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LETTER TO THE EDITOR

The validity of classical trajectory and perturbative quantal methods for electron-impact ionization from excited states in H-like ions

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Abstract

To test the validity of classical trajectory and perturbative quantal methods for electron-impact ionization of H-like ions from excited states, we have performed advanced close-coupling calculations of ionization from excited states in H, Li^{2+} and B^{4+} using the *R*-matrix with pseudo states and the time-dependent close-coupling methods. Comparisons with our classical trajectory Monte Carlo (CTMC) and distorted-wave (DW) calculations show that the CTMC method is more accurate than the DW method for H, but does not improve with n and grows substantially worse with Z, while the DW method improves with Z and grows worse with n.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Over the past decade, significant progress has been made in the development of advanced close-coupling methods for solving three-body Coulomb scattering problems. One of the most important of these problems is the electron-impact ionization of hydrogen and hydrogen-like ions. The accuracy of these non-perturbative methods for one-electron targets is only limited by the numerical accuracy of the two-electron continuum and the completeness of the partial-wave expansion. In addition, these methods have been applied successfully to ionization of multi-electron atoms, where the solution also depends on the accuracy of the target wavefunctions.

The majority of such non-perturbative calculations has been for ionization from the ground state of the target. In addition, such calculations for ionization from the lowest energy excited states of hydrogen [1, 2] and several multi-electron targets [3–5] have been performed.

However, with the exception of a CCC calculation from the $n = 3$ subshell of Li [6], there have been no advanced close-coupling calculations of ionization from more highly excited states, and these are of significant interest from both a fundamental and applied perspective. Excited-state ionization is a much more sensitive probe of collision dynamics because of the stronger coupling between such states and the target continuum. Energy scales are smaller and angular coupling is larger, resulting in a more difficult three-body Coulomb scattering problem. Furthermore, accurate electron-impact ionization cross sections from excited states of atoms and ions are of critical importance to the modelling of laboratory and astrophysical plasmas [7]. In a plasma environment, excited states are populated by charge exchange reactions, excitation from ground and metastable states, and for multi-electron species, dielectronic recombination. Ionization cross sections grow rapidly with principal quantum number, and at sufficiently high electron densities, ionization out of excited states can dominate the total ionization rate [8].

Results from these advanced close-coupling methods have proven to be in excellent agreement with each other and with more recent measurements for ionization from the ground state. However, application of advanced close-coupling methods to ionization from highly excited states presents a formidable computational challenge to atomic physics. The excited target orbitals extend out to large radii, which makes an accurate representation of continuum wavefunctions much more difficult; furthermore, the small ionization energies of these excited states lead to strong coupling between a larger number of scattering channels than for ionization from the ground state. For these reasons, plasma-modelling calculations have employed excited-state ionization cross sections determined from classical and perturbative quantal methods. However, no tests of the accuracy of such methods for ionization out of the more highly excited states currently exist.

Here we report on the first advanced close-coupling calculations for ionization out of states above the ground and lowest-energy excited states. In particular, we compare R-matrix with pseudostates (RMPS) and time-dependent close-coupling (TDCC) cross sections with perturbative distorted-wave (DW) and classical trajectory Monte Carlo (CTMC) cross sections for ionization from states through $n = 4$ of H, Li^{2+} and B^{4+}. Since the RMPS and TDCC cross sections should provide extremely accurate results for excited-state ionization in these H-like targets, we can use them as benchmarks to test the validity of the classical trajectory and perturbative quantal methods as a function of principal quantum number (n) and ionization stage (Z).

2. Description of the calculations

Although our implementation of the RMPS method has been explained elsewhere [9, 10], its application to ionization out of more highly excited states is only now computationally feasible through the recent development of our parallel suite of R-matrix programs [11]. We employ a set of Laguerre radial wavefunctions to provide the L_2-basis representation of the target continuum. The ionization cross section from a given term is determined by summing over the excitation cross sections to all pseudostates above the ionization limit. For the RMPS calculations presented here, we employed spectroscopic orbitals for all subshells through $n = 4$ and pseudo-orbitals from 5 s through 12 h. The $n = 5$ and $n = 6$ pseudostates are bound and all others are in the continuum. It is the size of the pseudostate expansion as well as the large L_2-basis needed to represent the incident and scattered electrons accurately that makes these calculations computationally demanding. Calculations with exchange were run for all $LS\Pi$ partial waves with $L = 0$–13, and were supplemented by no-exchange R-matrix calculations with $L = 14$–40.

