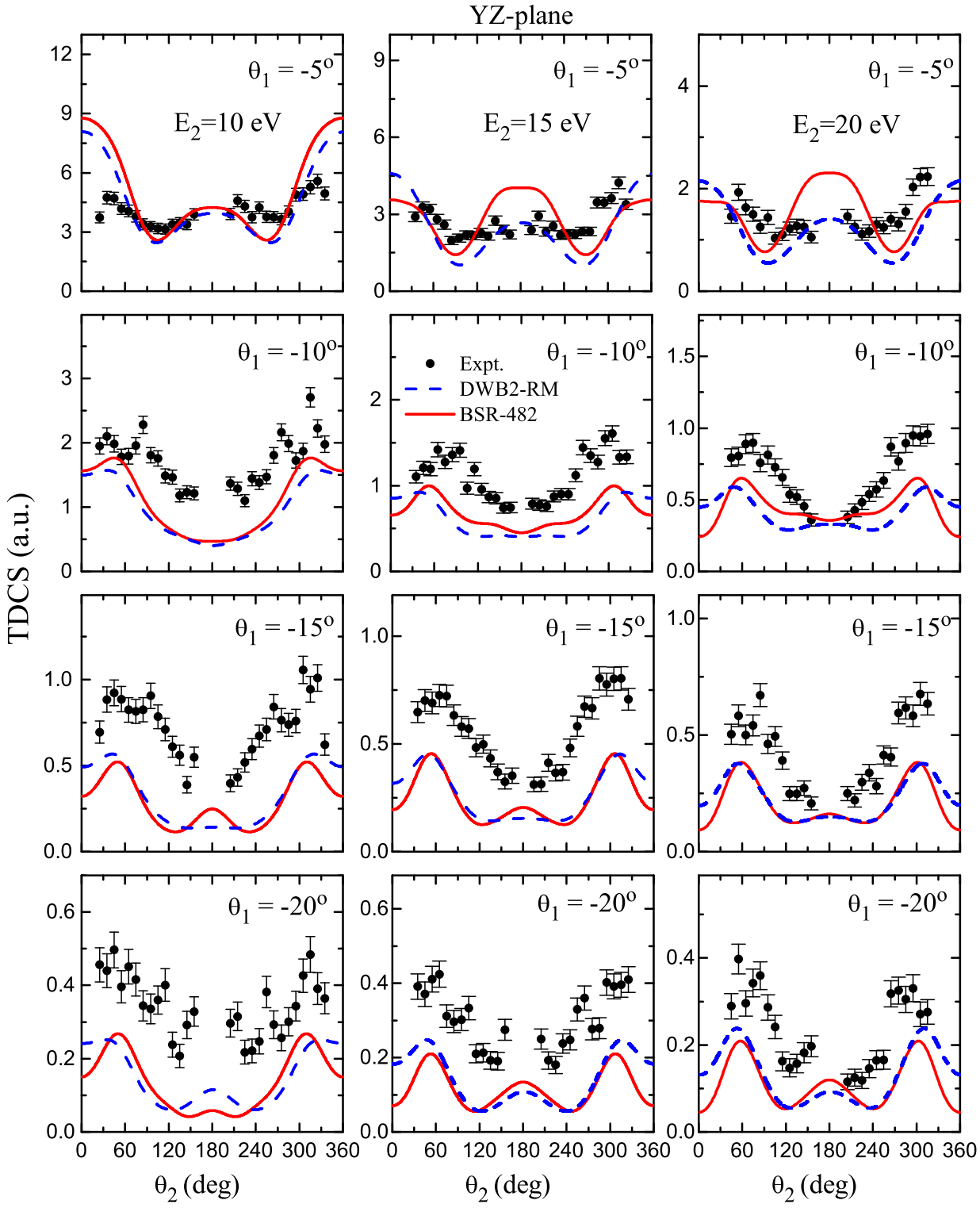

FIG. 2. (Color online) Same as Fig. 1, except that the slower of the two outgoing electrons is detected in the YZ-plane.

