Electron-Impact Excitation and Ionization of Complex Atoms

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Abstract. Taking advantage of significant improvements in multi-hit detector technology and algorithm development, together with the rapid increase of computational power, significant advances have recently been reported in the experimental and theoretical studies of electron-impact excitation and ionization processes. 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 excitation and ionization processes. Non-perturbative approaches, such as convergent close-coupling (CCC) [1, 2], R-matrix with pseudo-states (RMPS) [3, 4], time-dependent close-coupling (TDCC) [5, 6], and exterior complex scaling (ECS) [7], have been highly successful, especially for light quasi-one and quasi-two electron targets, in which the structure description is relatively simple (one or two outer electrons and, if necessary, a core potential), and relativistic effects are essentially negligible.

While the R-matrix method (see, for example, the compilation volume by Burke and Berrington [8] for an overview), particularly the widely used program package RMATRIX-I [9], is capable of treating complex open-shell targets, the target structure itself, and a consistent description of both the N-electron target and the (N+1)-electron collision problems, can become a significant challenge in the calculation of accurate atomic collision data.

The present paper describes two approaches that offer a partial solution to these problems. The first of these is the B-spline R-matrix (BSR) method [10, 11] and the corresponding software package [12], which was recently extended to a full-relativistic Dirac-based (DBSR) framework [13, 14]. It has been very successful in describing atomic structure properties as well as photo-ionization and electron-impact excitation processes, especially in the near-threshold resonance regime. The second is a hybrid distorted-wave Born plus R-matrix (DWB-RM) approach for electron-impact ionization processes. The basic idea is the description of a “fast” charged projectile interacting on a target as a perturbation, which can be treated by plane or distorted waves to first or second order [15-18], while the initial bound state and the ejected-electron−residual-ion interaction are handled via a convergent R-matrix expansion. Although the formulation neglects the proper Coulomb three-body boundary condition [19] at large separations of the two outgoing electrons and the residual ion, we will illustrate below that it has significant advantages over other methods that incorporate this boundary condition, but at the price of being less accurate in the spatial domain near the target center, where the actual ionization process occurs.

Due to space limitations, only very brief descriptions of the methods and a few key examples will be presented below. Unless specified otherwise, atomic units (a.u.) are used throughout this manuscript.
2. The B-Spline R-Matrix (BSR) Method for Electron Scattering from Atoms and Ions

This method is based on the close-coupling expansion. As such, it is a non-perturbative approach, whose accuracy is, in principle, only limited by the number and the quality of the target states accounted for in the expansion, including the coupling to the ionization continuum. The distinguishing features of the BSR method are i) the ability to use term-dependent, and hence non-orthogonal, sets of one-electron orbitals (Dirac spinors in the fully relativistic case) in the target description and ii) B-splines as the underlying, effectively complete basis to expand the wavefunction of the projectile. It is an all-electron approach, and hence core-valence correlation effects (e.g., core polarization) are described ab initio.

The use of non-orthogonal bound orbital sets generally allows for a much higher accuracy in the description of the target states than in traditional approaches with orthogonal orbitals. Since they are optimized in separate calculations, the high level of accuracy can be achieved with compact configuration interaction expansions. Regarding the close-coupling expansion of the total collision wavefunction, certain \((N + 1)\)-electron bound configurations must often be included to compensate for orthogonality constraints imposed on the continuum orbitals. However, it can be difficult to keep the expansion fully consistent, and any inconsistency may lead to pseudo-resonance structure. Using non-orthogonal continuum orbitals avoids the introduction of these \((N + 1)\)-electron terms and thus may drastically reduce the pseudo-resonance problem.

Although the technical implementation of the method is significantly more complicated than a formulation using a single set of orthogonal orbitals to describe the target and projectile electrons, the examples below clearly demonstrate that it is worth the effort. As a first illustration, Fig. 1 exhibits the differential cross section (DCS) for electron-impact excitation of two states from the \(2p^53p\) manifold in Ne, measured at two fixed scattering angles as a function of the incident energy [20]. For these situations, the near-threshold resonance features are particularly pronounced and thus permit a detailed comparison of the observed and calculated resonance profiles. The agreement between theory and experiment is excellent not only in terms of resonance energies and widths, but also in the shapes (peaks, dips, or more complicated Fano profiles).

