Electron-Impact Ionization-Excitation of Atoms

Klaus Bartschat
Department of Physics and Astronomy, Drake University, Des Moines, IA 50311, USA
E-mail: klaus.bartschat@drake.edu

Abstract. As a highly correlated process, simultaneous electron-impact ionization-excitation presents a major challenge to experimentalists and theorists alike. Taking advantage of significant improvements in multi-hit detector technology and the rapid increase of computational power, a number of advances have recently been reported. The current state-of-the-art in this field is illustrated by a few key examples.

1. Introduction
In recent years, much progress has been made in the theoretical and computational treatment of electron-impact ionization processes. Non-perturbative approaches, such as exterior complex scaling (ECS) [1], time-dependent close-coupling (TDCC) [2, 3], convergent close-coupling (CCC) [4], or R-matrix with pseudo-states (RMPS) [5–7] are now able to predict the total (TCS), single-differential (SDCS), double-differential (DDCS), and triple-differential (TDCS) cross section very accurately for the atomic hydrogen target. Similar success has been achieved, particularly by the CCC method, for ionization of helium — provided the ion is left in the He\(^+\)(1s) ground state, i.e., one of the two target electrons is essentially a spectator [8, 9].

The situation, however, does not look as good for more complex targets, such as ionization of the heavy noble gases leaving the ion in the outer \((n_s^1 n_p^5)^2P\) or \((n_s n_p^6)^2S\) states, ionization plus simultaneous excitation of \(\text{He}\) and other quasi-two-electron targets such as \(\text{Mg}\), the role of resonances and autoionizing states, and the additional complexity when the linear momenta of the incoming projectile and the two outgoing particles (electrons in this paper) are no longer in the same plane. Interestingly, out-of-plane ionization [13] and ionization via autoionizing states without excitation [14] both seem to be sensitive to higher-order effects, very similar to simultaneous ionization-excitation in coplanar kinematics [15].

The present paper is an update to previous reports [16–18]. In addition to the theoretical advances mentioned above, there have been significant developments on the experimental front, including multi-hit detector technology, the ability to measure over increasing angular ranges in and out of the scattering plane, and concentrated efforts to cross-normalize the data taken at different energy and angle settings in otherwise identical setups. While making experimental cross sections truly absolute remains a significant, and usually unmet challenge, proper cross-normalization reduces the number of unknown factors between experiment and theory to a single overall factor, instead of one factor for each setting. As a result of these efforts, new benchmark data have become available, which can be used for a much more detailed assessment of theoretical models than what was possible just a few years ago. Following a brief summary of the basic ingredients used in theoretical models today, some examples will be discussed below.
2. Theoretical formulation

As mentioned above, fully non-perturbative methods such as CCC, RMPS, TDCC, or ECS have not yet been applied to the fully correlated problem involving three or more active electrons with well-defined initial (the projectile) and final (the two outgoing electrons) linear momenta. Hence, the theoretical description often starts with the first-order amplitude [19]

\[ I_{L_0M_0S_0M_{S_0}M_{\mu_0} \rightarrow L_fM_fS_fM_{S_f}M_{\mu_2}}(k_0,k_1,k_2) = - \frac{1}{(2\pi)^{5/2}} \langle \varphi^{(-)}_{k_1\mu_1}(x) \psi^{\mu_2(-)}_{k_2}(X) | V(x,X) | \Psi_{L_0M_0S_0M_{S_0}}(X) \varphi^{(+)}_{k_0\mu_0}(x) \rangle. \]  

(1)

Here \( X = \{r_1, \sigma_1; r_2, \sigma_2; \ldots; r_{N+1}, \sigma_{N+1}\} \) denotes a set of electronic spatial and spin coordinates in the \((N+1)\)-electron atom, while \( x = \{r, \sigma\} \) represents the coordinates of the colliding electron. The Coulomb potential \( V(x,X) = \sum_{n=1}^{N+1} \frac{Z_n}{|r-r_n|} \) describes the interaction between the projectile and the atomic electrons as well as the nucleus. The integration in the matrix element is performed over the \((x,X)\) coordinates of all \( N + 2 \) electrons.