The TDCC method is described in more detail in Pindzola and Robicheaux [12]. Again these calculations from excited states are only feasible because of the development of advanced parallel computer programs and the availability of massively parallel computers. The calculation for H(3s) was similar to that described in Witthoeft *et al* [2] for H(2s). For the Li^{2+}(2s) ionization calculation, we employed the same Fourier-transform TDCC method used for the Li^{2+} ground-state calculation by Colgan *et al* [13]. Finally, because of the very large number of coupled channels required to achieve convergence, the TDCC calculation for Li^{2+}(4s) was very time consuming even using a large number of parallel processors and was, therefore, performed at only a single electron energy.

The DW calculations are based on a triple partial-wave expansion of the first-order scattering amplitude, including both direct and exchange terms. Here we employ two different forms of this perturbative method. In the first (the prior form), the incident and scattered electron wavefunctions are calculated in the V^N potential of the initial target and the ejected-electron wavefunction is calculated in the V^{N-1} potential of the ionized target [14]. In the second (the post form), all three continuum wavefunctions are calculated in the field of the V^{N-1} potential of the ionized target [15].

With the CTMC method [16], one solves Hamilton's equations to compute a classical cross section from the probability that an incoming electron with an impact parameter, b, ionizes the atom. The probability for ionization is determined from the fraction of trajectories for which both electrons have positive energy after the collision. For H-like species, the distribution of initial conditions for the bound electron is a microcanonical ensemble, which approximates the quantum spatial and momentum distributions with increasing accuracy at higher n. The incident electron starts with a certain incident energy at an impact parameter, b, and propagates in a potential with charge $Z - 1$ until it reaches the starting distance from the atom. The two-electron simulation starts with the incident electron at a large distance from the atom and ends when one of the electrons reaches a comparably large distance.

3. Results

In figure 1, we compare advanced close-coupling and DW ionization cross sections for H(ns) from $n = 1$ to $n = 4$. It is important to note how rapidly the ionization cross sections shown in this figure increase with principal quantum number. Clearly, at sufficiently high electron densities, ionization out of excited states will have a significant impact on plasma-modelling studies.

For H(1s) and H(2s), we see that the RMPS results are in excellent agreement with the earlier TDCC [2, 12] and convergent close-coupling (CCC) [1] cross sections, and the experimental measurements [17, 18]. In addition, the present TDCC calculation for H(3s) is in good agreement with the RMPS calculation. This provides assurance that the RMPS calculation for H(4s) should be accurate as well. For ionization from the excited states, the prior form DW cross sections are significantly larger than those from the post form DW; part of this difference arises from a shape resonance in the excited-state cross sections due to the combination of potentials employed in the prior-form DW approximation [19]. Regardless, the significant differences between the DW cross sections and those from the advanced close-coupling calculations indicate that the effects of inter-channel coupling and (in this neutral species) polarization of the target, which are not included in the DW calculations, have significant effects on ionization out of excited states. Furthermore, these effects appear to increase slowly with n.

RMPS calculations for ionization from excited states show a large variation with l. For example, for ionization of H(4l), the cross sections increase significantly with l and the peak

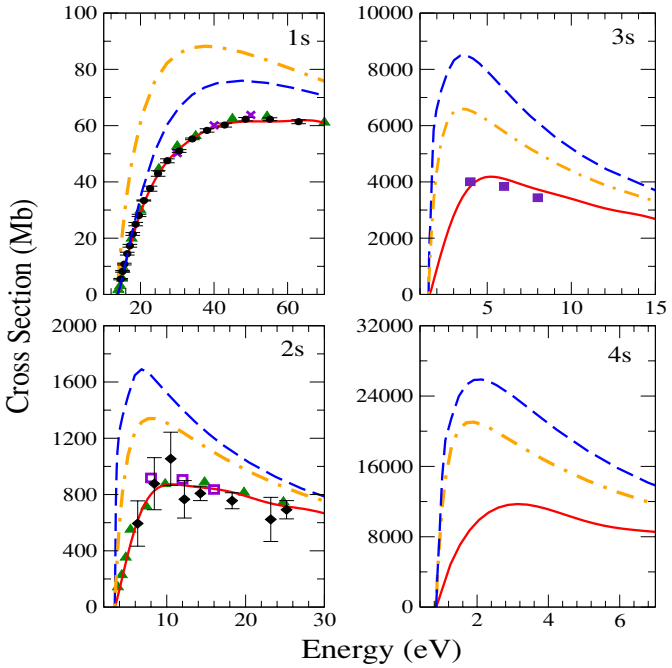

Figure 1. Electron-impact ionization cross sections for H(ns) as a function of n. Dot–dashed lines, DW (post form); dashed lines DW (prior form); solid lines, RMPS; crosses, TDCC from Pindzola and Robicheaux [12], open squares, TDCC from Witthoeft *et al* [2]; solid squares, present TDCC; solid triangles, CCC from Bartschat and Bray [1]; solid circles, experimental measurements of Shah *et al* [17]; and solid diamonds, measurements of DeFrance *et al* [18].