Next, Fig. 2 illustrates significant improvements achieved in describing the metastable excitation function of xenon and the excitation function of the \((6s6p)^3P_1\) state in Hg. Although our 31-state semi-relativistic BSR calculation (BSR-31) is in far better agreement with the experimental data of Buckman

![Figure 1](image)

**Figure 1.** Resonant features in differential cross sections for excitation of two \(2p^53p\) states in Ne. Experiment is shown by the ragged (red) line, theory by the smooth (blue) line. (From Allan et al [20].)
The experimental data are from Khakoo et al. [27] than any previously published attempt, only the Dirac-based DBSR method can reproduce the resonance structure in the Xe excitation function in a satisfactory way.

Despite its label as a triplet state by the dominant spin character of its wavefunction, the $(6s6p)^3P_1$ state of mercury can decay optically to the ground state by the emission of a 254 nm UV photon. These photons, after conversion to visible light, are the dominant source of light originating from mercury-based discharge lamps. Hence, understanding the details of this particular transition and its driving mechanism is crucial for modeling such lamps [22].

The current DBSR-36 results are in excellent agreement with the most recent experimental data of Erdevdi et al. [23], which were obtained with an energy resolution of 18 meV and hence show the threshold peak in significantly more detail than the measurements by Ottley and Kleinpoppen [24], which we show as one representative of several earlier experimental investigations of this particular excitation function. Note that the $(6s6p^2)^3P_{5/2}$ resonance in the excitation function of the $(6s6p)^3P_1$ state is mainly responsible for the outcome of the famous Franck-Hertz experiment [25, 26].

The most important problem with the BSR method, at the present time, is the lack of accounting for coupling to the target ionization continuum. This is illustrated in Fig. 3, which exhibits the DCS for electron-impact excitation of the $5p^56s$ states in Xe at an incident electron energy of 20 eV. Especially for excitation of the metastable states with total electronic angular momentum $J = 0$ and 2, the results are very sensitive to the number of states included in the close-coupling expansion. While the 75-state model contains a few pseudo-states, these are still insufficient to account for all the coupling to the ionization continuum.

**Figure 2.** Metastable excitation function of xenon (left) and angle-integrated cross section for electron-impact excitation of the $(6s6p)^3P_1$ state of mercury (right).

**Figure 3.** DCS for electron-impact excitation of the $5p^56s$ states in Xe at an incident energy of 20 eV. The experimental data are from Khakoo et al. [27].
### 3. The DWB-RM hybrid method for ionization and ionization-excitation

As mentioned above, fully non-perturbative methods such as CCC, RMPS, TDCC, or ECS have not yet been applied to the fully correlated ionization 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 [15]

\[
f_{L_0 M_0 S_0 M_{S_0}; \mu_0} \rightarrow L_f M_f S_f, \mu_1 \mu_2 (k_0, k_1, k_2) = \frac{1}{(2\pi)^{5/2}} \langle \varphi_{k_1 \mu_1}^{(-)} (x) \mid \varphi_{k_2 \mu_2}^{(-)} (x) \rangle V(x, X) \mid \Psi_{L_0 M_0 S_0 M_{S_0}} (X) \rangle \varphi_{k_0 \mu_0}^{(+)} (x). \tag{1}
\]

Here \( X = \{ r_1, \sigma_1; r_2, \sigma_2; \ldots; r_N, \sigma_N \} \) denotes a set of electronic spatial and spin coordinates in the \((N+1)\)-electron atom, \( x = \{ r, \sigma \} \) represents the coordinates of the colliding electron, and \( V(x, X) \) is the Coulomb interaction between the projectile and the atomic electrons as well as the nucleus.

The functions \( \varphi_{k_0 \mu_0}^{(\pm)} (x) \) and \( \varphi_{k_1 \mu_1}^{(-)} (x) \) represent the incident and outgoing projectile, respectively. In the simplest case, they are chosen as plane waves and the integral over the projectile coordinates is performed analytically through the Bethe integral [18]. 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 \( \varphi_{k_2 \mu_2}^{(-)} (x) \) 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 DWB-RM hybrid method. Here the ejected-electron–residual-ion interaction is treated by an \( R \)-matrix (close-coupling) expansion. 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, which is calculated using the same expansion. In the general computer code of Bartschat [16], 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. Due to the asymmetric treatment of the two electrons, however, 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 [17] for a distorted-wave treatment of the projectile and in Fang and Bartschat [18] 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.

Recall that Eq. (1) ignores the proper three-body Coulomb boundary condition [19] 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 employed such functions in ionization treatments [28, 29], albeit with mixed success. Improvements in the agreement between theory and experiment was achieved for ionization of atomic hydrogen [30], but significant problems remained for more correlated processes such as ionization and ionization-excitation of helium [31].

