Complete numerical solution of electron-hydrogen collisions

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Declaration

I declare that this thesis is my own account of my research and contains as its main content work which has not previously been submitted for a degree at any tertiary education institution.

Philip Lindsay Bartlett

For my mother Janet (1927–2003)

Abstract

This thesis presents an extensive computational study of electron-impact scattering and ionisation of atomic hydrogen and hydrogenic ions, which are fundamental to many diverse disciplines, from astrophysics and nuclear fusion to atmospheric physics. The non-relativistic Schrödinger equation describes these collisions, though finding solutions for even hydrogen, the simplest electron-atom collision, has proven to be a monumental task. Recently, Rescigno *et al* [Science 286, 2474 (1999)] solved this equation in coordinate space using exterior complex scaling (ECS), and presented the first electron-hydrogen differential cross sections for ionisation that matched with experiment without requiring uncontrolled approximation. This method has significant potential for extension to larger collision systems, but its large computational demand has limited its energy range and target configurations, and its application to discrete final-state collisions has been largely unexplored.

Using radically different numerical algorithms, this thesis develops methods that improve the computational efficiency of ECS by two orders of magnitude. It extends the method to calculate discrete final-state scattering cross sections and enhances the target description to include hydrogenic ions and excited initial states. In combination, these developments allow accurate solutions over a broad range of energies and targets, for both scattering and ionisation, including the important near-threshold energy region where accurate calculations have been unavailable. The refined ECS method implemented in this work now offers complete numerical solutions of electron-hydrogen collisions, and its computational efficiency will facilitate its future application to more complex targets. The thesis culminates with the first *ab initio* quantum mechanical confirmation of ionisation threshold laws for electron-hydrogen collisions [Bartlett and Stelbovics, 2004, Phys. Rev. Lett. 93, 233201], which have resisted confirmation through the complete solution of the Schrödinger equation for more than half a century.

Contents

List of Tables

List of Figures

List of Publications

During the candidacy for this PhD project thirteen manuscripts have been published in refereed journals along with one book chapter. Ten of these publications emanate from the research presented in this thesis, and four publications relate to research undertaken in the previous Honours year. Due to the length of some of these publications, only their reference and abstract are included here.

1. Williams, J.F., P.L. Bartlett and A.T. Stelbovics. 2005. Threshold electron-impact ionization mechanism for hydrogen atoms. *Phys. Rev. Lett.* Submitted.

   > The near-threshold evolution of electron-impact ionization of hydrogen is revealed by interpreting accurate measurements of the angular and energy correlations of the outgoing electrons with recent scattering theory. A dual wedge-and-strip detector on a single toroidal energy analyzer is used to measure single, double and triple differential cross sections in the 'perpendicular plane', simultaneously and with avoidance of many experimental problems. The experimental and calculated data are in excellent agreement, within the experimental uncertainty of $\pm 10\%$, providing strong evidence that the accurate solution of the Schrödinger equation provides a complete description of the physics of near-threshold ionization. Interpretation of the observations with propagating exterior complex scaling (PECS) quantum calculations indicates a gradual evolution of the three-body scattering interactions with changing phases between s and d partial waves.

2. Williams, J.F., P.L. Bartlett, I. Bray, A.T. Stelbovics and A.G. Mikosza. 2005. Differential cross sections for excitation to the 3s, 3p and 3d states of atomic hydrogen by electron impact at energies from 16.5 to 54 eV. *J. Phys. B: At. Mol. Opt. Phys.* Submitted.

   > The excitation of atomic hydrogen from the ground state to each of the 3s, 3p and 3d states has been studied for incident electron energies from 16.5 to 54 eV. The measured total and differential excitation cross sections (DCSs) for scattered electron angles from 5° to 150° are in agreement, within the experimental uncertainty of 10%, with values calculated using the propagating exterior complex scaling (PECS) and convergent close-coupling (CCC) methods. DCS calculations for all s, p, d and f final states with $n \leq 4$ are also presented over this energy range, and reveal a systematic trend with respect to increasing n, final-state angular momentum and incident energy.