in the 4f cross section is just over 50% higher than the peak in the 4s cross section. CTMC calculations intrinsically include an initial statistical distribution over the angular momentum of the target electron so as to produce a cross section that depends only on n. However, by standard methods of binning the bound orbitals by the corresponding quantal l, we have also run a CTMC simulation for H(4l). Although the CTMC 4l cross sections are all larger than the corresponding RMPS cross sections, their variation with l is remarkably similar to that of the RMPS cross sections.

For fusion-modelling studies of H-like systems, collisions in a plasma with protons tend to distribute the nl states statistically; therefore, it makes sense to employ n-bundled cross sections that have been averaged statistically over the angular momentum of the initial target states. Plots comparing CTMC, prior-form DW, and RMPS n-bundled cross sections are shown in figure 2. For the excited states, the CTMC cross sections are in closer agreement with the RMPS results than the prior-form DW cross sections. Although the differences are smaller, this is also true when we employ post-form DW cross sections; this indicates that the inclusion of the full three-body interactions in the CTMC calculation is more important for ionization of H than the quantal effects included in the DW approximation.

On the basis of the correspondence principle, one might expect that the accuracy of cross sections based on classical trajectories should improve with principal quantum number. Therefore, it is somewhat surprising that through $n = 4$, there is no improvement with n in the CTMC results; in fact, the differences between the CTMC and RMPS cross sections increase slightly with principal quantum number. This difference is not caused by the exchange

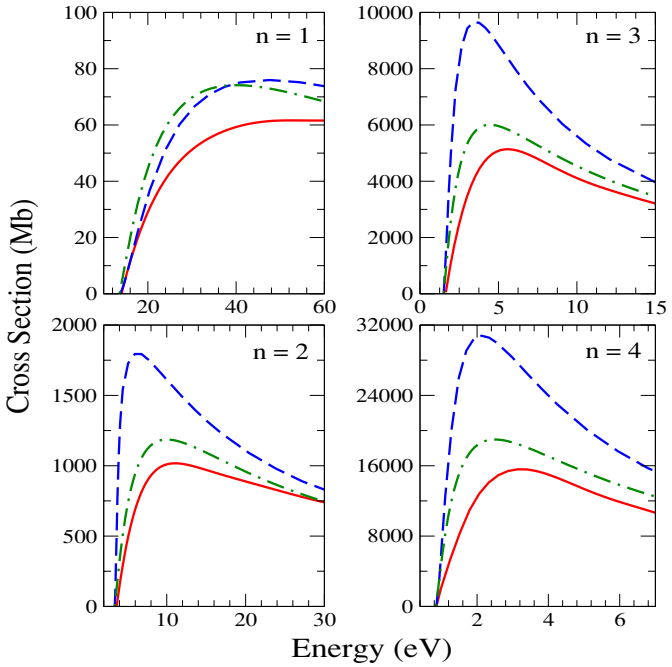

Figure 2. n-bundled electron-impact ionization cross sections for H as a function of n. Dashed lines, DW (prior form); dot–dashed lines, CTMC; and solid lines, RMPS.

interaction, since when we repeated the RMPS calculation without electron exchange, we found that the resulting cross sections were close to the RMPS cross sections with exchange shown in figure 1. The question remains as to whether the accuracy of the CTMC method will begin to improve with still higher values of n.

To test the validity of the DW method as a function of ionization stage, we compare advanced close-coupling and DW cross sections for ionization from $Li^{2+}(ns)$ in figure 3. There is clearly good agreement between the prior-form DW calculations, the TDCC calculations of Colgan *et al* [13], the present RMPS calculations, and the experimental measurements of Tinschert *et al* [20] for ground-state ionization. Furthermore, the agreement between the RMPS and present TDCC results for ionization from Li^{2+}(2s) and Li^{2+}(4s) is excellent. However, the cross sections from the prior-form and post-form DW calculations, which are in much better agreement with each other, are still well above the RMPS cross sections for ionization from excited states; furthermore, this difference between DW and RMPS increases with principal quantum number. Thus, inter-channel coupling effects on ionization out of the excited states of this doubly ionized species are still important.

