Solving Momentum-Space Coupled-Channels
Equations for Electron-Atom Scattering
Using a Rotated-Contour Method

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BSc (Hons)

This thesis is presented for the degree of Doctor of Philosophy
at Murdoch University

Division of Science, Murdoch University
March 2002
Declaration

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

[Signature]

Anthony John Blackett
Abstract

In the last twenty years, electron-atom scattering theory has witnessed significant theoretical developments. One of these advances is the use of the momentum-space convergent close-coupling approach to fully incorporate target atom continua. This theoretical framework is based on the momentum-space Lippmann-Schwinger equation, an integral form of the Schrödinger equation. Although the approach has been highly successful in its application to atomic scattering theory, computing numerical solutions is inherently difficult because the momentum-space LS equation is a singular integral equation. Standard numerical integration techniques are normally employed to solve the problem and as computing power has increased, calculations have improved. However, there remains the problem of the integral’s singular nature, which demands complicated methods for selecting integration points, particularly near the energy-dependant singularity. The rotated-contour method uses a complex-variable approach that solves the momentum-space LS equation by integrating along a deformed contour in the complex momentum plane away from the singularities. This method has the potential for simplifying the numerical integrations associated with the close-coupling equations.

A rotated-contour method is first applied to a simple scattering model – electron scattering from the Yukawa potential. This gives some insight into the difficulties that arise when calculating potential matrix elements for complex momenta. The method is then applied to the s-wave model of the electron-hydrogen scattering problem and finally, the full
Abstract

problem. Existing FORTRAN software written to solve the momentum-space LS equations for electron-hydrogen scattering using standard techniques has been converted to C++. Extensive modification of the code has resulted in a flexible Windows-based program with a graphical user interface that runs on any modern computer using PC architecture. The program can calculate results using either a conventional method (no rotation) or a rotated-contour method.

Using a rotated-contour method to solve the momentum-space LS equations necessitates detailed knowledge of the analytic nature and singularity structure of the coupled-channels potentials. This is achieved through the extensive use of the computer symbolic algebra system Maple to compute closed-form solutions for the direct potentials and for a range of partial-wave direct and exchange potentials. It is found that logarithmic branch point singularities are present on the real momentum axis for an extensive class of partial-wave direct-potential matrix elements. The analysis reveals that a rotated-contour method cannot be applied to the full atomic scattering problem due to these analytic problems which are associated with the long-range nature of the Coulomb potential.
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Acknowledgements

I must first give my appreciation and thanks to Professor Andris Stelbovics, my PhD supervisor, for his guidance and helpful support not only throughout this thesis, but through my entire undergraduate and postgraduate studies. Andris’ depth of knowledge over a broad spectrum of scattering theory has been invaluable, and he has always been willing and able to provide expert help whenever it was required. His continued support in the face of apparently insurmountable problems gave me renewed vigour which ultimately resulted in the completion of this thesis.

My sincere gratitude goes to my wife Carol who has suffered immeasurably over the many years that it has taken to reach this conclusion of my studies. Without her continued support at home, completing this thesis would have been impossible. We can now look forward to enjoying our future together free of study and the lonely nights and weekends that have been an inescapable aspect of our life over the past thirteen years since starting my undergraduate studies as a part-time student.

My thanks also goes to Associate Professor Stephen Thurgate, who first directed me onto this path of study in physics, and his support throughout my studies is very much appreciated. I’m also indebted to Associate Professor Ken Harrison for his fascinating undergraduate course on the Complex Variable, and for listening to and answering my many questions concerning complex variable techniques. I would also like to extend my
Acknowledgements

appreciation for the contribution of moral support given by Professor Igor Bray in the latter stages of the thesis and for his willingness to help wherever possible.

My appreciation is also offered to Dr Bill Scott for his helpful discussions on Maple, its idiosyncrasies, and for his generous provision of a copy of maple7 at a most fortuitous time. Appreciation is also given to Dr Chris Lund for his moral support and for the financial support that he gave in the form of work that allowed me to survive this difficult time.

I would also like to acknowledge my fellow students, Tony Shackleton and Philip Bartlett, for the many discussions we had on numerical and algebraic computing, and to Katrina Lyon and Dr Chris Lund for the use of their colour laser printer in the production of this thesis.

Finally, financial support for this work was provided primarily by the Australian Federal Government through the Australian Postgraduate Award Scheme and without which, this work would not have been undertaken.
Chapter 1

Introduction

Quantum theory is arguably one of the most successful theories of modern physics. Following the conception of quantum mechanics in the mid 1920's, physicists soon discovered the complete closed-form solution to Schrödinger's equation for a bound pair of charged particles. Atomic hydrogen is the classic instance for such a two-body quantum mechanical problem. For positive energies, the continuum solutions are also known in closed form. However, the situation is radically different for electron-atom scattering, in which a continuum electron interacts with a bound system. The simplest example of this problem is embodied in the quantum mechanical description of scattering an electron from hydrogen and the complete solution to what appears on the surface, to be a relatively simple problem, has proven to be remarkably difficult. Despite engaging theorists' endeavours for well over half a century, a complete numerical solution to this atomic scattering problem still remains elusive.

1.1 Momentum-Space Coupled-Channels Equations

Nearly twenty years ago, McCarthy and Stelbovics (1983) made a valuable contribution to solving the electron-atom scattering problem by developing an elegant technique for solving systems of coupled transition matrix Lippmann-Schwinger equations in momentum space. Prior to this development, coupled-channels equations for scattering problems were
usually solved in coordinate-space using methods such as the R-matrix formalism (Burke & Smith, 1962; Burke & Robb, 1975). Solving the coupled-channels equations in momentum space laid the foundations for improved methods of solution, leading to convergent close-coupling (CCC) methods (Bray & Stelbovics, 1992), which have been applied with promising results to a diverse range of electron excitation and ionisation scattering on various atomic targets over the last decade. These targets include: hydrogenic atoms (Bray, 1994), lithium-like atoms (Bray 1995), cesium (Bartschat & Bray, 1996) and helium (Bray, Fursa & McCarthy, 1994; Fursa & Bray, 1995; 1997a; Bray & Fursa, 1996). Positron-hydrogen scattering has also been studied with success using CC (Mitroy, 1996) and CCC methods (Kadyrov & Bray, 2000).

