COMPLETE NUMERICAL SOLUTION OF
ELECTRON-HYDROGEN COLLISIONS

Philip Lindsay Bartlett B.Sc. (Hons)

This thesis is presented for the degree of Doctor of Philosophy of Murdoch University, Perth, Western Australia, 2005.
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)
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.
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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.


   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 ±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.


   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.

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 $P_3$ parameter in the vicinity of 30$^\circ$.


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.


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.

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.


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.


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. \textbf{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. \textbf{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 \textbf{55}, 2024 (1997)] \((\sigma \propto \exp((-6.87 \pm 0.01)E^{-1/6}))\) for the singlet Temkin-Poet model.

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.


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)].


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.


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.


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.
The interactions between photons, electrons, atoms and molecules are fundamental to the processes of life, the universe and almost everything. From the radiation of light from the Sun and stars to its photosynthesis in plants, from the phosphorescent glow of our computer screens to the flicker of fluorescent lighting, atomic and molecular collisions pervade our everyday life. The quest of science is to understand these natural phenomena.

Since the pioneering research of Rutherford and Thompson in the late 1800s, science has sought to understand the structure of atoms and their interactions with electrons, photons and each other. The development of Quantum Theory in the early 1900s at last provided a theoretical basis for solving atomic collisions. Unfortunately, the equation fundamental to modelling these collisions, the Schrödinger equation, only possesses analytic solutions for two-body systems. One of the most fundamental of atomic collisions, an electron impacting with a hydrogen atom (e–H), which is the subject of this work, has no known analytic solution. It is a testament to the complexity of collision problems that proceeding from two-body collisions to a three-body system has taken a further century to formulate and solve numerically.

There are three possible outcomes for e–H collisions: elastic scattering of the incident electron, inelastic scattering where the target is left in an excited state (which subsequently decays) and a breakup collision where the target is ionised and gives two free electrons. The excitation and ionisation channels may be closed or open depending on whether the incident electron exceeds the required excitation and ionisation threshold energies, respectively. Though a “simple” collision system, the measured cross sections (interaction probabilities) for each of these channels have many structural features that vary with impact energy and angular distribution of the final-state particles. The richness of these structures, along with the large body of available experimental data, makes
this collision system an ideal test bed for new computational methods.

For nearly a century, atomic physicists have used approximation techniques in an
effort to find analytic and numerical solutions to the fundamental e–H collision. Many
of the modern numerical techniques have evolved from the close-coupling (CC) expan-
sion first introduced by Massey and Mohr (1932), which expands the wave function for
electron-atom collisions in terms of eigenstates of the target atom. Though, the very
limited computational resources available in this era meant that other more restrictive,
but numerically tractable, approaches were developed including perturbation methods
such as the Born approximation [e.g. see Massey and Mohr (1934), Mott and Massey
(1949) and Omidvar (1965)].

With the increasing availability of computing resources in the second half of last
century, attention returned to the CC expansion technique. Burke and Taylor (1966)
were successful in describing the elastic and inelastic non-breakup collisions below the
ionisation threshold by introducing extra basis functions in the target space in addition
to essentially exact low-lying excited states. When applied at higher energies, their re-
sults exhibited non-physical pseudo-resonance structures. It was soon realised that these
resonance features were simply an artifact of the limited basis set. A further calculation
with larger basis set leading to a denser distribution of positive-energy pseudostates,
and hence a better description of the effect of the continuum ionisation channel, helped
resolve this problem (Burke and Webb 1970). Using a model problem, Bray and Stel-
bovics (1992b, 1995b) demonstrated that with a sufficiently large basis of eigenstates
and positive-energy pseudostates convergent total scattering cross sections could be ob-
tained, for all discrete and ionisation processes, without unphysical resonance structures
at all energies. Both this method, convergent close-coupling (CCC) (Bray and Stelbovics
1992a, 1995a), and the intermediate energy R-matrix (IERM) method of Burke, Scott,
Sholtz and coworkers (Burke et al 1987, Scott et al 1989, Scholz et al 1991) were now
able to accurately calculate total scattering cross sections for e–H collisions over a wide
range of energies.

The ionisation channel has proven the most difficult to solve for e–H collisions; the
electrostatic forces have a long-ranged interaction and perturbation methods could not
account for measurements of the ionisation cross sections at low and intermediate electron energies. Bray and Stelbovics (1993) showed that the positive-energy pseudostates included in their CCC calculations could be used to evaluate ionisation cross sections, and obtained the first e–H total ionisation cross section (TICS) results that were in complete agreement with experiment over a wide range of energies. In addition to CCC and IERM, other state-of-the-art time-independent methods include the R-matrix with pseudostates (RMPS) method of Bartschat and Bray (1996) and the hyperspherical close-coupling (HSCC) method of Kato and Watanabe (1995), which also use close-coupling methods and discretise the ionisation continuum into positive-energy pseudostates. All these methods are now in good agreement with e–H experiments for all reaction channels over a wide range of energies and spatial distributions of the final-state particles. Given a sufficiently large basis of pseudostates, these methods provide ab initio solutions.

However, it is well known that in practice the IERM, RMPS and CCC methods exhibit large unphysical oscillations in their ionisation single-differential cross section (SDCS) results (with respect to energy sharing of the outgoing electrons) that are smoothed with various integral-preserving (Bray 2000) and least-squares fitting (Scott et al 2002) techniques. As discussed by Bray (1997) and Stelbovics (1999), it appears to be a feature of the CC expansions that the energy-sharing SDCS that they predict are not symmetric about equal energy-sharing, but rather exhibit a step-function behaviour.

In an effort to obtain fully ab initio solutions for e–H ionisation that do not exhibit unphysical oscillations in the SDCS results, direct solutions for the Schrödinger equation have been explored recently. These direct methods are relatively simple to implement and the rapid increase in supercomputing performance has made them attractive in recent years. Rescigno, Baertschy, McCurdy and coworkers (Rescigno et al 1999, Baertschy et al 2001a) demonstrated that the exterior complex scaling transformation (Nicolaides and Beck 1978, Simon 1979), based on that used for atomic resonance calculations, could be applied successfully to ionisation problems. They obtained the first direct solution for the scattering wave functions for e–H ionising collisions in coordinate space and did not require explicit knowledge of the boundary conditions at the outer edges of the grid. The method calculates ionisation cross sections from the scattering wave
functions using a surface integral method (Peterkop 1977, McCurdy et al 2001) that relies on an approximation of the final-state asymptotic continuum waves. The ECS method obtained convergent cross sections, though the phase of the ionisation amplitudes calculated with this approximation were ambiguous, as were the phases calculated using the above CC methods.

In a recent series of papers, Kadyrov et al (2003, 2004) gave the first formally correct asymptotic boundary conditions for the Coulomb three-body problem that are valid in all asymptotic domains, and include a partial-wave expansion suitable for use with numerical methods. An important outcome of this work, was that it gave a formal justification for the final-state continuum wave approximation used in the ECS method, leading to converged magnitudes of the ionisation amplitudes and furthermore ensured convergent phases as well. Thus, ECS can be considered a fully *ab initio* method for calculating both the scattering wave functions and ionisation cross sections, in all energy-sharing arrangements and spatial distributions of the breakup particles. All approximations used by ECS to calculate the wave functions and ionisation cross sections are *controlled*¹ and can be calculated to arbitrary accuracy.

Another direct method, the time-dependent close-coupling (TDCC) method of Pindzola, Robicheaux, Colgan and coworkers (Colgan et al 2002a), is used to compute solutions to the *time-dependent* Schrödinger equation for *e–H* collisions in momentum space. This method is in good agreement with other modern calculations, and like ECS, obtains *ab initio* results without knowledge of the final-state boundary conditions.

Apart from their markedly different theoretical development, the main points of difference of the direct methods, ECS and TDCC, from the close-coupling methods, RMPS, IERM and CCC, are in their ability to calculate the differential ionisation cross sections without application of empirical smoothing techniques. Also, the ECS method extracts scattering and ionisation amplitudes from the computed scattering wave function using

³We use the term *controlled* here, and throughout this thesis, to emphasise that convergence of the results with respect to all numerical and computational approximations are demonstrated in practice, with presently available computing resources. Given sufficient computing resources, the results can be calculated to arbitrary accuracy.
a rigorous surface integral formulation. As these direct methods are evolved in the future to solve collisions with multiple active electrons, where the \textit{a priori} assumption that the SDCS is smooth may not be valid, these features will be a distinct advantage.

The ECS and TDCC methods have very similar computational demands (Colgan \textit{et al} 2002a). For $e$–H collisions at intermediate incident energies (above 50 eV) both methods use large amounts of computing resources, and neither method is currently able to include sufficient partial-waves to demonstrate complete convergence (Baertschy \textit{et al} 2001a, Colgan \textit{et al} 2002a). Extrapolation techniques are used to overcome this limitation, but the \textit{ab initio} nature of the calculations is compromised. Unlike the CC methods, the ECS method for $e$–H collisions has thus far been limited to the ionisation channel; discrete final-state collisions, excited state targets and hydrogenic ions have not been considered.

Collisions at energies very close to the ionisation threshold energy are problematic for all the state-of-the-art methods discussed thus far. To maintain accuracy as energy approaches threshold, the direct methods require increasingly larger grids, while CC methods require an increasingly larger basis of pseudostates, and computational resource limits are quickly reached. ECS is unable to yield converged solutions for energies much closer than 1 eV from the ionisation threshold (Baertschy \textit{et al} 2001a), due to the computational demands of these very large grids. Also, there is evidence that the iterative method for solving the large sparse-matrix equations used in the $e$–H ECS method sometimes fail to converge (Baertschy and Li 2001) at these low energies. The application of the TDCC method at very low energies is largely unexplored, while the accuracy of the IERM, RMPS and CCC results is limited by significant energy-dependent oscillations [as is evident in the IERM, RMPS and CCC model calculations given in Scott \textit{et al} (1997)]. Consequently, a detailed exploration of the ionisation threshold region that gives convincing support for the Wannier (1953) and associated threshold laws has yet to be provided by any fully-quantal \textit{ab initio} method.

The impressive results and significant potential of the ECS method have given the impetus for the work undertaken in this thesis. The goal of this investigation is three-fold. Firstly, we will generalise the ECS method and solve the non-relativistic time-
independent Schrödinger equation for a complete\textsuperscript{2} range of \(e\–H\) collisions. Secondly, we will develop numerical and computational algorithms that markedly reduce the computational requirements of the ECS method for \(e\–H\) collisions and remove the near-threshold and higher-energy limitations. Lastly, we will undertake a thorough investigation of \(e\–H\) ionising collisions near the ionisation threshold in an effort to obtain the first fully-quantal \textit{ab initio} support for the classically derived Wannier (1953) and related threshold laws.

We will see in later chapters that solutions in this thesis are obtained on a numerical grid in coordinate space using both exterior complex scaling and an extension of the propagation algorithm used by Poet (1980) for model \(e\–H\) scattering problems. So as to differentiate the method developed in this thesis from that of Rescigno, Baertschy and McCurdy’s ECS method (Rescigno \textit{et al} 1999, Baertschy \textit{et al} 2001a), we will refer to the present work as the propagating exterior complex scaling method, and use the acronym PECS.

In Chapter 2 we will develop the theoretical foundation of the PECS method by extending the ECS method to include excited initial-state and charged hydrogenic targets, and develop a method to extract discrete final-state cross sections from the scattering wave functions. Chapter 3 gives the numerical developments of PECS, including the propagation method, finite-difference schemes and iterative schemes that greatly reduce computational effort. The computational implications of these numerical schemes are discussed in Chapter 4. We then test the accuracy and energy range of the PECS method in Chapter 5 by applying it to two commonly used \textit{model} problems. Chapter 6 demonstrates the application of PECS to a \textit{complete} range of \(e\–H\) collisions, followed by a comprehensive near-threshold investigation of \(e\–H\) ionising collisions in Chapter 7.

The significance of this work, however, is not limited to the \(e\–H\) collisions investigated here. Due to the efficient algorithms we have implemented, the prospect of the future application of the ECS method to multi-electron targets is encouraging.

\textsuperscript{2}In this context, \textit{complete} should be taken to mean: all reaction channels (elastic scattering, inelastic discrete final-state scattering and ionisation), for targets in the ground state and excited states, both neutral hydrogen atoms and charged hydrogenic ions, and energies that are accessible to experimental measurement, ranging from below ionisation threshold to moderately-high energies (within the constraints of the non-relativistic Schrödinger equation) where perturbation methods become accurate.
The benefits of using the ECS method to solve atomic collision problems numerically include the simplicity of its application and the high accuracy achievable over a wide range of energies and kinematics. The method is simple in its derivation as it solves the non-relativistic time-independent Schrödinger equation for the collision in a finite region of coordinate space, directly, completely and without knowledge of the boundary conditions, and as such is a fully \textit{ab initio} method. Also, it does not rely on any specialised expansion techniques, using only an expansion in terms of angular momentum, which is used in a vast range of quantum mechanical problems, and has a solid theoretical foundation. The high accuracy obtainable with ECS is due to the minimal number of approximations used in its derivation and numerical solution, all of which can be considered as controlled, and are readily estimated from convergence studies.

In Section 2.1 we give an overview of the ECS transformation, and demonstrate its features with a simple one-dimensional example. This is followed in Section 2.2 by the derivation of the partial-wave differential equations for the scattering wave function. It should be noted that, to date, ECS implementations for electron-hydrogen collisions have only considered neutral ground-state targets (Rescigno \textit{et al} 1999, Baertschy \textit{et al} 2001b), so the derivation presented in this section is the first of its type to consider both charged hydrogenic targets and excited initial states\footnote{When referring to \textit{previously published methods} or stating that the results or methods are \textit{the first of their type}, throughout this thesis, we exclude those publications that have emanated directly from the work undertaken for this thesis. These publications are listed in the List of Publications at the start of this thesis.}.

In Section 2.3 we derive equations that extract discrete final-state scattering amplitudes from the scattering wave functions using a surface integral method. We believe that this is the first time that discrete final state scattering amplitudes have been calculated from a direct solution of the scattering wave function for $e$–H collisions. However,
McCurdy *et al* have undertaken investigations with model problems using the optical theorem (McCurdy *et al* 1997) and the surface integral method (McCurdy *et al* 2002) that is further developed here. An excellent summary of their work is given in McCurdy *et al* (2004).

In the initial application of ECS to \(e^{-}H\) ionising collisions, Rescigno *et al* (1999) calculated ionisation cross sections from the outgoing flux of the scattering wave functions. The cross sections were not radially converged, and their numerical grid could not reach the very large radii required for convergence \((\gg 100 \text{ a.u.})\), so extrapolation techniques were used. The extrapolated results proved to be inaccurate for highly asymmetric energy-sharing of the outgoing electrons, which for moderate energy collisions is the region that has the highest contribution to the TICS. In later publications (McCurdy *et al* 2001, Baertschy *et al* 2001a) they used the Peterkop (1977) integral method to overcome this problem, and obtained convergent ionisation cross sections with significantly smaller radii than required by the flux method. In Section 2.4 we detail our derivation of the ionisation amplitude using the integral formulation of Peterkop, which extends beyond that published by Baertschy *et al* by allowing for charged hydrogenic and excited targets, and also discuss the ionisation amplitude phase ambiguity of this method.

The conventions used throughout this thesis, unless stated otherwise, are: All quantities and equations are in atomic units (a.u.), where \(\hbar\), the electron mass \(m_e\) and the proton charge \(Z_p\) are set to unity; the imaginary unit number is represented using the roman font, i.e. \(i = \sqrt{-1}\); vectors and functions dependent upon vectors are given in bold font, e.g. \(\Psi(r_1, r_2)\), while scalars and functions dependent only upon scalar quantities are given an italic font, e.g. \(\psi(r_1, r_2)\).

### 2.1 Exterior complex scaling

The use of an ECS transformation to obviate the need for asymptotic boundary conditions when solving atomic and molecular collisions was first introduced by Nicolaides and Beck (1978), and independently suggested by Simon (1979). Many decades prior to this the complex rotation of the radial coordinates had been used for atomic resonance
2.1: EXTERIOR COMPLEX SCALING

Figure 2.1: (a) Graphical representation of the rotation by $\theta$ radians into the complex plane of the radial coordinate $z(r)$ at the start of the complex scaling region $R_0$. (b) Result of complex scaling of $\psi(r) = \sin(z(r))$. (c) Regions of complex scaling in a two dimensional coordinate system.

problems. However, it was not until 1997 that Rescigno et al began exploring the use of ECS for three-body ionising collisions, which culminated in their landmark publication in Science (Rescigno et al 1999) of the first complete solution to the e–H breakup problem. These publications should be referenced for a detailed description and theoretical justification of the method, though we will look at a simple one-dimensional example to give some insight into the workings of ECS.

The ECS transformation rotates the radial coordinates into the complex plane by a fixed angle $0 < \theta < \pi/2$ at a finite distance from the origin ($R_0$) using the transformation

$$z(r) \mapsto \begin{cases} r, & r < R_0 \\ R_0 + (r - R_0)e^{i\theta}, & r \geq R_0. \end{cases} \quad (2.1)$$

This is depicted graphically in Figure 2.1a. If we apply this transformation to a one-dimensional outgoing wave $\psi(r) = e^{+ir}$, for $r > R_0$ we obtain

$$\psi(r) \mapsto \psi(z(r)) = e^{-(r-R_0)\sin\theta}e^{i(R_0+(r-R_0)\cos\theta)} \xrightarrow{r \to \infty} 0, \quad (2.2)$$

which demonstrates that outgoing waves diminish exponentially beyond $R_0$ under this transformation. Figure 2.1b shows the real part of this wave function (with arbitrary units), where it is evident that the wave function diminishes by 99.9% within 1.5 osci-
lations from $R_0$. When solving differential equations numerically with the ECS method, we may use this point ($R_{\text{max}}$) as the edge of our grid and set the boundary condition at this point to zero with minimal loss of accuracy. It should be observed that there is a discontinuity in the first derivative of the transformed wave function at $R_0$. We will discuss this further in Section 3.1 when we consider the grid spacing required in this region. An important outcome of the theoretical investigation into ECS by Rescigno et al (1997) is that the transformation is valid for use with finite difference methods, provided that the point of rotation into the complex plane $R_0$ is one of the points on the numerical grid.

If we now consider a one-dimensional incoming wave $\psi(r) = e^{-ir}$, for $r > R_0$ we obtain

$$\psi(r) \rightarrow \psi(z(r)) = e^{(r-R_0)\sin \theta} e^{-i(R_0+(r-R_0)\cos \theta)} \rightarrow \infty,$$  \hspace{1cm} (2.3)

which demonstrates that incoming waves diverge under this transformation. It is important, therefore, to ensure that equations solved using ECS do have outgoing waves beyond $R_0$ and don’t have incoming waves beyond $R_0$. We will discuss this point further in Section 2.2.

The ECS transformation is applied separately to each radial coordinate. The equations solved in this thesis have two radial coordinates, and Figure 2.1c demonstrates the four regions where $r_1$ and $r_2$ are either real or complex. The solutions obtained using ECS are only valid in the region where both coordinates are real, $r_1, r_2 \leq R_0$.

We will now turn our attention to the Schrödinger equation of the collision systems addressed by this thesis, to which the ECS transformation will be applied.

### 2.2 Schrödinger equation

The time-independent Schrödinger equation for an $e-$HZ collision\(^2\) is given by

$$\left( \hat{H} - E \right) \Psi^{S(+)}_i = 0,$$  \hspace{1cm} (2.4)

\(^2\)We use the notation $e-$HZ to represent the collision of an electron with hydrogen or a hydrogenic ion with central charge $Z \geq 1$.\)
where $\hat{H}$ is the Hamiltonian operator, $E$ is the total energy of the system and $\Psi^{S(+)}_i$ is the outgoing wave function. The initial state of the system is given by the subscript $i$, and represents the momentum of the incident particle $k_i$ and the initial state $|n_i l_i m_i⟩$ and nuclear charge $Z$ of the hydrogenic target. The spin angular momentum $S$ of the system is an observable quantum state that is conserved in the collision, and each spin state may be solved separately. Using ECS to solve this equation in its present form results in all boundary conditions becoming zero and our numerical methods will find the trivial solution of $\Psi^{S(+)}_i = 0$. To resolve this problem we must rearrange the equation into an inhomogeneous form. This is achieved by separating the outgoing wave function into an incident wave function $\Psi^{S}_{i,inc}$ and an outgoing scattering wave function $\Psi^{S(+)}_{i,sc}$, which are related by

$$\Psi^{S(+)}_i = \Psi^{S}_{i,inc} + \Psi^{S(+)}_{i,sc}. \quad (2.5)$$

The Schrödinger equation for the collision becomes

$$\left( E - \hat{H} \right) \Psi^{S(+)}_{i,sc} = \left( \hat{H} - E \right) \Psi^{S}_{i,inc}, \quad (2.6)$$

where the right-hand-side is known analytically, and hence provides an inhomogeneous equation that is suitable for solution using ECS.

For the collision systems considered in this thesis, the nucleus of the target is sufficiently massive, relative to the incident electron, that it may be considered fixed in space and its kinetic energy operator ignored without affecting the accuracy of the calculations. The resulting Hamiltonian $\hat{H}$ of the interaction may then be split into one- and two-electron operators given by

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_{12}, \quad (2.7)$$

where

$$\begin{align*}
\hat{H}_1 &= -\frac{1}{2} \nabla^2_1 - \frac{Z}{r_1}, \quad (2.8) \\
\hat{H}_2 &= -\frac{1}{2} \nabla^2_2 - \frac{Z}{r_2}, \quad (2.9) \\
\hat{H}_{12} &= \frac{1}{|r_1 - r_2|} = \frac{1}{r_{12}}, \quad (2.10)
\end{align*}$$

and where $Z \geq 1$. 

Equation (2.6) requires solution in six dimensions, two radial and four angular, which makes numerical solution in the present form computationally intractable. We will use a partial-wave expansion to reduce the system to an infinite set of coupled radial equations, each having only two dimensions, where numerical convergence is obtained in practice with a small number of partial waves. The partial-wave expansion that we will use is

\[
\Psi_{i,sc}^{S(+)}(r_1, r_2) = \frac{1}{r_1 r_2} \sum_{l_1 l_2 L M} \psi_{i, l_1 l_2}^{L M S I H}(r_1, r_2) Y_{L M}^{l_1 l_2}(\hat{r}_1, \hat{r}_2), \tag{2.11}
\]

where \(Y_{l_1 l_2}^{L M}\) is a bipolar spherical harmonic function (see Section A.2), which is non-zero only when

\[
|l_1 - l_2| \leq L \leq |l_1 + l_2|, \tag{2.12}
\]

where \(L\) is the partial-wave angular momentum, \(M\) is the projection of \(L\) onto the z-axis and \(l_1\) and \(l_2\) are the angular momenta of each electron. This effectively separates the radial and angular components of the scattering wave function, and is a common strategy for solving quantum mechanical equations. We have introduced the label \(\Pi\) to specify the parity of the angular momentum state, which is conserved in the collision, and is given by

\[
(-1)^R = (-1)^{L+l_1+l_2}, \tag{2.13}
\]

where we have defined even (natural) parity as \(\Pi = 0\) and odd parity as \(\Pi = 1\).

Using the relations

\[
\nabla^2 = \frac{1}{r^2} \left( \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) \right) - \frac{\hat{L}^2}{r^2} \tag{2.14}
\]

\[
\frac{1}{r^2} \left( \frac{\partial}{\partial r} \left( r^2 \frac{\partial f(r)}{\partial r} \right) \right) = \frac{\partial^2 f(r)}{\partial r^2} \cdot \frac{1}{r}, \tag{2.15}
\]

and (A.1) we are able to transform the single-electron Hamiltonian operators so that they are independent of the angular coordinates, and only operate on the radial outgoing scattering wave function \(\psi_{i, l_1 l_2}^{L M S I H}(r_1, r_2)\), giving

\[
\hat{H}_{l_1} = -\frac{1}{2} \frac{\partial^2}{\partial r_1^2} - \frac{Z}{r_1} + \frac{l_1(l_1 + 1)}{2r_1^2}, \tag{2.16}
\]

\[
\hat{H}_{l_2} = -\frac{1}{2} \frac{\partial^2}{\partial r_2^2} - \frac{Z}{r_2} + \frac{l_2(l_2 + 1)}{2r_2^2}. \tag{2.17}
\]
2.2: SCHRÖDINGER EQUATION

We will now proceed to perform a partial-wave expansion of the left-hand-side (LHS) of (2.6) by substituting (2.7), (2.11), (2.16) and (2.17), which yields

\[
\text{LHS} = (E - \hat{H}) \Psi_{i,sc}^{S(+)} = \frac{1}{r_1 r_2} \sum_{l_1 l_2 LM} (E - \hat{H}_{l_1} - \hat{H}_{l_2} - \hat{H}_{12}) \psi_{l_1 l_2}^{LMSH} (r_1, r_2) Y_{l_1 l_2}^M (\hat{r}_1, \hat{r}_2).
\]  

(2.18)

To remove the angular dependence and the singularities at \( r_1 = 0 \) and \( r_2 = 0 \) we use the transformation

\[
\mathcal{T}(f) = r_1 r_2 \int d\hat{r}_1 \int d\hat{r}_2 \mathcal{Y}_{l_1 l_2}^{L'M'*} (\hat{r}_1, \hat{r}_2) f,
\]

(2.19)

where \( |l_1' l_2' L'M'| \) is an arbitrarily selected state of angular momentum. In bra-ket notation (2.18) becomes

\[
\mathcal{T}(\text{LHS}) = \sum_{l_1 l_2 LM} \langle l_1' l_2' L'M'| (E - \hat{H}_{l_1} - \hat{H}_{l_2} - \hat{H}_{12}) |l_1 l_2 LM \rangle \psi_{l_1 l_2}^{LMSH} (r_1, r_2).
\]

(2.20)

The orthogonality of the bipolar spherical harmonic function (A.11) ensures that \( E \) and the single-electron Hamiltonian operators, which have no angular dependence, are non-zero only when \( l_1' = l_1, \ l_2' = l_2, \ L' = L, \) and \( M' = M, \) allowing (2.20) to be simplified to

\[
\mathcal{T}(\text{LHS}) = (E - \hat{H}_{l_1} - \hat{H}_{l_2}) \psi_{l_1 l_2}^{LM'SH} (r_1, r_2) - \sum_{l_1 l_2 LM} \langle l_1' l_2' L'M' | \frac{1}{r_{12}} |l_1 l_2 LM \rangle \psi_{l_1 l_2}^{LM'SH} (r_1, r_2).
\]

(2.21)

Equation (A.25) gives an analytic non-integral expression for \( \langle l_1' l_2' L'M' | \frac{1}{r_{12}} |l_1 l_2 LM \rangle \), which is non-zero only when \( L = L' \) and \( M = M'. \) It is referred to as the reduced-matrix element of \( \frac{1}{r_{12}} \) and is represented by \( \langle l_1' l_2' || \frac{1}{r_{12}} || l_1 l_2 \rangle_L. \) We may now give our transformed partial-wave expansion of the LHS as

\[
\mathcal{T}(\text{LHS}) = (E - \hat{H}_{l_1} - \hat{H}_{l_2}) \psi_{l_1 l_2}^{LM'SH} (r_1, r_2) - \sum_{l_1 l_2 LM} \langle l_1 l_2 || \frac{1}{r_{12}} || l_1' l_2' \rangle_L \psi_{l_1' l_2'}^{LM'SH} (r_1, r_2),
\]

(2.22)

where we have reversed the primed and unprimed arguments, making \( \langle l_1 l_2 LM \rangle \) the arbitrarily selected state. We should note that the reduced matrix element does not connect states of different total parity, so the summation over \( l_1' l_2' \) is limited to those states that satisfy the parity relation \((-1)^H = (-1)^{L+l_1'+l_2'} \).
The derivation of Baertschy et al (2001b) for the incident wave function of an $e$–H collision used a plane wave $e^{i\mathbf{k}_i \cdot \mathbf{r}}$ to represent the incident electron moving in free space with initial momentum $\mathbf{k}_i$, multiplied by the wave function of the ground-state hydrogen target. However, to allow for scattering and ionisation from charged hydrogenic targets ($Z > 1$), we will use an incoming Coulomb wave $\Phi_c^-(Z-1; \mathbf{k}_i, \mathbf{r})$ to represent the electron moving in a field of central charge $Z-1$, multiplied by the wave function of a hydrogenic target $\Phi_i(\mathbf{r}_1)$. Here, the $i$ subscript represents the charge $Z$ and initial state $|n_i l_i m_i\rangle$ of the hydrogenic target.

As the incident and bound electrons are indistinguishable, we symmetrise the incident wave function with respect to exchange of the electron coordinates $r_1$ and $r_2$. This gives the incident wave function the final form

$$\Psi_{i,\text{inc}}^{S}(r_1, r_2) = \frac{1}{\sqrt{2}} \left( \Phi_i(r_1) \Phi_c^-(Z-1; \mathbf{k}_i, r_2) + (-1)^S \Phi_i(r_2) \Phi_c^-(Z-1; \mathbf{k}_i, r_1) \right), \quad (2.23)$$

where to ensure that our derivation is equivalent to Baertschy et al for $Z = 1$, the Coulomb wave is normalised so that

$$\Phi_c^-(0; \mathbf{k}, \mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}}. \quad (2.24)$$

Substituting (2.23) and the relations

$$\hat{H}_1 \Phi_i(r_1) = \epsilon_i \Phi_i(r_1), \quad (2.25)$$

$$E = \frac{1}{2} k_i^2 + \epsilon_i, \quad (2.26)$$

and

$$\hat{H}_2 \Phi_c^-(Z-1; \mathbf{k}_i, r_2) = \left( \frac{1}{2} k_i^2 - \frac{1}{r_2} \right) \Phi_c^-(Z-1; \mathbf{k}_i, r_2), \quad (2.27)$$

into the RHS of (2.6) gives

$$\text{RHS} = (\hat{H} - E) \Psi_{i,\text{inc}}^{S}(r_1, r_2) = \frac{1}{\sqrt{2}} \left\{ \left( \hat{H}_{12} - \frac{1}{r_2} \right) \Phi_i(r_1) \Phi_c^-(Z-1; \mathbf{k}_i, r_2) \right. \right. \left. \left. + (-1)^S \left( \hat{H}_{12} - \frac{1}{r_1} \right) \Phi_i(r_2) \Phi_c^-(Z-1; \mathbf{k}_i, r_1) \right\}. \quad (2.28)$$

To proceed, we use a partial-wave expansion for a Coulomb wave, normalised as given in (2.24)

$$\Phi_c^-(Z; \mathbf{k}, \mathbf{r}) = \frac{4\pi}{kr} \sum_{lm} Y_{lm}^*(\hat{k}) Y_{lm}(\hat{r}), \quad (2.29)$$
where \( \phi_i(Z; k, r) \) is the regular Coulomb radial wave function normalised as \( \phi_0(0; k, r) = \sin(kr) \), the Coulomb phase is given by

\[
\sigma_l(Z, k) = \arg \left( \frac{\Gamma(l + 1) - iz}{k} \right),
\]

and \( Y_{lm} \) is the spherical harmonic function (see Section A.1). We also separate the hydrogenic wave function into its radial and angular components using

\[
\Phi_i(r) = \frac{1}{r} \phi_{nl_i}(Z; r) Y_{lm_i}(\hat{r}),
\]

which yields

\[
\text{RHS} = \frac{2\sqrt{2\pi}}{r_1 r_2 k_i} \sum_{lmLM} i^l e^{-i\sigma_l(Z-1,k_i)} \left\{ \left( \mathbf{H}_{12} - \frac{1}{r_2} \right) \phi_{n_l_i}(Z; r_1) \phi_l(Z-1; k_i, r_2) Y_{lm_i}(\hat{r}_1) Y_{lm}(\hat{r}_2) \right. \\
+ (-1)^S \left( \mathbf{H}_{12} - \frac{1}{r_1} \right) \phi_{n_l_i}(Z; r_2) \phi_l(Z-1; k_i, r_1) Y_{lm_i}(\hat{r}_1) Y_{lm}(\hat{r}_2) \left. \right\} Y_{lm_i}^* \mathbf{\hat{k}}_i.
\]

Using the inverse relation (A.13) to transform the spherical harmonic functions (of \( \hat{r}_1 \) and \( \hat{r}_2 \)) into bipolar spherical harmonic functions, we obtain

\[
\text{RHS} = \frac{2\sqrt{2\pi}}{r_1 r_2 k_i} \sum_{lmLM} i^l e^{-i\sigma_l(Z-1,k_i)} Y_{lm_i}^* (\mathbf{\hat{k}}_i) \left\{ \left( \mathbf{H}_{12} - \frac{1}{r_2} \right) \phi_{n_l_i}(Z; r_1) \phi_l(Z-1; k_i, r_2) \right. \\
\times C_{l,m_l,m_i}^{LM} Y_{l,m_i}^{LM} (\hat{r}_1, \hat{r}_2) + (-1)^S \left( \mathbf{H}_{12} - \frac{1}{r_1} \right) \phi_{n_l_i}(Z; r_2) \phi_l(Z-1; k_i, r_1) \\
\times C_{l,m_l,m_i}^{LM} Y_{l,m_i}^{LM} (\hat{r}_1, \hat{r}_2) \left. \right\},
\]

which after transformation by (2.19) gives

\[
T(\text{RHS}) = \frac{2\sqrt{2\pi}}{k_i} \sum_{lm} i^l e^{-i\sigma_l(Z-1,k_i)} Y_{lm_i}^* (\mathbf{\hat{k}}_i) \left\{ \left( \mathbf{H}_1^L \mathbf{1}_2^L \parallel \frac{1}{r_1} \mathbf{L}_L \right) - \frac{1}{r_2} \delta_{l_1 l} \delta_{l_2 l} \right\} C_{l,m_l,m_i}^{LM'} \\
\times \phi_{n_l_i}(Z; r_1) \phi_l(Z-1; k_i, r_2) + (-1)^S \left( \mathbf{H}_1^L \mathbf{1}_2^L \parallel \frac{1}{r_1} \mathbf{L}_L \right) - \frac{1}{r_1} \delta_{l_1 l} \delta_{l_2 l} \right\} C_{l,m_l,m_i}^{LM'} \\
\times \phi_{n_l_i}(Z; r_2) \phi_l(Z-1; k_i, r_1) \left. \right\}.
\]

By convention we set the direction of the incident electron along the z-axis, without loss of generality, where the spherical harmonic function \( Y_{lm}(\mathbf{\hat{k}}_i) \) is non-zero only when \( m=0 \).
Using (A.5) along with the parity relation (2.13) and the Clebsch-Gordan and reduced matrix element symmetry relations [(A.20) and (A.29)] we arrive at our final form for the transformation of the RHS

$$T(RHS) = \frac{1}{k_i} \sum_{l} \sqrt{2\pi(2l+1)} C_{l,m_i \to 0}^{LM} i^l e^{-i\sigma_l(Z-1,k_i)} \left\{ \left( \langle l_1 l_2 \parallel l_i l \rangle_L - \frac{1}{r_2} \delta_{l_1 l} \delta_{l_2 l} \right) \right.$$

$$\times \phi_{n_i l_i}(Z; r_1) \phi_l(Z-1; k_i, r_2) + (-1)^{S+\Pi} (1 \leftrightarrow 2) \right\},$$

(2.35)

where \((1 \leftrightarrow 2)\) exchanges \(l_1\) with \(l_2\) and \(r_1\) with \(r_2\), and like the LHS we have exchanged the primed and unprimed variables. The summation is over all \(l\) such that

$$|l_i - l| \leq L \leq l_i + l,$$

(2.36)

and that parity is conserved (between the initial and final states), noting that by the properties of the Clebsch-Gordan coefficient (A.16) the equation has non-zero solutions only when \(M = m_i\).

We may now equate (2.22) with (2.35) to give the partial-wave expansion of the time-independent Schrödinger equation for the collisions considered in this thesis as

$$(E - \hat{H}_{l_i} - \hat{H}_{l_2}) \psi_{i,i_1;i_2}^{LMSH}(r_1, r_2) - \sum_{l_1, l_2} \langle l_1 l_2 \parallel l_i l \rangle_L \psi_{i,i_1;i_2}^{LMSH}(r_1, r_2) = \chi_{i,i_1;i_2}^{LMSH}(r_1, r_2),$$

(2.37)

where

$$\chi_{i,i_1;i_2}^{LMSH}(r_1, r_2) = \frac{1}{k_i} \sum_{l} \sqrt{2\pi(2l+1)} C_{l,m_i \to 0}^{LM} i^l e^{-i\sigma_l(Z-1,k_i)} \left\{ \left( \langle l_1 l_2 \parallel l_i l \rangle_L - \frac{1}{r_2} \delta_{l_1 l} \delta_{l_2 l} \right) \right.$$

$$\times \phi_{n_i l_i}(Z; r_1) \phi_l(Z-1; k_i, r_2) + (-1)^{S+\Pi} (1 \leftrightarrow 2) \right\}. $$

(2.38)

For the special case of ground-state hydrogen targets we set \(Z=1, n_i=1, l_i=0\) and \(m_i=0\), which gives \(M=0, \Pi=0, l=L, \sigma_l=0, \phi_L(0; k_i, r) = j_L(k_i r)\) and \(C_{L0}^{L0} = 1\), where \(j_L\) is the Riccati-Bessel function, and our derivation reduces to that given in Baertschy et al (2001b).