3. Bartlett, P.L., A.T. Stelbovics, G.M. Lee and I. Bray. 2005. H(2p) excitation by 54.4 eV electrons. *J. Phys. B: At. Mol. Opt. Phys.* 38: L95–L98.

In response to the recent measurements of the 54.4 eV e-H(2p) reduced Stokes parameters by Gradziel and O'Neill (2004 J. Phys. B: At. Mol. Opt. Phys. 37 1893) we perform corresponding calculations using two recently developed techniques. These are the propagating exterior complex scaling direct approach to the solution of the underlying Schrödinger equation, and the box-based convergent close-coupling method. We find the results to be almost identical to the Laguerre-based convergent close-coupling method of Bray and Stelbovics (1992 Phys. Rev. A 49 1066). Hence we are unable to explain the substantial discrepancy with experiment for the $\bar{P}_3$ parameter in the vicinity of 30°.

4. Bartlett, P.L. and A.T. Stelbovics. 2004. Threshold behavior of e-H ionizing collisions. *Phys. Rev. Lett.* 93: 233201.

We present accurate *ab initio* numerical solutions of the full Schrödinger equation for the electron-impact ionization of hydrogen near threshold using the propagating exterior complex scaling method. They provide strong support for the Wannier threshold law [Phys. Rev. **90**, 817 (1953)], giving $\sigma \propto E^{1.122\pm0.015}$, and also give the energy dependence of the electrons' angular distribution as $(\pi - \theta_{12})_{FWHM} \approx 3.0E^{1/4}$, in general agreement with classical and semiclassical predictions.

5. Bartlett, P.L. and A.T. Stelbovics. 2004. Differential ionization cross-section calculations for hydrogenic targets with $Z \leq 4$ using a propagating exterior complex scaling method. *Phys. Rev. A* 69: 040701(R).

A propagating exterior complex scaling (PECS) method, with iterative coupling, has been adapted for the electron-impact of charged hydrogenic targets. Using this fully *ab initio* method for solving the Schrödinger equation, which has no uncontrolled approximations, we present highly-accurate total, single-differential, double-differential, and triple-differential cross section calculations for the electron-impact ionization of hydrogenic targets with nuclear charge $Z \leq 4$ (H, He^+, Li^{2+}, Be^{3+}). For a fixed scaled energy, the total and differential cross-sections begin to converge with respect to increasing Z when scaled by Z^4 and Z^6 respectively, and converge more rapidly with increasing incident-electron energy. The angular distribution of the differential cross sections change systematically with increasing nuclear charge for energies above the peak total ionization cross section, but for some lower-energy kinematics the triple-differential cross section for charged targets is significantly different from that of atomic hydrogen.

6. Bartlett, P.L., A.T. Stelbovics and I. Bray. 2004. Propagating exterior complex scaling method for electron-hydrogen collisions. *J. Phys. B: At. Mol. Opt. Phys.* 37: L69–L76.

A newly-derived iterative coupling procedure for the propagating exterior complex scaling (PECS) method, is used to efficiently calculate the electron-impact wave functions for atomic hydrogen. An overview of this method is given along with methods for extracting scattering cross sections. Differential scattering cross sections at 30 eV are presented for the electron-impact excitation to the n=1,2,3 and 4 final states, for both PECS and convergent close coupling (CCC), which are in excellent agreement with each other and with experiment. PECS results are presented at 27.2 eV and 30 eV for symmetric and asymmetric energy-sharing triple differential cross sections, which are in excellent agreement with CCC and exterior complex scaling calculations, and with experimental data. At these intermediate energies, the efficiency of the PECS method with iterative coupling has allowed highly accurate partial-wave solutions of the full Schrödinger equation, for $L \leq 50$ and a large number of coupled angular momentum states, to be obtained with minimal computing resources.

7. Stelbovics, A.T., P.L. Bartlett, I. Bray and A.S. Kadyrov. 2004. Three-body Coulomb scattering above the ionization threshold. *Physica Scripta* T110: 247–251.

Recent progress in the calculation of electron-atom scattering, with particular reference to electron-hydrogen ionization is presented. There have been substantial developments and improvements computationally, and also perhaps unexpectedly, in the formal theory. We conclude that within the frame of non-relativistic scattering theory electron-hydrogen scattering is practically a solved problem.