The momentum space formalism of coupled-channels equations for solving electron-atom scattering problems is now well known and has enjoyed considerable success (Bray & Stelbovics, 1995a). However, as more complicated scattering systems are investigated, such as beryllium (Fursa & Bray, 1997b) and barium (Fursa & Bray, 1998; 1999), the need for numerically efficient computational methods has become increasingly more important for dealing with the principal-value integrals inherent in the Lippmann-Schwinger equation due to the free Green's function singularity. Although Green's function subtraction or regularisation (McCarthy & Stelbovics, 1983) has been used over many years to assist evaluating the principal-value integrals, sophisticated quadrature schemes are still needed to avoid singularity difficulties in numerical solving the momentum-space coupled-channels equations (Bray & Stelbovics, 1992).
These computational considerations constitute the primary motivation for the work undertaken in this thesis. A rotated-contour method formally applied to nuclear physics scattering problems (Stelbovics, 1977) is developed and its application investigated as an alternative numerical approach for solving the coupled integral equations arising from the quantum mechanical description of atomic scattering processes.

At a fundamental level, the rotated-contour approach involves solving the momentum-space Lippmann-Schwinger equation for the transition (T) matrix elements by integrating along a contour in complex-momentum space. The solution yields the usual on-shell T-matrix elements which are used to directly calculate the fundamental quantity of all scattering problems – scattering amplitudes. As an integral equation, the practical solution of the momentum-space Lippmann-Schwinger equation normally involves numerically evaluating a Cauchy principal-value integral that has a singular kernel arising from a singular Green’s function (Landau, 1996). Such singular kernels complicate numerical solutions and require careful consideration when evaluated using standard numerical techniques, particularly in selecting appropriate integration quadrature grids. In the atomic scattering case, as more target states are coupled, the task of selecting a suitable quadrature mesh that handles the various kernels becomes more difficult because the kernels are inevitably singular at different points. When rearrangement channels are present, the problem is further compounded by different channel Green’s functions producing a new class of singularities. Chapter 2 gives an overview of the momentum-space coupled-channels and the numerical difficulties in solving the momentum-space T-matrix Lippmann-Schwinger equation for the electron-hydrogen scattering problem.
The rotated-contour method offers an alternative strategy to solving the coupled-channels equations for the transition matrix elements by evaluating the momentum-space integrations along a contour in the complex plane of momentum space, rather than along the traditional real axis. For a suitably chosen complex contour, this method has the advantage that singularities normally encountered in the kernel simply vanish. A singularity-free kernel is an appealing property from a numerical point of view, as it allows a simpler quadrature scheme to be used for the numerical integration mesh, particularly when coupling many target states in a calculation. Under the rotated-contour approach, the kernels become well-behaved functions along the complex contour, and therefore, simplify the task of choosing the numerical quadrature grid. In Chapter 3, the mathematical basis of a rotated-contour method for solving singular integrals is developed. A strategy for analysing the analytic structure in complex-momentum space of the three-dimensional T-matrix via the Born-series expansion is also discussed in detail.

A rotated-contour method is then developed and applied in Chapter 4 to solving the momentum-space LS equation for Yukawa-potential scattering. This illustrates how a rotated-contour method can be used in a single-channel scattering problem and lays the foundations for extending the technique to an atomic scattering problem.

1.2 Numerical Software

In addition to developing the rotated-contour method for solving the momentum-space Lippmann-Schwinger equations, a substantial part of this thesis was devoted to developing software to demonstrate the method for the electron-atom scattering problem. To this end,
software was first developed for a simple electron-potential scattering problem, and then for the more involved problem of solving the coupled-channels equations for electron-hydrogen scattering. Software coded in FORTRAN 77, originally written to solve the momentum-space T-matrix elements for electron-hydrogen scattering, has been used as the basis for developing new software that implements a rotated-contour solution. Since this software was first developed, the original FORTRAN code has undergone some modifications and additions as scattering theory progressed, but in general, it has remained virtually unchanged for almost twenty years. There is no doubt that during this period of time, developments in computer technology have been spectacular. Not only has computer hardware changed dramatically with vastly increased speed, memory size and storage capacity, but the programming languages and design methodologies associated with software development have also undergone considerable paradigm transformations.

Today, popular languages for developing application software include C, C++, Java, Visual Basic and Delphi. Traditionally, FORTRAN has been the preferred programming language for scientific applications, particularly in physics. However, in many respects FORTRAN 77 has been left behind, making it difficult for programmers to adopt new programming practices when coding with this language. With the development of FORTRAN 90, many deficiencies have now been addressed and this more recent implementation of the FORTRAN language will undoubtedly gain popularity as the preferred language for scientific programming. FORTRAN developers also rely upon a wealth of existing code from a variety of sources, such as the Netlib Repository (www.netlib.org), to solve many specialised mathematical functions needed in scientific problem solving.
Although most new programming languages are not specifically designed for scientific problems, they do offer many advanced features that allow developers to focus on the problem at hand, rather than on the actual coding task. Concepts such as structured design, data abstraction, object-oriented programming (OOP), data encapsulation, inheritance and polymorphism are common in modern programming languages (Stern, 2000) and when used correctly, the resulting code tends to be self-documenting, easier to read, easier to understand, and certainly easier to maintain. Understandability and maintainability are two very important issues in software development. Software usability is also an important issue often overlooked by physicists when developing software. Many modern languages allow user-friendly interfaces that take advantage of easy to use graphical user interfaces like those offered by the Windows operating systems or X-Windows and Motif running under Unix and Linux operating systems.