We should note that \(\chi_{i,i_1;i_2}^{LMSH}\) contains both incoming and outgoing waves and, as incoming waves diverge under the ECS transformation, it must be truncated in the
2.3 Scattering amplitude

region \( r_1 > R_0 \) or \( r_2 > R_0 \). McCurdy et al (2001) observed that a sharp cut off at \( R_0 \) resulted in small diffraction effects (oscillations) in the extracted cross sections, so used a rapid, but smooth, cut off near the hyperradius \( \rho = \sqrt{r_1^2 + r_2^2} = R_0 \). We have used the same cut off method, where

\[
\tilde{\chi}_{1l_1l_2}^{LMSH}(r_1, r_2) = \left\{ \begin{array}{ll}
\exp \left[ -(\rho/R_0)^{3/2} \right] \chi_{1l_1l_2}^{LMSH}(r_1, r_2), & \rho \leq R_0 \\
0, & \rho > R_0.
\end{array} \right. \tag{2.39}
\]

This is the only systematic, though controlled, approximation used in the ECS method for calculating the scattering wave function.

We will now proceed to derive a method for extracting the scattering amplitudes and the differential and total cross sections for discrete final-state collisions from the partial-wave scattering wave functions.

2.3 Scattering amplitude

The scattering wave function \( \Psi_{i,sc}^{S(+)}(r_1, r_2) \), calculated using (2.11) and (2.37), gives the probability amplitude for finding the electrons at the positions \( r_1 \) and \( r_2 \) after the collision, but does not directly give information on the scattering processes open to the collision. In this section we will derive the scattering amplitude for elastic and inelastic discrete final-state collisions \( F_j^S(\hat{k}_j) \), in terms of the scattering wave function \( \Psi_{i,sc}^{S(+)}(r_1, r_2) \), which will give the probability amplitude of all possible observable outcomes of these collisions.

Formally, the asymptotic behaviour of the time-independent outgoing scattering wave function for discrete final-state scattering is defined in terms of the scattering amplitude

\[
\Psi_{i,sc}^{S(+)}(r_1, r_2) \sim \frac{1}{\sqrt{2}} \sum_{n_j l_j m_j} \Phi_j^S(r_1) e^{i(k_j r_2 + \frac{j}{2} - 1 \ln(2k_j r_2))} F_{ji}^S(\hat{k}_j), \tag{2.40}
\]

where we have arbitrarily chosen \( r_1 \) for the bound electron and \( r_2 \) for the scattered electron. The \( j \) subscript represents the nuclear charge \( Z \) and final state \( |n_j l_j m_j\rangle \) of the hydrogenic target, and the initial state \( i \) is as defined on page 11 (making \( F_{ji}^S(\hat{k}_j) \) also dependent on \( k_i \), which is directed along the \( z \)-axis in our derivations). The leading constant \( 1/\sqrt{2} \) ensures that this wave function is normalised to the symmetrised scattering
wave function calculated using (2.11) and (2.37), and the magnitude of the initial and
final momentum of the scattered electron are related by
\[ k_j^2 = k_i^2 - Z^2 \left( \frac{1}{n_i^2} - \frac{1}{n_j^2} \right). \]  
(2.41)

For ionising collisions, Peterkop (1977) gives the ionisation amplitude as
\[ I^S(k_1, k_2) \sim \int dr_1 \int dr_2 \Psi^S(r_1, r_2)(\hat{H} - E)\Phi_{k_1 k_2}^{S(-)*}(r_1, r_2), \]  
(2.42)
where, \( \Phi_{k_1 k_2}^{S(-)} \) is a wave function that satisfies the asymptotic final-state boundary con-
ditions of the ionising collision. We will define discrete final-state scattering amplitudes
by adapting this relation to the form
\[ I^S_{ji}(\hat{k}_j) \sim \int dr_1 \int dr_2 \Psi_i^{S(+)}(r_1, r_2)(\hat{H} - E)\Phi_j^{S(-)*}(k_j, r_1, r_2), \]  
(2.43)
where \( \Phi_j^{S(-)} \) is an incoming discrete final-state wave function whose form we specify later,
and proceed to verify that asymptotically \( I^S_{ji}(\hat{k}_j) \) and \( F^S_{ji}(\hat{k}_j) \) are related functions. This
approach was suggested and developed by McCurdy et al (2002) for model problems. We
have introduced \( S \) labelling in these equations as spin is conserved in the collision and the
scattering amplitudes for singlet and triplet spin states may be calculated independently.

Firstly, using the standard vector identity
\[ \Phi \nabla^2 \Psi - \Psi \nabla^2 \Phi \equiv \nabla \cdot (\Phi \nabla \Psi - \Psi \nabla \Phi), \]  
(2.44)
the divergence theorem \( \int_V \nabla \cdot A dv = \oint S A \cdot dS \) and the Schrödinger equation \( (\hat{H} - E)\Psi_i^{S(+)} = 0 \) we can transform (2.43) to a surface integral in one of the coordinates,
which gives (omitting dependent variables in these intermediate steps to improve clarity)
\[ I^S_{ji} \sim \frac{1}{2} \left\{ \int dr_1 \int_{S_2} \left( \Phi_j^{S(-)*} \nabla_2 \Psi_i^{S(+)} - \Psi_i^{S(+)} \nabla_2 \Phi_j^{S(-)*} \right) \cdot dS_2 \right. \]
\[ + \left. \int dr_2 \int_{S_1} \left( \Phi_j^{S(-)*} \nabla_1 \Psi_i^{S(+)} - \Psi_i^{S(+)} \nabla_1 \Phi_j^{S(-)*} \right) \cdot dS_1 \right\}, \]  
(2.45)
where the surface integrals are taken at \( r_2 \to \infty \) and \( r_1 \to \infty \), respectively. This can be
simplified further if symmetrised wave functions are used, as the two integral expressions
have the same value, giving
\[ I^S_{ji} \sim \int dr_1 \int d\hat{r}_2 r_2^2 \left\{ \Phi_j^{S(-)*} \frac{\partial}{\partial \hat{r}_2} \Psi_i^{S(+)} - \Psi_i^{S(+)} \frac{\partial}{\partial \hat{r}_2} \Phi_j^{S(-)*} \right\}, \]  
(2.46)
where we have replaced the outgoing full wave function $\Psi_1^{S(+)}$ with the outgoing scattering wave function $\Psi_{i,sc}^{S(+)}$ as the incident wave function does not contribute to the integral. We note that, for energies above ionisation threshold, $\Psi_{i,sc}^{S(+)}$ also contains ionisation information, but this does not affect the scattering amplitude calculated using (2.46) due to the orthogonality of a Coulomb wave representing the ionised electron $\Phi_c^-(Z; k_1, r_1)$ with all hydrogenic bound states of charge $Z$.

Finally, we use the freedom afforded by the fact that we only need specify the symmetrised asymptotic form of the incoming scattering wave function for discrete final-state collisions to write

$$
\Phi_j^{S(-)}(k_j, r_1, r_2) \sim \frac{1}{r_2 \to \infty} \frac{1}{\sqrt{2}} (\Phi_j(r_1) \Phi_c^-(Z-1; k_j, r_2))
$$

(2.47)

We then substitute (2.47), an asymptotic expansion of an incoming Coulomb wave

$$
\Phi_c^-(Z; k, r) \sim \delta(\hat{k} - \hat{r}) \frac{2\pi}{1kr} e^{ikr + i\frac{Z}{2} \ln(2kr)} + \frac{\hat{r} \times (-\hat{k} \cdot \hat{r})}{r} e^{-ikr - i\frac{Z}{2} \ln(2kr)}, \quad (2.48)
$$

(normalised such that $\Phi_c^-(0; k; r) = e^{-ikr}$) and (2.40) into (2.46), and remove terms that asymptotically approach zero, which gives

$$
F_{ji}^S(\hat{k}_j) = -\frac{1}{2\pi} I_{ji}^S(\hat{k}_j).
$$

(2.49)

We have not given the functional form for $\hat{f}$ since, through cancellation, only the first term of (2.48) contributes to the result. Therefore, in the asymptotic limit $F_{ji}^S(\hat{k}_j)$ and $I_{ji}^S(\hat{k}_j)$ are equivalent, apart from an overall multiplying constant, and our integral expression for the scattering amplitude becomes

$$
F_{ji}^S(\hat{k}_j) \sim \frac{1}{2\pi} \int dr_1 \int d\hat{r}_2 r_2^2 \left\{ \Phi_j^{S(-)*}(k_j, r_1, r_2) \frac{\partial}{\partial r_2} \Psi_{i,sc}^{S(+)}(r_1, r_2) - \Psi_{i,sc}^{S(+)}(r_1, r_2) \frac{\partial}{\partial r_2} \Phi_j^{S(-)*}(k_j, r_1, r_2) \right\}. \quad (2.50)
$$

In the previous sections we have given details on the ECS method for obtaining solutions for the $e$–$H_Z$ scattering wave functions directly with a single controlled approximation. The method we have developed for obtaining scattering amplitudes relies on applying an asymptotic integral at a finite radius. This is a controlled approximation,
as from a single scattering wave function we can easily investigate the radial convergence of (2.50), and therefore estimate the error introduced by applying the asymptotic integral at \( R_0 \).

We will now proceed to derive a partial-wave expansion of (2.50). Substituting the partial-wave expansions for the scattering wave function (2.11) and Coulomb wave function (2.29), the symmetrised discrete final-state wave function (2.47) (the second term is ignored as it is asymptotically zero), the hydrogenic wave function expansion (2.31), and the bipolar spherical harmonic relation (A.8), gives

\[
F_{ji}^S(\hat{k}_j) \sim \frac{-\sqrt{2}}{k_j} \sum_{lm} i^{-l} e^{i \sigma_i (Z-1, k_j)} Y_{lm}(\hat{k}_j) \sum_{l_1 LM} \sum_{m_1 m_2} C_{l_1 m_1 l_2 m_2}^{LM} \times \int d\hat{r}_1 Y_{l_1 m_1}^\ast (\hat{r}_1) Y_{l_1 m_1}(\hat{r}_1) \int d\hat{r}_2 Y_{l_2 m_2}^\ast (\hat{r}_2) Y_{l_2 m_2}(\hat{r}_2) \times \int dr_1 r_2 \phi_{n_j l_j}(Z; r_1) \left\{ \phi_l(Z - 1; k_j, r_2) \frac{\partial}{\partial r_2} \frac{1}{r_2} \psi_{l_1 l_2}^{LMS} (r_1, r_2) - \psi_{l_1 l_2}^{LMS} (r_1, r_2) \frac{\partial}{\partial r_2} \frac{1}{r_2} \phi_l(Z - 1; k_j, r_2) \right\} \tag{2.51}
\]

We note that the spherical harmonic orthogonality relation (A.3) results in the angular integrals becoming unity when \( l_1 = l_j \), \( m_1 = m_j \), \( l = l_2 \) and \( m = m_2 \), and zero otherwise. Also, from the Clebsch-Gordan condition (A.16), we see that \( m_2 = M - m_j \), so the scattering amplitude partial-wave expansion simplifies to

\[
F_{ji}^S(\hat{k}_j) = \sum_{l_2 LM} i^{-l_2} e^{i m_2 (Z-1, k_j)} C_{l_1 m_1 l_2 M - m_j}^{LM} Y_{l_2 M - m_j}(\hat{k}_j) f_{ji, l_2}^{LMS} \tag{2.52}
\]

where the summation is over all \( l_2 LM \) such that \( |l_j - l_2| \leq L \leq l_j + l_2 \), \( |M| \leq L \), which coherently sums all possible parity states, and where

\[
f_{ji, l_2}^{LMS} \sim -\frac{\sqrt{2}}{k_j} \int dr_1 r_2 \phi_{n_j l_j}(Z; r_1) \left\{ \phi_{l_2}(Z - 1; k_j, r_2) \frac{\partial}{\partial r_2} \frac{1}{r_2} \psi_{l_1 l_2}^{LMS} (r_1, r_2) - \psi_{l_1 l_2}^{LMS} (r_1, r_2) \frac{\partial}{\partial r_2} \frac{1}{r_2} \phi_{l_2}(Z - 1; k_j, r_2) \right\} \tag{2.53}
\]

The total scattering cross section for a given \( S \) is evaluated from the scattering amplitude using

\[
\sigma_{ji}^S = \frac{k_j}{k_i} \int d\hat{k}_j \left| F_{ji}^S(\hat{k}_j) \right|^2, \tag{2.54}
\]

and by using the spherical harmonic relation (A.3) the angular integral can be removed,
2.4: IONISATION AMPLITUDE

giving

\[ \sigma_{ji}^S = \frac{k_j}{k_i} \sum_{l_2LM} |f_{ji,l_2}^{LMs}\|^2. \]  
(2.55)

We have included an explicit summation over parity in (2.52) and (2.55) to emphasise the contribution of both parity states, but as parity is determined by \((-1)^H = (-1)^{l_1+l_2+L}\) its inclusion is redundant. The total cross section is the sum of the cross sections for each spin state multiplied by the spin weighting factor \(\frac{2S+1}{4}\),

\[ \sigma_{ji} = \sum_S \frac{2S+1}{4} \sigma_{ji}^S. \]  
(2.56)

and the spin-weighted differential scattering cross section is given by

\[ d\sigma_{ji} = \frac{k_j}{k_i} \sum_S \frac{2S+1}{4} |F_{ji}^S(k_j)|^2 d\hat{k}_j. \]  
(2.57)

A quantity related to the scattering cross section, and often the subject of experimental measurement, is the spin asymmetry, which gives the relative magnitude of the singlet and triplet cross sections. Spin asymmetry is defined in terms of the separate spin cross sections (without spin weighting) as

\[ A_{ji} = \frac{\sigma_{ji}^0 - \sigma_{ji}^1}{\sigma_{ji}^0 + 3\sigma_{ji}^1}, \]  
(2.58)

and is a dimensionless quantity in the range \(-\frac{1}{2} \leq A_{ji} \leq 1\).

This finalises our derivation for the scattering amplitude and scattering cross section equations for the elastic and inelastic discrete final-state collision of an electron with a hydrogenic target in an arbitrary initial state. In the following section we will derive equations for the ionisation amplitude of break-up collisions, also using the Peterkop integral method.

2.4 Ionisation amplitude

The integral formulation of the ionisation amplitude that we use in this thesis is discussed at length by Peterkop (1977), so we will not repeat his derivations, but simply give the relevant final equations. This method has been used successfully by Baertschy et al (2001a), though is modified slightly here for hydrogenic targets. The procedure
that Peterkop used is similar to that used in the previous section to derive an integral expression for the scattering amplitude. One significant difference is that Peterkop chose to use six-dimensional hyperspherical coordinates, and the surface integral was taken on a hypersphere of hyperradius $\rho$. The final form for the ionisation amplitude can therefore be given, excluding an overall phase factor (independent of $\rho$), as

$$F_S^{\ell}(k_1, k_2) \sim \frac{1}{8\pi^{5/2}} \int d\hat{r}_1 \int d\hat{r}_2 \int_0^{\pi/2} d\alpha \, \rho^5 \sin^2 \alpha \cos^2 \alpha \times \left\{ \Phi_{Z,k_1 k_2}^{(-)}(r_1, r_2) \frac{\partial}{\partial \rho} \Psi_{i,sc}^{S(+)}(r_1, r_2) \right. $$

$$- \left. \Psi_{i,sc}^{S(+)}(r_1, r_2) \frac{\partial}{\partial \rho} \Phi_{Z,k_1 k_2}^{(-)}(r_1, r_2) \right\},$$

(2.59)

where $\alpha = \arctan(r_2/r_1)$ is the hyperangle, $k_1$ and $k_2$ are the momenta of the continuum electrons after the collision, and $\Phi_{Z,k_1 k_2}^{(-)}$ approximates the asymptotic final-state incoming continuum waves for central charge $Z$. Note that a factor of $\sqrt{2}$ has been included in this equation, compared with Peterkop, to compensate for the $1/\sqrt{2}$ symmetrisation constant introduced in (2.23).

In order for (2.59) to converge in phase, Peterkop suggests that a product of two Coulomb functions can be used to approximate the asymptotic final-state incoming continuum waves for atomic hydrogen ($Z=1$), giving

$$\Phi_{1,k_1 k_2}^{(-)}(r_1, r_2) = \Phi_{c}^{(-)}(Z_1; k_1, r_1) \Phi_{c}^{(-)}(Z_2; k_2, r_2),$$

(2.60)

provided that the charges on the Coulomb waves satisfy

$$\frac{Z_1}{k_1} + \frac{Z_2}{k_2} = \frac{1}{k_1} + \frac{1}{k_2} - \frac{1}{|k_1 - k_2|},$$

(2.61)

which is known as the Peterkop condition. There is no known analytic form for this condition when (2.59) is expanded in partial waves, so it cannot be applied in our derivation. For the ionisation of ground state hydrogen, Baertschy et al (2001a) found that provided the same $\rho$ was used for all partial waves, the phase ambiguities introduced by using uniform charges ($Z_1=Z_2=1$) cancelled and the ionisation cross sections were radially convergent. As we are dealing with hydrogenic targets we will use the product of two Coulomb waves of charge $Z$ for the asymptotic final-state continuum waves

$$\Phi_{Z,k_1 k_2}^{(-)}(r_1, r_2) = \Phi_{c}^{(-)}(Z; k_1, r_1) \Phi_{c}^{(-)}(Z; k_2, r_2),$$

(2.62)
2.4: IONISATION AMPLITUDE

and in Section 6.3 we test that radially convergent ionisation cross sections are obtained for \( Z > 1 \).

The Peterkop formulation and phase factor divergence problem have been recently addressed in a series of papers by Kadyrov et al (2003, 2004). They showed by a general argument that the practical procedure of choosing \( Z_1 = Z_2 = 1 \) is optimal, though when applied at finite \( \rho \) the ionisation amplitude will contain radially-diminishing oscillations in both phase and magnitude. These oscillations are observed in our calculations presented in later chapters, though our calculations are generally performed at sufficiently large \( \rho \) that the magnitude of these oscillations are not significant. Importantly, their work supports the validity of this method for extracting ionisation cross sections, but does emphasise its inability to give correct and converged ionisation amplitude phase information. Kadyrov et al (2004) gives corrections to the method used here that will give formally correct ionisation amplitude phases. No measurements of ionisation amplitude phase have been made, but these corrections can be used should they become available in the future.

To obtain a partial-wave expansion for the ionisation amplitude we substitute (2.11), (2.29) and (2.62) into (2.59), which yields

\[
F_i^S(k_1, k_2) \sim 2 \sqrt{\frac{\pi}{k_1 k_2}} \sum_{l_1 m_1 l_2 m_2} \frac{1}{l_1 l_2} C_{l_1 m_1 l_2 m_2}^{LM} Y_{l_1 m_1}(\hat{k}_1) Y_{l_1 m_1}(\hat{k}_2) i^{-l_1 - l_2} e^{i(\sigma_l(Z,k_1) + \sigma_{l'}(Z,k_2))} \\
\times \int d\hat{r}_1 Y_{l_1 m_1}^*(\hat{r}_1) Y_{l_1 m_1}(\hat{r}_1) \int d\hat{r}_2 Y_{l_2 m_2}^*(\hat{r}_2) Y_{l_2 m_2}(\hat{r}_2) \\
\times \rho \int_0^{\pi/2} d\alpha \left\{ \phi_l(Z; k_1, r_1) \phi_{l'}(Z; k_2, r_2) \frac{\partial}{\partial \rho} \psi_{l_1 l_1 l_2}^{LMSII}(r_1, r_2) \\
- \psi_{l_2 l_2 l_2}^{LMSII}(r_1, r_2) \frac{\partial}{\partial \rho} \phi_l(Z; k_1, r_1) \phi_{l'}(Z; k_2, r_2) \right\}.
\]

(2.63)

We note that the spherical harmonic orthogonality relation (A.3) results in the \( \hat{r}_1 \) and \( \hat{r}_2 \) integrals becoming unity when \( l = l_1, m = m_1, l' = l_2 \) and \( m' = m_2 \), and zero otherwise, so the ionisation amplitude partial-wave expansion simplifies to

\[
F_i^S(k_1, k_2) = \sum_{l_1 l_2 LMSII} i^{-l_1 - l_2} e^{i(\sigma_l(Z,k_1) + \sigma_{l'}(Z,k_2))} Y_{l_1 l_2}^{LM}(\hat{k}_1, \hat{k}_2) f_{l_1 l_1 l_2}^{LMSII}(k_1, k_2)
\]

(2.64)
where
\[ f_{i,l_1l_2}^{LMS} (k_1, k_2) \sim \frac{2}{\sqrt{\pi}} \frac{\rho}{k_1k_2} \int_0^{\pi/2} d\alpha \left\{ \phi_{l_1} (Z; k_1, r_1) \frac{\partial}{\partial \rho} \psi_{i,l_1l_2}^{LMS} (r_1, r_2) - \psi_{i,l_1l_2}^{LMS} (r_1, r_2) \frac{\partial}{\partial \rho} \phi_{l_1} (Z; k_1, r_1) \phi_{l_2} (Z; k_2, r_2) \right\}. \]

(2.65)

Once again, we have included an explicit summation over parity states in (2.64) to emphasise the coherent addition of parity states, though its inclusion is redundant.

The total ionisation cross section for a given \( S \) is evaluated from the ionisation amplitude using
\[ \sigma_i^S = \int_0^{E/2} d\epsilon_2 \int k_1 k_2 \frac{k_i}{k_i} |F_{i}^S (k_1, k_2)|^2, \]

(2.66)
where \( \epsilon_2 \) is the energy of one of the outgoing electrons. As the scattering wave function is symmetrised with respect to electron exchange, the energy integration is limited to \( E/2 \).

By using the spherical harmonic relation (A.3) the angular integrals can be removed, giving
\[ \sigma_i^S = \sum_{L^M^N^I} \int_0^{E/2} d\epsilon_2 \frac{k_1 k_2}{k_i} |f_{i,l_1l_2}^{LMS} (k_1, k_2)|^2. \]

(2.67)

The total ionisation cross section (with spin weighting) is given by
\[ \sigma_i = \sum_S \frac{2S + 1}{4} \sigma_i^S, \]

(2.68)
the fully-differential ionisation cross section (with spin weighting) is given by
\[ d\sigma_i (k_1, k_2) = \sum_S \frac{2S + 1}{4} \frac{k_1 k_2}{k_i} |F_{i}^S (k_1, k_2)|^2 d\hat{k}_1 d\hat{k}_2 d\epsilon_2, \]

(2.69)
and the spin asymmetry is as defined in (2.58), though with suitable adjustment of the subscripts so as to refer to the ionisation cross sections.

This finalises our derivation for the ionisation amplitude and ionisation cross section equations for the electron-impact ionisation of a hydrogenic target in an arbitrary initial state. In the following chapter we will discuss methods for obtaining numerical solutions to the scattering wave function equations and the scattering and ionisation cross section equations that have been developed in this chapter.
In Chapter 2 we derived the partial-wave time-independent Schrödinger equation for \( e^{-}\text{H}_2 \) collisions with arbitrary initial state. There is no known analytic solution to this equation, however, the equation is a relatively simple, coupled, second-order differential equation that can be solved using numerical approximation techniques if sufficient boundary conditions are known. Two known boundary conditions are

\[
\psi_{i,l_1l_2}(r_1,0) = 0 \quad \text{and} \quad \psi_{i,l_1l_2}(0,r_2) = 0,
\]

and with exterior complex scaling (2.1) we can closely approximate the outer boundary conditions by

\[
\psi_{i,l_1l_2}(r_1,R_{\text{max}}) \approx 0 \quad \text{and} \quad \psi_{i,l_1l_2}(R_{\text{max}},r_2) \approx 0,
\]

where \( R_{\text{max}} \) is made sufficiently larger than \( R_0 \) (the start of the complex scaling region) such that exponential damping of the outgoing wave function results in an outer boundary condition that can be set arbitrarily close to zero. We now have sufficient boundary conditions to solve (2.37) numerically.

The Coulomb interaction is a long-range force, and the charged final-state particles of an ionising collision continue interacting until their separation becomes infinite. Does this require the numerical grid to be infinite, and thus make numerical methods impractical? Rescigno et al (1999) demonstrated that radially convergent solutions are obtained for \( e^{-}\text{H}_2 \) collisions at low-intermediate energies by setting the grid size sufficiently large (\( R_0 \approx 100 \text{ a.u.} \)), ensuring that the Coulomb interactions are effectively complete. However, a large number of \( (l_1, l_2) \) states were necessary for good convergence, which, combined with the large \( R_0 \) and sufficiently fine grid spacing, resulted in an extremely large set of coupled linear equations (giving a sparse-matrix equation of the order of 6 million columns for each \( LS \) partial wave). Solving these equations required a massively-parallel supercomputer. As the total energy approaches ionisation threshold
an increasingly larger $R_0$ is required for convergence, and at higher energies or for excited initial-states an increased number of $L$ partial waves and coupled states of angular momentum $(l_1, l_2)$ must be included. With present supercomputer technology, these significantly larger calculations are impractical with their $e$–H ECS implementation.

In this chapter we will develop an alternative method for finding solutions to the ECS equations that has proven to be extremely computationally efficient. This method allows very-low energy, higher energy, and excited state collisions of hydrogen and hydrogenic ions to be explored easily with moderate computing resources.

3.1 Numerical grid

Selecting an appropriate grid is the first step towards minimising the computational effort required to numerically solve $e$–H$_Z$ collisions. Though the ECS technique has been demonstrated with both finite element and finite-difference numerical methods (Rescigno et al 1997, 1999), we will restrict our discussion to numerical grids that support finite-difference methods suitable for use with the propagation technique introduced in Section 3.3.

If we consider the symmetry of the $e$–H$_Z$ scattering wave function with respect to exchange of the radial coordinates

$$\psi^{LMSII}_{l_1,l_2} (r_1, r_2) = (-1)^{S+L+l_1+l_2} \psi^{LMSII}_{l_1,l_2} (r_2, r_1),$$

then we have two choices for solving the wave functions that minimise duplicate computations. We can solve for a) a square grid $r_1, r_2 \leq R_{\text{max}}$ and only $l_1 \leq l_2$, as undertaken by Rescigno et al (1999), or b) a triangular grid $r_2 \leq r_1 \leq R_{\text{max}}$ for all $(l_1, l_2)$.

For the present, let us make the simplistic assumption that finding solutions to our coupled grid equations requires $O(N^x)$ mathematical operations, where $N$ is the number of points in our grid, $x > 1$, and that we only consider even parity. For $L = 0$, where $l_1 = l_2$, method b) requires half of the grid points, resulting in a $O(2^x)$ reduction in computational effort. For odd $L$, where $l_1 \neq l_2$, both methods are equivalent, and for even $L$ method b) has a $O([4/3]^x)$ reduction for $L=2$, but diminishing to unity for higher $L$. 

3.1: NUMERICAL GRID

Figure 3.1: Triangular grid bounded by $r_2 = 0$, $r_1 = R_{\text{max}}$ and $r_1 = r_2$, with variable grid spacing. Real grid points are at intersecting blue lines ($r \leq R_0$) and complex grid points are at intersecting red lines ($r > R_0$). The inset shows the grid spacing $h$ and $t$, either real or complex, and the grid column and row numbers $i$ and $j$ in the $r_1$ and $r_2$ directions, respectively. The grid expansion (or contraction) ratios $\alpha$ and $\beta$ may be either real or complex, where $\alpha = \beta = 1$ would represent uniform grid spacing about the grid column $i$ and row $j$.

Clearly, using a triangular grid gives computational advantages, especially for the $L = 0$ partial waves that are used in most model calculations, hence this grid system will be used in this thesis. Triangular grids have been used successfully for model $e$–$H$ scattering (Poet 1980) and ionisation (Jones and Stelbovics 1999) problems and for the full $e$–$H$ scattering problem (Wang and Callaway 1993, 1994).

The second consideration when attempting to minimise computational effort is to maximise grid spacing (reducing grid points) while maintaining the required numerical accuracy. Previous model calculations (Jones and Stelbovics 2002) showed that finer grid spacing is required near the nucleus (where Coulomb potentials are stronger) than for the outer region, which is consistent with ECS calculations (Baertschy et al. 2001b).
A representative grid is shown in Figure 3.1, which uses varying spacing in the real region and finer spacing about the transition to complex scaling \((R_0)\) where the scattering wave function has discontinuous derivatives (see Fig. 2.1b). Further details on the grid spacing used for our calculations will be given in Section 5.2. For now though, it is sufficient to note that the grid spacing is symmetric with respect to exchange of \(r_1\) and \(r_2\), and that the finite difference scheme used to solve \(\psi^{LMS}_{i_1i_2}\) at the point \((i,j)\) must allow different spacing in each direction as well as a transition from real to complex spacing of one or both coordinates.

Having defined our grid we will now consider a finite-difference scheme to solve (2.37) numerically.

### 3.2 Numerov formulae

To simplify our discussion, we will initially consider a one-dimensional evenly spaced grid. These grids are suitable for simple finite difference methods (Abramowitz and Stegun 1965, p884) that estimate second-order derivatives using \(n \geq 3\) evenly spaced grid points \((n\) is odd\) and have an error \(O(\{(h^{n-1})\psi^{(n+1)}_i\})\), where \(h\) is the grid spacing and \(\psi^{(n+1)}_i\) is the \((n+1)\)’th derivative of \(\psi\) at the \(i\)’th grid point. In fact, these formulae were used by Baertschy et al (2001b) for their ECS implementation, though adapted for variable grid spacing. There is, however, a very accurate 3-point Numerov finite-difference formula that can be used to evaluate second-order differential equations that have no first-derivative terms, as in (2.37). In one dimension, these equations have the form

\[
\frac{d^2}{dr^2} \psi(r) + \Omega(r) = 0,
\]  
(3.4)

and the Numerov formula relates three successive points of \(\psi\) \((i - 1, i\) and \(i + 1)\) along \(r\) by

\[
\psi_{i+1} = 2\psi_i - \psi_{i-1} - \frac{h^2}{12} (\Omega_{i+1} + 10\Omega_i + \Omega_{i-1}),
\]  
(3.5)

and has a leading-order error of

\[
\frac{h^6}{240} \psi^{(6)}_i.
\]  
(3.6)
This error is comparable to the standard 7-point finite-difference method, though the sparse-matrix linear equation built using the Numerov formulae has fewer non-zero diagonals, giving a significant computational advantage (see Section 4.1).

The Numerov formula has been used successfully for $e$–H model problems for scattering (Poet 1980) and ionisation (Jones and Stelbovics 1999) and the full $e$–H scattering problem (Wang and Callaway 1994), and to our knowledge has not previously been adapted for variable grids. Jones and Stelbovics (2002) used a grid-doubling method that allowed their grid spacing to be increased by integer multiples (whilst continuing to use evenly spaced points for the Numerov formula), this technique is not suitable for the transition from real to complex coordinates at $R_0$ in our grid. Therefore, we need to derive a Numerov-like formula that will allow for completely variable, and complex, changes in grid spacing.

Firstly, we will propose that a variable-spacing Numerov formula has the form

$$
\psi_{i+1} = A\psi_i - B\psi_{i-1} - \frac{h^2}{12} \left( C\Omega_{i+1} + D\Omega_i + E\Omega_{i-1} \right),
$$

(3.7)

where $h$ is the grid spacing between $r_{i-1}$ and $r_i$, and $h\alpha$ is the grid spacing between $r_i$ and $r_{i+1}$. By substituting Taylor series expansions of $\psi_{i-1}$ and $\psi_{i+1}$, about $\psi_i$, we solve the unknown coefficients, giving

$$
\psi_{i+1} = (\alpha + 1)\psi_i - \alpha\psi_{i-1} - \frac{h^2}{12} \left\{ (\alpha^2 + \alpha - 1)\Omega_{i+1} + (\alpha^3 + 4\alpha^2 + 4\alpha + 1)\Omega_i 
\right.
\left. + (-\alpha^3 + \alpha^2 + \alpha)\Omega_{i-1} \right\},
$$

(3.8)

and a leading-order error of

$$
\left( \frac{\alpha^5}{180} + \frac{\alpha^4}{72} - \frac{\alpha^2}{72} - \frac{\alpha}{180} \right) h^5 \psi^{(5)}_i,
$$

(3.9)

which is of the same order of magnitude as the variable-grid 7-point finite-difference formulae derived by Baertschy et al (2001b). Note that the error increases as a function of $\alpha^5$, so large increases in grid spacing should be avoided unless $h$ is sufficiently small. Equation (3.8) reduces to (3.5) for fixed grid spacing ($\alpha = 1$), and (3.9) reduces to zero. In this case the error is given by the next term in the series, which for $\alpha = 1$ reduces to (3.6).
CHAPTER 3: NUMERICAL METHODS

This one-dimensional formula can be readily extended to two dimensions using similar techniques to Poet (1980). The significant algebra involved in its derivation was undertaken with the Maple algebraic computing software, and checks were made to ensure that the results reduce to previously published two-dimensional formula (Poet 1980, Wang and Callaway 1993) for the special case \( \alpha = 1 \). The length of the derivation, however, precludes its inclusion in this thesis, and we simply present the final formulae in Appendix B.

There is an additional complexity when reforming the scattering wave equation (2.37) into the form of (3.4), \( \Omega_0 \) has a singularity at \( r = 0 \) due to the Coulomb potentials and the expansion of the \( \nabla^2 \) operator [see (2.14)]. For \( l = 0 \), there is a \( 1/r \) singularity, and for \( l > 0 \) there is also an \( 1/r^2 \) singularity. We resolve this problem in the same way as Wang and Callaway (1993), using the known limiting behaviour of the \( e^{-\text{H}_Z} \) scattering wave function

\[
\psi_l(r) \to ar^{l+1} \text{ as } r \to 0,
\]

where \( a \) is a constant. We can then use a polynomial approximation for \( \psi_l \) at the points \( i=0, 1, 2 \) (in one dimension),

\[
\psi_l(r) \to r^{l+1} \left( a_0 + a_1 r + a_2 r^2 + \cdots \right),
\]

when deriving the Numerov formula. We therefore require several variations of the Numerov formula to estimate \( \psi_{ij} \) depending on whether \( r_{i-1} \) and/or \( r_{j-1} \) are zero, and whether \( l_1 \) and/or \( l_2 \) are zero. All of these variations are presented in Appendix B.

It is clear from Figure 3.2 that one or more of the nine grid points required for the two-dimensional Numerov formula fall outside of the triangular grid when \( i = j \) or \( i = j + 1 \). In this case we use the symmetry of the scattering wave functions given in (3.3) to replace \( \psi_{ij} \) of state \( (l_1 l_2) \) with \( \psi_{ji} \) of state \( (l_2 l_1) \) multiplied by \( (-1)^{S+L+l_1+l_2} \). This imposes two conditions on our numerical grids: The grid must be symmetric with respect to exchange of \( r_i \) and \( r_j \), and both \( (l_1 l_2) \) and \( (l_2 l_1) \) states must be included in the coupled-state calculation when \( l_1 \neq l_2 \).
3.3: PROPAGATION METHOD

Figure 3.2: Grid points marked with hollow circles, needed for the two-dimensional Numerov formula, fall outside of the triangular grid \((r_j \leq r_i, r_j = 0\) and \(r_i = R_{\text{max}}\)) when the central grid point is at A) \(i = j\), or B) \(i = j + 1\), and must be obtained using the symmetry properties [see (3.3)] of the scattering wave function.

3.3 Propagation method

Using the grid described in Section 3.1 and the Numerov formulae in Appendix B, it is now possible to construct and solve a single matrix equation for the \(e-\text{H}_2\) scattering wave functions for each \(|LMS\Pi\rangle\) state. Indeed, this single-equation approach was used by Baertschy et al., and required a massively parallel supercomputer to obtain solutions (Baertschy and Li 2001). Though we expect computational savings for some partial waves by using a triangular grid, and additional savings by using the Numerov formula, there are limitations to using this approach. The matrix equations are of such large magnitude that they are computationally intractable using sparse-matrix LU-factorisation algorithms that require \(O(N^2)\) mathematical operations. Baertschy et al. found that a conjugate gradient squared (CGS) algorithm could iteratively solve the matrix equation with \(O(N^{3/2})\) operations by using an approximate solution as a preconditioner. They also found that solutions to the uncoupled scattering wave equations (which require significantly less computational resources) could be used for these preconditioners. However, at total energies close to the ionisation threshold, the strong electron correlation made these uncoupled solutions unsuitable for use as a preconditioner, and the CGS
iterations did not converge. For this reason the ECS method has been unable to solve
$e^{-}H$ collisions below 1 eV from threshold with the CGS iterative algorithm. For calculations
above 50 eV, more $L$ states and coupled $(l_1, l_2)$ states are required for convergence,
and they found that their available supercomputing resources were exceeded (Baertschy
et al 2001a), and the results had significant numerical error (Baertschy 2000).

In an attempt to minimize computational overhead we will use the propagation
method, based on Poet (1980), that was recently used by Jones and Stelbovics (2000)
for model $e^{-}H$ ionisation problems. However, to allow for the inhomogeneous term $\chi$
in the scattering wave (2.37), this procedure requires modification.

Rather than solving one large matrix equation (using complex arithmetic) for the
whole grid, the propagation method “solves” one column (or vector) of grid points $\vec{\psi}^{(i)}$
at a time by finding a propagating matrix $D^{(i)}$ that relates it to the next column $\vec{\psi}^{(i+1)}$.
This requires $i_{\text{max}}$ small matrix equations to be solved ($i_{\text{max}}$ represents the grid column
number associated with $R_{\text{max}}$). As a starting point, we propose that the propagation
equation has the form

$$\vec{\psi}^{(i)} = D^{(i)} \cdot \vec{\psi}^{(i+1)} + \vec{E}^{(i)}, \quad (3.12)$$

where the propagation vector $\vec{E}^{(i)}$ is introduced into our derivation to allow for the
inhomogeneous term in (2.37).

The two-dimensional variable-grid Numerov formula (B.2) is then reformed into a
matrix equation

$$A^{(i)} \cdot \vec{\psi}^{(i-1)} + B^{(i)} \cdot \vec{\psi}^{(i)} + C^{(i)} \cdot \vec{\psi}^{(i+1)} = \vec{F}^{(i)} \quad (3.13)$$

that relates the $i-1$, $i$ and $i+1$ columns of the grid using the eight nearest neighbours for
each point $\psi_{ij}$ in the column. We should note that all coupled $(l_1, l_2)$ angular momentum
states for the $LMS\Pi$ partial wave must be solved simultaneously, and if we let $n_c$
represent the number of $(l_1, l_2)$ states required for convergence of the partial wave, we
must solve $n_c$ triangular grids simultaneously. Therefore, each $\vec{\psi}^{(i)}$ vector will contain
$n_c i$ grid points. The boundary points with $r_j = 0$ are not included in these vectors.