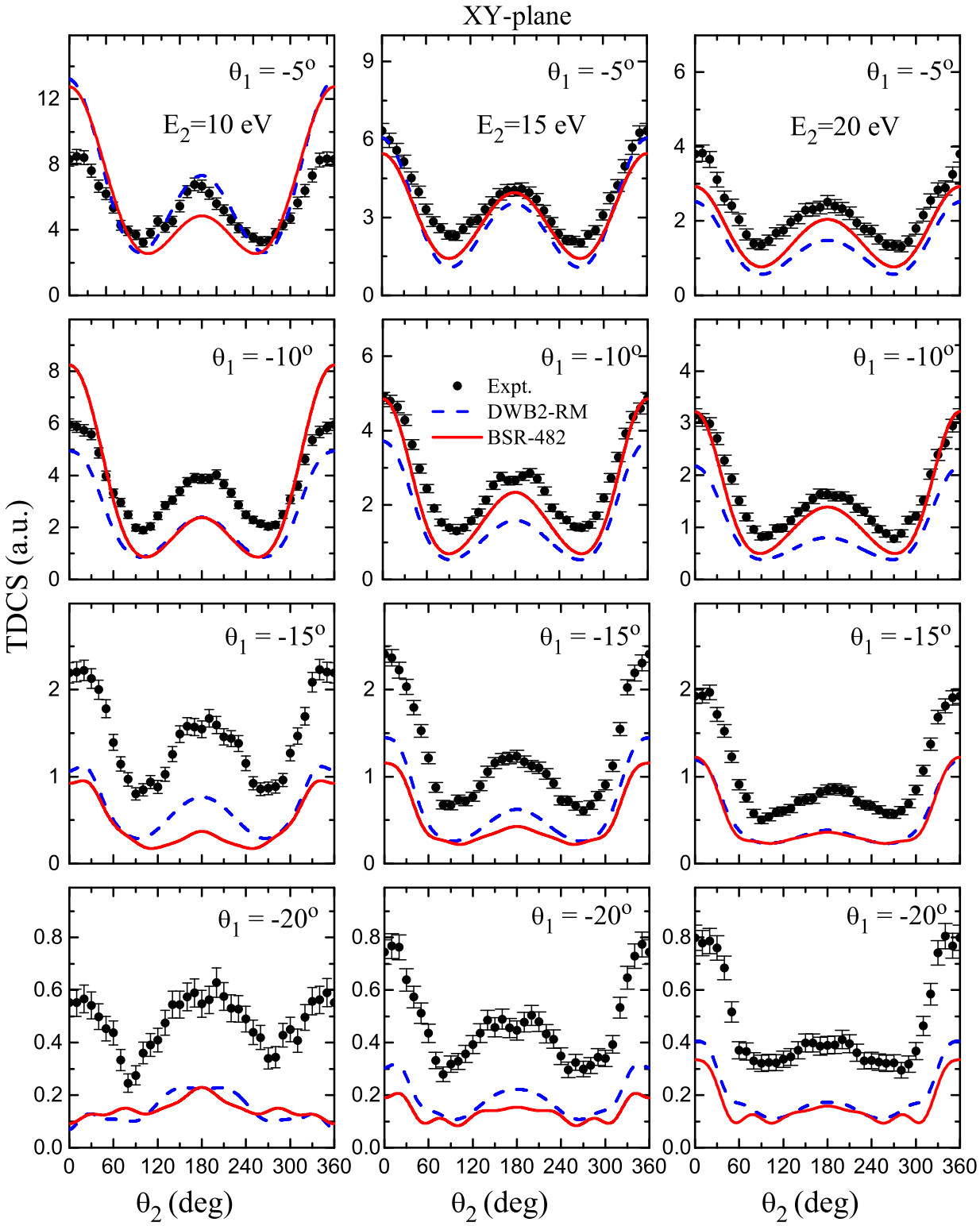

FIG. 3. (Color online) Same as Fig. 1, except that the slower of the two outgoing electrons is detected in the XY-plane.