With these considerations in mind, C++ was chosen as the programming language for software development in this thesis. Two existing FORTRAN 77 programs, one originally developed to solve the momentum-space coupled-channels equations for electron-hydrogen scattering, the other to compute differential and total cross sections, were converted to C++. The translated code was then developed into a single Windows-based program called TCrossWin, which computes T-matrix elements either conventionally or by the rotated-contour method, as required by the user. Program settings associated with computations are configurable at run time via a point and click-styled user interface. Where practical, some code has been rewritten to take advantage of object-oriented design.
Numerical data calculated under a rotated-contour scheme for partial-wave potentials, second-Born T-matrix amplitudes, full T-matrix amplitudes and differential cross sections are presented and discussed in Chapter 4 for Yukawa-potential scattering and Chapter 6 for e-H scattering in the s-wave model using software developed in this thesis. The enclosed CDROM includes copies of numerical software TMatrix and TCrossWin.

1.3 Symbolic Computer Algebra

Another recent advance in computational software that is emerging as a useful tool for theorists is in the field of symbolic algebraic computing. Considerable use has been made of this newly developing software technology in this thesis, with analytic analysis being done using the computer algebra system called Maple (Char, Geddes, Gonnet, Leong, Monagan, & Watt, 1992; see also Heck, 1993; Baylis, 1994; Gander & Hreбиcek, 1997). Computer algebra software like Maple not only provides new ways for teaching quantum mechanics (Horbatsch, 1995), but also furnishes physics researchers with the means to explore complicated mathematical theory to a much deeper level with relative ease, even on desktop computers. Maple has certainly been an invaluable research tool in this thesis, where it has been used extensively to discern the complicated analytic structures needed to study the T-matrix amplitudes in complex-momentum space. In Chapter 4, Maple is used to analyse the analytic structure of Yukawa-potential matrix elements and map the singularity structure of terms in the Born-series expansion of the T-matrix. Computer algebra is also used to evaluate direct and exchange partial-wave potentials in closed-form for the electron-hydrogen scattering problem in Chapters 5 and 7. From these closed-form expressions, analytic structures are ascertained in detail in Chapter 5 for the s-wave model
Introduction

e-H potentials and then for more general e-H potentials in Chapter 7. Differential cross-section data calculated from the coupled-channels equations using the rotated-contour method for the s-wave model of e-H scattering are then compared with results calculated using standard principle-value methods in Chapter 6. The results show that the rotated-contour method can be used to solve this restricted form of the full scattering problem. However, the analysis presented in Chapter 7 demonstrates that the rotated-contour method cannot be used to solve the full e-H scattering problem. The closed-form potentials reveal that nearly all e-H partial-wave direct potentials are not analytic functions. This finding suggests an underlying reason for convergent solutions to the momentum-space coupled-channels equations being so difficult to obtain for the electron-atom scattering problem.

References that are made to Maple in this thesis imply that the version being used is maple6, unless stated otherwise. The current version of Maple at the time of writing is maple7, a copy of which was only obtained as the final stages the thesis was being completed. Maple is a registered trade mark of Waterloo Maple Inc. More information on Maple can be found at their web site www.maplesoft.com.

1.4 Notation and Conventions

Vectors are shown in bold type, such as \( \mathbf{k} \), while unit vectors are shown in bold type with a circumflex, such as \( \hat{\mathbf{k}} \), while magnitudes are shown using italic type, such as \( k \).

Throughout this thesis, the notation used for momentum that is on the energy shell is \( \mathbf{k} \) and is usually referred to as being on-shell. These correspond to values of momenta which have wave numbers related to the system's total energy. Arbitrary values of momenta which are
generally off the energy shell, and unrelated to the system's total energy, are denoted by $p$ and referred to as \textit{off-shell} momenta. When the magnitude $p$ of off-shell momentum is either continued or rotated into complex-momentum space, it is denoted by $z$.

For purpose of this thesis, the contour-rotation angle is denoted by a positive angle $\alpha$ and lies in the range $[0, \frac{\pi}{2}]$. Contour rotation is therefore effected by multiplying momentum quadrature mesh points by the complex factor $e^{-i\alpha}$.

For convenience in writing large equations, atomic units are used throughout so that the fundamental constants are $\hbar = 1$, $m_e = 1$, $e = 1$. 
Chapter 2

Atomic Scattering Amplitudes: A Computational Overview

During the last few decades of the twentieth century, atomic collision theory has enjoyed considerable success. Much of this success can be attributed to rapid advancements in computer technology over the past twenty years. Refinements to existing numerical techniques and applying new methods of computation (Stelbovics & Bransden, 1989) have also contributed to this progress. McCarthy & Stelbovics' (1983) contribution to solving the electron-hydrogen scattering problem was to solve the coupled-channels equations in momentum space, rather than using conventional coordinate-space integro-differential equations. However, despite the success of this approach, even the simplest problem in atomic scattering theory, electron-hydrogen scattering, remains a difficult numerical problem to solve. Modern computers make the task far less tedious from a computational standpoint, although numerical difficulties still persist (Bray & Stelbovics, 1995a), which need to be addressed in order to enable the extension of present technology to the next order of magnitude of computations.

A primary objective of atomic scattering theory is to provide an accurate model for the evolution of a collision event, so that ultimately, theory can be reconciled with experimental data. Thus, calculating observable quantities is essential, although the theorist's first task is generally to find the complex-valued scattering amplitude, which
contains a complete quantum mechanical description of the scattering process. Not only
does the scattering amplitude relate the initial and final states of an interacting system, it
is also directly related to the differential cross-section – an observable that is directly
measurable by experimental methods in the laboratory.