Substituting (3.13) into (3.12) gives

$$D^{(i)} = -\tilde{B}^{(i)} \cdot C^{(i)} \quad (3.14)$$
and

\[ \mathbf{E}^{(i)} = \mathbf{B}^{(i)} \cdot (\mathbf{F}^{(i)} - \mathbf{A}^{(i)} \cdot \mathbf{E}^{(i-1)}) \], \quad (3.15) \]

where

\[ \mathbf{B}^{(i)} = (\mathbf{B}^{(i)} + \mathbf{A}^{(i)} \cdot \mathbf{D}^{(i-1)})^{-1}. \quad (3.16) \]

For a triangular grid $\mathbf{A}^{(i)}$, $\mathbf{B}^{(i)}$, $\mathbf{B}^{(i)}$, $\mathbf{C}^{(i)}$, $\mathbf{D}^{(i)}$, $\mathbf{E}^{(i)}$ and $\mathbf{F}^{(i)}$ must have [row,column] dimensions of $[n_{c}i, n_{c}(i-1)]$, $[n_{c}i, n_{c}i]$, $[n_{c}i, n_{c}(i+1)]$, $[n_{c}i, n_{c}i]$, $[n_{c}i, n_{c}(i+1)]$, $[n_{c}i, 1]$ and $[n_{c}i, 1]$, respectively. Also, we should note that $\mathbf{A}^{(i)}$, $\mathbf{B}^{(i)}$ and $\mathbf{C}^{(i)}$ are band matrices with $3n_{c}$ diagonals and that $\mathbf{B}^{(i)}$ and $\mathbf{D}^{(i)}$ are dense matrices. The matrices are real for $i < i_{R_{0}}$ and complex for $i \geq i_{R_{0}}$, whereas the vectors are always complex.

To begin the propagation at the first column ($i = 1$) we note that $\mathbf{A}^{(1)}$ is a null vector and $\mathbf{D}^{(0)}$ and $\mathbf{E}^{(0)}$ are not required to be known, and in fact are also null. We can therefore reduce (3.14) and (3.15) to

\[ \mathbf{D}^{(1)} = - (\mathbf{B}^{(1)})^{-1} \cdot \mathbf{C}^{(1)} \]

(3.17)

and

\[ \mathbf{E}^{(1)} = (\mathbf{B}^{(1)})^{-1} \cdot \mathbf{F}^{(1)}, \]

(3.18)

respectively. Alternatively, these equations can be re-derived from (3.13) using the boundary condition $\mathbf{\Psi}^{(0)} = \mathbf{0}$.

After solving $\mathbf{D}^{(1)}$ and $\mathbf{E}^{(1)}$, the remaining $\mathbf{D}^{(i)}$ and $\mathbf{E}^{(i)}$ are evaluated in ascending $i$ order, followed by $\mathbf{\Psi}^{(i)}$ in reverse order ($i = i_{\text{max}} - 1$ to $i = 1$) using (3.12) and the ECS boundary condition $\mathbf{\Psi}^{(i_{\text{max}})} = \mathbf{0}$. Hence, the PECS method solves the coupled scattering wave equation in $2(i_{\text{max}} - 1)$ steps, where the vast majority of the computational effort is devoted to the $i_{\text{max}} - 1$ matrix inversions in (3.16). It should be stressed that this method does not rely on an initial approximation for $\psi_{L_{i_{1}i_{2}}}$, or iterative refinement, as in the ECS/CGS method, and will find solutions for collisions at total energies very close to ionisation threshold.
3.4 Iterative-coupling method

The vast majority of the computations required by the PECS method are devoted to the matrix inversion in (3.16), which is independent of $\vec{F}$. In this section we will show how this feature can be exploited to obtain a highly efficient iterative coupling scheme for the PECS method.

The iterative coupling scheme for PECS was inspired, in part, by the ECS/CGS method, which solves the sparse linear equations for $e$–H collisions using an uncoupled solution as a preconditioner followed by iterative refinement. This suggests that coupling for $e$–H collisions may be treated as a perturbation to the uncoupled solutions, at least for energies greater than 1 eV above threshold. The Schrödinger equation for $e$–H$_2$ collisions (2.37) and (2.39) can be rearranged into an iterative form, where the first iteration finds the uncoupled solution, equivalent to the preconditioner used in the ECS/CGS algorithm (Baertschy et al 2001b). Further iterations incorporate estimates for the coupled wave functions based upon the previous iteration, and the results converge toward the fully coupled solutions. To simplify the labelling of our iterative scheme, the labels $a$ and $b$ are used to represent the $b$th iteration of the $a$th coupled state $|LMSII_l^a_{12}\rangle$, where $1 \leq a \leq n_c$ and $n_c$ is the number of states required to achieve convergence of the $LMSII$ partial wave. The iterative equivalent of (2.37) becomes

$$ (E - \hat{H}_1(r_1) - \hat{H}_2(r_2) - \langle l_1^{pa} \ | \ r_{12} \ | \ l_2^{pa} \rangle L \bar{\psi}_{LMSII_l^a_{12}, b+1}(r_1, r_2) = \bar{\tau}_{LMSII_l^a_{12}, b+1}(r_1, r_2), \quad (3.19) $$

where $b \geq 0$, and

$$ \bar{\tau}_{LMSII_l^a_{12}, b+1}(r_1, r_2) = \bar{\chi}_{LMSII_l^a_{12}, b+1}(r_1, r_2) + \sum_{a' \neq a} \langle l_1^{pa'} | r_{12} | l_2^{pa'} \rangle L \bar{\psi}_{LMSII_l^{a'}_{12}, b}(r_1, r_2), \quad (3.20) $$

where setting $\bar{\psi}_{LMSII_l^{a'}_{12}, 0}(r_1, r_2) = 0$ ensures that no coupling of other states occurs on the first iteration ($b = 0$). The net result of this rearrangement is that coupling of wave functions with different $(l_1, l_2)$ is moved to the RHS. For subsequent iterations ($b > 0$) estimates for coupled wave functions ($a' \neq a$) are obtained from the previous iteration. The overbar in (3.19) and (3.20) are used to differentiate the iteratively-coupled approximation from a fully-coupled solution.
We can see from (3.13) and (B.1) that reforming the Schrödinger equation in this way affects the construction of the $A^{(i)}$, $B^{(i)}$ and $C^{(i)}$ matrices, though they remain the same for each iteration, while $\overrightarrow{F}^{(i)}$ changes with each iteration. Consequently, $\hat{B}^{(i)}$ (and its associated matrix inversion) are only evaluated during the first iteration and subsequent iterations require minimal computational effort.

In Section 4.1 we derive estimates for the number of mathematical operations\(^1\) required to calculate the scattering wave functions using this method. For now though, we note that this iterative technique offers an $n_c^2$ increase in computational efficiency.

In Section 6.1 we will discover that this iterative method only converges at a moderate rate, and its performance can be significantly improved by using the latest estimate for $\overrightarrow{\psi}_{LMS}^{\Pi,l_1a_1,l_2a_2,b+1}(r_1,r_2)$ as soon as it becomes available. This is achieved simply by replacing (3.20) with

$$
\overrightarrow{\psi}_{LMS}^{\Pi,l_1a_1,l_2a_2,b+1}(r_1,r_2) = \overrightarrow{\psi}_{LMS}^{\Pi,l_1a_1,l_2a_2,b+1}(r_1,r_2) + \sum_{a' \leq a} \langle l_1a_1 l_2a_2| r_{12}^{-1} | l_1a' l_2a' \rangle \overrightarrow{\psi}_{LMS}^{\Pi,l_1a_1,l_2a_2,b+1}(r_1,r_2)
+ \sum_{a'' > a} \langle l_1a_1 l_2a_2| r_{12}^{-1} | l_1a'' l_2a'' \rangle \overrightarrow{\psi}_{LMS}^{\Pi,l_1a_1,l_2a_2,b+1}(r_1,r_2),
$$

(3.21)

where for each iteration we assume that wave functions are calculated sequentially, in ascending order of $a$.

As with the ECS/CGS iterative method, iterative coupling of the PECS equations gives diverging solutions at low energies, due to very strong electron correlation. This will be investigated in Section 6.1. However, it is possible to reach lower total energies by fully-coupling groups of partial waves, and iteratively coupling these groups. For example, if $n_c$ coupled $|LMSII_{l_1}^{n},l_2^{n}\rangle$ states are required for convergence of the $LMSII$ partial wave, we can order these into $n_g$ groups (or sets) such that $\sum_{g=1}^{n_g} n(g) = n_c$, where $n(g)$ gives the number of states\(^2\) in each group $g$. The iteratively coupled Schrödinger

\(^1\)A mathematical operation in this context refers usually to one multiplication and one addition or subtraction. Most floating-point units on modern CPUs can perform these operations concurrently, so they are counted as one operation.

\(^2\)Normally we select uniform size groups, but this is not essential. However, for simplicity of the discussion in later chapters, we will assume in this thesis that $n_c/n_g$ is an integer.
equation becomes
\[
E - \hat{H}_{l_1} (r_1) - \hat{H}_{l_2} (r_2) - \sum_{a' \in g} \langle l_1^{a' l_2} || |l_1^{a' l_2'}\rangle_L \overline{\psi}_{i, l_1^{a' l_2}, b+1}(r_1, r_2) = \overline{\xi}_{i, l_1^{a' l_2}, b+1}(r_1, r_2),
\]
(3.22)
where
\[
\overline{\xi}_{i, l_1^{a' l_2}, b+1}(r_1, r_2) = \chi_{i, l_1^{a' l_2}}(r_1, r_2) + \sum_{a'' \in g} \langle l_1^{a'' l_2} || |l_1^{a'' l_2'}\rangle_L \overline{\psi}_{i, l_1^{a'' l_2}, b+1}(r_1, r_2)
\]
(3.23)
and where $\in$ and $\notin$ have their standard set notation meaning. The grouping and iterative coupling of states in this manner is used when iterative convergence becomes marginal, and is also used to satisfy the requirement that states $(l_1^{a' l_2}, l_1^{a'' l_2})$ are solved simultaneously, and hence fully coupled (see Section 3.2). Assuming that the size of each group is the same, the speed increase of this coupling method compared with the fully-coupled solution is approximately $n_g^2$. We should note that for $n_g = 1$, (3.22) and (3.23) simplify to (2.37) and (2.39), respectively, and for $n_g = n_c$ (3.23) simplifies to (3.21).

The convergence (or divergence) behaviour of each of these methods of iterative coupling will be discussed in detail in Section 6.1. It is worth noting that though this iterative-coupling method was conceived independently, based upon computational features of the PECS method, it is similar to an iterative technique used successfully by Allison (1970) for one-dimensional Schrödinger equation problems.

### 3.5 Energy perturbation method

The PECS iterative coupling technique provides a dramatic improvement in computational efficiency, though we will see in Section 6.1 that it fails to converge for energies close to ionisation threshold. Here we will explore another iterative refinement technique that does converge over a broad range of energies, including near threshold, that allows us to efficiently calculate scattering wave functions for many finely spaced energies. This energy-perturbation method may be used in combination with the iterative
coupling technique described in the previous section if iterative coupling alone provides converging solutions.

After evaluating the scattering wave functions for total energy $E$ we can iteratively approximate the scattering wave functions for energy $E' = E + \Delta E$ using (3.22), where

$$
\tilde{\chi}_{LMS\Pi_i,l_{1}l_{2},b+1}(r_1, r_2) = \chi_{LMS\Pi_i,l_{1}l_{2}}(r_1, r_2) + \sum_{a'<a} \langle l_{12}^{a''} | l_{12}^{a'} \rangle L \psi_{LMS\Pi_i,l_{1}l_{2}}(r_1, r_2) - \Delta E \psi_{LMS\Pi_i,l_{1}l_{2}}(r_1, r_2),
$$

and begin the iteration by equating $\psi_{LMS\Pi_i,l_{1}l_{2},0}$ to the scattering wave solution for energy $E$. As the left hand side of (3.22) is unchanged from the evaluation of energy $E$, the same $A^{(i)}$, $B^{(i)}$, $C^{(i)}$ and $D^{(i)}$ matrices are used to evaluate energy $E'$ and no additional matrix inversions are required. Consequently, scattering wave functions can be evaluated for many closely spaced energies with minimal computational resources. The grid spacing, $R_0$, $R_{\text{max}}$ and the coupled angular momentum states must be selected to provide good convergence at both $E$ and $E'$. The convergence behaviour with respect to the ratio $\Delta E/E$ is investigated in Section 6.1. Also, we will find that for energies close to ionisation threshold the iterative coupling method is not convergent and $n_g = 1$ must be used, yet the energy perturbation method remains convergent over a useful range of energies. This method is used extensively in Chapter 7 to investigate the threshold behaviour of $e^{-}H$ ionising collisions.

3.6 Other numerical considerations

We have now completed the mathematical description of the numerical methods that have been derived for this thesis. However there are important considerations when choosing standard numerical routines for integration, interpolation and Coulomb waves that deserve a brief discussion. In these discussions we will consider the integrand of the ionisation partial-wave amplitude [see (2.65)] at 54.4 eV for an $e^{-}H$ ground state collision at equal energy-sharing for the $L=0, S=0, l_1=l_2=0$ partial wave. This integrand is plotted in Figure 3.3 for hyperangles $\alpha$ from 0 to $\pi/2$, which shows the highly oscillatory nature
CHAPTER 3: NUMERICAL METHODS

Figure 3.3: Integrand of the partial-wave ionisation amplitude equation [see (2.65)] for an $e$-$\text{H}(1s)$ ionising collision at 54.4 eV incident electron energy (at hyperradius $\rho=110$ a.u. and for $L=0$, $S=0$, $l_1=l_2=0$ and $k_1=k_2$).

of these functions. The function becomes more oscillatory with increasing hyperradius, and is asymmetric with respect to $\alpha = \pi/4$ when $l_1 \neq l_2$ or $k_1 \neq k_2$.

3.6.1 Numerical integration

There are two significant features of the ionisation amplitude integrand shown in Figure 3.3 that the numerical integration routine must address. Firstly, it must cater for highly oscillatory integrals, and as the number of oscillations varies as a function of hyperradius and total energy it should use an adaptive mesh algorithm. Secondly, as the integrand oscillates about zero, there is very significant cancellation and the numerical integration must be capable of high accuracy.

For this thesis we have developed an adaptive routine, based on the 11-point Bode’s rule (Abramowitz and Stegun 1965, p886) (equally spaced abscissas) that doubles the number of grid points (in the required regions) until successive calculations agree within the required precision. This relatively simple method reuses function points as the grid is adapted and does not require weighting factors to be calculated as is required by more
3.6: OTHER NUMERICAL CONSIDERATIONS

complex integration routines (e.g. Gaussian integration). In the above example our integration routine required approximately 1000 integrand points, though significantly more points were required for the model calculations presented in Chapter 5, which extend to much larger hyperradii.

3.6.2 Wave function interpolation

In Section 2.4 we detailed our method for calculating ionisation cross sections, which uses values of the scattering wave function on a curved hypersphere of hyperradius $\rho$. As our grid uses Cartesian rather than hyperspherical coordinates, these values must be obtained through interpolation. The high accuracy required of the integration routine when calculating ionisation and scattering amplitudes makes accurate interpolation of the scattering wave functions essential. There is a conflicting requirement between computational efficiency when calculating the scattering wave functions, where we try to maximise grid spacing, and the accuracy of the interpolation, which is increased by reducing the grid spacing. Regardless of the accuracy obtained in calculating the wave functions, the accuracy of their interpolation will limit the accuracy of the extracted cross sections. As such, all the convergence studies presented in this thesis are undertaken with respect to the extracted ionisation and scattering cross sections rather than the scattering wave function.

As an example, we show two (partial) SDCS curves in Figure 3.4 calculated from the same scattering wave functions but using different interpolation methods; cubic spline interpolation and Chebyshev polynomial interpolation (Press et al 1992). Each interpolation method has been implemented using a $10 \times 10$ grid-point subset of the main grid that is centred on the required interpolation point. Inaccuracies in the cubic spline interpolation causes small unphysical oscillations in the differential cross sections, whereas the Chebyshev polynomial approximation shows no noticeable error. When increased grid spacing is used for rough calculations, the inaccuracy of the cubic spline method is more evident. Increasing the size of the sub-grid used for the cubic spline interpolation does not significantly reduce this problem, consequently, we will use Chebyshev polynomial interpolation throughout this thesis.
Figure 3.4: Comparison of Chebyshev polynomial and cubic spline interpolation methods for calculating single differential cross sections of an $e$-$\text{H}(1\text{s})$ ionising collision at 54.4 eV incident electron energy ($\rho=110$ a.u., $L=0$, $S=0$).

The partial-wave amplitude equations (2.53, 2.65) are also dependent on the first derivative of the scattering wave function, which we calculate using a five-point finite-difference formula (Abramowitz and Stegun 1965, p883). To minimise error in this calculation it is important that the same $10 \times 10$ grid is used to interpolate each of these finely spaced points, even when some points fall into a neighbouring grid square. Using different $10 \times 10$ grids in a derivative calculation results in slight discontinuities in the integrand of (2.53) or (2.65), which causes our adaptive integration procedure to significantly increase the number of integration points in this region to maintain accuracy. This problem would be avoided if all grid points ($r < R_0$) are used in the Chebyshev interpolation routine, but this imposes a large computational overhead and makes it impractical.

### 3.6.3 Coulomb wave function

Extracting ionisation amplitudes and scattering amplitudes ($Z > 1$) from a scattering wave function using (2.65) and (2.53) requires accurate calculations of the two-body
regular Coulomb radial wave function. The “Coul90” routine (Barnett 1996) is used in this thesis and generally provides sufficient accuracy for this purpose. However, this routine fails to achieve the required accuracy at highly asymmetric energy-sharing and hyperangles $\alpha$ approaching zero or $\pi/2$ (i.e. small $k$ and small $r$). In this case we are required to use an approximation for the Coulomb wave function by performing a series expansion of its analytic form with respect to $kr$. The details of this expansion are given in Appendix C. To prevent small discontinuities in the integrand of (2.65) it is important that a smooth transition occurs between the small-$kr$ approximation and the Coul90 results. This is discussed further in the Appendix C.

This completes the discussion of the numerical algorithms used in the PECS method. However, before we present our calculations it is worthwhile discussing some of the computational strategies that have been used, which we include in the following chapter.
In Chapter 2 we derived the partial-wave Schrödinger equation for electron collisions with hydrogenic targets, and the methods used to extract the scattering and ionisation amplitudes from the scattering wave functions. This was followed in Chapter 3 by a detailed description of the numerical methods that we have used to efficiently evaluate these equations. We will now discuss features of these numerical methods that can be exploited to maximise their computational efficiency, and analyse the computational resources required by the PECS method, both with and without iterative coupling and/or energy perturbation.

4.1 Floating point operations

The vast majority of the computational effort required to evaluate the scattering wave functions for $e$–$H_Z$ collisions using the PECS method is devoted to the floating-point numerical operations required to evaluate the matrix equations (3.12), (3.14), (3.15) and (3.16), which are repeated here to aid our discussion:

\[
\tilde{\psi}^{(i)} = D^{(i)} \cdot \tilde{\psi}^{(i+1)} + \tilde{E}^{(i)},
\]  

\[
D^{(i)} = -\tilde{B}^{(i)} \cdot C^{(i)},
\]  

\[
\tilde{E}^{(i)} = \tilde{B}^{(i)} \cdot \left( F^{(i)} - A^{(i)} \cdot \tilde{E}^{(i-1)} \right),
\]  

and

\[
\tilde{B}^{(i)} = (B^{(i)} + A^{(i)} \cdot D^{(i-1)})^{-1},
\]  

respectively.

In order to optimise the computational efficiency of these equations it is important to recognise the characteristics of their matrix and vector operands. In Table 4.1 we have summarised the size, density (banded or dense), number of diagonals (if banded)
## Table 4.1: Characteristics of the matrices and vectors used in equations (4.1) through (4.4), where $i$ is the grid column number (see Figure 3.1) and $n_s = n_c/n_g$ is the number of simultaneously (not iteratively) coupled wave functions, $n_c$ is the number of coupled wave functions and $n_g$ is the number of iterative groups (see Section 3.4), and $n_d$ is the number of non-zero diagonals in the matrix. The storage requirement of the matrices and vectors is a first-order estimate that assumes double-precision arithmetic (eight bytes per real floating-point number), and the total storage may be calculated by summing over all $i$ and multiplying by $n_g$.

<table>
<thead>
<tr>
<th>Matrix/Vector</th>
<th>Size</th>
<th>Density</th>
<th>Variable Type</th>
<th>Storage (bytes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mathbf{A}(i)$</td>
<td>$n_s i \times n_s(i - 1)$</td>
<td>Banded</td>
<td>$3n_s$ real complex</td>
<td>$24n_s^2i$ $48n_s^2i$</td>
</tr>
<tr>
<td>$\mathbf{B}(i)$</td>
<td>$n_s i \times n_s i$</td>
<td>Banded</td>
<td>$3n_s$ real complex</td>
<td>$24n_s^2i$ $48n_s^2i$</td>
</tr>
<tr>
<td>$\tilde{\mathbf{B}}(i)$</td>
<td>$n_s i \times n_s i$</td>
<td>Dense</td>
<td>– real complex</td>
<td>$8n_s^2i^2$ $16n_s^2i^2$</td>
</tr>
<tr>
<td>$\mathbf{C}(i)$</td>
<td>$n_s i \times n_s(i + 1)$</td>
<td>Banded</td>
<td>$3n_s$ real complex</td>
<td>$24n_s^2i$ $48n_s^2i$</td>
</tr>
<tr>
<td>$\mathbf{D}(i)$</td>
<td>$n_s i \times n_s(i + 1)$</td>
<td>Dense</td>
<td>– real complex</td>
<td>$8n_s^2i^2$ $16n_s^2i^2$</td>
</tr>
<tr>
<td>$\tilde{\mathbf{E}}(i)$</td>
<td>$n_s i \times 1$</td>
<td>– complex complex</td>
<td>$16n_s i$ $16n_s i$</td>
<td></td>
</tr>
<tr>
<td>$\tilde{\mathbf{F}}(i)$</td>
<td>$n_s i \times 1$</td>
<td>– complex complex</td>
<td>$16n_s i$ $16n_s i$</td>
<td></td>
</tr>
<tr>
<td>$\tilde{\psi}(i)$</td>
<td>$n_s i \times 1$</td>
<td>– complex complex</td>
<td>$16n_s i$ $16n_s i$</td>
<td></td>
</tr>
</tbody>
</table>

and the variable type (real or complex) of each of these matrices and vectors in both the real region of the grid ($i < i_{R_0}$) and the complex scaling region ($i_{R_0} \leq i < i_{\text{max}}$). The first important feature to note is that all the matrices associated with (4.4) are real for $i < i_{R_0}$; a large majority of the grid. A significant computational saving is obtained by using real arithmetic in this region, which requires 1/4 of the mathematical operations of complex arithmetic. By comparison, the ECS method (Baertschy et al 2001b) requires complex arithmetic for all matrix operations.

To minimise storage, all banded matrices are stored in band storage mode (Anderson et al 1999), which reduces storage to an array with dimensions of approximately $n_d \times n$, where $n_d$ is the number of non-zero diagonals and $n$ is the column dimension of
the matrix. Similarly, significant computational gains can be achieved by using matrix-algebra routines that recognise the banded structure of the arguments. For example, the band-matrix $\times$ dense-matrix multiplication in (4.4) requires of the order of $n^3$ mathematical operations using unbanded procedures and only $n_d n^2$ operations using banded procedures, reducing computation time by a factor of $n/n_d$. The PECS method also has the requirement to multiply complex arguments with real arguments, consequently, many variations of the matrix-algebra routines are required to cater for banded and unbanded arguments of both real and complex variables. Many of these routines are unavailable in standard linear algebra computational packages\(^1\), so were custom written for this project. Table 4.2 lists the various matrix-algebra procedures used in the PECS method, along with the density and type of their arguments and an estimate of the real arithmetic operations required for their evaluation. Clearly, when $n_d \ll n$, as is the case with the PECS method, the banded operations significantly reduce the computations required and the matrix inversions become the dominant computational operations.

It should be noted that the performance of the BLAS routines are generally optimised for the computer system architecture. Care was taken to maximise the performance of the custom linear algebra routines by optimising the use of the CPU’s memory cache, and hence minimising memory-CPU transfers.

We can now estimate the number of floating-point operations required for the linear algebra operations (4.1) through (4.4), for all columns and all coupled grids (using the Variable Type column of Table 4.1 and the Flop column in Table 4.2). For the first iteration ($b=0$) a first-order approximation of the floating-point operations is given by

\[
\text{Flop}_{b=0} \approx n_g \left\{ \sum_{i=1}^{i_{R_0}^{-1}} (n_{s i})^3 + (6n_s + 4)(n_{s i})^2 + \sum_{i_{R_0}}^{i_{\text{max}}^{-1}} 4(n_{s i})^3 + (24n_s + 8)(n_{s i})^2 \right\}
\]

\[
\approx n_g \left\{ n_s^3 \left( \frac{4}{3} i_{\text{max}} - \frac{3}{4} i_{R_0} \right) + 4i_{\text{max}}^3 - 7i_{R_0}^3 \right\} + \frac{1}{3} n_s^2 \left( 8i_{\text{max}}^3 - 4i_{R_0}^3 \right),
\]

(4.5)

\(^1\)The LAPACK (Anderson et al 1999) and Basic Linear Algebra (BLAS) packages for FORTRAN 90 were used in this thesis (via the Compaq/HP\(^\circ\) Alphaserver Supercomputer CXML Parallel library).
Table 4.2: This table details the various matrix and vector algebra procedures that were used in the development of the software for the PECS method, and whether they were custom developed or obtained from the LAPACK (Anderson _et _al_ 1999) or Basic Linear Algebra (BLAS) libraries. The number of floating-point operations (Flop) column gives a first-order estimate of the real arithmetic operations required to perform the given operation, where all matrices are approximated by a $n \times n$ matrix with $n_d$ diagonals (if banded) and vectors have dimension $n \times 1$.

\[
\text{Flop}_{b>0} \approx n_g \left\{ \sum_{i=1}^{i_{R_0}-1} (3n_s + 4)(n_s i)^2 + \sum_{i_{R_0}}^{i_{\text{max}}-1} (12n_s + 8)(n_s i)^2 \right\}
\]  
\[
\approx n_g \left\{ n_s^3 \left( 4i_{\text{max}}^3 - 3i_{R_0}^3 \right) + \frac{1}{3} n_s^2 \left( 8i_{\text{max}}^3 - 4i_{R_0}^3 \right) \right\}.
\]  

From these equations we can see that the computation time is approximately proportional to $n_g n_s^3 i_{\text{max}}^4$ for the first iteration, and $n_g n_s^3 i_{\text{max}}^3$ for subsequent iterations. It is important, therefore, that when selecting the grid size, grid spacing, complex scaling region and number of coupled angular momentum states for each partial wave that $n_s$ and $i_{\text{max}}$ are set to the minimum required to achieve convergence to the required accuracy.
4.2: STORAGE REQUIREMENTS

<table>
<thead>
<tr>
<th>Target</th>
<th>$E_0$ (eV)</th>
<th>$R_0$ (a.u.)</th>
<th>$L$</th>
<th>$n_s$</th>
<th>$n_g$</th>
<th>$i_{R_0}$</th>
<th>$i_{\text{max}}$</th>
<th>$b=0$</th>
<th>$b&gt;0$</th>
<th>Storage (Gb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Model $e$--$H$</td>
<td>27.2</td>
<td>100</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>553</td>
<td>587</td>
<td>45</td>
<td>–</td>
<td>0.6</td>
</tr>
<tr>
<td>b) Model $e$--$H$</td>
<td>27.2</td>
<td>400</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1303</td>
<td>1337</td>
<td>960</td>
<td>–</td>
<td>6.4</td>
</tr>
<tr>
<td>c) Model $e$--$H$</td>
<td>27.2</td>
<td>1400</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>3803</td>
<td>3837</td>
<td>56000</td>
<td>–</td>
<td>144</td>
</tr>
<tr>
<td>d) $e$--$H$</td>
<td>27.2</td>
<td>100</td>
<td>0</td>
<td>1</td>
<td>6</td>
<td>326</td>
<td>350</td>
<td>37</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>e) $e$--$H$</td>
<td>27.2</td>
<td>100</td>
<td>5</td>
<td>2</td>
<td>16</td>
<td>326</td>
<td>350</td>
<td>770</td>
<td>12</td>
<td>8.1</td>
</tr>
<tr>
<td>f) $e$--$H$</td>
<td>13.9</td>
<td>180</td>
<td>2</td>
<td>12</td>
<td>1</td>
<td>263</td>
<td>288</td>
<td>5300</td>
<td>71</td>
<td>11</td>
</tr>
<tr>
<td>g) $e$--$H$</td>
<td>13.9</td>
<td>400</td>
<td>0</td>
<td>5</td>
<td>1</td>
<td>926</td>
<td>979</td>
<td>43000</td>
<td>–</td>
<td>67</td>
</tr>
</tbody>
</table>

Table 4.3: List of $n_s$, $n_g$, $i_{R_0}$ and $i_{\text{max}}$ values used for several PECS calculations presented in this thesis. An estimate is given for the total mathematical operations (Gflop = $10^3$ real floating-point operations) required for the matrix algebra, using (4.5) and (4.6), and the estimated total storage requirement (Gb = $10^3$ bytes), using (4.7).

4.2 Storage requirements

The storage requirement for each of the matrices and vectors required by the PECS method is summarised in Table 4.1. Clearly, the storage of the dense matrices $\tilde{B}^{(i)}$ and $D^{(i)}$ dominates the storage requirement and so only these will be considered when approximating the total storage. Though $\tilde{B}^{(i)}$ and $D^{(i)}$ are required for iterative coupling calculations, we only retain $\tilde{B}^{(i)}$, which halves the storage requirement but incurs a slight computational overhead when recalculating $D^{(i)}$ using (4.2) on subsequent iterations. The total storage (bytes) for all coupled wave functions may then be estimated to first-order by

$$\text{Storage} \approx \sum_{i=1}^{i_{R_0}-1} 8n_g n_s^2 i^2 + \sum_{i=1}^{i_{\text{max}}-1} 16n_g n_s^2 i^2 \approx \frac{8}{3} n_g n_s^2 (2i^3_{\text{max}} - i^3_{R_0}).$$  (4.7)

In addition to this storage the software developed for the PECS method requires storage for many other variables, vectors and matrices, but this estimate is adequate for our discussion of the storage options.
So far we have discussed storage without regard to whether random access memory (RAM), with fast retrieval times, is necessary or whether hard-disk storage (with relatively slow access) is sufficient for the PECS method. This decision depends on whether iterative coupling or energy perturbation is required and the amount of storage required versus the number of floating-point operations, which in turn depends on the values of $i_{R_0}$, $i_{\text{max}}$, $n_c$ and $n_g$ used in the calculation. To aid this discussion we have presented the values of these constants in Table 4.3 for several of the calculations reported in later chapters.

The storage requirements of the model $e-H$ calculations a) and b) in Table 4.3 are well within the RAM available on a single supercomputer node\textsuperscript{2}, and all matrices can be retained in RAM. Though sufficient hard-disk storage is available, the estimated time to write and read back the matrices is approximately twice the computation time for a) and equal to the computation time for b), making their storage on hard disk an inefficient option.

For calculations c) and g), the storage requirements of 144 Gb and 67 Gb, respectively, greatly exceed the RAM and hard disk available on a single node. The calculations could be spread over many nodes so that sufficient RAM or hard disk is available (see Section 4.3) but we chose an alternate method. By writing $\hat{B}(i)$ matrices and $\vec{E}(i)$ vectors to disk for only certain milestone values of $i$ (when the available RAM on the node fills) during the forward pass of the propagation algorithm [evaluating (4.2), (4.3) and (4.4)] the hard-disk storage requirement is greatly reduced. Then, on the backward pass [evaluating (4.1)], the milestones are read from disk and all matrices between the milestone values of $i$ are recalculated. Though this results in an overall doubling of computation time, it allows very large grids to be evaluated on a single node without significant restrictions being imposed by either RAM or hard-disk capacity.

\textsuperscript{2}The Australian Partnership of Advanced Computing’s Compaq/HP® Alphaserver supercomputer was used for this thesis. It contains 127 nodes, each having 4 × 1 GHz CPUs with a peak performance of 1 Gflops (Gflop per second) per CPU and between 4 and 16 Gb of shared RAM. A dedicated hard disk for temporary storage is attached to each node, with capacity $>50$ Gb and maximum read/write performance of $\approx 50$ Mb/s. All discussion of computing performance and capacity in this thesis will relate to the configuration of this supercomputer.
The storage requirements of the remaining calculations in Table 4.3 were within the available RAM. However, as calculations d) and e) utilise iterative coupling \( n_g > 1 \), and f) utilises energy perturbation iterations to evaluate many closely spaced energies, they are not suited to the milestone method. The large storage requirement of the arrays in these calculations, combined with the very small computational requirement for the \( b > 0 \) iterations would make the computations extremely I/O bound if the matrices were not resident in RAM. Indeed, the time required to write and read the matrices would most likely exceed the performance gain of the iterative method. If more RAM storage is required by the iterative PECS methods than is available on a single node, the calculations must be distributed over multiple nodes.

### 4.3 Multiprocessor utilisation

Each partial-wave calculation presented in this thesis was able to be calculated on a single supercomputer node, while different \( LMSII \) partial waves were calculated in parallel on separate nodes. However, for calculations larger than those presented in this thesis, multiple supercomputer nodes may be required to calculate a single partial wave, so it is worthwhile examining features of the PECS method that affect the distribution of these computations over multiple CPUs and multiple nodes.

The main feature of the PECS method that complicates the distribution of its calculations over more than one CPU is its sequential nature: when propagating forwards the results of column \( i \) must be fully calculated before the calculation of column \( i + 1 \) can begin, iteration \( b \) must be evaluated for all states before iteration \( b + 1 \) can begin, and within a single iteration, group \( g \) of iteration \( b \) must be completed before group \( g + 1 \) of iteration \( b \) can begin. This limits the size (in respect of Flops) of the individual computational blocks that may be executed in parallel on different CPUs or nodes. Unfortunately, when distributing calculations over multiple CPUs, the smaller the computational block, the greater the speed that is required of the inter-processor communications, and the efficiency of the distributed calculation can easily be limited.
by the bandwidth of the inter-processor communications. Also, in the case of OpenMP, the efficiency of the calculation can be limited by the overhead required to establish, initialise and finalise multi-thread processes for each parallel computational block.

For the calculations undertaken in this thesis, a single shared memory node with four CPUs was used, which had a very high inter-processor communication speed and so was not significantly bandwidth limited. There was some evidence during iterative refinement \( b > 0 \), where the calculations are dominated by small matrix calculations, that the overhead of initiating multi-thread processes impacted the efficiency of the distributed calculation. Overall, however, we were able to attain CPU utilisation efficiency of approximately 96%.

Distributing, the PECS method to more than one node may be achieved in several ways, depending on the iterative method selected:

1. Non-iterative calculations (\( n_g = 1 \) and \( b = 0 \))

   In these calculations, the dense matrix inversion in (4.4) dominates the computation and were easily and efficiently evaluated using SCALAPACK routines. The efficiency of distributing the remaining matrix operations was very poor due to the inter-node communications bandwidth but did not significantly affect the overall computational efficiency.

2. Iterative calculations – first iteration (\( n_g > 1 \) and \( b = 0 \))

   During the first iteration, each iterative coupling group \( g \) can be calculated independently and hence in parallel. Rather than use SCALAPACK to calculate each group, sequentially, over all nodes, LAPACK routines (using OpenMP) can be used to dedicate a node to a group. Of course, if the number of nodes required exceeds the number of groups, then SCALAPACK must be used to distribute each

---

3OpenMP is the shared memory multiprocessor application program interface used for this thesis.
4SCALAPACK is a version of LAPACK (Anderson et al 1999) designed for processors with distributed memory.
5The APAC supercomputer used for this thesis used a fat tree topology (allows all CPUs to send/recieve simultaneously at the maximum transfer rate) for its inter-node communications that provided a <5 \( \mu \)s latency and 250 Mbyte/s bidirectional bandwidth.
group over a subset of the nodes. Once again, as the matrix inversion dominates the processing, this iteration will utilise all CPUs efficiently.

3. Iterative calculations – subsequent iterations ($n_g > 1$ and $b > 0$)

These iterations pose the greatest problem when distributing the PECS iterative algorithm over multiple nodes. In Section 3.4 we noted that the iterations converge much more quickly if the latest iterative estimates are used for subsequent iterative groups. This limits the calculation to one group $g$ at a time, and so each group must be distributed over all computing nodes. However, each matrix operation is relatively small, and does not scale efficiently to multiple nodes due to inter-processor bandwidth limitations. The efficiency of these subsequent iterations are significantly compromised.

Alternatively, if we use the first iterative algorithm presented in (3.19) and (3.20), each group can be processed in parallel and the computational efficiency is greatly improved, but the convergence rate is compromised. In practice, depending on the number of execution nodes required, a compromise between these two methods can be obtained, which results in the best overall efficiency.

This method was investigated, but as the calculations presented in this thesis are not dependent upon them, no further details will be given. It should be noted however, that many custom matrix-algebra routines were required to be developed in addition to those in the SCALAPACK library (as was the case with LAPACK presented in Table 4.2).