8. Bartlett, P.L. and A.T. Stelbovics. 2004. Complete direct method for electron-hydrogen scattering: Application to the collinear and Temkin-Poet models. *Phys. Rev. A* 69: 022703.

We present an efficient generalization of the exterior complex scaling (ECS) method to extract discrete inelastic and ionization amplitudes for electron-impact scattering of atomic hydrogen. This fully-quantal method is demonstrated over a range of energies for the collinear and Temkin-Poet models and near-threshold ionization is examined in detail for singlet and triplet scattering. Our numerical calculations for total ionization cross sections near threshold strongly support the classical threshold law of Wannier [Phys. Rev. **90**, 817 (1953)] ($\sigma \propto E^{1.128\pm0.004}$) for the $L = 0$ singlet collinear model and the semiclassical threshold law of Peterkop [J. Phys. B **16**, L587 (1983)] ($\sigma \propto E^{3.37\pm0.02}$) for the $L = 0$ triplet collinear model, and are consistent with the semiclassical threshold law of Macek and Ihra [Phys. Rev. A **55**, 2024 (1997)] ($\sigma \propto \exp((-6.87 \pm 0.01)E^{-1/6})$) for the singlet Temkin-Poet model.

9. Bartlett, P.L. and A.T. Stelbovics. 2004. Electron-impact ionization cross sections for elements Z=1 to Z=54. *At. Data Nucl. Data Tables* 86: 235–265.

The electron-impact ionization cross sections for all neutral ground-state elements Z=1 to Z=54 (H to Xe) have been calculated using the plane-wave Born approximation. The atomic orbital wave functions have been approximated by Roothaan–Hartree–Fock Slater functions, and the scattered and ejected electrons have been approximated by a plane-wave and Coulomb-wave respectively. Full orthogonalization of the Coulomb-wave with the occupied atomic orbitals has been performed, which improves the correlation with experimental data at low- and mid-energies. Results are presented for the total ionization cross section and the partial ionization cross sections of the largest contributing orbitals, for each atom.

10. Bartlett, P.L., A.T. Stelbovics and I. Bray. 2003. Threshold ionization laws for electron-hydrogen scattering and their dominant region of configuration space. *Phys. Rev. A* 68: 030701(R).

    A fully quantal calculation of the ^1S three-body wave function is performed for the Wannier model of electron-hydrogen scattering in the near ionization threshold region using an exterior complex scaling method. The region of configuration-space of the wave function that provides the dominant contribution to the total ionization cross section is demonstrated to be $r_1 \approx r_2$ in accord with the argument of Rau [A. R. P. Rau, Phys. Rev. A **4**, 207 (1971)], but only in the so-called Coulomb zone. The work confirms to a high precision ($E^{1.128\pm0.004}$) the Wannier threshold law for the total ionization cross section, which is strictly valid only at threshold. A threshold law for the ^3S total ionization cross section is determined to be $E^{3.37\pm0.02}$, in agreement with the semi-classical calculations of Rost [J.-M. Rost., J. Phys. B **28**, 3003 (1995)].

11. Bartlett, P.L., I. Bray, S. Jones, A.T. Stelbovics, A.S. Kadyrov, K. Bartschat, G.L. Ver Steeg, M.P. Scott and P.G. Burke. 2003. Unambiguous ionization amplitudes for electron-hydrogen scattering. *Phys. Rev. A* 68: 020702(R).

    According to quantum collision theory, scattering amplitudes are complex numbers, which are completely defined by their magnitude *and phase*. Although the phase information is generally not determined entirely in collision experiments, the phases are well-defined and can be used to check computational models. We use four state-of-the-art approaches to calculate the magnitude and phase of the electron-hydrogen ionization amplitude in the Temkin-Poet S-wave model. We demonstrate that the correct phase can be extracted for each method by using the appropriate final-state continuum functions.

12. Bartlett, P.L. and A.T. Stelbovics. 2003. Born total ionisation cross sections: An algebraic computing program using Maple. *Comput. Phys. Comm.* 154: 159–174.