The work of McCarthy & Stelbovics (1983) laid the foundations for numerically solving
coupled-channels equations in momentum space, establishing the method as a viable
solution to atomic scattering problems. Choosing the momentum space formalism has the
distinct advantage in that the momentum space representation of the T-matrix is the direct
solution of the equations and the T-matrix itself, is directly related to the scattering
amplitude. In this section, a standard numerical method for solving the momentum-space
T-matrix Lippmann-Schwinger equation is outlined. This is followed by an overview of
the momentum-space coupled-channels equations and the method of their solution
formulated by McCarthy & Stelbovics. The discussion provides the background necessary
for the application of the rotated-contour method of solution developed in the next chapter.

2.1 One-Channel T-Matrix and Scattering Amplitudes

In most atomic scattering experiments, a beam of incident mono-energetic electrons with
known energy \( E \) is scattered by a target atom which is in a known initial state, typically the
ground state. Essential elements of the scattering experiment are shown in Figure 2.1,
where a suitable detector positioned at \( r \) measures particles scattered with momentum \( k' \)
into the solid angle \( d\Omega \). The natural scattering case to consider is a non-relativistic beam
of electrons incident upon an atomic target.
In its simplest form, such as scattering of a single particle with total energy $E$ by a potential field $V(r)$, the quantum mechanical description of the scattering process aims to solve Schrödinger’s non-relativistic, wave equation

$$(E - H_0) \psi_k(r) = V \psi_k(r) \quad (2.1)$$

for the unknown distorted scattered wave function $\psi_k(r)$. Here, $H_0$ is the free particle Hamiltonian operator. An incident beam consisting of free particles with energy $E = \frac{1}{2} k^2$ is described by the plane-wave $\varphi_k(r) = N e^{i k r}$, where $N$ is a normalisation constant which is often chosen as $N = (2\pi)^{-3/2}$. The asymptotic form of the scattered particles from a short-range potential is assumed to be an outgoing spherical-wave defined by

$$\psi_k^S(r) = f(\theta, \varphi) N e^{i k r} \quad \text{as } r \to \infty, \quad (2.2)$$

where the function $f(\theta, \varphi)$ is the scattering amplitude. The system’s total wave function is the sum of the plane-wave and scattered wave functions

$$\psi_k(r) = \varphi_k(r) + \psi_k^S(r). \quad (2.3)$$

![Figure 2.1: Basic atomic scattering experiment in which an incident beam of particles with momentum $k$ is scattered by a target. Scattered particles with final momentum $k'$ are detected at position $r$ relative to the target.](image)
The Lippmann-Schwinger equation is the integral form of Schrödinger’s wave equation

$$
\psi_k^*(r) = \phi_k(r) + \int \! dr' \, G_0^*(E, r, r') V(r') \psi_k^*(r').
$$

(2.4)

In this expression, $G_0^*(E, r, r')$ is the outgoing free Green’s function and the wave function $\psi_k^*(r')$ is the sum of the incoming plane-wave $\phi_k(r)$ and the scattered spherical-wave with an outgoing wave boundary condition. Hence, the boundary condition is built into the Lippmann-Schwinger equation. The scattering amplitude is identified, using the asymptotic form derived from $G_0^*(E, r, r')$, as

$$
f(\theta, \varphi) = -4\pi^2 \int \! dr' \, \phi_k^*(r') V(r') \psi_k^*(r').
$$

(2.5)

Equations describing the scattering problem can be written in more compact, abstract form using transition (T) matrix elements and potential (V) matrix elements. For a scattered electron with momentum changing from $k$ to $k'$, the momentum-space T-matrix is

$$
T(k, k') = \int \! dr' \, \phi_k^*(r') V(r') \psi_k^*(r').
$$

(2.6)

Similarly, the potential or V-matrix is defined by

$$
V(k, k') = \int \! dr' \, \phi_k^*(r') V(r') \phi_k(r').
$$

(2.7)

From the Lippmann-Schwinger equation (2.4) and the definitions (2.6) and (2.7), the T-matrix satisfies the linear integral equation

$$
T(k', k) = V(k', k) + \int \! dp \, V(k', p) G_0^*(E, p) T(p, k),
$$

(2.8)

with the outgoing free Green’s function defined by
\[ G_0^*(E, p) = \frac{1}{E - \frac{1}{2} p^2 + i\epsilon}. \]  \hspace{1cm} (2.9)

For the remainder of this thesis, notation for the outgoing free Green's function will be contracted to \( G_0(E, p) \). Note that there is an implied limit \( \varepsilon \to 0 \) here, which is only taken after integration. Equation (2.8) is known as the one-channel momentum-space T-matrix Lippmann-Schwinger equation and is the basis of the coupled-channels description in electron-atom scattering theory. This is the fundamental equation that this thesis is concerned with studying.

### 2.2 Solving the Lippmann-Schwinger Equation

For simplicity, this discussion on solving the Lippmann-Schwinger equation is limited in the first instance to the case of an electron elastically scattered by a local potential \( V(\mathbf{r}) \). A coordinate system is selected so that the initial momentum \( \mathbf{k} \) is directed along the positive \( z \)-axis. The scattered electron has momentum \( \mathbf{k}' \) directed away from the initial direction at a polar angle \( \theta \) and azimuth angle \( \varphi \). The momentum-transfer vector \( \mathbf{K} \) is defined by

\[ \mathbf{K} = \mathbf{k} - \mathbf{k}', \]  \hspace{1cm} (2.10)

and is in the same plane as \( \mathbf{k} \) and \( \mathbf{k}' \), but directed at an angle \( \Theta \) from the initial direction of \( \mathbf{k} \). Comparing equations (2.5) and (2.6) shows that in this simplified case, the on-shell T-matrix element is proportional to the scattering amplitude \( f(\theta, \varphi) \), the relationship being given by the simple expression

\[ f(\theta, \varphi) = -4\pi^2 T(k', k). \]  \hspace{1cm} (2.11)