4. Energy perturbation – subsequent iterations ($n_g = 1$ and $b > 0$)

When performing energy perturbation iterations without iterative coupling, there are no alternative coupling algorithms available to improve the efficiency of the iterations when multiple nodes are used. However, as the matrices are generally much larger in these calculations (as all coupled wave functions are solved simultaneously) the required inter-processor communication bandwidth is lower than the iterative coupling calculations discussed in the previous item, and computational efficiency is improved.
This completes our discussion of the theoretical, numerical and computational development of the PECS method. In the following chapter we will test the procedures developed in this and previous chapters with two commonly used model e–H problems.
Chapter 5
Model Problems

In previous chapters we developed the theoretical, numerical and computational framework of the PECS method for solving \( e-H_Z \) collisions. Rather than immediately applying these methods to the full \( e-H_Z \) problem, it is common practice to test new methods with *model \( e-H \) problems* that retain the essence of the full problem but have lower computational demands. As a large proportion of the computing algorithms were custom developed for this thesis, this approach allows them to be tested, and their results verified against accurate benchmark calculations, before tackling the computational demands of the full \( e-H_Z \) problem.

The complexity of the full \( e-H_Z \) problem arises from the electron-electron potential \( \hat{H}_{12} \), which causes the partial-wave expansion of the Schrödinger equation (developed in Section 2.2) to couple scattering wave functions for all states with the same \( LMS\Pi \). The Temkin-Poet model (Temkin 1962, Poet 1978) (TP) and the collinear model (Peterkop and Rabik 1972, Temkin and Hahn 1974) (CL) for \( e-H \) collisions that we will discuss in this chapter use approximations for this potential that remove the requirement to couple scattering wave functions of different \( (l_1, l_2) \). This greatly simplifies the calculations but, to varying degrees, the results are unphysical. Nevertheless, both approximations realistically model the complexities associated with the long-range electron-core potential. They also allow the integral formulations for extracting scattering and ionisation cross sections, developed in Sections 2.3 and 2.4, to be thoroughly tested.

In this chapter we will give a brief theoretical background of the TP and CL models, undertake a convergence study with respect to grid spacing, grid size and complex scaling, give results for scattering and ionising collisions with ground-state targets and investigate the TICS behaviour of each model when impact energies approach the ionisation threshold.
5.1 Model theory

5.1.1 Temkin-Poet model

The TP model for e–H collisions is a special case of the full e–H problem where all angular momenta are set to zero and the target is initially in the ground state. Effectively, it is a solution of the $\vert LSMIII_l_1l_2 \rangle = \vert 0S0000 \rangle$ state of the full problem, without coupling non-zero states of $l_1$ and $l_2$. This gives a non-analytic electron-electron potential of

$$\hat{H}_{12} = \langle 00 \parallel \frac{1}{r_{12}} \parallel 00 \rangle = \frac{1}{r_\gg},$$

(5.1)

where $r_\gg$ is the greater of $r_1$ and $r_2$. As a result, (2.37) and (2.38) of the full problem reduce to

$$(E + \frac{1}{2} \frac{\partial^2}{\partial r_1^2} + \frac{1}{2} \frac{\partial^2}{\partial r_2^2} + \frac{1}{r_\ll}) \psi^{(TP)}(r_1, r_2) = \chi^{(TP)}(r_1, r_2),$$

(5.2)

and

$$\chi^{(TP)} = \sqrt{\frac{2\pi}{k_i}} \left\{ \left( \frac{1}{r_\gg} - \frac{1}{r_\ll} \right) \phi_{ls}(r_1) \sin(k_i r_2) + (-1)^S (1 \leftrightarrow 2) \right\},$$

(5.3)

where $r_\ll$ is the smaller of $r_1$ and $r_2$. We will see in the following section that the non-analytic nature of this potential introduces radial convergence issues that are not evident in the full e–H$_Z$ problem. The most accurate calculations undertaken for this model are those recently published by Jones and Stelbovics (2002) using the finite-difference method (FDM). Though this project and the FDM method were developed at the same research institution, it should be noted that there is no commonality of software coding, FDM and PECS use a different grid structure and Numerov formulae, and whereas the FDM method directly solves the ionisation and scattering amplitudes at the grid boundary using asymptotic approximations, the PECS method computes the scattering wave function over the entire grid and extracts the scattering and ionisation amplitudes from it. The FDM method has not been extended beyond the TP model, and has not been applied to the CL model. Having highlighted the differences between FDM and PECS, the FDM method should be acknowledged for demonstrating that the propagation technique used (though adapted) for this project was numerically stable for the very large hyperradii required to extract accurate ionisation amplitudes in the TP model.
5.1.2 Collinear model

The total single-ionisation cross section of an atomic target was predicted by Wannier (1953), using classical arguments, to have an energy dependence of $E^\eta$ at ionisation threshold, where $\eta$ has an analytic form that depends on the charge of the target. For a neutral atomic target $\eta$ is approximately 1.127. To derive this relationship Wannier used the classical approximation $\hat{r}_1 = -\hat{r}_2$, that is, at threshold the electrons leave the nucleus in opposite directions. The CL model (Peterkop and Rabik 1972, Temkin and Hahn 1974) is a low-energy quantum-mechanical approximation of the full $e$–$H$ problem that retains the essence of Wannier’s argument by setting the electron-electron potential to

$$\hat{H}_{12} = \frac{1}{r_1 + r_2} \quad (5.4)$$

(the potential obtained if the incident and bound electrons exit in opposite directions), but the model does not restrict the ejection angles.

The partial-wave expansion of the Schrödinger equation for the CL model can be obtained from (2.37) by replacing the reduced matrix element with (5.4), which has no angular dependence, giving

$$(E - \hat{H}_{11} - \hat{H}_{22} - \frac{1}{r_1 + r_2})\psi_{i,l_1l_2}^{LMSII(CL)}(r_1, r_2) = \chi_{i,l_1l_2}^{LMSII(CL)}(r_1, r_2), \quad (5.5)$$

where

$$\chi_{i,l_1l_2}^{LMSII(CL)}(r_1, r_2) = \frac{1}{k_i} \sum_{l} \sqrt{2\pi(2l+1)} C_{\ell_i, m_i, l_0}^{LM} \frac{1}{r_1 + r_2} \delta_{\ell_1, \ell_2} \delta_{l_1, l_2}$$

$$\times \phi_{n_1, l_1}(Z; r_1) \phi_{l}(Z - 1; k_i, r_2) + (-1)^{S + \Pi} (1 \leftrightarrow 2). \quad (5.6)$$

If we consider scattering from the ground state ($n_i=0, l_i=0, m_i=0$) it should be noted that only the $(l_1, l_2) = (0, L)$ and $(l_1, l_2) = (L, 0)$ angular momentum states contribute to the scattering wave function, as the delta functions ensure that $\chi_{i,l_1l_2}^{LMSII(CL)}$ is zero for all other states. For $L > 0$ only one term within the braces of (5.6) survives, so for $(l_1, l_2) = (0, L)$ the singlet and triplet states will be identical, and for $(l_1, l_2) = (L, 0)$ the singlet and triplet states will have equal magnitude but opposite signs. Therefore, for...
$L > 0$, the magnitude of extracted cross sections (without spin weighting) for the triplet case will be equal to the singlet case, and must consequently have the same threshold behaviour. In this thesis we will only consider the $L=0$ partial wave, and when we refer to the CL model, $L=0$ is implied.

As in the TP model, the CL model simplifies the calculations by removing the coupling between scattering wave functions with different $(l_1, l_2)$. Unlike the TP model however, the electron-electron potential is analytic. Also, as the CL model is an approximation based on the behaviour of ionising collisions near threshold, we would expect this model to exhibit characteristics similar to the full $L=0$ e–H problem, at least for impact energies near the ionisation threshold.

5.2 Convergence studies

The PECS method uses numerical approximation techniques, rather than analytic methods, to solve the Schrödinger equation for e–H$_2$ collisions. Also, the integral methods used to extract scattering and ionisation amplitudes from the scattering wave function rely upon asymptotic approximations. It is important, therefore, that errors introduced into the calculations by these approximations are controlled so that the standard error of the calculations can be estimated. We will now summarise the approximations used by the PECS method (which were introduced in previous chapters) and discuss how the magnitude of their resultant errors can be controlled and estimated.

1. Scattering wave function approximations

   (a) Grid spacing (finite difference and interpolation)

   In Section 3.1 we found that the error of the Numerov finite difference method derived for this thesis was approximately $\frac{h^6}{240} \psi_i^{(6)}$ for fixed grid-spacing and approximately $\frac{\alpha^5}{120} h_{n\lambda}^5 \psi_i^{(5)}$ for variable grid-spacing, and additional grid-related errors are introduced when interpolating the scattering wave function. Evaluating the TICS and total scattering cross sections (TCS) for discrete final-states from scattering wave functions calculated with the same $E$, $R_0$, $R_{\text{max}}$, $\psi_i^{(5)}$ for variable grid-spacing, and additional grid-related errors are introduced when interpolating the scattering wave function. Evaluating the TICS and total scattering cross sections (TCS) for discrete final-states from scattering wave functions calculated with the same $E$, $R_0$, $R_{\text{max}}$,
θ and grid spacing regions, but decreasing \( h_n \) systematically, allows us to estimate the error introduced by the finite-difference and interpolation formulae (see Sections 3.2 and 3.6.2) in grid region \( n \). The error estimate is relative to the results obtained from a reference grid with very fine spacing, though the absolute error can be estimated from an extrapolation as \( h_n \to 0 \).

(b) Truncation of \( \chi \)

The initial-state wave functions (5.3) and (5.6), which are known analytically, contain incoming waves that diverge under the ECS transformation, and must be truncated at or before the complex scaling region. In this thesis we smoothly, but rapidly, truncate \( \chi \) just before \( R_0 \) using (2.39). By studying the TICS and TCS results from separate wave functions calculated with increasing \( R_0 \), the asymptotic behaviour of the results can be estimated. The estimated error based upon this asymptotic extrapolation will include the \( \chi \)-truncation as well as other radially-dependent approximations given in 1c), 2a), and 2c) below.

(c) Finite grid size

The electron-core and electron-electron potentials have a long-range interaction that diminishes as a function of \( 1/r \), and will therefore continue to influence the scattering wave function for very large distances. Calculating the scattering wave function on a finite grid size will introduce an error that diminishes with increasing \( R_0 \). This error can be estimated in combination with other radially-dependent approximations.

(d) Complex scaling

The boundary conditions used at \( r_1, r_2 = R_{\text{max}} \) given in (3.2) are approximations that become more accurate as the exponential damping of the ECS transformation increases. If we study the behaviour of the TICS and TCS results of calculations with increasing complex scaling length \( (R_{\text{max}} - R_0) \), the error introduced by this approximation of the boundary conditions can be estimated. The effect of complex scaling angle \( \theta \) and grid spacing in the complex region can also be examined.
In Sections 2.1 and 3.1 we discussed the effect of the discontinuous first derivative of the scattering wave function at $R_0$, the start of the ECS transformation. The error introduced by the Numerov finite-difference formula at this point is likely to vary with the grid spacing and the “sharpness” of this discontinuity, which in turn is likely to depend on where the transformation starts with respect to the oscillations in the outgoing scattering wave function. To estimate this error, the TICS and TCS results obtained from separate calculations with varying grid spacing in the region of $R_0$, and varying $R_0$, need to be investigated. The variation of $R_0$ should span at least one oscillation of the outgoing scattering wave function.

(e) Iterative coupling and energy perturbation

The error introduced by the iterative refinement techniques detailed in Sections 3.4 and 3.5 is easily estimated by examining the convergence (or divergence) behaviour of the TICS and TCS with respect to increasing iteration $b$. The converged results should also be compared with results obtained using the fully-coupled non-iterative method. As the TP and CL models only solve a single state, iterative coupling cannot be tested, and further discussion of these errors will be left to later chapters.

2. Scattering and ionisation amplitude approximations

(a) Asymptotic final-state continuum-wave approximation

The ionisation amplitude derived from the Peterkop integral formulation given in Section 2.4 is based upon an asymptotic approximation of the final-state continuum waves that is formally correct for $r_1, r_2 \sim \infty$. The error of applying this asymptotic formalism on the finite grids used in PECS can be estimated by studying the convergence behaviour of the extracted cross sections with respect to increasing hyperradius $\rho$ [see (2.65)]. Note that for a single wave function calculation with grid size $R_0$, the ionisation amplitudes can be calculated for any $\rho$ in the range $0 < \rho \leq R_0$, though this error cannot be distinguished from other radially-dependent errors.
(b) Peterkop condition

In order to obtain the correct ionisation amplitude phase using the Peterkop integral formulation for $e$–H collisions, the Peterkop condition (2.61) must be satisfied. As there is no known method of applying this condition for partial-wave scattering wave functions, two Coulomb waves of fixed charged are used in this thesis, and an error in phase will result (though a phase error in the TP or CL models will not affect the cross section results). Recently, Kadyrov et al (2004) have shown that not only is a phase error introduced by using fixed charges, but oscillations in the magnitude of the ionisation amplitude will occur, which diminish with increasing $\rho$. This error cannot be distinguished from other radially-dependent errors.

(c) Asymptotically zero terms

The derivation of the scattering amplitude in Section 2.3 relies upon an asymptotic form for the scattering wave function [see (2.40)] and is also based on the Peterkop asymptotic integral formulation. Using these at finite $\rho$ introduces radially-diminishing errors, as discussed in 2a). In addition to these errors, the final form of the scattering amplitude (2.53) excludes many asymptotically zero terms of the form $\frac{1}{r^2} e^{ikjr^2}$, which causes radially-diminishing oscillations in the scattering amplitude. This error can be minimised by averaging the oscillations near $R_0$.

The errors introduced by the above approximations can be investigated under three broad categories: grid spacing, grid size (and hyperradius) and complex scaling, which we will now discuss in more detail. The TP model is used for this convergence study as very similar convergence behaviour is exhibited by the CL model, except where highlighted in the discussion.

5.2.1 Grid spacing

The grid spacing regions used in this convergence study of the TP model were selected based upon characteristics of the scattering wave function in different regions, as in-
Grid Spacing $h_n$ (a.u.)

<table>
<thead>
<tr>
<th>Region ($n$)</th>
<th>Start (a.u.)</th>
<th>Length (a.u.)</th>
<th>Reference Grid</th>
<th>Converged Grid</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0</td>
<td>0.2</td>
<td>0.005</td>
<td>0.02</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>1.8</td>
<td>0.005</td>
<td>0.06</td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>18.0</td>
<td>0.050</td>
<td>0.20</td>
</tr>
<tr>
<td>4</td>
<td>20.0</td>
<td>180.0</td>
<td>0.100</td>
<td>0.40</td>
</tr>
<tr>
<td>5</td>
<td>200.0</td>
<td>2.0</td>
<td>0.005</td>
<td>0.10</td>
</tr>
<tr>
<td>6</td>
<td>202.0</td>
<td>18.0</td>
<td>0.200</td>
<td>0.70</td>
</tr>
</tbody>
</table>

TICS (a.u.) 0.06721 0.06734
1s-1s TCS (a.u.) 0.4117 0.4111

Table 5.1: Grid spacing regions used for convergence testing of the TP model at $E_0=1.0$ a.u. (27.2 eV) with $R_0 = 200$ a.u. and $\theta = 0.8$ rad. Measurements are made along the real axis, except $h_6$, which is measured along the complex contour. The converged grid column represents the maximum grid spacing able to maintain a standard error of 0.2% in the TICS.

The relationship between the magnitude of the relative error (with respect to the results obtained with the very fine reference-grid spacing given in Table 5.1) and the grid spacing in each region is shown in Figure 5.1 for both TICS and elastic-scattering cross sections. Some interesting conclusions can be drawn from these results.

Firstly, the error of the ionisation and scattering cross sections demonstrate similar dependence on the grid spacing in each region, even though the major contribution
5.2: CONVERGENCE STUDIES

![Figure 5.1](image)

**Figure 5.1**: Relative percentage error of the (a) TICS, and (b) elastic-scattering cross section, for varying grid spacing in each grid region $h_n$ (excluding $h_5$). All results are calculated for the singlet TP model at $E_0=1.0$ a.u. (27.2 eV), $R_0=200$ a.u., $R_{\text{max}}=220$ a.u. and $\theta=0.8$ rad. All errors are calculated relative to the results of the reference-grid calculation shown in Table 5.1.

...to each comes from different regions of the scattering wave function: the dominant contribution to ionisation comes from the region where both $r_1$ and $r_2$ are large ($h_4$ region), whereas the dominant contribution to elastic scattering is in the region where one of $r_1$ or $r_2$ is small ($h_1$ and $h_2$ region). From this we can infer that errors introduced by the spacing in one region affects the accuracy of the scattering wave function in other regions.

The results show an approximate power-law relationship between estimated error and grid spacing, though the $h_1$ and $h_2$ regions have a different slope (and hence power-law) to the remaining regions. The approximate relationships for the example grid and kinematics are as follows. For $n = 1, 2$ the error is approximately $a_n h_n^2$ and for $n = 3, 4, 6$ is approximately $a_n h_n^4$, where $a_n$ is a constant of proportionality. Note that these estimates are the combined error of the two-dimensional variable-grid Numerov formula, two-dimensional Chebyshev-polynomial interpolation and the sensitivity of the
Peterkop integral equations to errors in various regions of the grid, and cannot be directly related to the theoretical error of the Numerov formulae given in (3.6) and (3.9).

Lastly, the results conclusively demonstrate that finer grid spacing is required in the inner regions of the grid (small \( r \)), and may be increased with increasing \( n \) (increasing \( r \)). The relative error in both graphs shows an instability for grid spacing \( h_4 > 0.7 \), which gives an upper limit to the grid spacing in the real region of the grid at this energy.

We also found that the inner grid spacings \( h_1 \) and \( h_2 \) are relatively insensitive to the energy of the incident electron, but vary as a function \( Z \) (the charge on the nucleus) and the initial-state of the target. The grid spacing in the outer regions is influenced by the energy of the incident electron, and we can readily estimate the relationship between them. If we consider the outer regions of the scattering wave function, the most oscillatory area corresponds to elastic scattering \( (r_1 \ll r_2 \text{ or } r_1 \gg r_2) \), where the scattered electron has maximum energy \( (E_0) \) and maximum momentum \( (\sqrt{2E_0}) \). The wavelength of the scattering wave function in this region will be inversely proportional to the momentum. Assuming that, to maintain accuracy, the number of grid points per oscillation must be maintained when \( E_0 \) is varied, the grid spacing required in the \( h_4 \) region can be approximated by

\[
h_4 \approx \frac{(h_4)_{27.2eV}}{\sqrt{E_0}},
\]

where \((h_4)_{27.2eV}\) is obtained from Figure 5.1 depending on the accuracy required. For example, \((h_4)_{27.2eV}=0.4\) a.u. will give approximately 0.1% accuracy and \((h_4)_{27.2eV}=0.7\) a.u. will give approximately 1.0% accuracy in this region. The energy scaling of \( h_6 \) can be obtained in a similar way, and a rough estimate for \( h_3 \) can be obtained using

\[
h_3 \approx \frac{h_2 + h_4}{2}.
\]

This relationship between grid spacing and incident-electron energy is only a rough approximation and many other factors (especially \( R_0 \)) will influence the final error estimate. To obtain highly accurate results a convergence study should be undertaken for the \( E_0 \), \( Z \) and initial target-state of the collision.

The effect of grid spacing near \( R_0 \) is difficult to analyse as the error varies with the “sharpness” of the discontinuity in the first derivative of the scattering wave function at
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Figure 5.2: Relative percentage error of the (a) TICS, and (b) elastic-scattering cross section, for various grid spacing $h_5$ in the region of $R_0$. All results are for the singlet TP model at $E_0=1.0$ a.u. (27.2 eV) with $R_0 - R_{\text{max}}=20$ a.u. and $\theta=0.8$ rad. Errors are relative to an $h_5=0.05$ a.u. calculation.

$R_0$, which varies with $R_0$. In Figure 5.2 we have plotted the relative error of the TICS and elastic-scattering cross section results from scattering wave functions calculated at various $R_0$ and $h_5$. There are, however, many radially-dependent errors in addition to $h_5$ that affect the accuracy of the results. Indeed, at $R_0=200$ a.u. these errors are larger than those due to the discontinuity. In order to isolate the $h_5$ error, we assume that these additional errors are independent of $h_5$, and subtract the results of the reference calculations ($h_5=0.05$ a.u.) from the $h_5=0.1$, 0.2 and 0.4 a.u. results. This gives the net $h_5$ radially-dependent error that is plotted in Figure 5.2.

The TICS and elastic cross sections show similar errors with respect to $h_5$ and a similar dependence upon $R_0$. Each curve has a minima, which occurs when the change in gradient (“sharpness”) of the scattering wave function at $R_0$ (on average over the edges of the hypercube) is minimised. The position of this minima varies with $h_5$ and converges as $h_5$ is reduced. It is clear from the plots presented that a significant error (approximately 0.3%) is introduced into the results if the $h_4$ grid spacing (0.4 a.u.) is
used at $R_0$, and is significantly reduced when $h_5 \ll h_4$. As this region is very narrow ($\approx 1$ a.u.), finer $h_5$ grid spacing only marginally increases $i_{R_0}$ and $i_{max}$ and does not significantly increase the overall computation time.

5.2.2 Grid size ($R_0$) and hyperradius ($\rho$)

The radial dependence of the TICS is shown in Figure 5.3a, where the convergence with respect to $\rho$ at a fixed $R_0=400$ a.u. is shown by a thin solid line, and the convergence with respect to $\rho = R_0$ (from separate scattering wave function calculations with $30 \leq R_0 \leq 400$ a.u.) are shown by crosses. Both curves show an approximately $\rho^{-3/2}$ convergence trend, which contributes 0.05% to the total estimated error at $\rho=400$ a.u. The $R_0=400$ a.u. curve also shows short-wavelength oscillations (with respect to $\rho$) modulated by a larger-wavelength oscillation, both of which diminish in magnitude with increasing $\rho$, but increase the uncertainty of the results at finite $\rho$. These oscillations, and the asymptotic convergence, are consistent with our earlier discussion regarding the $R_0$- and $\rho$-dependent approximations used in our calculations.

An interesting feature observed in Figure 5.3a is that variations of the $\rho = R_0$ results are bound by the $\rho$-oscillations of the $R_0=400$ a.u. calculation. From this, and other convergence studies undertaken, we can make the general observation that the magnitude of the oscillations near $\rho$ give an upper limit to the oscillatory error associated with the calculation at $\rho$, regardless of the $R_0$ used for the calculation. Also, the smoothed $0 < \rho \leq R_0$ results can be extrapolated to estimate the asymptotic result. The total standard error is estimated from these errors in addition to the error estimates obtained from the grid-spacing convergence tests. It is possible, therefore, to estimate the radially-dependent error of a TICS calculation using a single wave function calculation, and the magnitude of this error is readily controlled.

None of the results presented in this thesis are based on a radial extrapolation of the cross sections, but are made at sufficiently large $R_0$ that they are effectively converged. However, the estimated error of the results presented take into account the asymptotic extrapolation beyond $R_0$.

The discrete-final-state cross sections presented in Figure 5.3b also exhibit a radially-
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Figure 5.3: TP model singlet (a) TICS, and (b) 1s-1s and 1s-5s discrete final-state scattering cross sections, with respect to hyperradius $\rho$ [see (2.53) and (2.65)]. Results are calculated at $E_0=1.0$ a.u. (27.2 eV). The 1s-5s results are multiplied by 135. Thin solid lines represent results extracted from a single scattering wave function ($R_0=400$ a.u.) with hyperradius $30 \leq \rho \leq 400$ a.u., in 1 a.u. increments. Crosses represent results extracted from separate scattering wave functions with $R_0 = \rho$. The dashed line in (a) is a best fit of the $R_0=400$ a.u. results to the function $f(\rho) = a + b\rho^{-3/2}$.

diminishing oscillatory behaviour. Beyond $\rho \approx 4n_f^2$ a.u., where $n_f$ is the final-state orbital quantum number, averaging the $\rho$-dependent oscillations of the discrete final-state cross sections gives a well-converged result. The magnitude of the oscillations, however, diminish relatively slowly at a rate proportional to $\rho^{-1}$, reducing from $\pm 0.8\%$ at $\rho=100$ a.u. to $\pm 0.2\%$ at $\rho=400$ a.u. For elastic scattering (1s-1s), the results obtained from the $R_0 = \rho$ calculations closely match the results extracted from the $R_0=400$ a.u. calculation at the same $\rho$. A greater deviation between these two sets of results is evident for the 1s-5s scattering cross sections, though they converge with increasing $R_0$. We note that at finite $\rho$ the 1s-5s scattering amplitude has significant contributions from regions of the scattering wave function that also contribute significantly to the ionisation amplitude. Formally, the orthogonality of the final-state ionisation continuum waves and the discrete
**Figure 5.4:** Singlet SDCS results at $E_0 = 1.0$ a.u. (27.2 eV) for various hyperradii $\rho$ for (a) TP model, and (b) CL model. The FDM TP results of Jones and Stelbovics (2002) are shown for comparison.

final-states should prevent interference between the ionisation and discrete final-state channels. However, the difference between these two sets of results (smoothed) has a $\rho$-dependence similar to that observed in the TICS results in Figure 5.3b. This indicates that, in practice, there is a small amount of interference from the ionisation channel when scattering amplitudes are calculated using the Peterkop integral formulation at finite $R_0$, which diminishes with increasing $R_0$ and is negligible for small $n_f$.

So far, we have discussed convergence with respect to the total ionisation and scattering cross sections. In the TP and CL models, only the $L = l_1 = l_2 = 0$ angular momentum states are considered, and hence the differential cross sections are constant with respect to their angular distribution and will have the same convergence characteristics as the total cross sections. However, for ionisation, the SDCS with respect to energy sharing of the outgoing electrons may exhibit convergence characteristics that vary with the energy fraction $E_1/E$, where $E_1$ is the energy of one of the outgoing electrons. The radial-convergence of the SDCS for the TP and CL models is shown in Figure 5.4. The TP results indicate that convergence near $E_1/E = 0.5$ is not obtained until $\rho$ becomes
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very large. Indeed, even at $\rho=1400$ a.u., the results have not converged completely in this region, and the rate of convergence indicates that the SDCS may be much smaller at this point. At $\rho=1400$ a.u. our TP results are in very good agreement with the FDM results of Jones and Stelbovics (2002). Interestingly, the TICS of these calculations, for all $\rho > 100$ a.u. agree to within 0.2%, so the large variations near $E_1/E = 0.5$ are offset by variations in other regions.

On the other hand, the CL SDCS results in Figure 5.4b show good convergence at $\rho=200$ a.u. for all energy sharing. The convergence problem of the TP model at equal energy-sharing is believed to be an artifact of the discontinuous derivatives of the electron-electron potential (5.1) at $r_1 = r_2$. The CL model has an analytic electron-electron potential (5.4) and does not exhibit the same radial-convergence problem. For the full $e$–$H_Z$ problem, the ionisation amplitude near $r_1 = r_2$ is highly suppressed due to electron repulsion, and we will find in Section 6.1 that its SDCS radial-convergence behaviour is closer to that of the CL model. For both the TP and CL models, there are unphysical oscillations in the SDCS with respect to $E_1/E$ that diminish with increasing $\rho$, and whose wavelength varies with $E$. Therefore, the magnitude of the SDCS error is greater than the TICS error estimate as the integration of the SDCS undertaken to obtain the TICS averages the effect of these oscillations.

5.2.3 Complex scaling

Provided that the region of complex scaling ($R_{\text{max}} - R_0$) gives sufficient exponential damping of the outgoing scattering wave function, we have found that the angle of rotation into the complex plane and the complex scaling length of the radial coordinates has negligible effect on the ionisation and scattering cross section calculations. This is consistent with the results of Baertschy et al (2001b).

Figure 5.5a shows the relative error in TICS with respect to complex scaling length. At $E_0=1.0$ a.u. the relative error introduced when $R_{\text{max}} - R_0 = 5$ a.u. is negligible, and beyond 7 a.u. the TICS remains constant (to six significant figures). At this impact energy, this complex scaling length represents approximately one oscillation of the scattering wave function. This is consistent with the complex-scaling length example
Figure 5.5: Relative error in the TP singlet TICS versus (a) complex scaling length \((R_{\text{max}} - R_0)\) with fixed \(\theta = \pi/4\) radians, and (b) complex scaling angle \(\theta\). Results are calculated at \(E_0 = 1.0\) a.u. (27.2 eV) with \(R_0 = 200\) a.u., and errors are relative to the \((R_{\text{max}} - R_0) = 20\) a.u., \(\theta = \pi/4\) calculation.

in Section 2.1. Using this criterion, we can estimate the scaling length required using

\[
R_{\text{max}} - R_0 \gtrsim \frac{5.0}{\sqrt{2E}},
\]

when \(\theta \approx \pi/4\).

The variation in the TICS with respect to the complex scaling angle \(\theta\) is shown in Figure 5.5b, where it should be noted that the complex-scaling length was varied with \(\theta\) to ensure that the same damping was provided by the ECS damping factor at \(R_{\text{max}}\) \([e^{-(r-R_0)\sin \theta}\) in (2.2)]. The same grid spacing in the complex-scaling region was used for each of these calculations, consequently, a significant contribution to the error shown in this figure may be attributed to using fixed spacing when the period of oscillation and damping rate of the outgoing scattering wave function varies with \(\theta\). Throughout this thesis a complex scaling angle of \(\theta = 0.8 \approx \pi/4\) radians is used, and all convergence studies are undertaken using this angle. Clearly, complex scaling angle has little effect on the accuracy of the PECS calculations, provided that the appropriate complex-scaling
5.3: RESULTS

Table 5.2: TP model singlet ($\sigma_{ns}^0$) and triplet ($\sigma_{ns}^1$) electron-impact discrete final-state scattering cross sections of a ground-state target, with spin weighting, where $n$ is the final orbital quantum number. $E_0$ is the incident-electron energy, and all columns are given in a.u. Superscripts represent powers of 10, e.g. $1.327^{+1} = 1.327 \times 10^1 = 13.27$.

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Table 5.2: TP model singlet ($\sigma_{ns}^0$) and triplet ($\sigma_{ns}^1$) electron-impact discrete final-state scattering cross sections of a ground-state target, with spin weighting, where $n$ is the final orbital quantum number. $E_0$ is the incident-electron energy, and all columns are given in a.u. Superscripts represent powers of 10, e.g. $1.327^{+1} = 1.327 \times 10^1 = 13.27$.

5.3: RESULTS

Table 5.2: TP model singlet ($\sigma_{ns}^0$) and triplet ($\sigma_{ns}^1$) electron-impact discrete final-state scattering cross sections of a ground-state target, with spin weighting, where $n$ is the final orbital quantum number. $E_0$ is the incident-electron energy, and all columns are given in a.u. Superscripts represent powers of 10, e.g. $1.327^{+1} = 1.327 \times 10^1 = 13.27$.

5.3 Results

We have now completed our convergence study for the TP and CL model calculations, and will proceed to present discrete final-state cross sections (elastic and inelastic), TICS, SDCS and ionisation amplitude phase calculations for both models at various electron-impact energies.

5.3.1 Discrete final-state cross sections

Tabulated TP singlet and triplet discrete final-state cross sections, with spin weighting\(^1\), are presented in Table 5.2 for electron-impact energies in the range $0.1 \leq E_0 \leq 2.0$.

\(^1\)Unless otherwise stated all results for a single spin-state presented in this thesis will be spin weighted (multiplied by the spin-weighting factor $\frac{2S+1}{2}$).


Table 5.3: Percentage variation of selected PECS TP discrete final-state scattering cross sections presented in Table 5.2 to CCC calculations (Bray and Stelbovics 1994) ($E_0 = 0.4$ a.u.) and FDM calculations (Jones and Stelbovics 2002) ($E_0 \geq 1.0$ a.u.).

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The variation between our results and FDM benchmark calculations (Jones and Stelbovics 2002) ($E_0 \geq 1.0$ a.u.) or CCC calculations (Bray and Stelbovics 1994) ($E_0 = 0.4$ a.u.) are shown in Table 5.3. All energies presented in Table 5.2 that match energies in these publications were chosen for this comparison. The stated error estimate of the FDM results is 0.1%, and our results agree with these calculations to better than 0.1% for all energies and $n_f$. This is significantly better than our estimated maximum error and demonstrates the improvement in accuracy that is obtained by averaging the $\rho$-dependent oscillations. There is also very good agreement with CCC results at $E_0=0.4$ a.u., except for the $2s$ triplet result. We believe that this discrepancy is due to an increased error in this CCC calculation, though, as it is much smaller than the $1s$ triplet.
result, it is not significant. Overall, the excellent agreement between PECS, FDM and CCC provides convincing evidence of the efficacy of the integral method for extracting discrete final-state cross sections that was developed in Section 2.3.

We present CL discrete final-state cross sections in Table 5.4, calculated using the same $R_0$ and grid spacing as the TP calculations. We are not aware of any published discrete final-state cross sections for the CL model, and estimate the standard error to be similar to the PECS TP calculations.

The CL model triplet elastic cross section at $E_0=0.1$ a.u. is three orders of magnitude smaller than at other energies, and Figure 5.6 shows that this is the result of a wide resonance structure. The singlet resonance is centered at $E_0=0.051$ a.u. and the triplet resonance is centered at $E_0=0.097$ a.u., both of which are unphysical, which highlights that the CL model is not a good model for $e^{-}H$ scattering below the ionisation threshold.

 Examination of the cross section data in Tables 5.2 and 5.4 reveals the distinctly different behaviour of the CL and TP models. The singlet elastic cross sections of the CL model are three times larger than the TP model above ionisation threshold, whereas

---

### Table 5.4: CL model singlet and triplet electron-impact discrete final-state scattering cross sections of a ground-state target, with spin weighting. See Table 5.2 for column details.

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Figure 5.6: Low-energy resonance structure of the CL model singlet \((S=0)\) and triplet \((S=1)\) elastic cross sections.

The triplet elastic cross sections are of similar magnitude. Below threshold, comparison of the elastic cross sections is difficult due to the wide resonance in the CL model. The peak singlet \(n_f\) inelastic cross section of each model are of similar magnitude, but are consistently shifted to lower energies in the CL model. The peak triplet \(n_f\) inelastic cross sections of each model also have similar magnitude, and are shifted to lower energies in the CL model, but to a lesser extent than the singlet case. At energies below the cross sections peak, the CL model results are larger.

5.3.2 Ionisation cross sections

The TP singlet and triplet ionisation cross sections, with spin weighting, are presented in Table 5.5, and were extracted from the same scattering wave functions used in the previous section. The TICS results are presented along with SDCS results at energy sharing \(E_1/E=0.0, 0.25\) and \(0.50\), and the percentage variation from the accurate benchmark FDM calculations of Jones and Stelbovics (2002) is also given, where available.

The estimated standard error of our TICS calculations, based upon convergence studies, is 0.2\% for all energies presented, while the estimated standard error of the
5.3: RESULTS

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<td>0.000(^{+0})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.9</td>
<td>1</td>
<td>1.978(^{-3})</td>
<td>3.545(^{-2})</td>
<td>5.998(^{-3})</td>
<td>0.000(^{+0})</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>1</td>
<td>3.092(^{-3})</td>
<td>0.16</td>
<td>4.442(^{-2})</td>
<td>-0.39</td>
<td>7.542(^{-3})</td>
<td>-1.19</td>
<td>0.000(^{+0})</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>1</td>
<td>7.778(^{-3})</td>
<td>0.11</td>
<td>5.936(^{-2})</td>
<td>-0.08</td>
<td>8.994(^{-3})</td>
<td>0.52</td>
<td>0.000(^{+0})</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>1</td>
<td>9.750(^{-3})</td>
<td>0.02</td>
<td>5.384(^{-2})</td>
<td>-0.08</td>
<td>6.947(^{-3})</td>
<td>0.24</td>
<td>0.000(^{+0})</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 5.5:** TP singlet and triplet TICS and SDCS calculations, with spin weighting, for selected energy-sharing (\( E_1/E \)). Percentage variation from FDM calculations (Jones and Stelbovics 2002), are given where available. All units are a.u.

SDCS results is increased to 0.5% due to slight oscillations with respect to energy sharing, and \( \gg 1\% \) at equal energy-sharing due to insufficient \( R_0 \) for complete convergence. The stated error of the FDM calculations is 0.1% in the TICS and SDCS, increasing to 1% for the SDCS at equal energy-sharing. The PECS and FDM calculations agree to within these estimated errors. However, there are large differences between the PECS and FDM SDCS results at equal energy-sharing. At \( E_0=1.0 \) a.u., PECS results were calculated using \( \rho=1400 \) a.u., but were not fully converged at \( E_1=E_2 \), while the higher-energy results were calculated using \( \rho=400 \) a.u. and were less converged at equal energy-sharing. Though the FDM and PECS equal energy-sharing results agree to within 1% at \( E_0=1.0 \) a.u., we believe that the estimated error of the FDM results in this region are underestimated. The slow rate of the convergence of the PECS SDCS results at equal energy-sharing indicates that for very large \( R_0 \) the SDCS is significantly lower.
CHAPTER 5: MODEL PROBLEMS

Table 5.6: CL singlet and triplet TICS and SDCS calculations, with spin weighting, at selected energy-sharing ($E_1/E$). All units are a.u.