    The software described in this paper uses the Maple algebraic computing environment to calculate an analytic form for the matrix element of the plane-wave Born approximation of the electron-impact ionisation of an atomic orbital, with arbitrary orbital and angular momentum quantum numbers. The atomic orbitals are approximated by Hartree-Fock Slater functions, and the ejected electron is modelled by a hydrogenic Coulomb wave, made orthogonal to all occupied orbitals of the target atom. Clenshaw-Curtis integration techniques are then used to calculate the total ionisation cross-section. For improved performance, the numerical integrations are performed using FORTRAN by automatically converting the analytic matrix element for each orbital into a FORTRAN subroutine. The results compare favourably with experimental data for a wide range of elements, including the transition metals, with excellent convergence at high energies.

13. Bartlett, P.L. and A.T. Stelbovics. 2002. Electron impact ionisation cross-sections of the transition metals. In *Current Developments in Atomic, Molecular, and Chemical Physics with Applications*, ed. M. Mohan, 167–172. New York: Plenum Publishers.

14. Bartlett, P.L. and A.T. Stelbovics. 2002. Calculation of electron-impact total-ionization cross sections. *Phys. Rev. A* 66: 012707.

    A computationally efficient analytic form of the Born-approximation electron-impact ionization amplitude is derived for general neutral-atom targets. High-quality Hartree-Fock-Slater orbitals are used to model the target wave function. Full orthogonalization of the continuum Coulomb wave to all occupied orbitals of the target atom is enforced. Results are presented for noble-gases (Ne, Ar, Kr, and Xe), selected transition metals (Fe, Cu, and Ag) and elements from the fourth, fifth, and six column of the periodic table (Si, Ge, Sn, P, As, Sb, S, Se, and Te) where theoretical comparisons are lacking. Full orthogonalization significantly improves agreement with experimental data for the noble gas series compared to previous Born models. Overall agreement with all elements is uniformly good and variations within each series are systematic.

Acknowledgements

Now that this thesis is complete, I have the opportunity to reflect upon the three years taken for its development. My emotions are mixed: I look back at this time with a sense of pride of my scholarly accomplishments, a genuine appreciation of those whom helped and encouraged me during this time, but a profound sadness for my personal loss that dominated much of this period.

Sadly, eight months after starting this project, my mother was diagnosed with terminal breast cancer. She had lived alone in a small country town, so there was no alternative but for her to live with me and my partner Kim in Perth. We cared for her for nine months as her health deteriorated, until her death on 25th June 2003. I have dedicated this thesis to her as throughout my life she has been my most avid supporter, always offered encouragement, and was so immensely proud of me, her youngest son. Much of the tenacity and drive that was required to complete this thesis I inherited from her. When my PhD is awarded, I will be proud, yet deeply sad that she will not be part of my celebration.

This thesis would not have been possible without the towering efforts of my partner Kim, whom not only helped my mother during her illness, which allowed me to devote some of my time to research, but gave *me* such immense support and good counsel during this very stressful time.

On matters more academic, I must acknowledge the incredible assistance of my principal supervisor Professor Andris Stelbovics. He has given constant encouragement and always shown the most genuine interest and enthusiasm for my research. I am fortunate to have had the tutoring and guidance of a researcher with such vast experience and solid reputation. The large volume of research and publications that have emanated from this project has demanded a significant amount of his time, which has always been given generously, even considering the onerous demands made on his time with his duties as Pro Vice Chancellor (Research). I also thank him for putting up with my oscillating

moods during this time!

I must also acknowledge the tremendous support of my co-supervisor Professor Igor Bray. Though not intimately involved with the "nuts and bolts" of this project, he obtained the large amount of computer time required, organised financial assistance for attending conferences, gave invaluable advice on publications, offered encouragement, allowed open access to his extensive database of CCC results and undertook many CCC calculations for me to include as comparisons in this thesis. This assistance has been invaluable.

Finally, I would like to thank the many eminent researchers that I have had the good fortune to meet and discuss this project with: Professors Phil Burke, Klaus Bartschat, Bill McCurdy, Ravi Rau and Jim Williams. Their positive comments have helped boost my enthusiasm for my research.