Once the on-shell T-matrix element is calculated, it is a relatively simple task to calculate scattering amplitudes, differential cross sections and total cross sections. Computational
difficulties are mainly encountered in numerically calculating the T-matrix elements in the first place. The general form of the momentum-space T-matrix $T(k', k)$ is expressed in the Lippmann-Schwinger equation

$$T(k', k) = V(k', k) + \int dp \frac{V(k', p) T(p, k)}{E - \frac{1}{2} p^2 + i\epsilon},$$  \hspace{1cm} (2.12)$$

where $E = \frac{1}{2} k^2$ is the total energy and $V(k', k)$ is the potential or Born matrix. Equation (2.12) is an integral equation which is a Fredholm integral equation of the second kind (Smithies, 1958). Fredholm integral equations are solved numerically by well-established matrix methods (Delves & Mohamed, 1985), although, these numerical techniques are impractical for solving the three-dimensional form of equation (2.12). However, the techniques are applicable to solving a sequence of one-dimensional integral equations of similar form to standard Fredholm equations. Such equations are derived from a partial-wave expansion of the momentum-space T-matrix elements.

### 2.2.1 Partial-wave expansions

The full three dimensional momentum-space Lippmann-Schwinger equation is

$$T(p', k) = V(p', k) + \int dp \frac{V(p', p) T(p, k)}{E - \frac{1}{2} p^2 + i\epsilon},$$  \hspace{1cm} (2.13)$$

which gives half-off-shell T-matrix elements when $p'$ is an arbitrary off-shell value of momentum. At some point, $p'$ takes the on-shell value $k'$, and in this particular case the on-shell T-matrix element (2.12) is given. In practice, the three-dimensional LS equation (2.13) is not solved, instead a partial-wave expansion is used to form a one-dimensional LS equation for partial-wave T-matrix amplitudes.
Expanding (2.13) using an angular momentum basis or partial-wave expansion, the required T-matrix $T(p', k)$ is expressed as a sum of partial-wave T-matrix elements $T_l(p', k)$. These matrix elements then satisfy a one-dimensional Lippmann-Schwinger equation that can be expressed in Fredholm form and solved (Bransden, Noble & Hewitt, 1993). The T-matrix is then calculated from its partial-wave expansion (Landau, 1996)

$$T(p', k) = \frac{1}{2\pi^2} \sum_{l=0}^{\infty} (2l + 1) T_l(p', k) P_l(\hat{p}', \hat{k}).$$

(2.14)

Using this expansion in equation (2.13), the momentum-space partial-wave T-matrix satisfies the integral equation

$$T_l(p', k) = V_l(p', k) + \frac{2}{\pi} \int_0^{\infty} dp \, p^2 \frac{V_l(p', p) T_l(p, k)}{E - \frac{1}{2} p^2 + i\epsilon}.$$  

(2.15)

Note that the half-off-shell partial-wave T-matrix can only be calculated if the half-off-shell and off-shell partial-wave potentials are known. Naturally, the partial-wave expansion has an analogue form for the on-shell T-matrix

$$T(k', k) = \frac{1}{2\pi^2} \sum_{l=0}^{\infty} (2l + 1) T_l(k', k) P_l(\hat{k}', \hat{k}),$$

(2.16)

with the on-shell partial-wave T-matrix obtained from half-off-shell potentials using

$$T_l(k', k) = V_l(k', k) + \frac{2}{\pi} \int_0^{\infty} dp \, p^2 \frac{V_l(k', p) T_l(p, k)}{E - \frac{1}{2} p^2 + i\epsilon}.$$  

(2.17)

Therefore, the on-shell partial-wave T-matrix can only be calculated if the on-shell and half-off-shell partial-wave potentials are also known.
2.2.2 Cauchy principal-value integral – regularisation

An obvious difficulty in solving equation (2.15) for $T_i(p', k)$ is finding a satisfactory method for dealing with the integrand’s denominator, which arises from the outgoing free Green’s function $G_0$. The first step towards a numerical solution uses the identity

$$\int_0^\infty dp \frac{f(p)}{E - \frac{1}{2} p^2 + i\epsilon} = \mathcal{P} \int_0^\infty dp \frac{f(p)}{E - \frac{1}{2} p^2} - i\pi \frac{f(k)}{k},$$  \hspace{1cm} (2.18)$$

where $\mathcal{P}$ denotes the Cauchy principal-value operator, formally defined as

$$\mathcal{P} \int_0^\infty dp \frac{f(p)}{\frac{1}{2} (k^2 - p^2)} = \lim_{\eta \to 0} \left[ \left( \int_0^{k - \eta} dp + \int_{k + \eta}^\infty dp \right) \frac{f(p)}{\frac{1}{2} (k^2 - p^2)} \right].$$  \hspace{1cm} (2.19)$$

Thus, equation (2.15) can be written in a simpler form

$$T_i(p', k) = V_i(p', k) + \frac{2}{\pi} \int_0^\infty dp \, p^2 \, V_i(p', p) \, G_0(E, p) \, T_i(p, k),$$  \hspace{1cm} (2.20)$$

where $G_0(E, p)$ is the Green’s matrix element incorporating the Cauchy principal-value operator $\mathcal{P}$ and in this case, is denoted by

$$G_0(E, p) = \frac{1}{E - \frac{1}{2} p^2 + i\epsilon} = \mathcal{P} \frac{1}{\frac{1}{2} (k^2 - p^2)} - i\pi \frac{\delta(k - p)}{k}. \hspace{1cm} (2.21)$$