<table>
<thead>
<tr>
<th>$E_0$</th>
<th>$S=0$</th>
<th>$S=1$</th>
<th>$E_1/E=0.00$</th>
<th>$E_1/E=0.25$</th>
<th>$E_1/E=0.50$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$S=0$</td>
<td>$S=1$</td>
<td>$S=0$</td>
<td>$S=1$</td>
<td>$S=0$</td>
</tr>
<tr>
<td>0.6</td>
<td>1.887$^{-2}$</td>
<td>1.276$^{-4}$</td>
<td>3.673$^{-1}$</td>
<td>7.440$^{-3}$</td>
<td>3.781$^{-1}$</td>
</tr>
<tr>
<td>0.7</td>
<td>2.837$^{-2}$</td>
<td>7.378$^{-4}$</td>
<td>2.806$^{-1}$</td>
<td>2.173$^{-2}$</td>
<td>2.840$^{-1}$</td>
</tr>
<tr>
<td>0.8</td>
<td>3.198$^{-2}$</td>
<td>1.720$^{-3}$</td>
<td>2.157$^{-1}$</td>
<td>3.418$^{-2}$</td>
<td>2.129$^{-1}$</td>
</tr>
<tr>
<td>0.9</td>
<td>3.260$^{-2}$</td>
<td>2.845$^{-3}$</td>
<td>1.697$^{-1}$</td>
<td>4.304$^{-2}$</td>
<td>1.622$^{-1}$</td>
</tr>
<tr>
<td>1.0</td>
<td>3.176$^{-2}$</td>
<td>3.944$^{-3}$</td>
<td>1.372$^{-1}$</td>
<td>4.873$^{-2}$</td>
<td>1.256$^{-1}$</td>
</tr>
<tr>
<td>1.5</td>
<td>2.282$^{-2}$</td>
<td>7.516$^{-3}$</td>
<td>6.074$^{-2}$</td>
<td>5.199$^{-2}$</td>
<td>4.357$^{-2}$</td>
</tr>
<tr>
<td>2.0</td>
<td>1.584$^{-2}$</td>
<td>8.427$^{-3}$</td>
<td>3.463$^{-2}$</td>
<td>4.347$^{-2}$</td>
<td>1.920$^{-2}$</td>
</tr>
</tbody>
</table>

than the results presented in Table 5.5. The limitation of $\rho \leq 1400$ a.u., imposed by computational resource limitations, prevents an accurate extrapolation of the SDCS equal-energy results for the TP model.

Our CL model singlet and triplet TICS results and selected SDCS results, with spin weighting, are presented in Table 5.6. The estimated standard error of these calculations is the same as the TP model, except that at equal energy-sharing our SDCS results are fully converged with an estimated standard error of 0.5%. There are no tabulated TICS or SDCS results available for the CL model to perform an accurate comparison with our results, however, the digitised CL singlet TICS published by Kato and Watanabe (1996) are in good agreement with the present calculations for $E_0 > 0.6$ a.u. (see Figure 5.12).

Plots of the singlet and triplet SDCS for the TP and CL models (at energies consistent with Tables 5.5 and 5.6) are presented in Figures 5.7 and 5.8. The CL singlet plots have been normalised at equal energy-sharing to highlight the change in shape as a function of incident-electron energy. At $E_0=0.6$ a.u. the SDCS shows a 4% reduction at $E_1 = 0$, compared with $E_1 = E_2$, and becomes flat at $E_0=0.7$ a.u. Above this energy, the SDCS becomes markedly asymmetric. There are no fully-quantal CL model SDCS results available for comparison, however the energy-dependence of the SDCS shape, changing from concave to convex as energy approaches threshold, is supported by the semiclassical
5.3: RESULTS

Figure 5.7: Singlet SDCS results, with spin-weighting, for (a) TP model, and (b) CL model, at various incident electron energies \( E_0 \). The CL model results have been normalised to 1.00 at equal energy-sharing \((E_1=E_2)\), and the original SDCS results (a.u.) may be obtained by multiplying by the constant \( \alpha \). The FDM TP singlet results of Jones and Stelbovics (2002) are shown by crosses.

Figure 5.8: Triplet SDCS results, with spin-weighting, for (a) TP model, and (b) CL model, at various incident electron energies \( E_0 \). The FDM TP triplet results of Jones and Stelbovics (2002) are shown by crosses.
calculations of Rost (1994). In both models the triplet SDCS are suppressed near the equal energy-sharing region due to the Pauli exclusion principle.

It should be noted that the PECS scattering wave functions are symmetric or antisymmetric with respect to exchange of electrons, consequently, all SDCS calculations are symmetric about $E_1/E = 0.5$. As such, all SDCS calculations in this thesis are presented for the range $0.0 \leq E_1/E \leq 0.5$.

### 5.3.3 Ionisation amplitude phase

Figure 5.9 shows the SDCS for the TP model using several choices for the final-state continuum waves [$\Phi$ in (2.59)]. Using two Coulomb waves (2.60) (CC) provides a very smooth SDCS, and with sufficiently large $\rho$ provides results very close to the FDM results of Jones and Stelbovics (2002). This method was first used by McCurdy et al (2001), and is able to accurately calculate the magnitude of the ionisation amplitude for both models considered in this thesis, as well as the full $e$–H problem (Baertschy et al 2001a). Unless otherwise stated, this method is used to calculate all ionisation cross sections presented in this thesis.
However, it is known that using (CC) for the TP model leads to a divergent ionisation amplitude phase (Rescigno et al 2003), as the correct asymptotic continuum waves for ionisation in the TP model is a Coulomb wave for the slow electron and a plane wave for the fast electron (where the central charge is shielded by the slow electron), giving

\[ \Phi_{1,k_1,k_2}^{(-)}(r_1,r_2) = \phi_{l_1}^{(-)}(1;k_1,r_1) \sin(k_2r_2), \quad k_1 < k_2. \]

(5.10)

When (5.10) is used with TP scattering wave functions, however, the SDCS oscillates wildly due to interference from discrete final-state scattering that is also contained in the scattering wave function. To remove this interference we have made the \( < r\mid k > \) function orthogonal to the first \( N \) bound states of hydrogen (with \( l = 0 \)) using the relation

\[ < r\mid k >_{\perp} = \sum_{n=1}^{N} < r\mid n00 > < n00 \mid k >, \]

(5.11)

where \( N \) can be made arbitrarily large. As \( < r\mid k >_{\perp} \leq < r\mid k > \) when \( r \to \infty \), the orthogonalisation of the plane wave has no effect upon the asymptotic value of (2.59). For the finite values of \( \rho \) used in our calculations, orthogonalisation of the plane wave removes interference from discrete final-state scattering channels, and \( N=10 \) was sufficient for this purpose.

Previously, for a short-range potential model problem, McCurdy and Rescigno (2000) demonstrated that using a projection operator to project out the elastic channel from the scattering wave function removes the wildly oscillatory behaviour caused by the discrete channels of the problem. Orthogonalisation of the plane-wave is equivalent to their procedure.

Figure 5.9 shows that the SDCS results using a Coulomb wave and an orthogonalised plane-wave (CO) removes interference from the discrete channels, and gives results very similar to the (CC) results, but with minor fluctuations of the order of 1%. These fluctuations diminish with increasing \( \rho \). For the case of two orthogonalised plane-waves (OO), good results are obtained near equal energy-sharing, but significant oscillations are apparent at asymmetric energy-sharing.

Figure 5.10 shows the phase of the TP and CL ionisation amplitudes extracted at various \( \rho \). The Coulomb phase(s) \( e^{i\sigma(Z,k)} \) in (2.64)] has been excluded from all phase
For the TP model, it is apparent that the phase is divergent when (CC) are used for the final-state continuum waves, which is consistent with the known logarithmic phase behaviour of this final state. However, the phase is convergent when (CO) are used for the final-state continuum waves. The slight \( \rho \)-dependent phase differences near \( E_1/E=0 \) in the (CO) plots do not indicate a slowly diverging phase. Convergence studies showed that our primary grid spacing (0.40 a.u. at this energy) was required to be halved in order to provide fully converged phase results with respect to increasing \( \rho \), indicating that convergence of the ionisation amplitude phase is much more sensitive than the magnitude to numerical errors introduced by the Numerov finite-difference method.

For the CL model shown in Figure 5.10b, neither the (CC) nor (CO) final-state continuum waves provide convergent phase results, as neither describes the correct asymptotic behaviour when \( k \) approaches zero.
5.3: RESULTS

totic form of the final-state continuum waves in this model (which are not known analytically).

Recently, Rescigno et al (2003) demonstrated that the ionisation amplitude phase for both the TP and CL models could be made convergent, and for the TP model match the (CO) results presented in Figure 5.10a. Their procedure may be applied for any choice of charges for the final-state Coulomb waves ($Z_1$ and $Z_2$), by adding logarithmic phase factors, including the Peterkop phase. Their phase adjustment equations for the two models are

$$
\phi_{TP} = \left( \frac{1}{k_<} - \frac{Z_1}{k_1} - \frac{Z_2}{k_2} \right) \ln(2K\rho), \tag{5.12}
$$

$$
\phi_{CL} = \left( \frac{1 - Z_1}{k_1} + 1 - \frac{Z_2}{k_2} - \frac{1}{k_1 + k_2} \right) \ln(2K\rho), \tag{5.13}
$$

where $K = \sqrt{2E}$ and

$$
Q(k; Z) = \arg(\Gamma(1 - i\frac{Z}{k}) + 2\frac{Z}{k} \ln(k/K)). \tag{5.14}
$$

The phase adjustment for the TP model is therefore zero for the (CO) case, and $\phi_{TP} + Q(k_>, 1)$ for the (CC) case. The phase adjustment for the CL model is $\phi_{CL}$ for the (CO) case and $\phi_{CL} + Q(k_>, 1)$ for the (CC) case. These phase adjustments have been applied separately to our TP and CL model results in Figure 5.10, and demonstrate that the adjustments give $\rho$-convergent phases that are independent of the $Z_1$ and $Z_2$ choice for the final-state asymptotic continuum waves.

Figure 5.11 shows the ionisation amplitude phase for the TP model singlet and triplet states at various incident-electron energies using the (CO) final-state asymptotic continuum waves. The phase is clearly energy dependent, and the plots also demonstrate a systematic flattening (with respect to the $E_1/E$ energy fraction) with increasing $E_0$. These plots were extracted at varying hyperradii (400-1000 a.u.), where good convergence of the SDCS were obtained, and demonstrate only minor fluctuations in the phase with respect to energy fraction, though oscillations increase near equal energy-sharing in the triplet plots, where the ionisation amplitudes are highly suppressed and errors are larger.

The TP and CL model calculations in this section demonstrate that $\rho$-convergent ionisation amplitude phases cannot be obtained directly from the Peterkop integral formulation unless the correct asymptotic form for the asymptotic final-state continuum
Figure 5.11: TP ionisation amplitude phases at various incident-electron energies, using a Coulomb wave for the slow electron and an orthogonalised plane wave for the fast electron, for the (a) singlet state, and (b) triplet state.

waves are used. We will discuss this issue in relation to the full $e-H_Z$ problem in Section 6.1.

5.4 Threshold behaviour

Since Wannier proposed the threshold law for electron-atom ionising collisions, based on classical mechanics, there has been a large number of theoretical and computational studies undertaken in an effort to give quantum-mechanical confirmation for this law. We will leave the detailed discussion of these studies until we investigate the threshold behaviour of the full $e-H$ problem in Chapter 7. In summary though, all theoretical and computational studies undertaken to verify this relationship have made significant a priori assumptions in order to make the calculations tractable.

Calculations near ionisation threshold using coordinate-space methods are difficult due to the very large grid sizes required to achieve convergent results, which are approximately inversely proportional to the total energy ($R_0 \propto 1/E$). The CL model simplifies
the calculations by approximating the predicted electron-electron potential of the full problem near ionisation threshold, and Kato and Watanabe (1996) were able to confirm that this model is consistent with Wannier’s predictions. In this section we will investigate the threshold behaviour of the CL model using the PECS method, and compare our results with these and other calculations.

Theoretical and computational studies of the TP model ionisation threshold behaviour have also been undertaken, though, as the electron-electron potential of this model is unphysical, the threshold behaviour is significantly different to that of the full e–H problem. This makes an investigation of the threshold behaviour of the TP model a somewhat “academic” exercise, but there is sufficient disagreement between available calculations to warrant an investigation using PECS.

5.4.1 Collinear model

The results of our PECS CL model TICS calculations near ionisation threshold are shown in Figure 5.12 along with other recent calculations. Clearly, there is good agreement between our results and those of Kato and Watanabe (1996) for energies greater than 0.05 a.u., and our results exhibit a significant reduction in energy-dependent oscillations at lower energies. However, it should be noted that the Kato and Watanabe values were obtained by scanning and digitising their published results, which may have introduced additional errors. Our calculations are in good agreement with the ECS results of McCurdy et al (2001) for energies above 0.01 a.u., and with the time-dependent results of Robicheaux et al (1997) above 0.03 a.u., while both of these data sets show significant errors below these energies. The results presented in the singlet plot have been divided by $E^{1.127}$ to highlight their threshold behaviour, where it is expected that the gradient of the plots should approach zero as the energy approaches threshold, if the Wannier threshold law holds for the CL model. This is indeed the case for our results and those of Kato and Watanabe.

For total energies between 0.2 a.u. and 0.04 a.u. an overall estimated error of 0.2% in our total ionisation cross section results was maintained. At 0.2 a.u. this required $R_0 = 600$ a.u. and at 0.04 a.u. $R_0 = 1400$ a.u.. Below 0.04 a.u., $R_0$ was limited to 1400
Figure 5.12: (a) Singlet TICS, and (b) triplet TICS, for the CL model (with spin weighting) as a function of total energy near ionisation threshold. The results are compared with those of Kato and Watanabe (1996), McCurdy et al (2001) and Robicheaux et al (1997). The singlet and triplet results are divided by $E^{1.127}$ and $E^{3.38}$ respectively, to emphasise their threshold behaviour.

Due to limits on our computational resources. As a result, the estimated error of these very low-energy calculations increased to 0.5-1.0%.

We used a nonlinear fitting procedure, similar to that described by Kato and Watanabe, over the energy range 0.005-0.2 a.u., by fitting to the function $\sigma = E^\eta g(E)$, where an $n$th order series expansion of $g(E)$ was made. Our fitting gave

$$\sigma_{S=0}^{\text{CL}} = E^{(1.128\pm0.004)} \left( (0.386\pm0.007) - E(1.69\pm0.08) + E^2(4.1\pm0.5) - E^3(4.6\pm1.1) \right),$$

which shows a three-fold improvement in estimated error compared with Kato and Watanabe’s result of $\sigma \propto E^{1.124\pm0.013}$.

With this fitting procedure, both the value of $\eta$ and its estimated error are dependent upon the number of terms in $g(E)$ and the estimated error of each of our data points. Our initial nonlinear fit was based upon the estimated errors of our results, and the
5.4: THRESHOLD BEHAVIOUR

Table 5.7: Coefficients for singlet CL model TICS nonlinear fitting for $E = 0.005-0.200$ a.u. Figures in brackets are the estimated standard error of the least significant figure.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$\chi^2$</th>
<th>$E^n$</th>
<th>$a_0$</th>
<th>$a_1E$</th>
<th>$a_2E^2$</th>
<th>$a_3E^3$</th>
<th>$a_4E^4$</th>
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<tbody>
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<td>164.5</td>
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<td>0.142(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>117.0</td>
<td>1.071(2)</td>
<td>0.300(3)</td>
<td>-0.76(1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>50.7</td>
<td>1.112(2)</td>
<td>0.359(3)</td>
<td>-1.35(2)</td>
<td>2.01(6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>46.5</td>
<td>1.128(4)</td>
<td>0.386(7)</td>
<td>-1.69(8)</td>
<td>4.1(5)</td>
<td>-4.6(11)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>46.3</td>
<td>1.148(5)</td>
<td>0.43(1)</td>
<td>-2.4(2)</td>
<td>12(2)</td>
<td>-43(9)</td>
<td>75(16)</td>
</tr>
</tbody>
</table>

The fitting function was then used to calculate the standard deviation of our results in each of four energy regions of equal size. These standard deviations were then used as an improved estimate for the absolute error of the points in that region, and a new value of $\eta$ was calculated. This procedure was performed iteratively until convergence of the fitting function coefficients was obtained.

The results of our $n = 0$ to $n = 4$ nonlinear fits are detailed in Table 5.7. The $n = 3$ polynomial for $g(E)$ was selected as the best fit, and is used for our estimate of the threshold behaviour given above. From the table we can see that the $\chi^2$ parameter reduces with increasing $n$, indicating an increasingly better fit. The difference between the $\chi^2$ of the $n = 3$ and $n = 4$ fits is not significant, indicating that over this energy range $g(E)$ can be suitably represented by a third-order polynomial. As our calculations have numerical errors, increasing the degrees of freedom of the fitting function beyond the $n = 3$ case did not improve the $\chi^2$ result and necessarily increased the standard error of the coefficients. In order to select the best fit of our results we have consistently chosen $n$ such that $\chi^2$ approaches its minimum while the maximum standard error of the coefficients remains below 25%, and the polynomial coefficients do not increase exponentially.

We also performed a nonlinear fitting of the singlet data over the smaller energy range 0.005-0.05 a.u., and present these results in Table 5.8. As this region is closer to threshold, it was anticipated that $g(E)$ would be suitably represented be a lower order
polynomial. However, due to the fewer number of points, and the increased estimated error of the points in this region, there is some uncertainty as to whether \( n = 1 \) or \( n = 2 \) provides the best fit in this region. However, the coefficients of the \( n = 1 \) fit are consistent with the \( n = 3 \) fit from Table 5.7, while the error of the \( a_2 \) coefficient for \( n=2 \) exceeds our limit for the maximum allowable error of the coefficients. As a test of the fitting function (5.15) we performed a linear fit of the transformed data, over the same energy intervals, and obtained the same values of \( \eta \), within their estimated standard error.

Using semiclassical methods, the threshold power law for the triplet wave function for three-body breakup was first proposed by Klar and Schlecht (1976) to be \( E^{3.881} \). This incorrect result was repeated in subsequent publications (Greene and Rau 1982, 1983), but was correctly calculated by Peterkop (1983) to be \( E^{3.381} \). This matched subsequent derivations (Feagin 1984, Rost 1995), also using semiclassical methods. It should be noted that the threshold laws for the singlet and triplet \( L = 0 \) partial waves of the full hydrogen problem are predicted to be the same as the \( L = 0 \) CL model (Peterkop 1977, 1983, Rost 1995). Also, the threshold law for the \( L > 0 \) singlet and triplet partial waves for the full hydrogen problem is the same as the \( L = 0 \) singlet partial wave (Roth 1972, Klar and Schlecht 1976, Greene and Rau 1982, 1983).

Similar fitting procedures were applied for the CL triplet TICS presented in Figure 5.12b, over the energy range 0.01-0.2 a.u., which gave a fitting function (in a.u.)

<table>
<thead>
<tr>
<th>( n )</th>
<th>( \chi^2 )</th>
<th>( E^\eta )</th>
<th>( a_0 )</th>
<th>( a_1 E )</th>
<th>( a_2 E^2 )</th>
<th>( a_3 E^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>55.5</td>
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<td>1</td>
<td>19.7</td>
<td>1.129(2)</td>
<td>0.386(3)</td>
<td>-1.48(3)</td>
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<td></td>
</tr>
<tr>
<td>2</td>
<td>16.7</td>
<td>1.152(8)</td>
<td>0.43(2)</td>
<td>-2.3(3)</td>
<td>7(3)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>17.9</td>
<td>1.14(2)</td>
<td>0.40(4)</td>
<td>-1.9(9)</td>
<td>8(16)</td>
<td>-56(125)</td>
</tr>
</tbody>
</table>

**Table 5.8**: Coefficients for singlet CL model TICS nonlinear fitting for \( E = 0.005-0.050 \) a.u.
of

\[ \sigma_{S=1}^{\text{CL}} = E^{(3.365 \pm 0.009)} ((0.56 \pm 0.02) - E(3.59 \pm 0.25) + E^2(11 \pm 1) - E^3(14 \pm 3)). \] (5.16)

No other triplet calculations, or fits to the predicted threshold law, are available for comparison.

When fitting of the triplet results was made over a smaller energy range, or compared with the results of a linear fit of the transformed data, \( \eta \) did not coincide within the stated error, and the polynomial coefficients changed significantly (as they are very sensitive to small changes in \( \eta \)). We have therefore increased our estimated standard error, and give the \( L = 0 \) CL triplet threshold power law as \( E^{3.37 \pm 0.02} \). This result is consistent with the semiclassical theoretical calculations of Peterkop (1983). The estimated error for \( \eta \) is larger than our singlet result due to using fewer data points, limiting \( R_0 \) to 400 a.u., and the suppression of the triplet cross sections, all of which resulted in an increase in the estimated error or our plot points.

From our results presented in this section, it is clear that PECS can provide very accurate TICS results for the CL model for energies very close to ionisation threshold. From these results we have shown that the CL model strongly corroborates the Wannier and Peterkop ionisation threshold laws for singlet and triplet states, respectively. However, as the CL model uses similar \textit{a priori} assumptions to those used to derive these laws, the analysis presented here cannot be considered to give complete quantum-mechanical confirmation for these laws. In Chapter 7, however, we will undertake a similar investigation using the PECS method for the full \( e-H \) problem, which \textbf{will} provide full \textit{ab initio} quantum-mechanical support.

\subsection*{5.4.2 Temkin-Poet model}

An interesting observation was made of the TP model in the \textit{classical} regime: Friedrich \textit{et al} (1999) showed that ionisation cannot occur below a total energy of 1/6 a.u. even though it is energetically allowed. Quantum mechanically, therefore, we would expect a tunnelling suppression of the TICS near this energy, causing a significant deviation of this model from the Wannier threshold law.
For the singlet TP model Macek and Ihra (1997) made a fully-quantal prediction for the threshold power law of

$$\sigma_{S=0}^{\text{TP}} \propto \exp(-6.870E^{-1/6} + 3.680E^{1/6}). \quad (5.17)$$

Later, Miyashita et al (1999) performed a fit of their results (ignoring the $E^{1/6}$ term) and obtained (in a.u.)

$$\sigma_{S=0}^{\text{TP}} = \pi(104 \pm 1) \exp(-(6.75 \pm 0.02)E^{-1/6}) \quad (5.18)$$

at energies approaching threshold. They also replaced $E^{-1/6}$ with $E^{-\alpha}$ and calculated $\alpha$ from their numerical fit. There is justification for this as the derivation of $E^{-1/6}$ relied on some theoretical approximations (Macek and Ihra 1997). This gave a threshold behaviour of

$$\sigma_{S=0}^{\text{TP}} \propto \exp(-(8.4 \pm 0.1)E^{-0.149\pm0.008}). \quad (5.19)$$

Our TP singlet TICS results are plotted in Figure 5.13a, where we have divided our results by the two Miyashita et al fitting functions to emphasise their near-threshold behaviour. With the logarithmic energy scale of this figure, we would expect the gradient of our plots to approach zero as we approach threshold, if our results support the predicted threshold behaviour as the ionisation threshold is approached. It appears, therefore, that the threshold prediction of (5.18) better describes the near threshold behaviour of our results.

Using nonlinear fitting procedures we were able to fit our data to the function $\exp(aE^{-1/6})(b + cE)$ over the energy range 0.005-0.100 a.u., and obtained (in a.u.)

$$\sigma_{S=0}^{\text{TP}} = \pi \exp(-(6.868 \pm 0.007)E^{-1/6})\{(142 \pm 2) - (224 \pm 8)E\}, \quad (5.20)$$

which matches Macek and Ihra, within estimated error.

Our fitting to the function $\exp(aE^{-\alpha})(b + cE)$ over the same energy range gave

$$\sigma_{S=0}^{\text{TP}} = \pi \exp(-(6.7 \pm 0.3)E^{-0.169\pm0.004})\{(117 \pm 39) - (181 \pm 73)E\}. \quad (5.21)$$

The significant errors of this fit limit the conclusions that we can draw from our results, and many more data points would be required to accurately fit our data to this function.
5.4: THRESHOLD BEHAVIOUR

![Graphs showing TICS vs total energy for singlet and triplet TP models.]

**Figure 5.13:** (a) Singlet, and (b) triplet TP TICS, with spin weighting, versus total energy. Singlet results are divided by the two fitting functions calculated by Miyashita et al (1999), and the triplet results are divided by the fitting function calculated by Ihra et al (1997). Miyashita et al (1999) TP singlet results are displayed with long dashes, and are mostly indistinguishable from our results. Their lower-energy results are not displayed due to significant errors in digitizing their published figures.

However, the $E^{-0.169\pm0.004}$ term is again consistent with the Macek and Ihra prediction of an $E^{-1/6}$ dependence, and in disagreement with the $E^{-0.149}$ dependence proposed by Miyashita et al (1999).

In Figure 5.13b we present our triplet TICS results, divided by the threshold form calculated by Ihra et al (1997)

$$\sigma_{S=1}^{TP} \propto \frac{1}{2E + 1} \exp(-15.766E^{-1/6} - 1.162E^{1/6}). \quad (5.22)$$

Once again, the gradient of the plot approaches zero as $E$ approaches zero, supporting their estimate of the threshold behaviour for the TP triplet model. When a nonlinear fit of our results was made to this functional form, the estimated error of all the coefficients were too large to allow any conclusions to be made. This was due to the very small cross section near threshold and the limited number of data points.
It should be noted that our fitting functions for the Temkin-Poet model [(5.20) and (5.21)] were very sensitive to the energy range chosen for the fit, and the number of terms in the modifying polynomial. Though our results match the $E^{-1/6}$ functional form within our estimated error, giving evidence of its validity, the possibility of alternate forms for the threshold law that closely match our results in the energy range considered cannot be discounted.

This completes our investigation of scattering and ionisation cross sections for the TP and CL models. The PECS method is clearly able to provide very accurate results, equal to or better than all previous benchmark calculations for these models, over a wide range of energies. In summary, this $e$–H model study

• is the first to demonstrate that accurate discrete final-state scattering cross sections can be obtained from the ECS scattering wave functions,

• provides the first published discrete final-state scattering cross sections for the CL model,

• provides the first test of the phase correction formulae of Rescigno et al (2003) for the CL model,

• is the most accurate fully-quantal confirmation of the Wannier threshold law undertaken to date,

• is the first fully-quantal confirmation of the ionisation threshold law for the $L=0$ triplet partial wave proposed by Peterkop (1983), and

• supports the TP ionisation threshold laws proposed by Macek and Ihra (1997) and Ihra et al (1997).

Having demonstrated the utility of this method for these model calculations, we will now proceed to apply PECS, and its iterative coupling techniques, to the full $e$–H$_2$ problem.
Chapter 6
Hydrogen and Hydrogenic Ions

The ECS method has thus far been applied to $e$–H($1s$) ionising collisions (Rescigno et al 1999, Baertschy et al 2001a) for electron-impact energies in the range 14.6 to 54.4 eV, and provided highly accurate results that are consistent with experiment and other state-of-the-art computational methods. In this chapter we will demonstrate that the PECS method can be applied to a complete range of electron-hydrogen collisions by considering discrete final-state collisions, both above and below ionisation threshold, ionising collisions over a wide range of energies and electron collisions with excited-state and charged hydrogenic targets. We will see that the excited-state and hydrogenic collision systems are far more computationally demanding than those considered by the ECS method, thus demonstrating the significant computational advantage of the PECS method and its iterative coupling and energy perturbation techniques.

6.1 Convergence studies

In Section 5.2 we considered the convergence of the PECS results with respect to grid spacing, grid size and complex scaling parameters for $e$–H model problems. These studies are also applicable to the full calculations presented here and will not be repeated. However, there are many more convergence issues that must be considered with the full problem, which we will address here.

Firstly, we will consider the convergence behaviour of the iterative coupling and energy perturbation techniques that we have developed for the PECS method. We will then investigate the behaviour of the partial cross sections for $e$–H$_2$ collisions with respect to angular momentum, which will give insight into how the computational demand of the problem scales with changes in impact energy and the state and charge of the target. Lastly, we will examine the radial convergence of both the total and differential cross sections (DCS).
Figure 6.1: (a) Error in ionisation cross sections versus iteration number, and (b) maximum relative change in magnitude of the scattering wave function for each iteration. Calculations relate to the $L=0$ $S=0$ partial waves of $e^{-}H(1s)$ at $E_0=1.0$ a.u. with $n_g=6$, $\rho=R_0=100$ a.u. and $l_1 = l_2 \leq 5$. The error in (a) is relative to the solution obtained without iterative coupling ($n_g=1$).

6.1.1 Iterative coupling

The rate of convergence of the PECS iterative-coupling technique is shown in Figure 6.1 for an $e^{-}H$ collision at $E_0=1.0$ a.u. The behaviour shown by the $L=0$ $S=0$ partial wave used in this example is representative of other partial waves, though the rate of convergence is dependent upon many parameters, which we will see in subsequent graphs. Two significant features of the iterative coupling technique can be observed in these plots. Firstly, once a converging trend is demonstrated for all coupled partial waves ($b \geq 8$ in this example), the error of the partial cross sections shown in (a) are closely matched by the maximum relative change in magnitude of their associated scattering wave function, shown in (b). This is an important observation because the ionisation cross section calculations are much more computationally intensive than a simple difference calculation, so the contribution of iterative coupling to the estimated
Figure 6.2: Iterative-coupling error of an e–H scattering wave function for various iteration numbers $b$ along (a) a contour of fixed hyperradius $\rho=100$ a.u., and (b) the radial $\alpha = \pi/4$ (where $r_1=r_2$). The $l_1=l_2=0$ partial wave from Figure 6.1 was used for this analysis, and the errors are relative to the $n_g=1$ solution. Both plots use the same legend.

The absolute error of the cross sections can be constantly monitored using the latter without incurring a large computational overhead. Throughout this thesis iterative coupling is continued until all coupled states converge to better than 0.1%. Secondly, the states with the largest contributions to the TICS are the first to converge, and will therefore be converged to a much greater accuracy. In this example, $(l_1,l_2)=(5,5)$ converges to better than 0.1% by $b=20$ at which point the total cross section for this $L=0 \ S=0$ partial wave has an error of approximately 0.0001% (relative to the solution obtained without iterative coupling). As such, iterative coupling has a negligible contribution to the estimated error of the calculations presented in this thesis.

The absolute error of the $L=S=l_1=l_2=0$ scattering wave function in different coordinate regions, for various iteration numbers, is shown in Figure 6.2. It is apparent that at small and large hyperangles, when one of $r_1$ or $r_2$ is small, convergence is much more rapid. When both $r_1$ and $r_2$ are large convergence is slower; this region has the largest
Figure 6.3: Iterative-coupling iterations required to converge $e$–H scattering wave functions (to better than 0.1%) for varying (a) total energy $E$ ($L=0$), and (b) partial-wave angular momentum $L$ ($E_0=1.0$ a.u.). The scattering wave functions were calculated using $R_0=100$ a.u. and maximum $n_g$, except $L=2$ (circled), which used a reduced $n_g$ to improve the rate of convergence.

contribution to the ionisation cross section. This convergence behaviour is consistent with the magnitude of the coupling coefficient [see (2.37) and (A.24)], which has a radial dependence of $r^\lambda_1/r^\lambda_{>1}$ and gives maximum coupling when $r_1 \approx r_2$. Figure 6.2b shows that when both $r_1$ and $r_2$ are small, convergence is also rapid.

The iterative coupling convergence rate is different for each spin state and is strongly related to the energy of incident electron. In Figure 6.3a we can see that the number of iterations required to achieve convergence increases rapidly with decreasing total energy. At energies near the ionisation threshold the iterative coupling technique becomes divergent. The triplet spin state, however, requires much fewer iterations to converge and does not become divergent until energies very close to ionisation threshold are reached. Though the $L=0$ triplet wave function in this example becomes increasingly suppressed as energy approaches zero, due to the Pauli exclusion principle, the iterative-coupling convergence rate for all triplet states is similar. Likewise, when the target is initially in
6.1: CONVERGENCE STUDIES

Figure 6.4: Iterative-coupling iterations required to converge \( e-H \) scattering wave functions (to better than 0.1%) for (a) varying total energy \( E \), \( n_g \) and iterative-coupling method \((L=0 \ S=0 \ R_0=100 \ \text{a.u.})\), and (b) varying grid size \( R_0 \) \((E_0=1.0 \ \text{a.u.} \ L=0 \ \text{method}=[B])\). Method [A] couples results of last iteration (equations 3.20) and method [B] couples latest available results (equation 3.21 and 3.23).

an excited state with \( l_i \geq 1 \) (when odd parity is allowed) the odd parity states (both singlet and triplet) converge much more quickly than even parity states.

The number of iterations can be reduced significantly when the convergence rate is marginal by relaxing the 0.1% maximum error for all scattering wave functions and allowing a much larger error for those states that do not contribute significantly to the TICS. However, this may result in an increase in the error of the angular-differential cross sections for some kinematics, so has not been used in this thesis.

The rate of convergence of the iterative coupling technique is also dependent upon the angular momentum \( L \) of the partial wave. Generally, the \( L \) that has the largest contribution to the TICS requires the most iterations. The results for \( E_0=1.0 \ \text{a.u.} \) are shown in Figure 6.3b, noting that for \( L=2 \) (which provides the largest contribution to the TICS [see Figure 6.6]) a smaller value of \( n_g \) was required to achieve an acceptable convergence rate. Convergence for higher-\( L \) and all triplet states was rapid.
CHAPTER 6: HYDROGEN AND HYDROGENIC IONS

The dependence of the iterative-coupling convergence rate on the iterative-coupling method was discussed in Section 3.4, and in Figure 6.4a we can see that using the latest iterative estimate for the coupled states (method [B]) converges more quickly than when only the results of the previous iteration are used (method [A]), and is convergent to much lower total energies. The convergence rate of method [B] can be further improved, and used at energies closer to ionisation threshold, by reducing the number of iterative-coupling groups \( n_g \). However, this also increases the memory requirement and calculation time, as discussed in Sections 4.1 and 4.2. Figure 6.4b shows that the number of iterations increases with increasing grid size.

When convergence of the PECS iterative coupling technique becomes marginal or diverges, there are several strategies in addition to decreasing \( n_g \) that improve the rate of convergence. Firstly, an average of two or more previous iterations can be used instead of the previous iteration only, e.g. \( (\psi_{b-1} + \psi_{b-2} + \psi_{b-3})/3 \). Though initial convergence is slower with this method, it is smoother with less pronounced oscillations and convergence can often be achieved when using \( \psi_{b-1} \) alone is divergent. Also, the order in which the \( (l_1, l_2) \) states are distributed amongst the \( n_g \) coupling groups affects the rate of convergence. In the convergence studies presented here, the \( (l_1, l_2) \) states with the lowest \( l_1 + l_2 \) are allocated to the first group, the next lowest to the second group, and so on, which does not necessarily provide the best convergence rate. In some circumstances the convergence rate is improved if the \( (l_1, l_2) \) states are distributed as evenly as possible amongst the coupling groups so that each group will contain wave functions of large magnitude and small magnitude. In Table 6.1 we have summarised the effect of different PECS parameters upon the rate of convergence of the iterative-coupling technique.

In Section 3.5 we developed an iterative method for solving the PECS scattering wave functions when the energy is perturbed by \( \Delta E \) from its initial value \( E \). Unlike iterative coupling, though, this method is convergent over a broad range of energies, including those near and below ionisation threshold. Figure 6.5 shows the range of \( \Delta E/E \) for which convergent results can be obtained, for several total energies. Generally, good convergence is obtained for perturbations in total energy of \( \pm 5\% \), and if iterative-coupling is
6.1: CONVERGENCE STUDIES

<table>
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<tr>
<th>Parameter</th>
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</tr>
<tr>
<td>$R_0$</td>
<td>Increase with increasing $R_0$</td>
</tr>
<tr>
<td>$n_c$</td>
<td>Increase with increasing $n_c$</td>
</tr>
<tr>
<td>$n_g$</td>
<td>Increase with increasing $n_g$</td>
</tr>
<tr>
<td>$L$</td>
<td>Reduce with increasing $L$ (beyond peak $L$)</td>
</tr>
<tr>
<td>$S$</td>
<td>Reduce for $S=1$ (triplet)</td>
</tr>
<tr>
<td>$\Pi$</td>
<td>Reduce for $\Pi=1$ (odd parity)</td>
</tr>
</tbody>
</table>

Table 6.1: Effect of PECS parameters on the rate of convergence of iteratively-coupled scattering wave functions.

**Figure 6.5**: Energy-perturbation iterations required to converge $e$–$H L=0 S=0$ scattering wave function (to better than 0.01%) for varying $\Delta E/E$ at $E=1.00$, 0.10 and 0.01 a.u., using $R_0=70$, 100 and 200 a.u., respectively, and $n_g=1$

Convergent at the desired energy, both iterative-coupling and energy perturbation iterations can be used simultaneously. The range of $\Delta E/E$ for the $E=0.01$ a.u. calculations is significantly larger than the other energies presented, though it should be noted that the $R_0$ used at this energy would not provide TICS results converged to the same accuracy as the other energies.
Though a relatively large number of iterations are required to achieve convergence for some partial waves with the PECS iterative-coupling method, the computational effort required for each iteration is very small. Overall, we estimate that iterative coupling provides a 100-fold reduction in computational effort for $e^{-}H$ calculations at intermediate energies, compared with solutions obtained without iterative coupling.

A direct comparison with the published ECS performance given in Baertschy and Li (2001) for the full $e^{-}H$ problem is difficult due to the limited details provided in this publication, and the different numerical methods used. Their $L=6$ $S=0$ partial wave at $E_0=20.4$ eV with 24 coupled states and $R_0=130$ a.u. (noting that this publication counts $(l_1,l_2)$ and $(l_2,l_1)$ as one state), required 96 processors for 500 minutes, which equals 800 CPU hours (where we assume that this partial wave was responsible for their largest quoted CPU time). Our equivalent calculation required 15 CPU hours (adjusted for the relative performance of the supercomputers used), a 50-fold improvement. There are many factors that make a direct comparison difficult: our grid spacing was larger, presumably due to the improved efficiency of the Numerov finite difference scheme, though our iterative coupling scheme required $n_g=4$ (instead of $n_g=24$) to obtain convergence at this energy. At $E_0=27.2$eV the PECS iterative coupling scheme converges with maximum $n_g$, providing much more dramatic improvements in performance at higher energies.