The functions \( \varphi^{(+)}_{k_0\mu_0}(x) \) and \( \varphi^{(-)}_{k_1\mu_1}(x) \) represent the incident and outgoing projectile, respectively. In the simplest case, they are chosen as plane waves, in which case the integral over the projectile coordinates can be performed analytically through the Bethe integral [20]. In more sophisticated treatments, they are represented by distorted waves via a partial-wave expansion, with the results then depending on the choice of the distortion potential. Another important aspect is the treatment of the ejected-electron–residual-ion interaction, i.e., the function \( \psi^{\mu_2(-)}_{k_2}(X) \) in (1). A common approximation is to write this function as a product of the residual ionic state and another distorted wave for the ejected electron. In addition, the dependence of the radial orbitals for the spectator electrons (i.e., those remaining in the ion) on the charge state and the various angular momentum coupling is often ignored.

The description of the initial bound state, the final ionic states, and the ejected-electron–residual-ion interaction can be improved significantly in the hybrid method described by Bartschat and Burke [19], following early work by Jakubovics and Moores [21]. In this method, the ejected-electron–residual-ion interaction is described by an \( R \)-matrix (close-coupling) expansion, as in electron scattering from the ion with slightly modified boundary conditions since the ejection of the electron only corresponds part of the full collision. In principle, coupling a large number of discrete and pseudo-states will ultimately lead to a converged result for this collision problem, as well as for the initial bound state. The latter is calculated using the same expansion, once again with appropriately modified boundary conditions. In the general computer code of Bartschat [22], it is straightforward to use multi-configuration expansions for the ionic states. This automatically results in such an expansion for the bound state, and it also yields orthogonality between the initial bound state and the ejected-electron–residual-ion wavefunction. On the other hand, due to the asymmetric treatment of the two electrons, the calculation of the exchange amplitude is not straightforward in the hybrid method and has been omitted in all calculations to date. Consequently, the method is only expected to work reasonably well in strongly asymmetric kinematics.

The description of the projectile–target interaction can also be improved by treating, at least approximately, this interaction to second order. Details can be found in Reid et al [23] for a distorted-wave treatment of the projectile and in Fang and Bartschat [20] for the plane-wave case. At the present time, the remaining approximations in the evaluation of the second-order term include the use of only the pole term in a principal-value integral, the choice of an average
excitation energy for the intermediate state, and limiting the evaluation of integrals to within
the $R$-matrix sphere.

Note that equation (1) ignores the proper three-body Coulomb boundary condition [24]
between the two outgoing electrons and the residual ion, and in fact also the corresponding
modification to the projectile–target wavefunction in the initial state. In recent years, Madison
and co-workers have implemented the use of such functions in ionization treatments [25, 26],
albeit with overall mixed success. Improvements in the agreement between theory and
experiment was achieved for ionization of atomic hydrogen [27], while significant problems
remained for more correlated processed such as ionization–excitation of helium [15].

3. Results

3.1. Ionization of $\text{He} (1s^2)$ to $\text{He}^+ (1s)$ and $\text{He}^+ (n = 2)$

Figure 1 shows recent experimental data of Bellm et al [28] for ionization of $\text{He} (1s^2)$ without
excitation, i.e., leading to $\text{He}^+ (1s)$. The primary energy $E_0$ is 194.6 eV and the two final-
state electrons have average energies of 150 eV and 20 eV, respectively. For this case, the CCC
method is expected to be highly reliable. Indeed, its predicted angular dependence is in excellent
agreement with the measured results for all detection angles of the faster electron. Hence, the
CCC results were used to put the experimental data on an absolute scale, by employing a single
overall factor for all angles and also for the results for ionization–excitation shown below. This
was possible due to the careful cross-normalization of all experimental data.

![Figure 1. Experimentally derived and theoretical TDCSs for ionization of $\text{He} (1s^2)$ leading to $\text{He}^+ (1s)$. The primary energy $E_0$ is 194.6 eV and the two final-state electrons have average energies of 150 eV and 20 eV, respectively. The relative experimental data were normalized to the CCC results for a best overall visual fit using a single normalization constant. (Adapted from Bellm et al [28].) ](image)

Also shown in figure 1 are predictions from first-order and a second-order hybrid models
(labeled DW1-RM and DW2-RM, respectively), a first-order plane-wave Born approximation
(FBA), and a much more elaborate Four-Body Distorted Wave (4DW) calculation. In the latter
model, all particles in the continuum are described by distorted waves, and the Coulomb
interaction between the two outgoing electrons is included exactly. As can be seen, the DW2-RM
model, which contains a convergent RMPS expansion for $e - \text{He}^+$ scattering and the initial
bound state, performs well for the scattering angles $\theta_1 = 24^\circ$ and $32^\circ$. It deteriorates at $40^\circ$
and, therefore, was not used for $56^\circ$. On the other hand, all the other theoretical predictions
show significant disagreement with experiment at all angles. It is particularly disappointing to
see that the 4DW model, which yields reasonable agreement with the CCC and DW2-RM results
at $24^\circ$, joins the FBA in completely failing at $56^\circ$.