Writing the partial-wave T-matrix LS-equation in terms of a principal-value integral is then

$$T_i(p', k) = V_i(p', k) + \frac{2}{\pi} \mathcal{P} \int_0^\infty dp \, p^2 \, \frac{V_i(p', p) \, T_i(p, k)}{\frac{1}{2} (k^2 - p^2)} - i2 \, k \, V_i(p', k) \, T_i(k, k). \hspace{1cm} (2.22)$$

The problem is then dealing with the singularity at $p = k = \sqrt{2E}$. A number of methods have been developed to solve this numerical problem. Their relative strengths and weaknesses are discussed by Bransden et al (1993). A customary method of managing this numerical difficulty is regularisation of the integral (McCarthy & Stelbovics, 1983), which
effectively removes the singularity, transforming the principal-value into a definite integral that can be evaluated. Regularisation takes advantage of the well known Cauchy principal-value identity

\[ \mathcal{P} \int_{0}^{\infty} dp \frac{1}{k^2 - p^2} = 0, \]  

(2.23)

which implies that the following expression is also true:

\[ \frac{2}{\pi} \mathcal{P} \int_{0}^{\infty} dp \ k^2 \frac{V_i(p', k) T_i(k, k)}{\frac{1}{2} (k^2 - p^2)} = 0. \]  

(2.24)

Subtracting (2.24) from equation (2.22) eliminates the singularity, giving an equivalent equation which has a regular integrand

\[ T_i(p', k) = V_i(p', k) + \frac{2}{\pi} \int_{0}^{\infty} dp \ p^2 \frac{V_i(p', p) T_i(p, k) - k^2 V_i(p', k) T_i(k, k)}{\frac{1}{2} (k^2 - p^2)} \]

\[ - i 2 k V_i(p', k) T_i(k, k). \]  

(2.25)

In principle, this equation can be solved numerically. It should be noted here that the K-matrix formulation

\[ K_i(p', k) = V_i(p', k) + \frac{2}{\pi} \int_{0}^{\infty} dp \ p^2 \frac{V_i(p', p) K_i(p, k) - k^2 V_i(p', k) K_i(k, k)}{\frac{1}{2} (k^2 - p^2)} \]  

(2.26)

of Bray (1994) and Bray & Stelbovics (1995b) can also be used to calculate the momentum-space T-matrix elements, but this method is unsuitable for the rotated-contour method because the imaginary term \( i\epsilon \) in (2.15) is the origin of the complex contribution in (2.25) and as will be shown, is inherent in the rotated-contour formalism. An analytic continuation into the complex plane requires positioning of the Green’s function singularity off the real momentum axis. This is intrinsically impossible in the K-matrix kernel.
2. Atomic scattering computational overview

2.2.3 Quadrature integration – matrix solution

In practice, a numerical computation using an N-point quadrature sum is used to evaluate the definite integral in equation (2.25), resulting in the discretised form

\[
T_i(p', k) = V_i(p', k) + \frac{2}{\pi} \sum_{n=1}^{N} w_n \frac{p_n^2 V_i(p_n, k) T_i(p_n, k) - k^2 V_i(p', k) T_i(k, k)}{\frac{1}{2} (k^2 - p_n^2)} - i2 \, k \, V_i(p', k) T_i(k, k),
\]

(2.27)

where \( w_n \) is the weight associated with the \( n^{th} \) quadrature point \( p_n \). Forming a closed set of equations in which \( p' \) takes on values at each of the quadrature points \( p_n = p_1, \ldots, p_N \), and at the on-shell momentum \( p_0 = k' \), enables them to be solved simultaneously. This gives a set of \((N+1)\) equations defined by

\[
T_i(p_n, k) = V_i(p_n, k) + \frac{2}{\pi} \sum_{n=1}^{N} w_n \frac{p_n^2 V_i(p_n, k) T_i(p_n, k) - k^2 V_i(p_n, k) T_i(k, k)}{\frac{1}{2} (k^2 - p_n^2)} - i2 \, k \, V_i(p_n, k) T_i(k, k).
\]

(2.28)

In a simpler form, this equation is written as

\[
T_i(p_n, k) = V_i(p_n, k) + \sum_{n=0}^{N} K(p_n, p_n) T_i(p_n, k),
\]

(2.29)

where the kernels are given by \( K(p_n, p_n) = V_i(p_n, p_n) W(p_n) \), and \( W(p_n) \) are termed the super-weights defined by

\[
W(p_n) = \begin{cases} 
- \frac{2}{\pi} \left( \sum_{n=1}^{N} w_n \frac{p_n^2}{\frac{1}{2} (k^2 - p_n^2)} \right) k^2 - i2 \, k, & n = 0 \\
\frac{2}{\pi} \frac{w_n p_n^2}{\frac{1}{2} (k^2 - p_n^2)}, & n = 1, \ldots, N.
\end{cases}
\]

(2.30)

Writing equation (2.29) in matrix form
\[
\begin{pmatrix}
T_i(k',k) \\
T_i(p_1,k) \\
\vdots \\
T_i(p_N,k)
\end{pmatrix} =
\begin{pmatrix}
V_i(k',k) & \cdots & V_i(k',p_N) \\
V_i(p_1,k) & \cdots & V_i(p_1,p_N) \\
\vdots & \ddots & \vdots \\
V_i(p_N,k) & \cdots & V_i(p_N,p_N)
\end{pmatrix}
\begin{pmatrix}
W_0 & 0 & \cdots & 0 \\
0 & W_1 & \cdots & 0 \\
\vdots & \vdots & \ddots & \vdots \\
0 & 0 & \cdots & W_N
\end{pmatrix}
\begin{pmatrix}
T_i(k',k) \\
T_i(p_1,k) \\
\vdots \\
T_i(p_N,k)
\end{pmatrix}
\]