### 6.1.2 Angular momentum states

The partial-wave expansion (2.11) used in the PECS method expands the scattering wave function of the collision into an infinite sum of $LMl_1l_2$ partial-wave scattering wave functions, where each $LMII$ state can be solved independently. In practice, accurate results can be obtained with a relatively small set of partial waves, though the number required varies considerably depending on the target state, target charge and the incident electron energy.

The $L$ partial-wave contributions to the singlet cross sections of various targets for both ionisation and elastic scattering are presented in Figure 6.6. For $H(1s)$ ionisation, the peak contribution is from the $L=2$ partial wave at the energies presented, with an exponential decay with increasing $L$. The slope of this decay reduces with increasing en-
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Figure 6.6: Angular momentum partial cross sections for (a) ionisation, and (b) elastic scattering. Results are presented for the singlet channel only at \( E_0 = 20.4, 27.2 \) and 54.4 eV for a ground-state (1s) hydrogen target, \( E_0 = 217.7 \) eV for a ground-state \( \text{He}^+ \) target and \( E_0 = 14.8 \) eV for an excited-state (2s) hydrogen target.

Energy, and consequently higher-energy collisions require more partial waves to be included to maintain similar accuracy. The smoothness of the decay allows the error introduced by truncating the infinite sum to be easily estimated. For \( E_0 = 14.8 \) eV ionisation of H(2s), the peak occurs considerably higher at \( L = 5 \) and exhibits a similar decay slope to that of \( E_0 = 54.4 \) eV H(1s). The impact energies of both collisions are approximately the same number of threshold units\(^1\) above threshold. The peak cross section for \( E_0 = 217.7 \) eV ionisation of \( \text{He}^+(1s) \) occurs at \( L = 2 \) and has a similar decay slope as the H(\( n_i s \)) collisions at the same number of threshold units. The trend of the peak \( L \) increasing with \( n_i \) and the relationship between decay slope and threshold energy units is consistent with all other calculations presented in this thesis.

\(^1\)One threshold unit (t.u.) is defined as the ionisation energy of the target, and for hydrogenic targets equals \( Z^2/(2n_i^2) \) atomic units (a.u.). In t.u., the impact energy is related to the total energy by \( E_0 = E + 1 \). For example, one t.u. for H(1s) is 0.5 a.u. (13.6 eV), for H(2s) is 0.125 a.u. (3.40 eV) and for Be\(^{3+}(1s)\) is 8.0 a.u.
Figure 6.7: Partial ionisation cross sections of $n_L$ groups of angular momentum states for (a) $L=0$, and (b) $L=5$, where $n_L = (l_1 + l_2 - L - \Pi)/2$. Results are presented for the singlet channel only at $E_0=20.4$, 27.2 and 54.4 eV for a ground-state (1s) hydrogen target, $E_0=217.7$ eV for a ground-state He$^+$ target and $E_0=14.8$ eV for an excited-state (2s) hydrogen target.

The partial-wave contributions to the elastic cross section for $S=0$ are presented in Figure 6.6b. The peak contribution for H(1s) targets is at $L=0$, and $L=2$ for H(2s). The energy dependence of their slopes is not as marked as the ionisation results, and the slope diminishes with increasing $L$. This decay rate is characteristic of elastic cross sections; inelastic scattering cross sections have a relatively constant exponential decay. Though the total elastic cross section can be calculated accurately with a similar number of partial waves as the TICS, we will see in later sections that accurate DCS calculations for discrete final-state collisions requires a much larger set of partial waves to achieve good convergence.

In addition to truncating the $L$ series of the partial-wave expansion, for each $L$ it is necessary to truncate the number of coupled $(l_1, l_2)$ states. In the PECS method we have chosen to group these states by the parameter $n_L = (l_1 + l_2 - L - \Pi)/2$. As an example, we have tabulated the constituent angular momentum states for $L=5$ and $n_L \leq 5$ in
Table 6.2 shows the partial ionisation cross sections with respect to $n_L$ for the $L=0$ and $L=5$ singlet partial waves of various targets. The shape of the distribution is similar for all 1s targets, which exhibits a rapid exponential decay with increasing $n_L$, while the decay for the H(2s) target is significantly slower, and so requires many more $(l_1, l_2)$ states to be coupled to achieve good convergence. The peak contribution for ionisation is from $n_L=1$ for ground state targets and $n_L=3$ for H(2s), while $n_L=0$ provides the major contribution to the $L=5$ ionisation cross section. The general trend exhibited by all targets is that as $L$ is increased, the rate of decay with respect to $n_L$ increases and convergence can be achieved to the desired accuracy with fewer $n_L$ groups.

The number of $(l_1, l_2)$ states for each $n_L$ equals $L+1$, and must therefore be truncated for large $L$ so as to minimise the memory requirement of the PECS calculations. The contribution of each $(l_1, l_2)$ to the $L=10$ ionisation cross section are shown in Figure 6.8, grouped by $n_L$. The shape of the distribution of the partial ionisation cross sections is similar for both targets and all $n_L$, and demonstrates a rapid exponential decay beyond the peak. Though the relative contribution of partial waves with small $l_1$ is also small, truncating small-$l_1$ partial-waves severely impacts the remaining partial waves. Only terms beyond the peak can be truncated. Also, as the present PECS method evaluates the scattering wave function using a triangular grid, both $(l_1, l_2)$ and $(l_2, l_1)$ states must be included. This limits the states that can be truncated to those where both $(l_1, l_2)$ and $(l_2, l_1)$ are well beyond the peak, which generally does not occur until $L \geq 12$ for $n_i = 1$.

<table>
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<td>5</td>
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</tr>
</tbody>
</table>

Table 6.2: Angular momentum states of $L=5$ $H=0$ partial wave for $n_L \leq 5$. 
targets and $L \geq 18$ for $n_i = 2$ targets, for the energies considered in these examples.

In this section we have shown the systematic behaviour of the contributions of the $LMl_1l_2$ angular momentum states to the total ionisation and discrete final-state cross sections of various targets. It is clear that calculations for excited state targets require many more coupled ($l_1, l_2$) states to be calculated for each $L$, and many more $L$ states, making these calculations significantly more computationally intensive than ground-state targets.

The error introduced by truncating the number of terms in the partial-wave expansion has been estimated by extrapolating the observed decay rate of the series with respect to $L$, $n_L$, and $l_1$. For all $e$–H(1s) targets, the contribution to the total estimated error of the TICS introduced by this truncation was maintained at less than 0.05% throughout all calculations presented in this thesis, and increased to 0.3% for the charged and excited state target calculations. For example, to achieve this accuracy the $E_0=27.2$ eV ionisation calculations included $L \leq 12$ and the number of coupled ($l_1, l_2$) states ranged between 6 and 32 for each $L$. The largest calculation undertaken was the $H(2p)$ target

Figure 6.8: Contribution of $(l_1, l_2)$ angular momentum states to the $L=10$ singlet ionisation cross section for (a) ground state (1s) $e$–H target at $E_0=54.4$ eV, and (b) excited state (2s) $e$–H target at $E_0=14.8$ eV.
at $E_0=14.8$ eV, which included $L \leq 25$ for singlet and triplet, $M=0$ and $M=1$ and both even and odd parity; totalling 152 separate calculations. The number of coupled $(l_1,l_2)$ states ranged between 8 and 60 for each partial wave, giving a total of 6,460 partial-wave scattering wave functions.

### 6.1.3 Grid size ($R_0$) and hyperradius ($\rho$)

In Section 5.2.2 we investigated the radial convergence of the $e$–H model problems. Many of the approximations used in the PECS method for extracting cross sections from the scattering wave functions are radially dependent, so it is important to verify that the full $e$–H problem demonstrates similar convergence behaviour. The radial convergence of $e$–H TICS and discrete final-state cross sections at $E_0=27.2$ eV are presented in Figure 6.9. In contrast to the model calculations (see Figure 5.3), the TICS of the full problem converges much more quickly, with significantly reduced oscillations ($\pm 0.05\%$ compared with $\pm 0.5\%$ in the TP model at $\rho=100$ a.u.). There is also excellent agreement between the TICS results calculated with grid sizes of $R_0=60$ a.u. and 100 a.u., indicating that truncation of the incident-state wave function $\chi^{LMS\Pi}_{l_1,l_2}$ at these much smaller $R_0$ has negligible effect on the results. The discrete final-state cross sections also show reduced oscillations and improved $\rho$-convergence. We are therefore able to calculate accurate cross sections for the full $e$–H problem with significantly smaller grids than suggested by the model problems.

The integral formulation for extracting ionisation and scattering cross section has not previously been used for charged targets with the ECS method. For ionisation, we approximate the final-state continuum waves by two Coulomb waves with charge equal to the charge $Z$ of the nucleus, and for scattering the final-state is represented by the analytic excited-state hydrogenic ion wave function and a Coulomb wave with charge $Z-1$. To ensure that this method produces radially convergent results for charged targets, we investigate the $\rho$ convergence of the TICS and discrete final-state scattering results for $\text{He}^+$ at $E_0=108.8$ eV in Figure 6.10. These ionisation and scattering results converge in a similar way to the H(1s) results presented in Figure 6.9, demonstrating reasonably rapid convergence with respect to increasing hyperradius and oscillations that...
diminish with increasing hyperradius. Thus, the integral methods developed in Chapter 2 for extracting ionisation and scattering amplitudes are suitable for both charged and neutral targets.

In the previous chapter we also found that the SDCS results of the TP and CL models showed different convergence behaviour at equal energy-sharing. In Figure 6.11 we have plotted the variations in the SDCS of the full $e$–H problem at several hyperradii (with respect to the $\rho=100$ a.u. calculation), which shows no convergence problems in any energy-sharing region. Though the SDCS contains unphysical oscillations, their magnitude is small (< 0.5%) and diminish with increasing $\rho$.

In Section 5.3.3 we found that the phase of the ionisation amplitude is divergent unless the correct asymptotic final-state continuum waves are used for $\Phi$ in (2.59). Baertschy et al (2001a) found that when the product of two Coulomb waves is used for the final-state continuum waves, the phase error for each partial wave at fixed $\rho$ is the same and the phase errors did not affect differential cross section calculations. If the phase errors were not the same for each partial wave we would expect that the triple differential
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Figure 6.10: Convergence of $e$–$\text{He}^+(1s) \ E_0=108.8\ \text{eV}$ singlet total cross sections with respect to hyperradius $\rho$ for (a) ionisation, and (b) discrete final-state scattering.

Figure 6.11: Variation of $e$–$\text{H} \ E_0=1.0\ \text{a.u.}$ singlet differential cross sections with respect to hyperradius, relative to $\rho=100\ \text{a.u.}$, for (a) SDCS, and (b) coplanar TDCS ($E_1=2\ \text{eV}, \ \theta_2=20\ \text{degrees}$).
cross sections (TDCS), which are calculated from a coherent sum of the partial-wave complex amplitudes, would not be convergent with respect to $\rho$. In Figure 6.11b we have plotted the TDCS variations at several hyperradii (with respect to $\rho=100$ a.u.) for a representative kinematics, which demonstrates good radial convergence and supports the findings of Baertschy et al. It should be noted that the variation percentages are calculated relative to the maximum TDCS so that large relative variations in the regions with small cross sections do not overly influence the interpretation of the results.

This completes our investigation of convergence issues for the full $e$–H$_z$ problem that were not addressed in the study of model problems. It is clear from this analysis that the PECS method in combination with iterative coupling techniques can obtain results converged to a very high accuracy. Moreover, the iterative-coupling technique demonstrates an almost linear increase in computation time with respect to the number of coupled states. This has allowed full Schrödinger equation calculations for high impact-energy and excited initial-state collisions that have not been previously possible to such high accuracy.

### 6.2 Ground-state hydrogen results

Electron collisions with ground-state hydrogen targets have been the subject of innumerable experimental and computational studies over many decades. There is now good agreement over a wide range of kinematics between experiment and modern computational techniques for solving the Schrödinger equation. While the ECS method is potentially the most accurate computational method developed thus far, it has only been applied to ionising collisions and only over a limited range of energies. In this section we will demonstrate that the PECS method has the same high accuracy as the ECS method, can solve collisions over a much broader range of energies, and is able to calculate accurate solutions for discrete-final state collisions above and below ionisation threshold.
6.2: GROUND-STATE HYDROGEN RESULTS

<table>
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<tr>
<th>$E_0$</th>
<th>$n_j$</th>
<th>Method</th>
<th>$l_j=0$ (s-state) $A_s$</th>
<th>$l_j=1$ (p-state) $A_s$</th>
<th>$l_j=2$ (d-state) $A_s$</th>
<th>$l_j=3$ (f-state) $A_s$</th>
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<td>-</td>
<td>-</td>
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<tr>
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<td>1.62$^{+0}_{-1}$ 0.332</td>
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<td>-</td>
<td>-</td>
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<tr>
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<td>2.39$^{-1}$ 0.438</td>
<td>9.75$^{-2}$ 0.477</td>
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<td>Exp.</td>
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<td>(2.0 $\pm$ 0.4)$^{-1}$ -</td>
<td>(1.1 $\pm$ 0.1)$^{-1}$ -</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
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<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
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<td>-</td>
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<td>2</td>
<td>PECS</td>
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<td>-</td>
<td>-</td>
<td>-</td>
</tr>
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<td>PECS</td>
<td>3.60$^{-2}$ 0.123</td>
<td>3.69$^{-1}$ 0.047</td>
<td>5.50$^{-2}$ 0.078</td>
<td>-</td>
<td>-</td>
</tr>
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<td>CCC</td>
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<td>5.57$^{-2}$ 0.102</td>
<td>-</td>
<td>-</td>
</tr>
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<td>PECS</td>
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<td>1.29$^{-1}$ 0.057</td>
<td>2.44$^{-2}$ 0.091</td>
<td>7.75$^{-4}$ 0.118</td>
<td>-</td>
</tr>
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<td>2.52$^{-2}$ 0.113</td>
<td>8.87$^{-4}$ 0.160</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 6.3: Discrete final-state total scattering cross sections for $e$–H(1s) targets. Energy is given in eV, cross sections in a.u. and spin asymmetry ($A_s$) is dimensionless$^2$. CCC (Bray 2004) calculations and experimental results (Williams 2004) are presented for comparison.

6.2.1 Scattering

For our investigation of discrete final-state scattering cross sections for $e$–H(1s) targets, we have selected several energies in the low- to intermediate-energy region where there have been recent measurements and calculations for comparison. The PECS TCS results for excitation to each $n_j l_j$ final-state at these energies are given in Table 6.3 for $n_j \leq 4$. There is generally excellent agreement with CCC calculations at 30.0 and 54.4 eV, and based upon convergence studies, we estimate the standard error of our calculations range
from 1% for elastic collisions, increasing with \( n_j \) to 4% for \( n_j=4 \). There is reasonable agreement with the TCS measurements of Williams (2004) for the \( n_j=3 \) transitions at 16.5 eV. The 16.5 eV calculations were undertaken solely for the \( n_j=3 \) DCS calculations, and as we were not concerned with ionisation amplitude convergence, the calculations were limited to \( R_0=100 \) a.u. and included \( L \leq 20 \). We are yet to undertake an investigation of other higher-\( n_j \) transitions, but expect that these will require larger \( R_0 \) calculations to obtain good convergence.

In Figure 6.12 we present our DCS results at 30 eV for \( n_j=1 \) to \( n_j=4 \), which are in excellent agreement with CCC calculations. There is close agreement with the \( n_j=1 \) experimental results of Williams (1975) and the \( n_j=2 \) results of Grafe et al (2001), while the \( n_j=3 \) and \( n_j=4 \) results are in reasonable agreement with Sweeney et al (2001). A grid size of \( R_0=100 \) a.u. was used for our calculations and included partial waves \( L \leq 20 \).

A total of 48 CPU hours was required to calculate the wave functions and cross sections for all partial waves\(^3\), ranging from 0.1 CPU hours for the \( L = 0 \) triplet partial wave, using six coupled angular momentum states, to 2.0 CPU hours for the \( L = 5 \) singlet partial wave, using 32 coupled angular momentum states [where \((l_1, l_2)\) and \((l_2, l_1)\) pairs are counted separately].

The discrete scattering cross sections for \( L > 20 \) do not contribute significantly to the total cross section, however, their inclusion gives convergent differential cross sections at small scattering angles and removes oscillations at large backward scattering angles. Scattering amplitudes for partial waves \( 20 < L \leq 200 \) were included in our calculations by extrapolating the \( L \leq 20 \) results. We explicitly calculated the partial waves \( 20 < L \leq 50 \) to verify the smooth exponential decay of the scattering amplitudes that is necessary to ensure good extrapolation accuracy. This technique is used for all scattering cross sections presented in this thesis. In contrast, the CCC method uses an analytic extrapolation approximation to obtain convergent elastic cross sections and a Born-subtraction method for \( n_j > 1 \) to smooth the back-scattering region.

\(^2\)We use the commonly used abbreviation for spin asymmetry \((A_s)\) here, and throughout the remainder of this thesis, which is equivalent to our definition for spin asymmetry \((A_{ji})\) given in Chapter 2.

\(^3\)See Section 4.2 for specifications of the computer system used for all the calculations presented in this thesis.
6.2: GROUND-STATE HYDROGEN RESULTS

Figure 6.12: Differential scattering cross sections for $e^{-}$–H(1s) and $n_{j} \leq 4$ at $E_{0}=30$ eV. CCC calculations (Bray 2004) are mostly indistinguishable from the PECS calculations. Experimental results are given for Williams (1975) for $n_{j}=1$, Grafe et al (2001) for $n_{j}=2$ and Sweeney et al (2001) for $n_{j}=3$ and 4.

Recently, Williams (2004) made the first measurements of $e^{-}$–H(1s) differential cross sections for transitions to the 3s, 3p and 3d final-states. These measurements are presented in Figure 6.13 for $E_{0}=16.5$ eV and 54.4 eV, and match our PECS calculations within experimental error. Interestingly, PECS predicts a large back-scattering cross section at 16.5 eV for the 3s transition, yet this region was not included in the experimental measurements. Based on the angular range and magnitude of the other measurements presented, we believe that this region should be accessible to measurement, and encourage further measurements to verify the PECS prediction.

The total and differential cross sections presented thus far give strong evidence for the accuracy of the PECS method for calculating discrete final-state scattering ampli-
Figure 6.13: Differential scattering cross sections for \( e^{-}\text{H}(1s) \) 3s, 3p and 3d transitions at \( E_0=16.5 \) and 54.4 eV. Experimental results by Williams (2004).

However, calculation of the reduced Stokes parameters for the 1s-2p transition will provide the most stringent test of our method since they additionally contain information about the phase of the magnetic sub-level amplitudes, whereas the cross sections only provide information on the magnitude of these amplitudes. The reduced Stokes parameters are calculated using the relations

\[
\bar{P}_1 = 2\lambda - 1 \quad (6.1)
\]

\[
\bar{P}_2 = -2\sqrt{2}R \quad (6.2)
\]

\[
\bar{P}_3 = 2\sqrt{2}I, \quad (6.3)
\]

where the electron-photon correlation parameters are defined as

\[
\lambda = \frac{\langle |f_0^r| \rangle}{\sigma} \quad (6.4)
\]

\[
R = \frac{Re\langle f_1 f_0^* \rangle}{\sigma} \quad (6.5)
\]

\[
I = \frac{Im\langle f_1 f_0^* \rangle}{\sigma}, \quad (6.6)
\]

and where \( \sigma \) is the 1s-2p DCS summed over all magnetic sub-levels, the angle brackets represent the spin-averaged sum over singlet and triplet spin states and, using the
notation introduced in Chapter 2, the normalised scattering amplitude is given by

\[ f_{m_j} = \sqrt{k_j/k_i} F_{ji}^S. \]  

(6.7)

Several related parameters are the linear polarisation parameter \( P_l \), charge cloud alignment angle \( \gamma \) and excitation coherence parameter \( P^+ \), which are given by

\[ P_l = \sqrt{\bar{P}_1^2 + \bar{P}_2^2} \]  
\[ \gamma = \frac{1}{2} \arg(\bar{P}_1 + i\bar{P}_2) \]  
\[ P^+ = \sqrt{\bar{P}_1^2 + \bar{P}_2^2 + \bar{P}_3^2}. \]  

(6.8) \hspace{1cm} (6.9) \hspace{1cm} (6.10)

To improve their clarity, the dependence of these equations on the scattering angle is left as implied.

In a recent paper, Gradziel and ONeill (2004) presented measurements of \( \bar{P}_3 \) for electron-hydrogen collisions at 54.4 eV impact energy that disagreed with long-standing CCC calculations (Bray and Stelbovics 1992a). Yet the CCC method has accurately calculated this parameter for electron collisions with the alkali metals and helium (Bray et al 2002), and so the reasons for the apparent discrepancy for \( e-H \) collisions is not clear. It is thus highly desirable to provide an independent theoretical comparison to shed further light on the source of the discrepancy. We will therefore test our reduced Stokes parameter calculations at this energy.

In Figure 6.14 we present our results for the reduced Stokes and related parameters for electron-hydrogen 1s-2p scattering collisions at 54.4 eV, and include the original Laguerre-based CCC calculations (Bray and Stelbovics 1992a) and more recent CCC-B box-based calculations (Bray 2004) for comparison. Our calculations are in good agreement with CCC-L and almost indistinguishable from the later CCC-B results. The \( \bar{P}_1 \), \( \bar{P}_2 \), \( P_l \) and \( \gamma \) parameters are in excellent accord with the experimental results of Yalim et al (1999), which have significantly smaller standard errors than Gradziel and ONeill’s measurements. We have limited the scattering angle range of the \( \bar{P}_2 \) and \( \bar{P}_3 \) plots to give emphasis to the experimental points; PECS and CCC-B results show similar agreement in the region that is not displayed. Gradziel and ONeill state that the accuracy of their measurements for \( \theta \leq 10^\circ \) are open to question due to finite volume and solid angle.
CHAPTER 6: HYDROGEN AND HYDROGENIC IONS

Figure 6.14: Reduced Stokes parameters $\bar{P}_1$, $\bar{P}_2$ and $\bar{P}_3$ and related parameters $P_l$, $\gamma$ and $P^+$ for $e$–H $1s$-$2p$ scattering at $E_0=54.4$ eV. CCC Laguerre-based calculations (CCC-L) (Bray and Stelbovics 1992a), CCC box-based calculations (CCC-B) (Bray 2004) and measurements of Yalim et al (1999) and Gradziel and ONeill (2004) are also shown.

We have already noted that at large back-scattering angles a large number of partial waves must be included in the DCS calculations to reduce oscillations. In this region the coherent sum of the partial-wave scattering amplitudes causes the small-$L$ partial waves (with largest magnitude) to cancel. This cancellation is highly sensitive to the phase
of the partial-wave scattering amplitudes. It was noted in the convergence studies presented in the previous section that the scattering cross sections exhibit small $\rho$-dependent oscillations that diminish with increasing $\rho$, and arise from $\rho$-dependent oscillations in both the magnitude and phase of the scattering amplitudes. This causes $\rho$-dependent fluctuations in the back-scattering region $\theta > 150^\circ$, though it is generally not of significance as the fluctuations are only evident when the cross sections are much smaller than the small-angle scattering. However, the reduced Stokes parameters are calculated from ratios of cross sections and these fluctuations cause very large $\rho$-dependent deviations in the Stokes parameters at $\theta \geq 150^\circ$. Further investigation revealed that the $\rho$-dependent oscillation of the scattering amplitudes has a wavelength of $\rho \lambda = \frac{\pi}{k_j}$, and can be removed by averaging the scattering amplitudes calculated at $n$ intervals near $R_0$ separated by $\rho \lambda/n$. We used $n=4$, which removed all instability in the scattering amplitudes, cross sections and reduced Stokes parameters. We have used this averaging technique when calculating all discrete final-state scattering results presented in this thesis.

Finally, to demonstrate the suitability of our method for calculations below the ionisation threshold, we present scattering cross sections for energies in the range $E_0 = 11.6-12.08$ eV, where there are numerous resonance structures. Our results are shown in Figure 6.15 along with the benchmark RMPS calculations of Bartschat et al. (1996) (which matched both CCC and IERM calculations) and the measurements of Williams (1988). Our 2$s$ and 2$p$ results are almost indistinguishable from RMPS, and demonstrate remarkable agreement on the energy, width and magnitude of the resonance features, and are in good agreement with experiment. The visible variation in magnitude of the elastic cross sections is exaggerated by the expanded scale, and is less than one percent 1%, well within our estimated error and errors introduced from digitising Bartschat et al’s results. Once again, the resonance structures are in excellent agreement.

Our calculations included 97 energy points spaced at 0.005 eV intervals, and several additional points spaced at 0.001 eV intervals near $E_0=11.935$ eV to better define the large resonance peak. The energy range chosen is within 1.6 eV of the $n_j=2$ threshold, consequently $\rho \lambda$ for $n_j=2$ transitions reached 10 a.u. and large grids of $R_0=200$ a.u. were required to achieve convergence to better than 1% for the $n_j=2$ cross sections. Our
calculations included partial waves $L \leq 4$. They might appear to be a very large set of calculations, but for a large majority of these energy points we were able to use iterative coupling with maximum $n_g$ (iterative coupling groups), which reduced computational effort dramatically. Furthermore, we were able to use our energy perturbation technique (see Section 3.5) to solve energy points within $\pm 0.05$ eV of the initial energy, providing further significant reductions in computational effort. However, near sharp resonance features, iterative coupling fails to converge and the energy perturbation range narrows, but only for the partial wave(s) responsible for the resonance feature. The computa-
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The computational effort required for these calculations is increased as separate \( n_g=1 \) calculations are required for each energy.

This initial investigation into resonance features below the ionisation threshold excluded the highly resonant region \( E_0=12.080-12.094 \text{ eV} \) just below the \( n_j=3 \) threshold. However, we have confirmed that PECS can obtain accurate solutions in both this region and the resonance-free region that extends down to the \( n_j=1 \) threshold at 10.2 eV, though \( R_0 \) must be extended to around 400 a.u. for the latter. A more rigorous investigation may identify strategies for reducing the computational effort near resonance features, though below 10.2 eV, where only the elastic channel is open, a significant reduction in computational effort is expected.

6.2.2 Ionisation

Only in recent years have computational methods demonstrated good agreement with \( e^{-}\text{H} \) ionisation measurements over a wide range of kinematics. The ECS technique of Rescigno, McCurdy, Baertschy and coworkers (Rescigno et al 1999, Baertschy et al 2001a) made an impressive contribution in this area, and indeed was an essential prerequisite and gave inspiration for the work undertaken in this thesis. In this section we will directly compare results of the PECS method with published ECS results, as well as investigate the near-threshold energy of 13.88 eV (\( E=0.01 \text{ a.u.} \)) and a moderately high energy of 150 eV that approaches the region where the Born approximation becomes accurate. Both of these energies are believed to be inaccessible to the ECS method due to poor convergence (divergence) of the CGS sparse-matrix solver near the ionisation threshold and excessive computational demands at high energies.

We present TICS and spin asymmetry calculations for a broad range of energies in Table 6.4, which compare extremely favourably with ECS calculations (Baertschy et al 2001a) where available. The number of \( L \) states required for convergence (\( L_{\text{max}} \)) increases significantly with energy. At 54.4 eV the large computational requirements limited Baertschy et al’s calculations to \( L \leq 13 \) and extrapolation procedures were used for higher partial waves. They also noted that insufficient \( (l_1, l_2) \) states could be included for each \( L \) to obtain complete convergence with respect to angular momentum states.
Table 6.4: Total ionisation cross sections for $e$–H(1s) targets. Energy is given in eV, $R_0$ and cross sections are in a.u. and spin asymmetry is dimensionless. ECS results are from Baertschy et al (2001a).

These higher-energy calculations are readily solved with PECS, and rapid convergence of the iterative coupling procedure ensures minimal computing resources are required. Thus, explicit calculation of the higher partial waves and inclusion of sufficient angular momentum states were possible for energies up to 150 eV. Higher energy calculations are expected to be readily achievable.

Our 13.88 eV calculation was undertaken at limited $R_0$ and we estimate the standard error is 3.5%, with the increased error due solely to insufficient grid size. At this energy we expect convergence to better than 1% would require a grid size approaching 1500 a.u., which is beyond our current computational resources. Further discussion of our near-threshold results is presented in the Chapter 7.

The SDCS results (with respect to energy sharing) of several of our calculations are shown in Figure 6.16. We have included ECS results for 17.6 eV and 30 eV, which are largely indistinguishable from the present results. Both PECS and ECS results at 17.6 eV contain small oscillations in the SDCS, though the PECS oscillations are not readily observed at the scale presented. As discussed previously, the oscillations appear to be inherent to the surface integral method used by both PECS and ECS to extract cross sections from the scattering wave functions, and diminish with increased $\rho$. However, the magnitude of the ECS oscillations at this energy is approximately five times
6.2: GROUND-STATE HYDROGEN RESULTS

Figure 6.16: SDCS calculations for $e^{-}\text{H}(1s)$ at $E_0=13.88$, 17.6, 30.0 and 150 eV. Comparison is made with ECS (Baertschy et al 2001a) and CCC (Bray 2000, 2004) calculations. Note that the 150 eV SDCS has steep gradients in the highly asymmetric energy-sharing region and has been plotted with a log scale to help differentiate the curves presented.

larger than PECS. The grid size of the ECS calculations is not known, but given the good agreement of our remaining 17.6 eV results, it is unlikely that it was significantly smaller than that used by PECS (120 a.u.). Baertschy et al state that Wannier theory predicts this oscillatory behaviour at near-threshold energies. To preempt our near-threshold investigations in the following chapter, our results suggest a slight deviation from a linear SDCS at very low energies, but we find no evidence that indicates that this oscillatory behaviour is a physical effect, and propose that numerical errors may be responsible for the larger ECS oscillations.
We also present CCC SDCS results (Bray 2004) in Figure 6.16 at \( E_0 = 17.6, 30.0 \) and 150 eV. It is well known that CCC calculations exhibit unphysical oscillations in the SDCS [e.g. see Bray (2003)]. Though these oscillations are predicted to converge to the true solution given a sufficiently large pseudo-state basis, at low energies this is not computationally achievable. This problem is not unique to CCC and is exhibited by other pseudo-state methods such as IERM and RMPS. However, Stelbovics (1999) argues that at \( E/2 \) the CCC ionisation amplitudes will converge to half of their real value, regardless of basis size, and exhibit behaviour much the same as the truncated Fourier series of a step function, and hence gives 1/4 of the true cross sections at this point. Hence, the \textit{ab initio} character of the CCC calculations is retained at equal energy-sharing. CCC then constructs a smooth integral-preserving estimate of the SDCS that is four times larger than the raw results at \( E/2 \). Both the raw and smoothed CCC results are presented. At equal energy-sharing, the 17.6 eV CCC SDCS varies from PECS and ECS results by 5%, which is reasonable considering the difficulty of these low energy calculations. However, there is a marked deviation in the predicted shape. Given the \textit{ab initio} nature of the PECS and ECS calculations at asymmetric energy-sharing, and the Wannier prediction that the SDCS is nearly independent of electron energy-sharing near threshold, we believe that the shape of the PECS and ECS results provides a better representation of the true SDCS at 17.6 eV. At 30 eV, PECS and ECS are in excellent accord and CCC are in better agreement. At 150 eV, where the equal energy-sharing cross sections are relatively small, PECS is in good agreement with the \textit{raw} CCC results for \( E_1 \leq E_2 \).

The 13.88 eV PECS SDCS is given for calculations at \( \rho = 355 \) and 360 a.u. As discussed already, this calculation was performed using a restricted grid size, which increases the \( \rho \)-dependent variations of the TICS and the magnitude of the oscillations of the SDCS. The variation between these results gives an indication of the likely error of the SDCS. The integral of these cross sections varies by 2%, which helps confirm our estimate of the TICS standard error.

The triple-differential cross sections for \textit{e}-\textit{H} collisions at low energies have historically been the most difficult for computational methods to predict accurately. Our equal
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Figure 6.17: Coplanar equal energy-sharing TDCS calculations for $e$–H(1s) at $E_0=17.6$ eV. Comparison is made with ECS and CCC calculations and absolute measurement presented in Röder et al (2003).

energy-sharing coplanar TDCS calculations for $E_0=17.6$ eV are given in Figure 6.17 along with the updated measurements of Röder et al (2003) and the CCC and ECS calculations contained therein. $\theta_{12}=80^\circ$ ECS results are also presented from Baertschy et al (2001a). For $\theta_{12} \geq 120^\circ$ all calculations and measurements are in superb agreement. At $\theta_{12} \leq 100^\circ$ there are minor differences between the three calculations, but as these cross sections are small in comparison to the other kinematics, the variations are not considered significant. The agreement between CCC, ECS and PECS for these equal energy-sharing coplanar cross sections are exceptional. However, we saw in Figure 6.16 that there was a 5% variation between the CCC $E/2$ SDCS result and both PECS and ECS, which indicates that there may be larger variations in the out-of-plane equal
Figure 6.18: Coplanar equal energy-sharing TDCS calculations for $e^{-}\text{H}(1s)$ at $E_0=30$ eV. Comparison is made with ECS calculations (Baertschy et al. 2001a) and relative measurement (Röder et al. 1996).

equal energy-sharing TDCS results than are demonstrated by these coplanar results. Also, in light of the variations in the SDCS results at asymmetric energy-sharing, it would be useful to investigate asymmetric energy-sharing TDCS calculations at this energy should measurements become available.

Once again, Figure 6.18 demonstrates excellent agreement between PECS, CCC and ECS results for $E_0=30$ eV TDCS results at equal energy-sharing. There are however, differences of up to 5% in the peak TDCS of the theoretical methods, for some kinematics, but no systematic variation. All methods compare favourably with the experimental results of Röder et al. (1996).

Figure 6.19 gives PECS and CCC results for $E_0=27.2$ eV TDCS at both symmet-
Figure 6.19: Coplanar asymmetric and equal energy-sharing TDCS calculations for $e^{-}\text{H}(1s)$ at $E_0=27.2$ eV. Comparison is made with CCC (Bray 2003) and experimental results, as presented by Berakdar et al (1999), are internormalised for a given secondary energy.
ric and asymmetric energy-sharing. As far as we are aware, no published asymmetric energy-sharing TDCS results for the ECS method are available for comparison. Both PECS and CCC compare favourably with the available experimental data, however there are some minor differences in the magnitude of the calculations for some kinematics. The PECS results tend to be flatter and smaller than the CCC results for geometries where $\theta_1 \approx \theta_2$. This is most evident in the $\theta_1 = -\theta_2 \rightarrow 0$ region of the equal energy-sharing kinematics, which should be highly suppressed due to electron repulsion. These deviations are possibly due to errors introduced into the CCC method when estimating the scattering amplitudes at asymmetric energies.

The agreement between the PECS and CCC coplanar asymmetric energy-sharing

**Figure 6.20:** Coplanar TDCS calculations for $e$–H(1s) at $E_0$=150 eV. Comparison is made with CCC (Bray 2000) and absolute measurement (Ehrhardt et al 1986).
$E_0=150$ eV TDCS results presented in Figure 6.20 is very good. The position and shape of the peaks agree with the measurements of Ehrhardt et al (1986), as does the magnitude for kinematics with larger cross sections. There is only moderate agreement with the magnitude of the measured peaks for some kinematics with small cross sections.

This completes our presentation of results for electron collisions with ground-state hydrogen targets for the moment. We will return to them later in the following chapter when we consider ionisation threshold laws. In this section we have demonstrated that PECS produces highly accurate results for both scattering and ionisation, at energies below ionisation threshold, near the ionisation threshold and up to moderately-high energies where the Born approximation (and its derivatives) become accurate. We will now proceed to electron collisions with hydrogenic ions.

6.3 Hydrogenic ion results

The electron-impact ionisation of hydrogenic ions is fundamental to plasma modelling in astrophysics and nuclear fusion, where many highly charged ionic species exist in the very high temperature plasmas studied in these fields. Unfortunately, the small cross sections of these ions and difficulties in preparing suitable target gases makes absolute experimental measurements difficult, especially measurements of the differential cross sections. Consequently, plasma modelling is heavily dependent on accurate theoretical calculations. For large nuclear charges $Z$, the total ionisation and scattering cross sections are predicted to scale inversely to $Z^4$, and the differential cross sections are predicted to scale inversely to $Z^6$ (Thomson 1912, Burgess et al 1970, Stia et al 2000). In this section we will focus on the behaviour of the ionisation cross sections for low $Z$, where the scaling law approximation does not rigorously apply, which will give insight into the energies and $Z$ for which the scaling law becomes accurate.

To date, many of the published theoretical calculations for total and differential ionisation cross sections for low-$Z$ hydrogenic targets have relied upon approximation methods, including the distorted wave Born approximation (Younger 1980, Fang et al 1993) and the “BBK” method (Brauner et al 1989, Jia et al 1997). These methods
generally provide acceptable approximations when electron correlation effects are less
dominant, for example high energy collisions or when inter-particle separations are large.
For state-of-the-art methods that are known to provide accurate differential cross sections
over a large range of energies and kinematics, such as ECS (Baertschy et al 2001a), CCC
(Bray 2003), and time dependent close coupling (TDCC) (Colgan et al 2002a), the
published calculations for hydrogenic targets beyond hydrogen is limited. So far, CCC
has only been applied to He\(^+\) TICS and 1s-2s inelastic cross sections (Bray et al 1993).
TDCC (Colgan et al 2002b, Witthoeft et al 2003) has only been applied to He\(^+\) and
Li\(^{2+}\), while ECS has not been applied to charged targets. None of these methods have
reported differential ionisation cross sections for these collision systems.

6.3.1 Scattering

In Figure 6.21 we compare our PECS electron scattering cross sections for He\(^+\) 1s-2s
transition over a range of energies with CCC (Bray et al 1993) and TDCC (Witthoeft
et al 2003) calculations and experiment (Dolder and Peart 1973). All results are in
good agreement, which helps verify the efficacy of the PECS surface integral method for
evaluating scattering cross sections of charged targets.