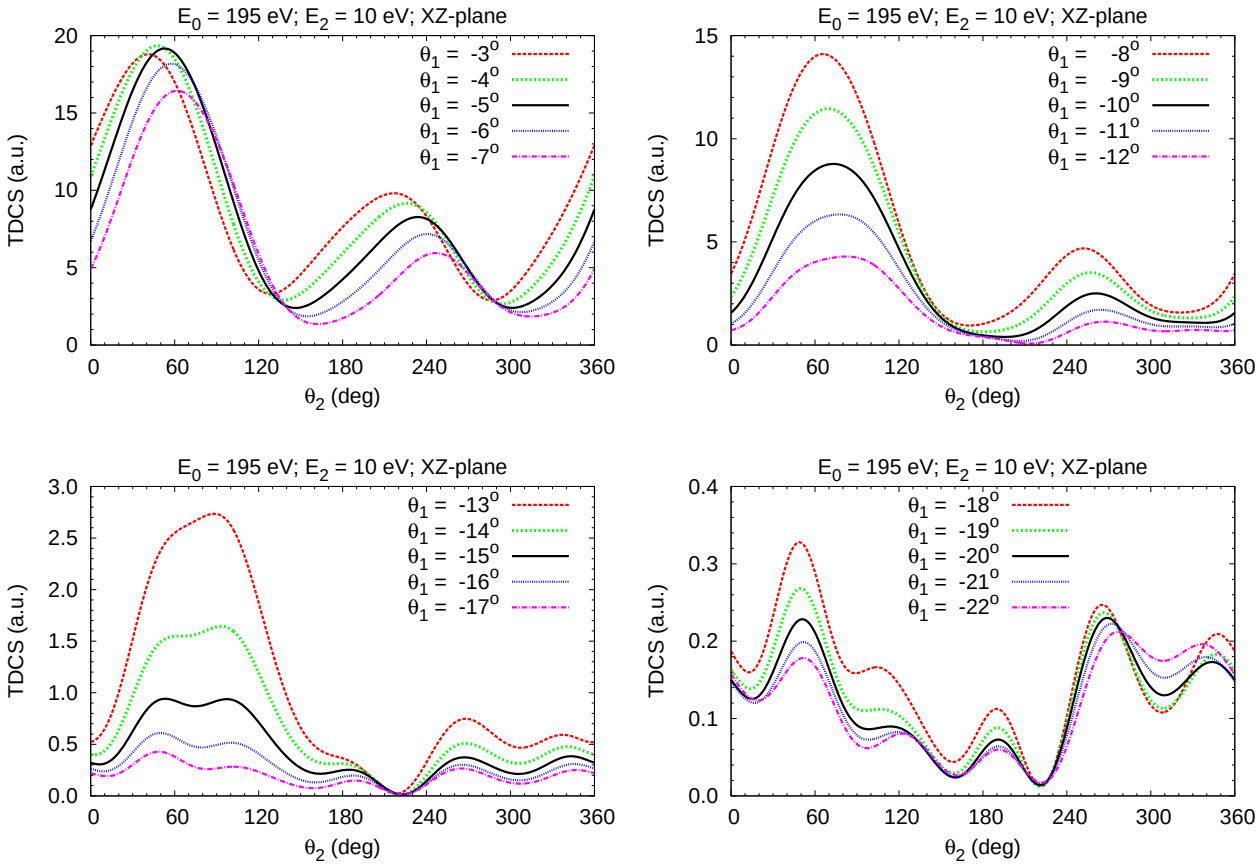

FIG. 4. (Color online) TDCS for electron impact ionization of Ar(3p) for an incident electron energy of $E_0 = 195$ eV. The faster of the outgoing electrons with an energy of $E_1 = 169$ eV is detected in the collision plane at fixed scattering angles $\theta_1 \in [-3^\circ, -7^\circ]$, $\theta_1 \in [-8^\circ, -12^\circ]$, $\theta_1 \in [-15^\circ, -17^\circ]$, and $\theta_1 \in [-18^\circ, -22^\circ$, respectively. The slower of the two outgoing electrons with energy $E_2 = 10$ eV is also detected in the collision plane at variable angles $0^\circ \leq \theta_2 \leq 360^\circ$.