(2.31)

illustrates how equation (2.29) for the partial-wave T-matrix elements is formulated into a matrix equation solvable using standard matrix algebra. This closed set of equations contains the required physical on-shell partial-wave T-matrix element \( T_i(k', k) \), and \( N \) half-off-shell matrix elements \( T_i(p_n, k) \). The matrix equation above is more simply expressed in operator form as

\[
T = V + K T,
\]

(2.32)

where the kernel matrix \( K = V W \), with \( V \) being a square and \( W \) a diagonal matrix. Solving this matrix equation for the T-matrix elements using matrix algebra yields the solution

\[
T = (1 - K)^{-1} V.
\]

(2.33)

All that remains to enable equation (2.33) to be solved is to calculate the partial-wave potential matrix elements \( V_i(p_n, p_n) \) for all combinations of off-shell quadrature points and the on-shell momenta. How this is done depends on the nature of the scattering potential. For a simple local potential, the partial wave potentials are calculated (Landau, 1996) using

\[
V_i(p', p) = \int_{0}^{\infty} r^2 j_i(p' r) V(r) j_i(p r).
\]

(2.34)

This simplified single-channel model provides an idealised example to illustrate the rotated-contour method of solving the Lippmann-Schwinger equation and will be discussed in Chapter 4.
A more practical problem involves scattering an electron from an atomic target. Atomic targets add another level of complexity to the problem because the atom has an internal structure and it is often possible for the incident electron to transfer energy to the target atom, exciting the target into a higher-energy state, resulting in both elastic and inelastic interactions as possible outcomes. The numerous possible projectile-target states that are involved in an interaction are called channels. A channel is considered open if the incident electron has sufficient energy to excite the target atom into the state associated with that particular channel. Hence, there are a finite number of open channels whenever the incident electron's energy is less than the ionisation threshold.

2.3 Overview of Solving Coupled-Channels Equations

The focus of this section is the calculation of momentum-space partial-wave T-matrix elements for electron scattering by single-electron atomic targets. An overview of the methods developed by McCarthy & Stelbovics (1983) for solving the momentum-space coupled-channels equations for electron-atom scattering is presented, highlighting some of the computational aspects of their solution. For convenience, the target atom is considered infinitely massive and positioned at the origin of a standard rectangular coordinate system. Initially, the incident electron's momentum is defined by \( \mathbf{k} \) and is directed along the \( z \)-axis with energy \( \frac{1}{2} k^2 \). The target atom's initial state is defined by \( |nlm\rangle \) and has energy \( \varepsilon_n \). Following the interaction, the scattered electron's momentum is \( \mathbf{k}' \) and its direction is in the plane containing the \( x \) and \( z \) axes so that \( \varphi = 0 \). The target's final state is denoted by \( |n'l'm'\rangle \) and has energy \( \varepsilon_{n'}. \) Momentum-transfer vector \( \mathbf{K} \) is defined in the usual manner by equation (2.10).
Computation of both the T and V-matrix elements is accomplished via partial-wave expansions over the total angular momentum quantum number $J$. For T-matrix elements, this expansion is defined by

$$
T_{n' l' m'}^{n l m} (p', k) = \langle p'; n' l' m' | T | n l m; k \rangle = \sum_{L'M'} \langle \hat{p}' | L'M' \rangle C_{M'm'M_j}^{L'J} T_{n L l}^{n' L' J} (p', k) C_{M_m M_j}^{L J} \langle L M | \hat{k} \rangle,
$$

(2.35)

where $p'$ is an arbitrary value of momenta, $k$ is the on-shell momentum for the incident channel and $T_{n L l}^{n' L' J} (p', k)$ are the partial-wave T-matrix elements given by

$$
\int d\hat{p}' \int d\hat{k} \sum_{M_m M_j} \langle L'M' | \hat{p}' \rangle C_{M'm'M_j}^{L'J} \langle p'; n' l' m' | T | n l m; k \rangle C_{M_m M_j}^{L J} \langle \hat{k} | L M \rangle.
$$

(2.36)

Potential matrix elements are also calculated using (2.35), simply by replacing $T$ with $V$.

Using an abbreviated channel notation, in which subscripts $i$ and $f$ refer to incident and scattered channels respectively, then $T_{fi}(p', k_i) = T_{n L l}^{n' L' J} (p', k_i)$, and the partial-wave T-matrix elements then consist of closed sets of coupled Lippmann-Schwinger equations of the form

$$
T_{fi}(p', k_i) = V_{fi}(p', k_i) + \sum_j \int_0^\infty dp \: p^2 \: V_{fj}(p', p) \: G_0(E_j, p) \: T_{ji}(p, k_j).
$$

(2.37)

Again, the Cauchy principal-value operator $\mathcal{P}$ is incorporated into the Green’s operator, which for this problem, is defined by

$$
G_0(E_j, p) = \mathcal{P} - \frac{1}{E_j - \frac{1}{2} p^2} - i \frac{\pi}{k_j} \delta(k_j - p),
$$

(2.38)

where $k_j$ is the on-shell momentum for channel $j$. The $p$’s are typically off-shell momenta, while the channel energy is $E_j = E - \epsilon_j = \frac{1}{2} k_1^2 + \epsilon_1 - \epsilon_j$ where $E$ is the total energy and $\frac{1}{2} k_1^2$
is the incident electron's energy. Therefore, the channel energy for a target initially in the ground state is

\[ E_j = \frac{1}{2} k_j^2 = \frac{1}{2} k_{1s}^2 + \frac{1}{2} \left( 1 - n_j^{-2} \right) \]  

(2.39)

Total angular momentum \( J \) and channel parity \( \Pi = (-1)^{J+1} = (-1)^{L+1} \) are considered the good quantum numbers and impose specific restrictions on the external electron's angular momentum quantum numbers \( L \) and \( L' \) such that, for a given channel \( j (\equiv n L I) \), \( L \) can only take the values satisfying the triangle inequality \( |J - I| \leq L \leq J + I \). In addition, only those channels which satisfy the condition of natural parity, \( \Pi(L + I) = \Pi(J) \), are coupled to the entrance channel.