There has been a large amount of work on the helium, especially regarding the highly correlated ionization-excitation process. For recent summaries of the current state-of-the-art for this target, we refer to the comprehensive paper by Bellm et al [31] and the many references therein. In short, only the DWB2-RMPS method is generally able to reproduce the experimental data for asymmetric kinematical situations, i.e., small scattering angles of the fast projectile and a significant difference in the energies...
of the two outgoing electrons – typically hundreds of eV for the projectile and less than about 20 eV of the ejected electron. When the energy of the projectile electron is lowered to about 100 – 150 eV, however, problems with the absolute normalization arise with the DWB2-RMPS method as well. While first-order theories generally underestimate the ionization-excitation cross section by a large amount, the second-order method starts to overestimate it for such low energies [32].

We suggested on several occasions [33, 34] 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 4 shows results from a recent study by Bolognesi et al [35] 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. The experimental results are 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. While the angular dependence of the triple-differential cross section (TDCS) is predicted very well by the theory, there is a magnitude difference of about a factor 2, whose origin is not understood at the present time.

Figure 4. TDCS for electron impact ionization of Mg ($3s^2$) for the Mg$^+$ 3s and 3p 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 ionic state are 2.2 times larger than the actual predictions. See Bolognesi et al [35] for details.

Special care is required when comparing experimental data and theoretical predictions in cases where resonances may play a role [36]. For ionization-excitation of He ($1s^2$) leading to He$^+ (n \neq 1)$, such resonances can be significant for ejected electron energies between approximately 5 eV and 14 eV. Consequently, special care has to be taken in the comparison of experimental and theoretical results, especially when the theoretical approach allows for the treatment of such resonances [36]. An extreme example is shown in Fig. 4 of [32].

Figure 5 shows results from a recent study by deHarak et al [37], 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 for He ionization leading to He$^+ (1s)$. 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 ab initio the measured angular dependence of the signal.

There have been numerous recent studies for electron impact ionization of heavy noble gases, including detailed comparisons between experiment and theory for Ne, Ar, and Xe targets, with progress in previously unexplored kinematical regimes [38] or angular ranges [39] that have just become accessible through a magnetic angle changer [40]. Using a reaction microscope, Ren et al [41] were able to extend these studies from the coplanar geometry to the full three-dimensional space. As seen in Fig. 6, there is good qualitative agreement between the measured and our calculated 3D angular distributions for ionization of a 3p electron in Ar, as well as the respective cuts through two representative planes.
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)D 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 θ₀ = 0. See deHarak et al [37] for details and the definition of θ₀.

Figure 6. 3D images (experiment left, theory right) of the ejected electron angular distribution in single ionization of Ar(3p) for an incident projectile energy of 200 eV and an ejected electron energy of 10 eV. The panels on the right show selected cuts for the scattering plane and the perpendicular plane.

4. Collaboration between data producers and data users

With the large number of data currently being produced for atomic collisions, it seems worthwhile to investigate to what extent these data can actually be used in practical modeling, for example, of plasma discharges. Figure 7 depicts results for a Ne discharge, in which oscillator strengths and electron collision data generated from the BSR approach, together with additional data for various other processes in the plasma, were employed to model the luminosity.

While there is excellent agreement between the modeled and the measured spectra, it is important to keep in mind that the model contains a large number of parameters. Consequently, the internal consistency of the results is of critical importance and actually allows for an assessment of the input data. Details can be found in Dodt et al [42], but the small residuals in the modeling of most lines suggests a very high quality of the BSR predictions. Even the deviations can be explained and are almost certainly due again to the neglect of coupling to the continuum.

This is a prime example of how data producers and data users can collaborate, even without
understanding all the details of their individual contributions to a given problem. A mutually beneficial collaboration, however, requires significant communication about the needs of the data users and the possibilities of the data producers. In the above example, it was critical to estimate reasonable uncertainties in the atomic input data.

5. Conclusions
The BSR and hybrid DWB-RM methods discussed in this paper are important numerical methods in the treatment of electron collisions with complex targets, for which currently available fully non-perturbative methods continue to struggle due to the difficulties associated with the target description and the handling of the full correlation between two outgoing electrons and a residual ion with structure itself. In the future, we will include a sufficient number of pseudo-states in the (D)BSR calculations to obtain converged results with the number of states in the close-coupling expansion also above the near-threshold regime. In some cases, this will allow for fully non-perturbative treatments of ionization as well. Where this remains essentially impossible with current algorithms and computational resources, we will extend the BSR package by adding the hybrid approach. Finally, we hope to continue our very fruitful collaborations with many colleagues in the field of atomic physics, while reaching out to those in related areas who can employ our data in practical modeling applications.

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