The scattering cross sections for hydrogenic targets with \(Z \leq 4\) are presented in
Table 6.5 for all \(n_j l_j\) final states with \(n_j \leq 4\) at total energies of 0.50, 1.00, 3.00 and 5.00
t.u. The estimated standard error of the results range from 1% for the 1s results to 4%
for the 4f results. The results have been multiplied by \(Z^4\) to highlight the convergence
behaviour of these cross sections with respect to \(Z\) and \(E\). For each scaled total energy
(t.u.) and final state, the cross sections form a converging series with respect to increasing
charge \(Z\) of the target. The 3d, 4d and 4f final states do not show consistent convergence
behaviour at \(E=0.5\) t.u., and calculations for larger \(Z\) are required to determine if a
converging series is eventually formed for these collisions. The larger estimated error
of these calculations may have influenced the apparent non-convergence of these series.
Apart from these minor exceptions, the results give strong evidence of a \(Z^4\) scaling of
the discrete final-state cross sections at large \(Z\) or high energy.

To highlight the convergence trends of the discrete final-state cross sections, the total
6.3: HYDROGENIC ION RESULTS

Figure 6.21: Scattering cross section of He\(^+\) 1s-2s transition. Comparison is made with CCC (Bray et al 1993) and TDCC (Witthoeft et al 2003) calculations and experiment (Dolder and Peart 1973).

\(n_j\) scattering cross sections for each \(Z\) and energy are plotted in Figure 6.22, divided by the \(Z=4\) cross section for the same energy and final states\(^4\). It is clear that the elastic cross sections (1s) converge much more quickly than the excited final-state cross sections, and the convergence rate of all final states increases at higher scaled total energies.

6.3.2 Ionisation

In this section we present our calculations for the TICS, SDCS, and selected double-differential cross sections (DDCS) and TDCS calculations for ground-state targets with \(Z \leq 4\) at total energies of 0.5, 1.0, 3.0, and 5.0 t.u. These results were extracted from the same scattering wave functions as used for discrete final-state scattering in Section 6.3.1.

Convergence studies indicate that our TICS calculations have a standard error of approximately 1%. To achieve this accuracy, partial waves up to \(L=10\) were included in the 0.5 t.u. calculations, increasing to \(L=30\) for the 5.0 t.u. calculations. The grid sizes

\(^4\)Though all of the plots intersect at \(Z=4\), they are not necessarily converged at this point. The purpose of Figure 6.22 is to show the rate of change of the cross sections with increasing \(Z\).
range from 100 a.u. for H at 0.5 t.u. (20.4 eV) to 15 a.u. for Be$^{3+}$ at 5.0 t.u. (1306 eV). The contribution to the estimated standard error of our TICS calculations are: grid size $R_0$ error (0.5%), grid spacing error (0.25%), limiting $L$ partial-waves (0.2%), limiting $(l_1, l_2)$ states for each $L$ (0.2%) and iterative coupling error (0.01%). It should be noted that these errors relate to the TICS, and we expect that the errors in the differential cross sections will be larger, though generally not discernible on the plots presented here.

Our TICS results, multiplied by $Z^4$, are presented in Figure 6.23, and are within 1% of the interpolated ECS and CCC calculations for H(1s), within 3% of the interpolated CCC results for He$^+$, though systematically lower, and consistent with experiment. The PECS results for Li$^{2+}$ are in reasonable agreement with TDCC and experiment, though
Figure 6.22: Convergence of scattering cross sections with increasing $Z$. The results in Table 6.5 have been summed for each $n_j$ and divided by the $Z=4$ result at the same energy and final state.

At 3.0 t.u. they are lower than interpolated TDCC results. It should be noted that the TDCC calculations use a distorted wave perturbation calculation beyond $L=6$ and the authors claim an accuracy of the order of 5%, and no estimate of the accuracy of the CCC calculations are given. The general agreement of our PECS results with these other theoretical calculations gives us confidence that our estimated error is justified.

It is clear from our calculations that by $E = 5.0$ t.u. the scaled TICS are converging quickly at higher $Z$, and that the rate of convergence decreases with decreasing energy. Clearly, the $Z^4$ scaling law (Stia et al 2000) for TICS, for large $Z$ or high $E$, is confirmed by our solutions.

Normalized SDCS at the selected energies are shown in Figure 6.24. They reveal a systematic increase in the contribution to the SDCS at asymmetric energy-sharing with increasing scaled total energy. Like the TICS, the shape of the SDCS converges quickly with increasing $Z$ at high energies, but more slowly at lower energies. In Table 6.6 we have included the normalization constants used to scale the results in Figure 6.24, from
Figure 6.23: TICS calculations for $Z \leq 4$ targets at total energies of 0.5, 1.0, 3.0, and 5.0 t.u. The energies of our PECS calculations are highlighted with vertical dashed lines. Comparison is made with ECS (Baertschy et al. 2001a) and the $l_{\text{max}} = 4$ CCC calculations of (Bartschat and Bray 1996) for H; CCC (Bray et al. 1993), TDCC (Witthoeft et al. 2003) and experiment (Peart et al. 1969) for He$^+$; and TDCC (Colgan et al. 2002b) and experiment (Tinschert et al. 1989) for Li$^{2+}$. All TICS have been multiplied by $Z^4$.

which our raw SDCS results can be derived. These constants have been divided by $Z^6$, and each column demonstrates a convergence trend similar to the scaled TICS. This supports the $Z^6$ scaling law for the differential cross sections of hydrogenic targets, for large $Z$ or high $E$.

Our DDCS results are plotted in Figure 6.25 for selected secondary electron energies and total energies. The shape of the DDCS in each sub-plot begins to converge with increasing $Z$, and this convergence is generally more rapid with increasing scaled total energy. Electrons ejected at low energy are more spatially dispersed than high energy electrons, and the dominance of back scattering of low-energy electrons decreases with increasing $Z$ and increasing total energy. The high-energy electrons are ejected in a
Figure 6.24: SDCS calculations for $Z \leq 4$ targets at total energies of 0.5, 1.0, 3.0, and 5.0 t.u. All curves have been normalised to 1.0 at equal energy-sharing ($E_1 = E_2$). The original SDCS can be calculated by multiplying by $\alpha(E, Z)/Z^6$, where the normalising constant $\alpha(E, Z)$ is given in Table 6.6.

<table>
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<tr>
<th>Z</th>
<th>0.5 t.u.</th>
<th>1.0 t.u.</th>
<th>3.0 t.u.</th>
<th>5.0 t.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>8.205</td>
<td>5.611</td>
<td>1.268</td>
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<td>2</td>
<td>He$^+$</td>
<td>10.93</td>
<td>6.608</td>
<td>1.397</td>
</tr>
<tr>
<td>3</td>
<td>Li$^{2+}$</td>
<td>12.11</td>
<td>7.141</td>
<td>1.441</td>
</tr>
<tr>
<td>4</td>
<td>Be$^{3+}$</td>
<td>12.84</td>
<td>7.479</td>
<td>1.502</td>
</tr>
</tbody>
</table>

Table 6.6: Normalisation constants $\alpha(E, Z)$ used in Figure 6.24. To recover the original SDCS in a.u., multiply by $\alpha(E, Z)/Z^6$. The energies shown are total energies in t.u.
In Figure 6.25, coplanar TDCS results are plotted for selected scaled total energies and selected secondary electron energies and directions. The shapes of the TDCS plots also converge with increasing Z, consistent with a $Z^6$ scaling law for differential cross sections, and converge more rapidly with increasing scaled total energy. At $E \leq 1.0$ t.u., there is a marked difference in the spatial distribution of the fast outgoing electron ($E_1=0.95E$) when $\theta_2=15^\circ$; for atomic hydrogen the minima in the TDCS is in the forward direction, whereas the charged targets have a maxima in this direction. The slight oscillations in the TDCS of the back-scattered fast electron for $E \geq 3$ t.u., which are 2-5 orders of magnitude smaller than the peaks, are expected to diminish as partial waves $L > 30$ are included. These very high partial waves were not included in these calculations as they have not converged sufficiently at the grid size selected.

These results demonstrate that the PECS method, with iterative coupling, is able to calculate highly accurate total and differential ionisation cross sections for charged
6.4 Excited-state hydrogen results

Scattering and ionisation cross sections of excited-state hydrogen targets are important in plasma modelling as excited atoms are formed in large quantities by the charge exchange reactions of energetic ions (Defrance et al. 1981). However, experimental measurement...
has thus far been limited to the metastable 2s state of hydrogen due to the short lifetime of the other excited states, and only limited state-of-the-art computational results are available. It is evident from the convergence studies in Section 6.1 that electron collisions with excited states of hydrogen require a large number of states of angular momenta to be coupled, making these problems particularly difficult to solve using partial-wave expansion techniques. To help verify the PECS results presented in this section, Bray (2004) has kindly undertaken CCC calculations for comparison.

So far in this chapter we have studied collisions with ground state hydrogen atoms and ions, which are restricted to $M=0$ states and even parity. Electron collisions with H(2s) are also restricted to these states, but there are no such limitations for H(2p) targets. Therefore, the $e$–H(2p) results presented in the following subsections serve as a check of the PECS equations derived in Chapter 2 for targets with arbitrary initial state.

### 6.4.1 Scattering

The scattering wave functions for electron collisions with H(2s) and H(2p) targets were calculated using an incident energy of 14.8 eV (which has the same total energy as a $E_0=25$ eV collision with a ground-state target) and a grid size of $R_0=100$ a.u. Partial waves with $L \leq 25$ were required to obtain good convergence of the ionisation amplitudes and total scattering cross sections. The $n_L$ used to achieve convergence with respect to angular momentum was: $n_L \leq 7$ for $L \leq 2$, $n_L \leq 6$ for $3 \leq L \leq 4$, $n_L \leq 5$ for $5 \leq L \leq 7$, $n_L \leq 4$ for $8 \leq L \leq 9$, $n_L \leq 3$ for $10 \leq L \leq 14$ and $n_L \leq 2$ for $L \geq 15$. The odd parity partial waves converged with smaller $n_L$: $n_L \leq 4$ for $L \leq 2$, $n_L \leq 3$ for $L \leq 7$ and $n_L \leq 2$ for $L \geq 8$.

The estimated standard error of our TCS results range from 1% for elastic collisions to 4% for $n_j=4$ final states.

Results for the electron-impact scattering cross sections for final states $1 \leq n_j \leq 4$ of both H(2s) and H(2p) targets are presented in Table 6.7 along with CCC results (Bray 2004), and show good agreement between these methods. The contributions from separate $M$ states are also given for the PECS calculations. The cross sections for 2s-2p and 2p-2s transitions, however, are not given as they are not convergent with
6.4: EXCITED-STATE HYDROGEN RESULTS

Table 6.7: $e$–H(2s) and $e$–H(2p) 14.8 eV discrete final-state scattering cross sections. CCC results from Bray (2004).

<table>
<thead>
<tr>
<th>$n_jl_j$</th>
<th>2s initial state</th>
<th>2p initial state</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total CCC</td>
<td>$M=0$ $M=\pm1$</td>
</tr>
<tr>
<td>1s</td>
<td>4.68$^{-1}$</td>
<td>4.86$^{-1}$</td>
</tr>
<tr>
<td>2s</td>
<td>1.27$^{+2}$</td>
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<tr>
<td>2p</td>
<td>–</td>
<td>–</td>
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<tr>
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<td>8.64$^{+0}$</td>
<td>8.82$^{+0}$</td>
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<td>1.64$^{+0}$</td>
<td>1.72$^{+0}$</td>
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<td>4p</td>
<td>4.95$^{+0}$</td>
<td>5.03$^{+0}$</td>
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<td>3.32$^{+0}$</td>
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<tr>
<td>4f</td>
<td>3.45$^{+0}$</td>
<td>3.22$^{+0}$</td>
</tr>
</tbody>
</table>

Table 6.7: $e$–H(2s) and $e$–H(2p) 14.8 eV discrete final-state scattering cross sections. CCC results from Bray (2004).

The differential scattering cross sections for the transitions presented in Table 6.7 are shown in Figures 6.27 and 6.28. Partial waves $L \leq 25$ were included in these calculations, and extrapolated amplitudes were included for $25 < L \leq 200$ to smooth the oscillations in the back-scattering region. The results agree with CCC (Bray 2004) for each $n_jl_j$ state, though to aid clarity only the total $n_j$ cross sections are shown for CCC. There is a slight variance between CCC and PECS near $\theta=180^\circ$, though this region is many orders of magnitude smaller than the peak and does not affect the accuracy of the total cross sections, and is probably beyond experimental determination. The important thing to note is that the PECS results remain relatively smooth in this computationally difficult
Figure 6.27: PECS $e$-H(2$s$) differential scattering cross sections at 14.8 eV for final states $n_j \leq 4$. Calculations include partial waves $L \leq 25$ and extrapolated partial wave amplitudes for $25 < L \leq 200$. CCC results from Bray (2004).

region, which highlights the stability of the phase of the scattering amplitudes. The close agreement of the PECS and CCC calculations presented here confirms the validity of the PECS theoretical development for excited-state targets undertaken in Chapter 2.

6.4.2 Ionisation

The ionisation cross sections presented here were extracted from the wave functions used in the previous section. The TICS and spin asymmetry for $e$–H(2$s$) and $e$–H(2$p$) collisions at 14.8 eV are presented in Table 6.8 and have an estimated standard error of 1%. These results are in good agreement with CCC (Bray 2004), and agree with experimental results (Defrance et al 1981) for the 2$s$ state (obtained by interpolating measurements at nearby energies). The SDCS for these collisions are presented in Figure 6.29, along
6.4: EXCITED-STATE HYDROGEN RESULTS

Figure 6.28: PECS e-H(2p) differential scattering cross sections at 14.8 eV for final states $n_j \leq 4$. Calculations include partial waves $L \leq 25$ and extrapolated partial wave amplitudes for $25 < L \leq 200$. CCC results are from Bray (2004).

<table>
<thead>
<tr>
<th>Method</th>
<th>$n_i$</th>
<th>$l_i$</th>
<th>$M$</th>
<th>$S=0$</th>
<th>$S=1$</th>
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<td>30.2</td>
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<tr>
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<td>18.6</td>
<td>30.5</td>
<td>0.186</td>
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<tr>
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<td>–</td>
<td>29 ± 3</td>
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<td>23.9</td>
<td>36.7</td>
<td>0.134</td>
<td></td>
</tr>
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</table>

Table 6.8: PECS $e^{-}\text{H}(2s)$ and $e^{-}\text{H}(2p)$ 14.8 eV TICS and spin asymmetry results. CCC (Bray 2004) calculations and experimental (Defrance et al 1981) results (interpolated) are presented where available. PECS calculations include partial waves $L \leq 25$, singlet and triplet results are spin weighted and are given in a.u.
with the separate $M$-state and parity contributions for the $2p$ target. The $2s$ SDCS is in good agreement with CCC, with only minor differences at near equal energy-sharing and highly asymmetric energy-sharing. This difference may be an artifact of the smoothing algorithm used in the CCC method. CCC differential cross sections for the $2p$ collision were not available for comparison, and there are no known measurements of the differential cross sections of the metastable state.

Fully-differential cross sections for $e^{-}\text{H}(2s)$ collisions at 14.8 eV are shown in Figure 6.30 for several kinematic arrangements. CCC results are in good agreement with our calculations, though contain some additional minor oscillations in the $\theta_2=30$ degree plots. As the PECS calculations used a larger set of angular momentum states, these additional oscillations would be expected to diminish with a larger CCC calculation. The TDCS results of the $\text{H}(1s)$ collision with the same excess energy are included so as to highlight the significantly different structure in the angular distribution of the slow electron. This is clearly demonstrated in the $E_1=1$ and 3 eV plots at $\theta_2=15$ degrees, where the excited target has three large peaks compared with a single dominant peak.
Figure 6.30: Coplanar TDCS results for an $e$-H($2s$) ionising collision at $E_0=14.8$ eV, compared with $e$-H($1s$) at $E_0=25.0$ eV, for various fixed angles of the fast electron ($\theta_2$) and energies of the slow electron ($E_1$). Both collisions are at the same total energy $E=11.4$ eV, and the $e$-H($1s$) results have been multiplied by 10. $1s$ calculations include $L \leq 12$ and $2s$ calculations include $L \leq 25$.

in the ground state collision. The physical reason for this difference may be due to the different number of nodes in the wave function of hydrogen $1s$ and $2s$ targets. We believe that the large differential cross sections of the metastable $2s$ state in these regions should encourage future experimental confirmation of the TDCS structure revealed by our calculations.

For completeness, we also present TDCS results for the H($2p$) target in Figure 6.31, for which there are no published results available, either theoretical or experimental.
Figure 6.31: Coplanar TDCS results for an e-H(2p) ionising collision at $E_0=14.8$ eV, compared with e-H(2s) at the same energy. The e-H(2p) partial cross sections for the component $M$-states are shown with dashed lines. Calculations include $L \leq 25$.

This completes our investigation of electron collisions with hydrogen and hydrogenic ions at low and intermediate energies. We have demonstrated that the PECS method can accurately calculate

- cross sections, spin asymmetry and angular correlation parameters for discrete final-state collisions, which has not previously been undertaken with ECS-based methods,
- below ionisation threshold resonance calculations,
• ionisation amplitudes over a much larger range of impact energies than has been demonstrated by the ECS method, and

• ionising collisions for both charged hydrogenic targets and excited initial-state targets.

Before we claim that the PECS method developed in this thesis is a complete numerical method for solving $e$–$H_Z$ collisions, in the following chapter we will apply it to what is arguably the last unsolved problem in electron-hydrogen collisions: an \textit{ab initio} quantum-mechanical confirmation of the Wannier and related threshold laws.
In previous chapters we have given the theoretical, numerical and computational development of the PECS method and demonstrated its utility and accuracy for model problems and the full \( e-H_2 \) problem over a wide range of energies, below and above ionisation threshold. However, the most computationally difficult calculations are near ionisation threshold where large grids are required to obtain convergent results for ionisation, and strong coupling between the \((l_1, l_2)\) angular momentum states of each partial wave cause iterative solution methods to fail; both the iterative coupling method of PECS and the CGS sparse matrix solver used by ECS. Fortunately, PECS can obtain solutions without iterative coupling, albeit with a higher computational overhead, so we will use PECS to investigate this energy region in this chapter. To date, no complete solution to the full Schrödinger equation has been undertaken with sufficient accuracy at energies approaching the ionisation threshold to confirm the threshold laws predicted using classical, semiclassical and approximate quantal methods. Before we apply PECS to these problems we will give a brief overview of the predictions made by these methods.

Wannier (1953) proposed an ionisation threshold law for all ionising collisions leading to two free electrons and a charged atomic ion in the final state. He divided coordinate space into three regions, the reaction zone, Coulomb zone and free zone, and argued that the probability of ionisation is determined by the behaviour of the these electrons in the Coulomb zone, where their motion can be described using classical mechanics. The reaction zone extends from the nucleus to approximately the Bohr radius, where the potential energy dominates the total energy of the system and quantum mechanics is required to describe the motion of the electrons. In the Coulomb zone the potential energy and total energy essentially cancel, and its outer boundary is given by \( \rho = (4Z - 1)/\sqrt{2E} \), which gives \( \rho E = 3/\sqrt{2} \approx 2 \) for \( Z=1 \). In the free zone, he postulated
that the outgoing electrons essentially move independently of each other. As the reaction zone is inaccessible to classical mechanics, he also postulated that the distribution of the two electrons in phase space is approximately uniform when they exit the reaction zone.

Using these postulates, and considering the energy dependence of the classical trajectories in the Coulomb zone and an approximation of the Coulomb potential energy in this region, Wannier was able to calculate the probability that the collision leads to ionisation is proportional to the total energy of the system, \( \sigma \propto E^\eta \), near ionisation threshold. \( \eta \) is a constant that depends on the charge of the final-state ion and can be expressed analytically as

\[
\eta = \frac{1}{4} \left( \frac{100Z - 9}{4Z - 1} \right)^{1/2} - 1. \tag{7.1}
\]

For the electron-impact of a hydrogen target this gives \( \eta \approx 1.127 \).

Wannier's threshold law applies to a vast range of atomic collisions, and consequently it continues to attract considerable interest five decades later. Experiments (McGowan and Clarke 1968, Cvejanović and Read 1973, Spence 1975, Pichou et al 1978, Donahue et al 1982) have given support to this threshold law, and numerous semiclassical and quantal studies (Peterkop 1971, Rau 1971, Roth 1972, Klar and Schlecht 1976, Peterkop 1983, Feagin 1984, Read 1984, Rost 1994), which utilise approximations to the Schrödinger equation, are in agreement with Wannier's conjecture.

Wannier theory also predicts that the ionised and scattered electrons emerge in opposite directions \( (\theta_{12} = \pi) \) at threshold. As total energy approaches threshold, \( \theta_{12} \) is predicted to have a Gaussian probability distribution, centered at \( \theta_{12} = \pi \), with a full-width-half-maximum (FWHM) related to total energy by \( (\theta_{12})_{\text{FWHM}} \propto E^{1/4} \) (Vinkalns and Gailitis 1967). Later investigations (Rau 1976, Feagin 1984, Read 1984, Altick 1985) concur with this prediction though they give a range of values for the constant of proportionality. However, an \textit{ab initio} investigation of these laws using a direct numerical solution of the full Schrödinger equation for the \textit{e}–\textit{H} system has been a rather remote goal until now due to the sheer scale of the computations.

Semiclassical and quantal investigations have given important insights into near-threshold collisions, but have relied on one or more \textit{a priori} assumptions to make the
computations tractable: They (a) consider only collisions with zero total angular momentum \((L=0)\) and use semiclassical arguments (Roth 1972, Klar and Schlecht 1976, Greene and Rau 1982) for similar scaling of the higher angular momentum states, (b) use Wannier’s conjecture that the interaction is limited to the Coulomb zone where \(\rho E \approx 2\) for \(Z=1\), (c) assume that the potential ridge at \(\theta_{12} = \pi\) and \(r_1 \approx r_2\) dominates the interaction, or (d) include a semiclassical approximation of the final-state wave function.

To-date, several state-of-the-art fully-quantal numerical methods have been used to explore near-threshold for \(e^-\text{H}\) ionising collisions. Kato and Watanabe (1997) used their HSCC method to investigate the Wannier exponent in a two dimension model, angular correlation of the outgoing electrons for the \(L=0\) singlet partial wave and calculated the TICS and spin asymmetry of the full problem near threshold. Scott \textit{et al} (1997) used IERM to investigate the \(L=0\) singlet TICS near threshold. Yet, none of these methods have been implemented with the necessary precision to calculate \(\eta\) or the energy dependence of \(\theta_{12}\) for the full \(e^-\text{H}\) collision. The most comprehensive set of calculations thus far include those presented in Section 5.4.1 and those of Kato and Watanabe (1996), both of which incorporate assumptions a) and c) and are consistent with the Wannier threshold law.

In this chapter we directly solve the Schrödinger equation for near-threshold \(e^-\text{H}\) ionising collisions using the PECS method. These calculations will be used to find the Wannier threshold law exponent \(\eta\) and investigate the behaviour of the spin asymmetry, SDCS (with respect to electron energy-sharing) and the energy dependence of \(\theta_{12}\) near threshold. These calculations provide the first successful investigation of the Wannier and related predictions using a fully-quantal \textit{ab initio} method.

\section*{7.1 Wannier threshold law}

We performed calculations at 261 total energies between 0.01-0.10 a.u., spaced at 0.00025 a.u. intervals below 0.05 a.u., and 0.0005 a.u. above. The TICS are converged, with respect to grid spacing and angular momenta, to around \(\pm 1\%\) over the energy range. For
all singlet calculations in this energy range the PECS iterative coupling method fails, and solutions were obtained using \( n_g = 1 \). However, the energy perturbation method does converge over a useful range of energies, allowing solutions to be obtained for \( \Delta E = 0.0025 \) a.u. below \( E = 0.05 \) a.u. and \( \Delta E = 0.0050 \) a.u. above \( E = 0.05 \) a.u.. This provided a many-fold reduction in computational effort. All calculations use the same grid spacing and grid size (\( R_0 = 180 \) a.u.), and include six partial waves (\( L \leq 5 \)) to achieve the stated convergence for all energies. Angular momentum states were included up to \( n_L = 5, 4, 3, 2, 2 \) and 1 for \( L = 0 \) through 5, respectively. As a test of the accuracy of our results, we compared our asymmetric energy-sharing DDCS results of these calculations at \( E_0 = 14.6 \) eV (\( E = 0.037 \) a.u., \( E_1 / E = 0.9 \) and \( R_0 = 180 \) a.u.) with recent CCC and ECS calculations and measurements (Childers et al 2004), which are shown in Figure 7.1. This is the lowest energy that differential ionisation calculations and measurements are available, and the good agreement with CCC and excellent agreement with ECS helps corroborate the claimed accuracy of our results. As differential cross sections are more demanding than the TICS with regard to including sufficient \( (l_1, l_2) \) angular momentum states, the

**Figure 7.1**: DDCS for \( E_0 = 14.6 \) eV and \( E_1 = 0.9 \) eV, compared with CCC and ECS calculations and measurements presented by Childers et al (2004).
close agreement with experiment demonstrates that our selected angular momentum states are sufficient in this near-threshold energy region.

In Figure 7.2 we plot our spin-weighted TICS and include several higher-energy calculations from Chapter 6 to demonstrate the deviation from near-linear behaviour above $E=0.05$ a.u. As discussed in previous chapters, the extracted cross sections contain smooth $\rho$-dependent oscillations that diminish with increasing $\rho$. In a similar manner, for fixed $\rho$ and varying energy there are slight $E$-dependent oscillations, clearly visible in Figure 7.3, that range from $\pm 0.2\%$ at 0.10 a.u., $\pm 0.5\%$ at 0.05 a.u., and reach $\pm 1.5\%$ at the lowest energy presented. Increasing $R_0$ to allow larger $\rho$ reduces these oscillations, but vastly increases computational effort. Overall, our estimated TICS error ranges between 1.5\% at 0.10 a.u. to 3\% at 0.01 a.u. Our results match the ECS calculation (Baertschy et al 2001a) at 0.0735 a.u. ($E_0=15.6$ eV, the only published ECS TICS result in this region) and are in good agreement with experiment (Shah et al 1987) and CCC calculations (Bartschat and Bray 1996) (with significantly reduced scatter).

Semiclassical studies (Roth 1972, Klar and Schlecht 1976, Greene and Rau 1982)
predicted that the TICS contribution from each $LS$ partial wave separately obeys the Wannier threshold law (with same $\eta$), with the exception of the $L=0$ triplet partial wave for $e^{-}\text{H}$ collisions. This partial wave is highly suppressed due to the Pauli exclusion principle and was predicted (Klar and Schlecht 1976, Greene and Rau 1982) to have $\eta \approx 3.88$, but later corrected by Peterkop (1983) to $\eta \approx 3.38$. In Figure 7.3 we present the TICS, and separate partial-wave cross section (PWCS) contributions of the angular momentum states ($L$) and spin-states ($S$) to the TICS, divided by $E^{1.127}$ to emphasise the low-energy results. With this scaling we would expect the curves to become linear (ignoring $E$-dependent oscillations) if the Wannier threshold law is valid as threshold is approached. This is indeed the case and confirms that both the TICS, and the $L$ and $S$ contributions to the TICS, are consistent with Wannier’s threshold law. Though, the linear dependence upon energy implies that it only strictly applies at threshold. It is also evident that the relative contribution of higher partial waves diminishes as threshold is approached. We have also included TICS results for several calculations undertaken with $R_0=360$ a.u., which are well within the estimated error of the $R_0=180$ a.u. results. The scaling in this plot emphasises the greatly reduced $E$-dependent oscillations of the PECS results compared with the RMPS and CCC calculations of Bartschat and Bray (1996).

The singlet and triplet spin-weighted ionisation cross sections for the $L=0$ partial wave shown in Figure 7.4 demonstrate the suppression of the $L=0$ triplet state, due to the Pauli exclusion principle, and the different scaling law as threshold is approached. The $L=0$ triplet channel is nearly five orders of magnitude smaller than the singlet channel at $E=0.01$ a.u. and shows an increasing suppression as threshold is approached. Though this partial wave has a different scaling law to the remaining partial waves, its very small cross sections near threshold ensures that it does not affect the threshold behaviour of the TICS, or arguments that rely on the same scaling of all partial waves.

In order to estimate the threshold power laws we performed non-linear fitting of our results presented in Figure 7.3 to the function $E^\eta \sum_{j=0}^{j_{\text{max}}} c_j E^j$. This method was used for the collinear model investigation in Section 5.4.1 and previously by Kato and Watanabe (1996), and has the advantage that it extracts accurate information near threshold by
7.1: WANNIER THRESHOLD LAW

**Figure 7.3:** Partial-wave cross section (PWCS) contributions from $S=0$ and $S=1$, and separate PWCS for $L \leq 5$ ($S=0$ and $S=1$ combined), for $e$–$H$ collisions with $E=0.01$–$0.10$ a.u. and $R_0=180$ a.u. All results are divided by $E^{1.127}$. TICS calculations for PECS at $R_0=360$ a.u., RMPS and CCC (Bartschat and Bray 1996) are also shown.

**Figure 7.4:** Spin-state contributions to $e$–$H$ $L=0$ PWCS for $E=0.01$–$0.10$ a.u.
fitting to a finite energy interval thus allowing for deviations from the power law further from threshold. The fitting function coefficients and their errors are sensitive to both \( j_{\text{max}} \) and the energy range chosen. We chose the largest \( j_{\text{max}} \) that minimised \( \chi^2 \) without resulting in exponential increases in \( c_j \) or large errors in \( c_{j_{\text{max}}} \). Our calculations were fitted over several ranges of energies (0.01-0.03 a.u. through 0.01-0.10 a.u., in 0.01 a.u. increments) and the average and standard deviation of \( \eta \) for these fits are shown in Table 7.1. This table includes fits for the TICS and the separate spin \( S \) and angular momentum \( L \) contributions to the TICS.

\[
\begin{array}{|c|c|}
\hline
\text{TICS} & 1.122 \pm 0.015 \\
\hline
S=0 & 1.107 \pm 0.040 \\
S=1 & 1.120 \pm 0.038 \\
L=0 & 1.092 \pm 0.018 \\
L=1 & 1.102 \pm 0.030 \\
L=2 & 1.109 \pm 0.031 \\
L=3 & 1.166 \pm 0.015 \\
L=4 & 1.131 \pm 0.048 \\
L=5 & 1.117 \pm 0.032 \\
\hline
\end{array}
\]

Table 7.1: Mean and standard deviation of \( \eta \) for the nonlinear fitting of: TICS, separate spin state partial-wave cross sections (over all \( L \)), and separate \( L \) (spin-weighted \( S=0 \) and \( S=1 \) combined).

Our result for the summed partial cross sections gives \( \sigma \propto E^{1.122\pm0.015} \), and hence provides strong support for the Wannier threshold law. The individual partial wave and spin-state results are also consistent with the Wannier threshold law, though the standard errors of our \( L=0 \) and \( L=3 \) partial-wave fitting appear low. Separate calculations for the \( L=0 \) singlet partial wave with \( R_0 = 400 \) a.u. give \( \eta = 1.124 \pm 0.016 \), providing strong evidence that these variations in \( \eta \) are resolved by calculations with larger \( R_0 \). However, a significantly larger \( R_0 \) for the full problem is beyond our present computational resources. It is worth noting that \( L=2 \) and \( L=1 \) provide the majority
contribution in this energy range rather than \( L=0 \) and \( L=3 \), and so the increased error of the \( L=0 \) and \( L=3 \) results does not significantly affect the accuracy of the summed (TICS) results. Non-linear fitting of the \( L=0 \) triplet PWCS gives \( \sigma \propto E^{3.36 \pm 0.02} \), in agreement with Peterkop (1983).

Given the consistency of our results with the classical and semiclassical results, we can give the constants of proportionality and first-order energy-correction coefficients of these threshold laws for \( e^{-H} \) collisions that best fit our results as

\[
\begin{align*}
\sigma &= E^{1.127} \{(7.49 \pm 0.03) - (8.7 \pm 1.1)E\} \\
\sigma_{L=0S=1} &= E^{3.38} \{(1.199 \pm 0.005) - (6.0 \pm 0.2)E\}.
\end{align*}
\]

These functions provide good fits to our results up to \( E=0.05 \) a.u.

### 7.2 Spin asymmetry

Classical mechanics is unable to predict spin asymmetry \( (A_s) \) as spin is a quantum-mechanical concept. Semiclassical analysis (Greene and Rau 1982) indicates that \( A_s \) should be independent of energy near threshold, based on the argument that singlet and triplet channels have the same Wannier power law exponent\(^1\). Though more recent quantal calculations (Bartschat and Bray 1996, Kato and Watanabe 1997) are consistent with this energy independence, their scatter or insufficient penetration into the threshold region leads to some uncertainty in the value at threshold. We present our results along with experiment (Fletcher et al 1985) and other calculations for \( A_s \) in Figure 7.5. They confirm a linear, nearly energy-independent behaviour below 0.05 a.u. and that the spin asymmetry approaches the limiting value \( A_s = 0.54 \pm 0.01 \). This is about 10\% higher than experimental data but it should be noted that the error bars below 0.3 a.u. are large.

---

\(^1\)This argument does not hold for individual partial waves where, for \( e^{-H} \) collisions, the \( L=0 \) triplet state has a different \( \eta \), but because this state is highly suppressed due to the Pauli exclusion principle, the argument does hold when all \( L \) states are summed.
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Figure 7.5: Spin asymmetry of e–H collisions for $E=0.01$–5.0 a.u. CCC (Bartschat and Bray 1996) and HSCC (Kato and Watanabe 1997) calculations and measurements Fletcher et al (1985) are also shown.

7.3 Single-differential cross section

The energy-sharing behaviour of the outgoing electrons is shown in Figure 7.6 by normalising the single-differential cross sections to 1.00 at equal energy-sharing for a range of energies. As threshold is approached the dominance of the asymmetric energy-sharing diminishes. Earlier calculations (Vinkalns and Gailitis 1967, Peterkop 1971) assert that the SDCS becomes independent of energy sharing near threshold. At 0.04 a.u. this is essentially correct, but as the energy is further decreased to 0.01 a.u. the $E_1=0$ normalised contribution drops to 0.96. This result is consistent with our previous e–H collinear model calculations presented in Section 5.4.1 and other classical (Read 1984) and semiclassical (Rost 1994) predictions. In Figure 6.16 in the previous chapter we noted that the SDCS at this energy is quite oscillatory, and though our results show a slight decrease in the asymmetric energy-sharing SDCS, relative to equal energy-sharing,
7.4: ELECTRON-ELECTRON ANGULAR DISTRIBUTION

Figure 7.6: SDCS (with respect to energy sharing) for \( e-H \) collisions near threshold normalised to 1.00 at equal energy-sharing \( (E_1 = E/2) \). Results for \( E=0.01 \) and 0.04 a.u. were calculated using \( R_0=360 \) a.u. grids.

the result of 0.96 is only approximate and has a standard error of \( \pm 0.02 \).

7.4 Electron-electron angular distribution

The remaining important prediction of the Wannier models that we investigate is the angular dependence of the outgoing electrons. We noted earlier that as the total energy approaches threshold, the size of the interaction region, the Coulomb zone, increases approximately as \( 1/E \). Therefore, it is reasonable to use \( \rho E \) as a suitable radial measure when investigating the radial convergence of the results for collisions with different total energies. The SDCS, with respect to \( \theta_{12} \), are presented in Figure 7.7 at several energies and constant \( \rho E=1.8 \) a.u. The cross sections peak at \( \theta_{12} = \pi \) and the positions of the half maxima (shown with filled circles) move towards \( \theta_{12} = \pi \) as the energy diminishes. This is consistent with classical (Vinkalns and Gailitis 1967) and semiclassical (Rau
Figure 7.7: SDCS (with respect to $\theta_{12}$) for $e$–H at various total energies and $\rho E=1.8$ a.u. The half maximum of each curve is shown with a filled circle.

1976, Read 1984, Feagin 1984) calculations, which report the relationship between total energy and the full-width-half-maximum as $(\theta_{12})_{FWHM} = \alpha E^{1/4}$.

In Figure 7.8 we present $(\theta_{12})_{FWHM}/E^{1/4}$ as a function of $\rho E$ at several total energies. For our results to confirm the $E^{1/4}$ power-law, then each curve within the threshold energy region should converge to the same constant $\alpha$. Though we cannot demonstrate complete radial convergence at all energies due to our limited $R_0$, all the curves overlap and have the same convergence behaviour with respect to $\rho E$, indicating that $\alpha$ converges to approximately 3.0 for $E \leq 0.05$ a.u. There is a slight deviation for the $E = 0.10$ a.u. curve, but we consider that this is outside of the applicable energy range of the threshold law.

In order to demonstrate full convergence at 0.01 a.u. we estimate that our calculations need to be extended to at least $\rho E=20$ ($R_0=2000$ a.u. at $E=0.01$ a.u.). As the computational effort of PECS scales as $O(N^4)$, where $N$ is the number of grid points along one dimension, these calculations are well beyond the capacity of our present supercomputing facilities. However, we have undertaken larger calculations for the $L=0$
and $L=2$ singlet partial waves at $E=0.01$ a.u. ($R_0=720$ a.u. and 360 a.u., respectively). The results of these larger calculations are shown in Figure 7.9, and confirm that the converging trend demonstrated in Figure 7.8 continues at larger $\rho E$. We note that different partial waves converge to different values of $\alpha$. We also present results for calculations at various maximum $n_L$. It is interesting to note that as $\rho$ is increased, more angular momentum states must be included to achieve convergence, however at smaller $\rho$ all calculations give the same results. Thus convergence of calculations with respect to angular momentum coupling must always be checked as a function of $\rho$, especially in the near threshold region, otherwise spurious convergence may be obtained. For our $L=0$ calculations at $R_0=180$ a.u., we used $n_L \leq 5$ to obtain convergence, whereas this must be extended to $n_L \leq 6$ for $\rho$ up to 720 a.u. Similar behaviour is exhibited by the $L=2$ partial wave, though in this case the $n_L \leq 3$ used for our $R_0=180$ a.u. calculations is also sufficient for convergence of the $R_0=360$ a.u. calculations. The increased number of angular momentum states required for the larger-$\rho$ calculations was suggested by Gailitis (1990). Our calculations support his conclusions that were based on semiclassical
modelling.