Figure 2 compares the DW1-RM, DW2-RM, 4DW, and FBA results to the $n = 2$ experimental
data. Recall that the CCC method cannot yet be applied to this ionization–excitation process.
Overall the second-order DW2-RM hybrid calculation provides the best description, although
Figure 2. TDCSs for transitions leading to the He\(^{+}(n = 2)\) states. The primary energy \(E_0\) is 235.4 eV and the two final-state electrons have average energies of 150 eV and 20 eV, respectively. The experimental data were put on an absolute scale using the results of CCC calculations for the \(n = 1\) transition. (Adapted from Bellm et al [28].)

it fails to describe the rapid fall-off at small values of \(\theta_2\). The first-order DW1-RM hybrid calculation performs significantly worse, underestimating the cross-section magnitudes at all values of \(\theta_1\).

Interestingly, in contrast to the \(n = 1\) case, the FBA predictions for the \(n = 2\) final ionic states are closer to the experimental values than those of the DW1-RM calculation. Not only does the FBA provide a better estimate of the magnitude of the cross-section maximum, but it also reproduces the rapid decrease in the TDCS magnitude for small values of \(\theta_2\). However, we believe that this results from a fortuitous cancellation of shortcomings in the FBA model, combining the well-known overestimate of direct processes with an underestimate of higher-order effects. Indeed, the FBA cannot reliably predict the cross-section ratio of ionization without excitation to ionization with excitation [28]. Compared to the FBA calculation, the 4DW calculation, in spite of its greater sophistication, provides a poor description of the experimental data. These findings illustrate that including more physics in an approximate model does not necessarily improve the overall results.

3.2. Ionization-excitation of Mg(3s\(^2\)) \(\rightarrow\) Mg\(^{+}\)(3s,3p,4s,3d)

It was predicted on several occasions [16, 29] that changing the target from He to Mg or Ca might result in an enhanced signal for ionization-excitation due to the strong \(p^2\) correlation in the 3s\(^2\) and 4s\(^2\) ground states of these atoms. Figure 3 shows results from a recent study by Bolognesi et al [30] on Mg. Indeed, the ratio of the experimental binary peaks for leaving the Mg\(^+\) ion in the 3s rather than the 3p state is about 25 in this case and, somewhat surprisingly, only about 15 when compared to the binary peak of the signal corresponding to Mg\(^+\) in either the 4s or the 3d state, which could not be resolved in the experiment due to the almost identical energy loss.

The experimental results are again compared with first-order and second-order hybrid calculations, this time approximating the ejected-electron–residual-ion interaction and the initial bound state by a 4-state close-coupling expansion. Second-order effects in the theory are small, thus indicating that most of the ionization-excitation is due to “shake-off”, i.e., correlation in the ground state. Since the largest correlation comes from the \(3p^2\) term in expansion of the ground-state wavefunction, it is not surprising that the magnitude of the theoretical prediction for generating Mg\(^+\) in either 4s or 3d is much smaller than experiment and also (in contrast to experiment) smaller than the result for generating Mg\(^+\)(3p). Interestingly, the angular dependence of the signal is well reproduced by the hybrid model, but more studies seem necessary to resolve the magnitude problem.
Figure 3. TDCS for electron impact ionization of Mg (3s^2) for the Mg^+ 3s, 3p, and 4s/3d final ionic states for $E_a = 400$ eV and $E_b = 20$ eV. The experimental data are compared with DWB1-RM4 and DWB2-RM4 predictions. Note that the theoretical values shown for the excited states are 2.2 and 14 times larger than the actual predictions. (Adapted from Bolognesi et al [30].)