The situation for the n-bundled cross sections for Li^{2+} shown in figure 4 is quite different from that of H. The DW cross sections are now in better agreement with the RMPS results than the CTMC cross sections, although the difference between the DW and RMPS cross sections increases with principal quantum number. Clearly the accuracy of the CTMC method appears to decrease with ionization stage, indicating that quantal effects are becoming more important in these H-like ions.

We have also completed DW, CTMC and RMPS calculations for ionization of $B^{4+}(nl)$ with n = 1–4. Since the effects of inter-channel coupling decrease with ionization stage, the differences between the DW and RMPS cross sections are smaller for this ion. For B^{4+}(3s)

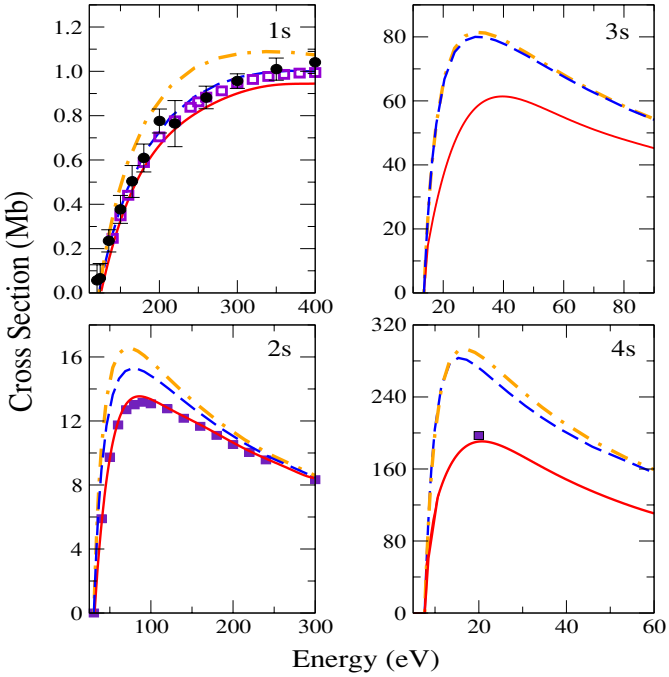

Figure 3. Electron-impact ionization cross sections for $Li^{2+}(ns)$ as a function of n. Dot–dashed lines, DW (post form); dashed lines DW (prior form); solid lines, RMPS; open squares, TDCC from Colgan *et al* [13]; solid squares, present TDCC; solid circles, experimental measurements of Tinschert *et al* [20].

ionization, the prior and post forms of the DW approximation agree well and yield cross sections about 15% above the RMPS cross section at the peak; this increases to about 25% for $B^{4+}(4s)$. On the other hand, the differences between the CTMC and the RMPS cross sections are about the same as they are for Li^{2+}, again indicating that classical-trajectory methods are not accurate for H-like ions.

In order to investigate the importance of these variations in cross section on plasma modelling, we have also carried out collisional-radiative calculations of partial effective ionization rate coefficients for hydrogen. The effective ionization rate coefficient, $S_{\rm eff}$, is the ground-state ionization rate coefficient, $S_{\rm gs}$, plus the sum of excited-state ionization rate coefficients weighted by their populations [8]. For modelling calculations, ionization from excited states through $n = 100$ or more are often included; however for our comparisons, $S_{\rm eff}$ includes excited levels only through $n = 4$, and the excitation rates were determined from the RMPS calculations of Anderson *et al* [21]. The results are given in table 1 for an electron density of 10^{14} cm^{-3} and temperatures from 10^4 K to 10^6 K. From a comparison of the RMPS values for $S_{\rm eff}$ and $S_{\rm gs}$, we see that ionization out of this limited number of excited states is extremely important at this density, especially at the lower temperatures. The CTMC method does reasonably well compared to the RMPS method, with the CTMC values of $S_{\rm eff}$ varying from 30% higher at 10^4 K to only 2% higher at 10^6 K. On the other hand, the prior-form DW value of $S_{\rm eff}$ is over 60% high at 10^4 K, but decreases to 13% at 10^6 K.