The $(\theta_{12})_{FWHM}$ calculations presented in Figure 7.9 are still not fully converged, and so the ionisation amplitude for each $(l_1, l_2)$ state must also not be fully converged. We explore this further in Figure 7.10, where it is clear that at $E=0.01$ a.u. and $\rho=720$ a.u. the PWCS contribution to the $L=0$ singlet TICS of all $(l_1, l_2)$ angular momentum states have not yet converged completely, though the TICS for the total partial wave (not shown) has converged to better than $\pm 1\%$. This gives further evidence for the significant exchange of angular momenta between the outgoing electrons, even at large $\rho$, and that the higher angular momentum states are suppressed at small $\rho$. To confirm that this is not an artifact of the asymptotic approximations used in the surface integral method for extracting the cross sections, we have plotted the magnitude squared of the scattering wave function (at $r_1 = r_2$), as a function of $\rho$, in Figure 7.10b (multiplied by $\rho$). As they represent the direct solution of the Schrödinger equation for these partial waves at $r_1 = r_2$, they are free from asymptotic approximations. The scattering wave functions have the same convergence trend as the partial cross sections, and corroborates our conjecture that exchange of angular momenta continues for very large distances at this low energy. Similar analysis of our results for higher-energy collisions indicate that good convergence of the largest contributing angular momentum states does not occur until $\rho E > 20$. This result is in contrast to Wannier’s arguments, and those of many semiclassical works (e.g. Rau (1971)), that assume the region of interaction of the electrons is restricted to the Coulomb zone. Certainly, this appears to be true for the TICS, but the angular distribution of the electrons appear to be much more sensitive to the long range Coulomb forces and require much larger $\rho E$ before approaching their asymptotic value.

From this analysis we are confident that the convergence trend of $\alpha$ demonstrated in Figure 7.8 is real, and estimate the threshold asymptotic value as $\alpha = 3.0 \pm 0.2$ in atomic units. Semiclassical calculations for $\alpha$ are reported as 2.66 Altick (1985), 2.71 Feagin (1984), 3.38 Rau (1976) and 3.55 Read (1984), and are markedly different from the experimental result of $1.6 \pm 0.1$ given by Cvejanović and Read (1973). Reasons for disagreement with experiment have been suggested as possible experimental error.
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**Figure 7.9:** Convergence of $(\theta_{12})_{FWHM}$ with respect to $\rho E$ for $L=0$ and $L=2$ singlet partial waves at $E=0.01$ a.u., and including $(l_1, l_2)$ states of angular momentum up to and including the maximum $n_L$ shown.

**Figure 7.10:** Convergence of PWCS and $|\psi|^2$ with respect to $\rho E$ for $L=0$ singlet partial waves at $E=0.01$, and $|\psi|^2$ only for $E=0.10$ a.u.
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Figure 7.11: Constants of proportionality for $E^{1/4}$ energy dependence of $(\theta_{12})_{FWHM}$: Experiment for He (Cvejanović and Read 1973) and best fit $\alpha = 1.6$, PECS $\alpha = 3.0$ and semiclassical predictions of 2.66 (Altick 1985), 2.71 (Feagin 1984), 3.38 (Rau 1976) and 3.55 (Read 1984).

(Read 1984) and that the single plane of measurement ($90^\circ$ to the incident electron) is not representative of the full problem (Altick 1985). However, despite the variation of the constant of proportionality across the various models, our calculations support the $E^{1/4}$ energy dependence of the FWHM, and our fit of $\alpha$ lies within the midrange of semiclassical calculations, shown in Figure 7.11.

To calculate $\alpha$ most semiclassical calculations assume a Gaussian shape for the $\theta_{12}$ SDCS [as in (Rau 1971) but in disagreement with (Read 1984)] and all are limited to $L=0$. Our SDCS results for the full $e$–H problem at $\rho E=1.8$ near threshold exhibit an approximate Gaussian shape, but deviate systematically from this shape with increasing $\rho$. To investigate this further, Figure 7.12 presents the normalised $\theta_{12}$ SDCS for the $L=0$ singlet partial wave at various hyperradii from 180 a.u. to 720 a.u. From this we see that as the hyperradius is increased the FWHM becomes narrower and the peak of the curve becomes flatter. For the 180 a.u. and 720 a.u. curves we also give the Gaussian curve
Figure 7.12: Deviation of singlet SDCS (with respect to $\theta_{12}$) from Gaussian shape at $E=0.01$ a.u. for the $L=0$ partial wave as hyperradius is increased.

that provides the best least-squares fit. It is clear that as the hyperradius increases the SDCS deviates further from the Gaussian approximation, and indeed the shape is closer to that predicted by Read (1984) in the region $\theta_{12} > 2.5$ radians. Our results support a non-Gaussian form, which gives a further reason for the variance between our estimate for $\alpha$ and the semiclassical estimates.

In summary, we have undertaken a wide-ranging investigation into $e$-H ionisation collisions at energies very close to threshold using the PECS method. Our solutions of the full Schrödinger equation give convincing evidence for the validity of Wannier’s threshold law for $e$-H ionising collisions, support classical and semiclassical predictions for the $E^{1/4}$ dependence of the angular distribution of the outgoing electrons and give an estimate for its constant of proportionality, give insight into the electron energy distribution and elucidate the spin asymmetry behaviour near threshold. The accurate numerical solution of the time-independent Schrödinger equation near-threshold has proven to be an enormous computational task but has at last provided convincing support for these classically and semiclassically derived threshold laws.
Chapter 8
Conclusion

We have now completed the theoretical and computational development of the PECS method, and have presented a large set of calculations together with comparisons with other state-of-the-art computational methods and measurements. In summary, we have

- Extended the theoretical development of the ECS method (Rescigno et al 1999, Baertschy et al 2001a) to include hydrogen and hydrogenic targets of arbitrary initial state and charge.

- Developed a method to extract scattering amplitudes from the scattering wave functions based on the Peterkop (1977) surface integral formulation.

- Extended the propagation algorithm of Poet (1980) to solve inhomogeneous equations and enhanced the Numerov formula to cater for arbitrary and complex changes in grid spacing in two dimensions, as is required by the exterior complex scaling technique.

- Developed highly efficient methods for iteratively coupling the PECS equations that lead to a 100-fold improvement in its efficiency at higher energies, and an iterative energy-perturbation technique that significantly reduces the computational effort required for calculations at closely-spaced energies.

- Presented a comprehensive convergence study for both model and the full $e$–$H_Z$ problem to demonstrate convergence with respect to grid spacing, grid size, angular momentum states and iterative coupling.

- Given benchmark solutions for the Temkin-Poet and collinear models at energies below (from $E_0=2.7$ eV) and above (up to $E_0=54.4$ eV) ionisation threshold, for both discrete final-state and ionising collisions, and investigated the ionisation threshold behaviour of each model to within 0.1 eV of threshold. The estimated
standard error of the TICS calculations were 0.2% and 0.5% for the SDCS calculations, at higher energies. At energies close to threshold, the estimated standard error of the TICS was maintained below 1%. The error of the discrete cross sections ranged from 0.5% for elastic scattering to 2.0% for excitation to the 5s state.

- Presented benchmark results for $e^{-}\text{H}$ scattering, including: resonance structure below ionisation threshold ($E_0=11.6-12.08$ eV), total and differential scattering cross sections for $n_j \leq 4$ above ionisation threshold (16.5 and 54.4 eV) and Stokes parameter calculations at 54.4 eV. We have also presented total and differential scattering cross sections for hydrogenic ions with $Z \leq 4$, which gave strong support for the $Z$-scaling laws, and 2s and 2p excited-state hydrogen targets. The estimated error of these calculations ranged from 1% for elastic collisions to 4% for $n_j=4$ collisions.

- Undertaken TICS, SDCS, DDCS and TDCS (symmetric- and asymmetric energy-sharing) ionisation calculations for hydrogen, hydrogenic ions ($Z \leq 4$) and H(2s) and H(2p) targets. Energies ranged from 0.27 eV above threshold to $E_0=150$ eV for hydrogen targets and 1.3 keV for Be$^{3+}$ targets. The estimated error of the TICS of these calculations, except near threshold, was of the order of 1%.

- Performed a detailed examination of the behaviour of $e^{-}\text{H}$ ionisation cross sections near the ionisation threshold ($E=0.27-2.7$ eV), including: TICS, SDCS with respect to energy sharing, SDCS with respect to angular distribution and spin asymmetry. This provided the first convincing fully-quantal ab initio support for the Wannier (1953) and related threshold laws for $e^{-}\text{H}$ collisions.

All PECS calculations presented in this thesis were in excellent agreement with other state-of-the-art computational methods and measurements, where available. We have shown that with the PECS method it is now possible to provide benchmark solutions for electron-hydrogen collision over the whole range of observables accessible by experiment. We consider that the method is complete in four important respects:

- Solutions are obtained by direct solution of the full Schrödinger equation, where
all approximations are controlled in the sense that errors due to numerical discretisation and solution on a grid can be demonstrated to converge consistently with grid size reduction, hyperradius extension and increasing the number of angular momentum states. Hence, \textit{ab initio} benchmark results are obtained for all electron energy-sharing and kinematic arrangements.

- Results can be obtained at all energies accessible to experiment, within the constraints of the non-relativistic Schrödinger equation. The high-energy calculations $[E_0=150 \text{ eV for H}(1s) \text{ and } E_0=1.3 \text{ keV for Be}^{3+}(1s)]$ given here required minimal computational resources and we expect that accurate results can be readily obtained at higher energies where perturbation methods become accurate. The energies near ionisation threshold were more problematic, due to the very large grid sizes required. The difficulty, however, is only one of providing sufficient computational resources, we found no evidence to suggest that the PECS method becomes unstable or divergent at energies closer to threshold than the calculations presented here.

- The method gives benchmark solutions for both discrete final-state and ionising collisions.

- PECS can be applied to hydrogenic targets with arbitrary nuclear charge and initial state.

With our generalisation of the ECS method for discrete final-state, excited initial-state and charged hydrogenic ion collisions, and our development of the highly efficient computational methods that have removed the lower and upper energy limits of the ECS method, we believe that we have achieved the stated goal of this project; to enhance the ECS method to provide a \textit{complete} numerical solution for $e$–H collisions. This is significant in that it is the first method to demonstrate benchmark \textit{ab initio} results over a complete range of $e$–H$_Z$ targets, impact energies and final-state kinematic arrangements.

The benefits afforded by the exterior complex scaling technique used in the PECS method, in combination with the highly efficient numerical and computational algorithms
developed in this thesis, promise enormous potential for its future application to other atomic collision problems.

There remain a number of electron-hydrogen collisions that warrant further investigation, including a more detailed examination of the resonance structure of discrete final-state collisions below threshold, excitation to high-$n$ final states and collisions with highly excited targets. These calculations will require substantial computing resources due to the large grids and/or large number of coupled angular momentum states. The ECS method has very recently been applied to other three-body problems including photon-helium collisions (Horner et al. 2004) and photoionisation of hydrogen molecules (Vanroose et al. 2004). Though, there remain many other three-body systems to which the PECS method can be applied, of which the positron-hydrogen collision system is a prime candidate.

The full solution to the Schrödinger equation for a four-body break-up collision is significantly more computationally demanding than the three-body collisions investigated here, and is the next logical progression for the development of the PECS method. We believe that the efficiency of PECS, combined with the ever-increasing power of modern supercomputers, will make this a realisable goal in the near future. The ECS method has very recently been applied to electron-helium collisions in the $S$-wave model using a time-dependent ECS method (Horner et al. 2005), and we expect that the PECS method will make similar progress with the time-independent solutions. Ultimately, a full four-body solution to electron-helium collisions will give accurate information on many processes that are inaccessible to existing three-body approaches, including double excitation, excitation-ionisation and double ionisation.

Certainly each new collision system will present its own difficulties and challenges, but we believe that the developments undertaken in this thesis will significantly aid these future efforts.
This section details the angular functions and relations used in the partial-wave expansions undertaken in Chapter 2. The primary reference used for these relations was Varshalovich et al (1988), with additional information obtained from Brink and Satchler (1993), and these texts should be referenced for a rigorous justification of the relations presented. Though many relations in this section are in common use in atomic physics, they are included in this appendix to ensure that the theoretical and computational development of the thesis is self contained.

A.1 Spherical harmonic function

The spherical harmonic function $Y_{lm}(\theta, \phi)$ is a single-valued, continuous and bounded complex function of $\theta$ and $\phi$, where $0 \leq \theta \leq \pi$, $0 \leq \phi \leq 2\pi$ and parameters $l$ and $m$ are integers with $l \geq 0$ and $|m| \leq l$. The spherical harmonic function plays an important role in quantum mechanics as it describes the angular distribution of a particle, with orbital angular momentum $l$ and projection $m$, moving in a spherically symmetric field. It is an eigenfunction of the square of the orbital angular momentum operator $\hat{L}^2$ such that

$$\hat{L}^2 Y_{lm}(\theta, \phi) = l(l+1)Y_{lm}(\theta, \phi)$$  \hspace{1cm} (A.1)

and

$$\hat{L}_z Y_{lm}(\theta, \phi) = mY_{lm}(\theta, \phi),$$  \hspace{1cm} (A.2)

where $m$ is the eigenvalue of $\hat{L}_z$, which is the projection of the orbital angular momentum operator on the quantisation axis.

The orthogonality and normalisation of the spherical harmonic function is given, in
spherical coordinates, by

$$\langle l_2 m_2 | l_1 m_1 \rangle = \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \, Y_{l_2 m_2}^* (\theta, \phi) Y_{l_1 m_1} (\theta, \phi) = \delta_{l_1 l_2} \delta_{m_1 m_2},$$  \hspace{1cm} (A.3)$$

and the complex conjugate is given by

$$Y_{l m}^*(\theta, \phi) = Y_{l m}(\theta, -\phi) = (-1)^m Y_{l -m}(\theta, \phi).$$  \hspace{1cm} (A.4)$$

The equivalence of the different representations of the angular coordinates in the spherical coordinate system should be noted, \((\theta, \phi) \equiv \hat{\Omega} \equiv \hat{r},\) as they are used interchangeably in this thesis. For the special case \(\theta = 0\) (\( \hat{z}\)-axis) the spherical harmonic function reduces to

$$Y_{lm}(0, \phi) = \delta_{m0} \sqrt{\frac{2l+1}{4\pi}}.$$

(A.5)

Care must be taken when calculating \(Y_{lm}(\theta, \phi)\) numerically using standard power series expansions, as large errors can be introduced when \(l\) is large and finite precision floating point arithmetic is used. The software for this thesis was based on “Numerical Recipes in FORTRAN 77” (Press et al 1992), which uses a numerically stable recurrence relation.

A relation used to derive the reduced matrix element in Section A.5 involves an integral over total solid angle of three spherical harmonic functions, which is given by

$$\int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \, Y_{l_1 m_1} (\theta, \phi) Y_{l_2 m_2} (\theta, \phi) Y_{l_3 m_3} (\theta, \phi) = \frac{[l_1][l_2][l_3]}{\sqrt{4\pi}} \begin{pmatrix} l_1 & l_2 & l_3 \end{pmatrix} \begin{pmatrix} 0 & 0 & 0 \\ m_1 & m_2 & m_3 \end{pmatrix},$$  \hspace{1cm} (A.6)$$

where \([l] = \sqrt{2l+1}\) and the symbols in round brackets are Wigner-3j symbols, defined in Section A.3.

A.2 Bipolar spherical harmonic function

The bipolar spherical harmonic function \(Y_{LM}^{L_1 L_2}(\hat{\Omega}_1, \hat{\Omega}_2)\) is used for systems that depend on two vector directions, with a common centre, where

$$\vec{L} = \vec{l}_1 + \vec{l}_2$$

(A.7)
and can be expressed in terms of the spherical harmonic function for each vector by

\[ Y_{L_{1}l_{1}}^{L_{2}m_{2}}(\hat{\Omega}_{1}, \hat{\Omega}_{2}) = \sum_{m_{1}m_{2}} C_{l_{1}m_{1}l_{2}m_{2}}^{L_{1}L_{2}} Y_{l_{1}m_{1}}(\theta_{1}, \phi_{1}) Y_{l_{2}m_{2}}(\theta_{2}, \phi_{2}), \]  

(A.8)

where \( C_{l_{1}m_{1}l_{2}m_{2}}^{L_{1}L_{2}} \) is a Clebsch-Gordan coefficient (see Section A.3). It is an eigenfunction of the square of the orbital angular momentum operator \( \hat{L}^{2} \) such that

\[ \hat{L}^{2} Y_{L_{1}l_{1}}^{L_{2}m_{2}} = L(L + 1) Y_{L_{1}l_{1}}^{L_{2}m_{2}} \]  

(A.9)

and

\[ \hat{L}_{z} Y_{L_{1}l_{1}}^{L_{2}m_{2}} = M Y_{L_{1}l_{1}}^{L_{2}m_{2}}, \]  

(A.10)

where \( M \) is the eigenvalue of \( \hat{L}_{z} \), which is the projection of the orbital angular momentum operator on the quantisation axis. The function is non-zero only when \( |l_{1} - l_{2}| \leq L \leq l_{1} + l_{2} \) and \( m_{1} + m_{2} = M \), due to properties of the Clebsch-Gordan coefficient.

The orthogonality and normalisation of the bipolar spherical harmonic function is given by

\[ \langle l'_{1}l'_{2}L'M'|l_{1}l_{2}LM \rangle = \int d\hat{\Omega}_{1} \int d\hat{\Omega}_{2} Y_{l'_{1}l'_{2}}^{L'M'*}(\hat{\Omega}_{1}, \hat{\Omega}_{2}) Y_{l_{1}l_{2}}^{L'M}(\hat{\Omega}_{1}, \hat{\Omega}_{2}) = \delta_{l_{1}l'_{1}} \delta_{l_{2}l'_{2}} \delta_{L'L'} \delta_{M'M'}, \]  

(A.11)

where

\[ \int d\hat{\Omega} \equiv \int_{0}^{2\pi} d\phi \int_{0}^{\pi} d\theta \sin \theta. \]  

(A.12)

We may find an inverse relation for (A.8) as follows (where we have removed the
angular variables to improve clarity)

\[
Y_{l_1l_2}^{LM} = \sum_{m_1m_2} \langle l_1m_1l_2m_2|LM \rangle Y_{l_1m_1} Y_{l_2m_2}
\]

\Rightarrow \sum_{LM} \langle LM|l_1'l_2'm_1'm_2' \rangle Y_{l_1l_2}^{LM} = \sum_{m_1m_2LM} \langle l_1m_1l_2m_2|LM \rangle \langle LM|l_1'l_2'm_1'm_2' \rangle \times Y_{l_1m_1} Y_{l_2m_2}

= \sum_{m_1m_2} \langle l_1m_1l_2m_2|l_1'l_2'm_1'm_2' \rangle Y_{l_1m_1} Y_{l_2m_2}

= \sum_{m_1m_2} \delta_{l_1l_1'} \delta_{m_1m_1'} \delta_{l_2l_2'} \delta_{m_2m_2'} Y_{l_1m_1} Y_{l_2m_2}

\Rightarrow Y_{l_1m_1} Y_{l_2m_2} = \sum_{LM} \langle LM|l_1m_1l_2m_2 \rangle Y_{l_1l_2}^{LM}

= \sum_{LM} \langle l_1m_1l_2m_2|LM \rangle Y_{l_1l_2}^{LM}, \quad (A.13)

where \( \langle l_1m_1l_2m_2|LM \rangle = C_{l_1m_1l_2m_2}^{LM} = \langle LM|l_1m_1l_2m_2 \rangle \).

### A.3 Clebsch-Gordan coefficient and Wigner-3j symbol

The Clebsch-Gordan coefficients are used for problems that involve the addition of orbital angular momentum of two particles. They represent the probability amplitude that for a system with total orbital angular momentum \( L \) and projection \( M \) that the individual particles have an orbital angular momentum and projection of \( (l_1m_1) \) and \( (l_2m_2) \). Two common, and equivalent, notations for these coefficients are

\[
C_{l_1m_1l_2m_2}^{LM} \equiv \langle l_1m_1l_2m_2|LM \rangle. \quad (A.14)
\]

The coefficients are real, and are non-zero only when

\[
|l_1 - l_2| \leq L \leq l_1 + l_2, \quad (A.15)
\]

and

\[
M = m_1 + m_2, \quad (A.16)
\]

where \( l_1, l_2, L \) are integer or half-integer non-negative numbers, \( m_1, m_2, M \) are integer or half-integer numbers, \( |m_1| \leq l_1, |m_2| \leq l_2, |M| \leq L \) and \( j_1 + m_1, j_2 + m_2, L + M \) and \( l_1 + l_2 + L \) are integer non-negative numbers.
The Clebsch-Gordan coefficient can be represented in terms of Wigner-3j coefficients. These are often used in place of Clebsch-Gordan coefficients due to their simpler symmetry properties. They are related by

\[
\begin{pmatrix}
  l_1 & l_2 & l_3 \\
  m_1 & m_2 & m_3
\end{pmatrix} = (-1)^{l_1+m_3+2l_1}[l_3]^{-1}C_{l_1-m_1 l_2-m_2}^{l_3 m_3},
\] (A.17)

with the inverse relation

\[
C_{l_1 m_1 l_2 m_2}^{l_3 m_3} = (-1)^{l_1-l_2+m_3}[l_3] \begin{pmatrix}
  l_1 & l_2 & l_3 \\
  m_1 & m_2 & -m_3
\end{pmatrix}.
\] (A.18)

The symmetry properties of the Wigner-3j symbol, with respect to exchange of columns are

\[
\begin{pmatrix}
  a & b & c \\
  \alpha & \beta & \gamma
\end{pmatrix} = \begin{pmatrix}
  b & c & a \\
  \beta & \gamma & \alpha
\end{pmatrix} = \begin{pmatrix}
  c & a & b \\
  \gamma & \alpha & \beta
\end{pmatrix} = p \begin{pmatrix}
  a & c & b \\
  \alpha & \gamma & \beta
\end{pmatrix} = p \begin{pmatrix}
  b & a & c \\
  \beta & \alpha & \gamma
\end{pmatrix},
\]

where \( p = (-1)^{a+b+c} \), and with respect to the change of sign of the momentum projections

\[
\begin{pmatrix}
  a & b & c \\
  \alpha & \beta & \gamma
\end{pmatrix} = p \begin{pmatrix}
  a & b & c \\
  -\alpha & -\beta & -\gamma
\end{pmatrix}.
\] (A.19)

A commonly used symmetry property of the Clebsch-Gordan coefficients, with respect to exchange of the state of each particle, is

\[
C_{l_1 m_1 l_2 m_2}^{l_3 m_3} = (-1)^{l_1+l_2-l_3}C_{l_2 m_2 l_1 m_1}^{l_3 m_3},
\] (A.20)

A.4 Wigner-6j symbol

The Wigner-6j symbols are used when calculating the coupling coefficients of three angular momenta, and are related to the Wigner-3j symbol through the relation

\[
\begin{pmatrix}
  a & b & c \\
  d & e & f
\end{pmatrix} = \sum (-1)^{d+e+f+\delta+\epsilon+\phi} \begin{pmatrix}
  a & b & c \\
  \alpha & \beta & \gamma
\end{pmatrix} \begin{pmatrix}
  a & e & f \\
  \alpha & \epsilon & -\phi
\end{pmatrix} \begin{pmatrix}
  d & b & f \\
  -\delta & \beta & \phi
\end{pmatrix} \begin{pmatrix}
  d & e & c \\
  \delta & -\epsilon & \gamma
\end{pmatrix},
\] (A.21)

where the summation is over all possible values of \( \alpha, \beta, \gamma, \delta, \epsilon \), and \( \phi \), with only three summation indices being independent. The Wigner-6j symbol is invariant under the permutation of its columns, or under interchange of the upper and lower arguments in each of any two columns.
APPENDIX A: ANGULAR MOMENTUM

The Wigner-6j symbol is related to the Racah coefficient, commonly used in angular momentum texts, by

\[
\begin{pmatrix} a & b & c \\ d & e & f \end{pmatrix} = (-1)^{a+b+d+e} W(abed; cf).
\]  

(A.22)

A.5 Reduced matrix element of \( \frac{1}{r_{12}} \)

The partial-wave expansion of \( \frac{1}{r_{12}} = \frac{1}{|r_1 - r_2|} \) is given by Brink and Satchler (1993) as

\[
\frac{1}{r_{12}} = \sum_{\lambda q} \frac{4\pi}{2\lambda + 1} \frac{r_\lambda^L}{r_\lambda^< + 1} Y_{\lambda q}(\hat{r}_1) Y_{\lambda q}^*(\hat{r}_2),
\]  

(A.23)

where \(-\lambda \leq q \leq \lambda\), \(0 \leq \lambda \leq \infty\), \(r_\lambda^< = \min(r_1, r_2)\) and \(r_\lambda^\geq = \max(r_1, r_2)\). Therefore, when transformed into integral notation, the matrix element \(\langle l'_1 l'_2 L'M'|\frac{1}{r_{12}}|l_1 l_2 L M \rangle\) becomes

\[
\langle l'_1 l'_2 L'M'|\frac{1}{r_{12}}|l_1 l_2 L M \rangle = \sum_{\lambda q} \frac{4\pi}{2\lambda + 1} \frac{r_\lambda^L}{r_\lambda^< + 1} \int \partial \hat{r}_1 \int \partial \hat{r}_2 Y_{l'_1 l'_2}^{LM}(\hat{r}_1, \hat{r}_2) Y_{\lambda q}(\hat{r}_1)
\times Y_{\lambda q}^*(\hat{r}_2) Y_{l_1 l_2}^{LM}(\hat{r}_1, \hat{r}_2).
\]  

(A.24)

The integrals can be removed using the relations (A.8), (A.4) and (A.6), and simplified using the relations (A.18) and (A.21) and the Wigner-6j and Wigner-3j symmetry relations, which gives

\[
\langle l'_1 l'_2 L'M'|\frac{1}{r_{12}}|l_1 l_2 L M \rangle = \sum_{\lambda} \frac{r_\lambda^L}{r_\lambda^< + 1} f_\lambda(l_1, l_2, l'_1, l'_2; L) \delta_{LM} \delta_{MM'},
\]  

(A.25)

where

\[
f_\lambda(l_1, l_2, l'_1, l'_2; L) = (-1)^{l_1 + l'_1 + l'_2[l_2][l_1][l'_1][l'_2]} \begin{pmatrix} l_1 & l_2 & L \\ l'_1 & l'_2 & \lambda \end{pmatrix} \left( \begin{array}{ccc} l_1 & \lambda & l'_1 \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} l_2 & \lambda & l'_2 \\ 0 & 0 & 0 \end{array} \right),
\]  

(A.26)

and where the \(\lambda\) summation is over all non-negative integers such that the Wigner-3j and Wigner-6j symbols are non-zero, which is given by

\[
\text{max}(|l_1 - l'_1|, |l_2 - l'_2|) \leq \lambda \leq \text{min}(|l_1 + l'_1|, |l_2 + l'_2|).
\]  

(A.27)

An important outcome of this matrix element is that it is non-zero only when \(L = L'\) and \(M = M'\), and has no dependence upon the projection of the angular momenta \(M\), \(m_1\) or \(m_2\). We refer to it as the reduced matrix element of \(\frac{1}{r_{12}}\), which is represented by

\[
\langle l'_1 l'_2 || \frac{1}{r_{12}} || l_1 l_2 \rangle_L \equiv \langle l'_1 l'_2 L'M'|\frac{1}{r_{12}}|l_1 l_2 L M \rangle,
\]  

(A.28)
and note from the Wigner-6j and Wigner-3j symmetry properties that

$$
\langle l_1' l_2' \parallel \frac{1}{r_{12}} \parallel l_1 l_2 \rangle_L = \langle l_2' l_1' \parallel \frac{1}{r_{12}} \parallel l_2 l_1 \rangle_L = \langle l_1 l_2 \parallel \frac{1}{r_{12}} \parallel l_1' l_2' \rangle_L.
$$

(A.29)

This derivation is equivalent to Equation (6.34) published by Brink and Satchler (1993), where it is noted that the condition that both \((\lambda + l_1 + l_1')\) and \((\lambda + l_2 + l_2')\) are even ensures that the reduced matrix element does not connect states of different total parity.
Appendix B
Numerov Formulae

In Section 3.2 we derived a one-dimensional variable-grid Numerov formula for solving second-order differential equations. However, it is necessary to derive nine variations of this Numerov formula in order to compute the $e^{-\mathbf{H}_Z}$ scattering wave function on a two-dimensional grid. The formula selection depends on whether $r_{i-1}=0$ and/or $r_{j-1}=0$, dictating whether a series expansion for $\psi_{ij}$ is used when deriving the formula [see (3.11)], and when this expansion is used, whether the angular momentum of the electron $l$ is zero or greater than zero. These Numerov formulae are used to solve equations of the form

\[
\left( \frac{\partial^2}{\partial r_i^2} + \frac{\partial^2}{\partial r_j^2} \right) \psi_{k,l}^{LMSS} (r_i, r_j) + \Omega_{k,l}^{LMSS} (r_i, r_j) = 0, \tag{B.1}
\]

and may be most simply presented as

\[
\sum_{i'=-1}^1 \sum_{j'=-1}^1 \left\{ \left( h^2 B_{i'} C_{j'} + t^2 A_{i'} D_{j'} \right) \psi_{k,l}^{LMSS} (r_{i+i'}, r_{j+j'}) \right. \\
\left. + h^2 t^2 B_{i'} D_{j'} \Omega_{k,l}^{LMSS} (r_{i+i'}, r_{j+j'}) \right\} = 0, \tag{B.2}
\]

where $\Omega_{k,l}^{LMSS}$ can be evaluated from (2.16), (2.17), (2.37) and (2.39), giving

\[
\Omega_{k,l}^{LMSS} (r_i, r_j) = \left\{ 2E + 2Z \left( \frac{1 - \delta_{i,0}}{r_i} + \frac{1 - \delta_{j,0}}{r_j} \right) - \frac{l_1 (l_1 + 1) (1 - \delta_{i,0})}{r_i^2} \\
- \frac{l_2 (l_2 + 1) (1 - \delta_{j,0})}{r_j^2} \right\} \psi_{k,l}^{LMSS} (r_i, r_j) - 2\tilde{\chi}_{k,l}^{LMSS} (r_i, r_j) \tag{B.3}
\]

Note that the $i$ subscript on the $\psi$ and $\tilde{\chi}$ functions uses bold font to differentiate this abbreviation for the initial state (see page 11) from the grid points in the $i$ direction. Also, note that the singularities in $\Omega_{k,l}^{LMSS}$ are removed by the use of delta functions.

The grid spacing is given by $h = r_i - r_{i-1}$ and $t = r_j - r_{j-1}$ in the $i$ and $j$ directions, respectively. Two further coefficients are used, $\alpha = (r_{i+1} - r_i)/h$ and $\beta = (r_{j+1} - r_j)/t$. 

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\( r_j/t \), which determine the expansion (or contraction) of the grid spacing in the \( i \) and \( j \) directions, respectively. Each grid measurement, \( h, t, \alpha, \) and \( \beta \) may be real or complex, and are displayed graphically in Fig. 3.1. The values of \( A, B, C \) and \( D \) vary depending on whether \( r_{i-1}=0 \) and / or \( r_{j-1}=0 \) and the angular momentum of the electrons.

Firstly, we shall consider only the \( i \) direction. If there is no singularity, \( r_{i-1} > 0 \), then

\[
\begin{align*}
A_{-1} &= 12\alpha \\
A_0 &= -12(\alpha + 1) \\
A_1 &= 12 \\
B_{-1} &= -\alpha^3 + \alpha^2 + \alpha \\
B_0 &= \alpha^3 + 4\alpha^2 + 4\alpha + 1 \\
B_1 &= \alpha^2 + \alpha - 1.
\end{align*}
\]

If there is a singularity \((r_{i-1} = 0)\) and \( l = 0 \) then

\[
\begin{align*}
A_{-1} &= 0 \\
A_0 &= (\alpha + 1)(3\lambda_1^2 \alpha^2 h^2 + 4\lambda_1^2 h^2 \alpha - 30\lambda_1 \alpha h + \lambda_1^2 h^2 - 24\lambda_1 h + 72) \\
A_1 &= -\lambda_1^2 h^2 - 6\lambda_1 \alpha h + 2\lambda_1^2 h^2 \alpha + 24\lambda_1 h - 72 \\
B_{-1} &= 6\alpha(\alpha^2 - \alpha - 1) \\
B_0 &= (\alpha + 1)(3\lambda_1 \alpha^2 h - 6\alpha^2 - 18\alpha + 4\lambda_1 \alpha h + \lambda_1 h - 6) \\
B_1 &= 2\lambda_1 \alpha^2 h - 6\alpha^2 + \lambda_1 \alpha h - \lambda_1 h - 6\alpha + 6,
\end{align*}
\]

or if there is a singularity and \( l > 0 \) then

\[
\begin{align*}
A_{-1} &= 0 \\
A_0 &= (1 + \alpha)^2 + (\alpha(2 + l)(l^2 + l + \lambda_2 + \lambda_1 h) - 6 - 9l + \lambda_2 - 3l^2 + \lambda_1 h) \\
A_1 &= \alpha^2 \lambda_1 h(l + 1) + \alpha(l^3 + 6l^2 + (\lambda_1 h + \lambda_2 + 11)l + \lambda_2 + 6) + 9l + 6 - \lambda_1 h - \lambda_2 + 3l^2
\end{align*}
\]
\[ B_{-1} = 0 \]
\[ B_0 = (1 + \alpha)^{2+l}(l\alpha + 2\alpha + 1) \]
\[ B_1 = (1 + \alpha)^2(l\alpha + \alpha - 1) \]

In these equations \( \lambda_1 = 2Z \), where \( Z \) is the charge on the nucleus, and \( \lambda_2 = -l(l+1) \), where \( l \) is the angular momentum of the electron (\( l_1 \) and \( l_2 \) for the \( i \) and \( j \) directions, respectively).

For the \( j \)-direction, the formulae are based on those given above and are selected depending on whether there is a singularity (\( r_{j-1} = 0 \)) and the angular momentum of the electron \( l = l_2 \). For the \( j \)-direction we use \( C \) in place of \( A \) and \( D \) in place of \( B \), and replace \( \alpha \) with \( \beta \) and \( h \) with \( t \).

These formulae were derived using the Maple algebraic computing language and checked to ensure that for equally spaced grids (\( \alpha = \beta = 1 \)) the equations reduce to those given by Wang and Callaway (1993) for \( l > 0 \) and Poet (1980)\(^1 \) for \( l = 0 \).

We now have the required values for \( A, B, C \) and \( D \) that are used in (B.2) to give the Numerov formula relationship between the nine grid points centred on \((i, j)\). By building a matrix equation and using the boundary conditions (3.1) and (3.2), \( \psi_{i,j,l_1l_2}^{LMSH} \) can be solved for all points on the grid.

\(^1\)Note that equation (14) in this publication is missing a factor of \( h^2 \) in the last two terms on the left-hand-side.
Coulomb Wave Small-\(k_r\) Approximation

In Section 3.6.3 we briefly discussed the inaccuracies encountered with the Coul90 routine (Barnett 1996) when calculating regular Coulomb radial wave functions for small values of \(k_r\). To overcome this problem we require a small-\(k_r\) approximation for this function [eg. (van Haeringen 1985)], however, at large values of electron angular momentum and small \(k_r\) when Coul90 becomes inaccurate, or fails, the small-\(k_r\) approximation requires more expansion terms to maintain accuracy than are normally published. We have therefore used algebraic computing to calculate a small-\(k_r\) approximation from first principles.

The analytic form of the regular Coulomb wave function is given by (van Haeringen 1985)

\[
\phi_l(Z; k, r) = C_l e^{ikr} (kr)^{l+1} _1F_1(l + 1 + i\gamma; 2l + 2; -2ikr), \quad (C.1)
\]

where \(\gamma = Z/k\), \( _1F_1 \) is the confluent hypergeometric function and

\[
C_l = 2^l e^{-\frac{1}{2} \pi \gamma} \left| \frac{\Gamma(l + 1 + i\gamma)}{(2l + 1)!} \right|. \quad (C.2)
\]

By performing a series expansion of \(\phi_l(Z; k, r)\) with respect to \(k_r\), using the Maple algebraic computing environment, we obtain the small-\(k_r\) approximation for this function, giving

\[
\phi_l(Z; k, r) = C_l (kr)^{l+1} \left\{ 1 + \frac{\gamma kr}{l+1} \frac{(kr)^2(2\gamma^2 - l - 1)}{2(l+1)(2l+3)} + \frac{\gamma(kr)^3(2\gamma^2 - 3l - 4)}{6(l+1)(2l+3)(l+2)} + \frac{(kr)^4(4\gamma^4 - 12\gamma^2 - 20\gamma^2 - 3l^2 + 9l + 6)}{24(l+1)(2l+3)(l+2)(2l+5)} + O((kr)^5) \right\}. \quad (C.3)
\]

Five terms in this series expansion is sufficient to ensure the necessary accuracy for all targets, energies and kinematics presented in this thesis. At small \(k_r\) the magnitude of the terms within the braces of (C.3) converge monotonically towards zero, from which the error of the truncated series can be easily estimated. This approximation for the regular Coulomb function is used in this thesis when its estimated error falls below 0.001 percent.