3.3. Resonance effects

Special care is required when comparing experimental data and theoretical predictions in cases where resonances may play a role [31]. For ionization—excitation of He (1s^2) leading to He^+ (n ≠ 1), such resonances can play a role for ejected electron energies between approximately 5 eV and 14 eV. An extreme example is shown in figure 4. The DWB2-RMPS model describes the angular dependence of the observed signal quite well, provided the theoretical results for a variety of ejected-electron energies are averaged corresponding to the experimental energy (and angle) resolution. On the other hand, the calculation at the nominal energy of 7.5 eV (very close to the n = 3 threshold) yields an entirely different angular dependence.

Figure 4. TDCS for ionization—excitation of He (1s^2) to He^+ (n = 2) by 105 eV electrons as function of the slow electron emission angle. The nominal energy of the ejected electron is 7.5 eV, but the theoretical predictions were averaged over a ±0.5 eV window to compare with the experimental data of Dürr et al [32]. Note the scale factors on the DWB2-RMPS calculations.

It is worthwhile to note that the experimental data of Dürr et al [32] were once again cross-normalized to well-established results for ionization without excitation, where CCC calculations and independent experimental data are available (see Dürr et al [33] for details). Consequently,
Figure 5. Out-of-plane ejected electron angular distributions for 488 eV electrons scattered through 20.5°. Left: Direct ionization with 34.1 eV ejected electrons. Right: Direct ionization plus autoionization via the \((2p^2)^1D\) intermediate state. The solid and dashed lines are DWB2-RMPS and DWB1-RMPS calculations, respectively, while the chained lines are Fano-fitted PWBA calculations. Theory and experiment are normalized to unity at \(\theta_0 = 0\). The angle \(\theta_0\) is defined in the plane perpendicular to the scattering plane, which also contains the momentum transfer direction (\(\theta_0 = 0\)) and its opposite (\(\theta_0 = 180\)). (Adapted from deHarak et al [14].)

Figure 6. Left: Same as figure 5 for two fixed ejected-electron energies of 34.10 eV and 35.35 eV. Right: The corresponding single-differential cross section. Note the difference between the DWB1-RMPS and DWB2-RMPS results near the \((2p^2)^1D\) intermediate state at 35.35 eV. It seems as if the DWB2-RMPS model overestimates the TDCS at the peaks while the DWB1-RMPS model still underestimates it. We suspect that 105 eV is too low an incident energy for the hybrid model to work properly, especially with exchange effects being neglected.

Figure 5 shows results from a recent study by deHarak et al [14], who investigated the effect of the autoionizing \((2p^2)^1D\) state (and other states) on the angular distribution of electrons emitted out of the scattering plane. The effect of the resonance is clearly seen by comparing the results when the ejected-electron energy is either away or very close to the resonance. Only the DWB2-RMPS theory is able to predict \textit{ab initio} the measured angular dependence of the signal. While the latter can be fitted with Fano parameters, these parameters have to be chosen vastly different from the values obtained from the ejected-electron—residual-ion interaction alone [14].

This finding suggests that the projectile has a significant effect on the observed resonance, with higher-order effect once again playing a role. Indeed, figure 6 shows a significant difference between the DWB1-RMPS and DWB2-RMPS results for both the TDCS and the single-differential cross section in the vicinity of the \((2p^2)^1D\) state at an ejected-electron energy of 35.35 eV. On the other hand, second-order effects are small away from the resonance.
4. Conclusions

Many currently open questions remain in the field of ionization—excitation. New experimental data are challenging theory, pushing into regions of energy-angle parameter space, where even the best currently available approaches seem insufficient. Fully non-perturbative are highly desirable, but such calculations are very demanding and have met serious challenges to date. Hence, improvements to existing perturbative models, e.g., by calculating an exchange amplitude and accounting at least approximately for the post-collision interaction, seem worth pursuing in order to better understand the physics in these highly correlated processes.

Acknowledgments

This work is supported by the US National Science Foundation under grant PHY-0757755. I would like to thank I. Bray, S. Bellm, A. Dorn, M. Dürr, D.V. Fursa, A. Harris, A.S. Kheifets, B. Lohmann, J. Lower, D.H. Madison, M. Stevenson, J. Ullrich, and E. Weigold for permission to include some of their unpublished results in this report and/or the oral presentation.