Although the CTMC method may provide reasonable estimates of $S_{\rm eff}$ for neutral H, this is not true for H-like ions. A similar collisional-radiative calculation for Li^{2+} or B^{4+} would yield much larger deviations between the CTMC and RMPS values of $S_{\rm eff}$ than those shown

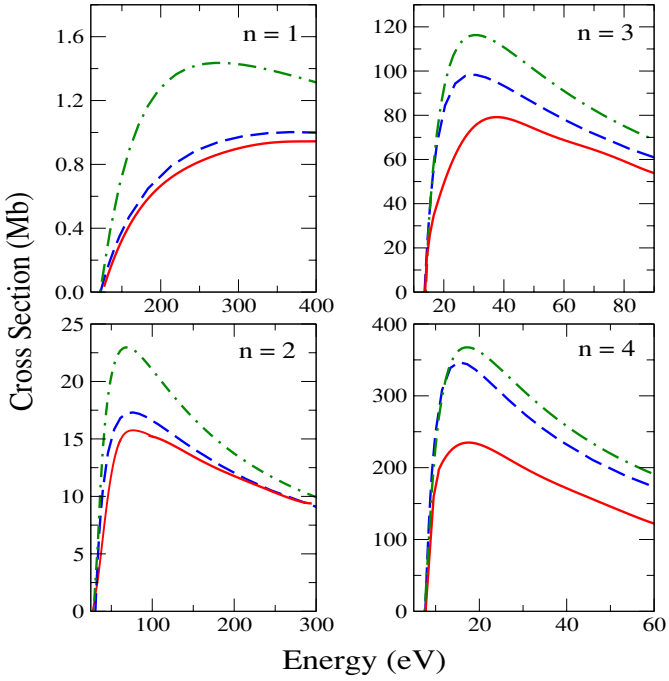

Figure 4. n-bundled electron-impact ionization cross sections for Li^{2+} as a function of n. Dashed lines DW (prior form); dot–dashed lines, CTMC; and solid lines, RMPS.

Table 1. The RMPS ground-state ionization rate coefficient (S_{gs}) and RMPS, prior-form DW, and CTMC partial effective ionization rate coefficients for H from $n = 1$ through $n = 4$ (S_{eff}) for an electron density of 10^{14} cm^{-3}. All rate coefficients are in units of (cm^3 s^{-1}), and a(b) represents a$\times 10^b$.

T (K)	S_{gs} RMPS	S_{eff} RMPS	S_{eff} DW	S_{eff} CTMC
1.00(4)	6.04(−16)	34.7(−16)	56.7(−16)	45.3(−16)
2.00(4)	2.56(−12)	8.41(−12)	11.5(−12)	10.5(−12)
5.00(4)	5.13(−10)	10.2(−10)	13.0(−10)	12.7(−10)
1.00(5)	3.60(−9)	5.82(−9)	7.17(−9)	7.08(−9)
2.00(5)	1.05(−8)	1.50(−8)	1.80(−8)	1.74(−8)
5.00(5)	2.09(−8)	2.69(−8)	3.12(−8)	2.90(−8)
1.00(6)	2.52(−8)	3.11(−8)	3.51(−8)	3.18(−8)

in table 1. On the other hand, for ions, the variation between the DW and RMPS values of the S_{eff} through $n = 4$ would be smaller than those shown in table 1. However, since the DW approximation grows worse with n, the use of DW data for the determination of values of S_{eff} that include ionization from more highly excited states may lead to substantial errors at low temperatures.

4. Conclusions

We have performed extensive advanced close-coupling, distorted-wave and classical trajectory Monte Carlo calculations for H-like species. The differences between the DW and advanced

close-coupling results clearly demonstrate the importance of inter-channel coupling to ionization out of excited states. The TDCC and RMPS calculations, which are by far the most accurate, are presently limited in terms of the largest possible principal quantum number. In contrast, the CTMC calculations can be scaled to any value of n. Thus, a combination of accurate RMPS cross sections for $n \leqslant 4$ with untested CTMC cross sections for $n \geqslant 5$ provides the best available data for neutral hydrogen. For H-like ions, the CTMC method is far less accurate, and formulae based on this method are not recommended. The overall agreement between DW and RMPS calculations improves with ionization stage, but for a given ion, there is no indication that the DW approximation improves with n; in fact, calculations through $n = 4$ indicate that it gets worse. Clearly there is a need for advanced close-coupling cross sections for ionization out of more highly excited states. However, even with use of massively parallel computers, extending these calculations to excited states as high as $n = 10$, for example, would require a daunting computational effort.

Acknowledgments

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