References

[1] Rescigno T N, Baertschy M, Isaacs W A, and McCurdy C W 1999 Science 286 2474
[2] Pindzola M S and Robicheaux F 1996 Phys. Rev. A 54 2142
[3] Colgan J P, Pindzola M S, Robicheaux F, Griffin D C, and Baertschy M 2002 Phys. Rev. A 65 042721
[4] Bray I, Fursa D V, Kheifets A S, and Stelbovics A T 2002 J. Phys. B 35 R117
[5] Bartschat K, Hudson E T, Scott M P, Burke P G, and Burke V M 1996 J. Phys. B 29 115
[6] Bartschat K and Bray I 1996 Phys. Rev. A 54 R1002
[7] Bartschat K 1998 Comp. Phys. Commun. 114 168
[8] Bray I 2002 Phys. Rev. Lett. 89 273201
[9] Stelbovics A T, Bray I, Fursa D V, and Bartschat K 2005 Phys. Rev. A 71 052716
[10] McCurdy C W, Horner D A, and Rescigno T N 2002 Phys. Rev. A 65 042714.
[11] Bartlett P L, Stelbovics A T, Rescigno T N, and McCurdy C W 2007 J. Phys.: Conf. Series 88 012011
[12] Pindzola M S, Robicheaux F, Colgan J P, Witthoef M C, and Ludlow J A 2004 Phys. Rev. A 70 032705
[13] Dürr M, Dimopoulou C, Najjari B, Dorn A, Bray I, Fursa D V, Chen Z, Madison D H, Bartschat K, and Ullrich J 2008 Phys. Rev. A 77 032717.
[14] deHarak B A, Bartschat K, and Martin N L S 2008 Phys. Rev. Lett. 100 063201
[15] Bellm S, Lower J, Bartschat K, Guan X, Weflen D, Foster M, Harris A L, and Madison D H 2007 Phys. Rev. A 75 042704
[16] Bartschat K in: Electron and Photon Impact Ionization and Related Topics, U. Ancarani (Ed.), IOP Conf. Proc. #172, Institute of Physics (2003) 57
[17] Bartschat K in: Correlations, Polarization, and Ionization in Atomic Systems, G.F. Hanne, L. Malegat, and H. Schmidt-Böcking (Eds.), AIP Conf. Proc. #697, American Institute of Physics (2003) 213
[18] Bartschat K in: Correlations, Polarization, and Ionization in Atomic Systems, A. Lahmann-Bennani, B. Lohmann, and J. Miraglia (Eds.), AIP Conf. Proc. #811, American Institute of Physics (2006) 203
[19] Bartschat K and Burke P G 1987 J. Phys. B 20 (1987) 3191 and 21 (1988) 2969
[20] Fang Y and Bartschat K 2001 J. Phys. B 34 L19
[21] Jakubowicz H and Moores D L 1981 J. Phys. B 14 3733
[22] Bartschat K 1993 Comp. Phys. Commun. 75 219
[23] Reid R H G, Bartschat K, and Raeker A 1998 J. Phys. B 31 563; corrigendum 2000 J. Phys. B 33 5261
[24] Brauner M, Briggs J S, and Klar H 1989 J. Phys. B 22 2265
[25] Jones S and Madison D H 1998 Phys. Rev. Lett. 81 2886
[26] Prideaux A, Madison D H, and Bartschat K 2005 Phys. Rev. A 71 (2005) 032702
[27] Chen Z, Madison D H, Whelan C T, and Walters H R J 2004 J. Phys. B 37 981
[28] Bellm S, Lower J, Weigold E, Bray I, Fursa D V, Bartschat K, Harris A L, and Madison D H 2008 Phys. Rev. A, submitted
[29] Bartschat K, Weflen D, and Guan X 2007 J. Phys. B 40 3231
[30] Bolognesi P, Pravica L, Veronesi S, Fainelli E, Avaldi L, Bartschat K 2008 J. Phys. B 41 065203
[31] Fang Y and Bartschat K 2001 Phys. Rev. A 64 020701(R)
[32] Dürr M, Dorn A, Ullrich J, and Bartschat K 2008, in preparation
[33] Dürr M, Dimopoulou C, Dorn A, Najjari B, Bray I, Fursa D V, Chen Z, Madison D H, Bartschat K, and Ullrich J 2006 J. Phys. B 39 4097.