Applying regularisation to the Cauchy principal-value integral and discretising the coupled-channels equations (2.37) using the quadrature grid \( p_{jn} \), in which the Gaussian quadrature points are \( p_{jn} = p_2 \ldots p_{N+1} \), and the on-shell momentum is \( p_{j1} = k_j \), the coupled equations form the closed set of \( N + 1 \) equations

\[ T_{ji}(p_{jn'}, k_i) = V_{ji}(p_{jn'}, k_i) + \sum_{j} \sum_{n=1}^{N+1} K_{ff}(p_{jn'}, p_{jn}) T_{ji}(p_{jn}, k_i), \] 

(2.40)

where the kernels are \( K_{jj}(p_{jn'}, p_{jn}) = V_{jj}(p_{jn'}, p_{jn}) W_j(p_{jn}) \), and \( W_j(p_{jn}) \) are the superweights. How the super weights are defined depends on whether \( p_{jn} \) is an on-shell momentum value or an off-shell quadrature point. They are given by

\[
W_j(p_{jn}) = \begin{cases} 
-k_j^2 \left( \sum_{n=1}^{N+1} \frac{w_n}{(k_j^2 - p_n^2)} \right) - i\pi k_j, & n = 1 \\
\frac{p_n^2 w_n}{\frac{1}{2} (k_j^2 - p_n^2)}, & n = 2, \ldots, N + 1. 
\end{cases}
\] 

(2.41)
Although the coupled-channels equations have been regularised to avoid singularity problems associated with the Green’s function in the Cauchy principal-value integral, the numerical formulation described by the matrix equation (2.40) and super-weights (2.41) can encounter problems, particularly when coupling large numbers of channels in a calculation. These problems are discussed later in section 2.6 and are the source of motivation for investigating the rotated-contour approach.

As final note, T-matrix elements satisfy a symmetry relation in which swapping the channel order also requires swapping the momenta and is simply stated as

\[ T_{fi}(p', p) = T_{if}(p, p') \]  

(2.42)

This symmetry also applies to V-matrix elements and is often used to reduce the number of potentials that need to be calculated in practice to solve the momentum-space T-matrix Lippmann-Schwinger equation.

### 2.4 Calculating Potential Matrix Elements

In the discussion that follows, the external electron is labelled by subscript 1, while subscript 2 identifies the bound electron. Using this notation, the potential \( V_1 \) then refers to the interaction between the external electron and the atomic core, whereas, \( V_2 \) is the interaction between the bound electron and the core and \( V_{12} \) is the two-electron potential due to the bound and free electron interaction.

Momentum-space partial-wave direct potentials are calculated using a near closed-form expression needing a single integration over a direction cosine, whereas, the exchange
potentials require the evaluation of a double coordinate-space integral. For the direct potentials, one equation is used to calculate contributions for both the two-electron interaction and the electron-core interaction, although it is not immediately obvious how the electron-core matrix elements are obtained from the two-electron potential. Similarly, the exchange-potential calculation can be separated into an energy dependent term and a two-electron term, and again, one equation is used to calculate both contributions.

Bound states of the one-electron target atom are expressed in the form of Slater basis functions, such that

$$
\langle \mathbf{r} | n l m \rangle = \sum_{\mu=1}^{n-1} c_\mu A_\mu \, r^{n_r-1} \, e^{-\alpha r} \, Y_{l m}(\theta),
$$

(2.43)

with $A_\mu = \left[(2 \alpha_\mu)^{2n_r-1} / (2n_\mu)! \right]^{1/2}$. It is well known that these functions are particularly suitable for atomic structure problems and are also convenient for this application because they have a simple analytic structure. It is also worthy of noting here that the Laguerre basis used for convergent close coupling methods (Bray & Stelbovics, 1992) are simply linear combinations of Slaters, except that the coefficients $\alpha_\mu$ are fixed for a given partial wave. Therefore, the applicability of the rotated-contour method also extends to CCC formulations. For hydrogen, the Slater parameters are easily calculated from the principal quantum number $n$ and orbital quantum number $l$, where

$$
\begin{align*}
  n_\mu &= l + \mu, \\
  \alpha_\mu &= \frac{1}{n}, \\
  c_\mu &= (-1)^{\mu-1} \frac{(2 \alpha_\mu)^{-1/2} \, \alpha_\mu[(n-l-1)! \, (n+l) \, (2n_\mu)!]}{(n-n_\mu)! \, (l+n_\mu)! \, (\mu-1)!}.
\end{align*}
$$

(2.44)
2.4.1 Electron-electron direct matrix elements

The two-electron interaction involves the potential operator $V_{12}$, for which, the direct-potential matrix is given by

$$V_{nm}'^{ll'}(k', k) = \langle k'; n'l'm' | \frac{1}{|r_1 - r_2|} |nlm; k \rangle. \quad (2.45)$$

This two-electron direct potential has the same symmetry property (2.42) as the T-matrix and has a closed-form solution (Blackett & Stelbovics, 1999)

$$V_{nm}'^{ll'}(K) = \frac{1}{2\pi^2 K^2} 4\pi \sum_{l''m''} i^{l''} (-1)^{l''} \frac{\hat{n} \hat{m} \hat{l}}{(4\pi)^{1/2}} \begin{pmatrix} l'' & l' & l \\ m'' & m' & -m \end{pmatrix} \begin{pmatrix} l'' & l' & l \\ 0 & 0 & 0 \end{pmatrix} \langle \hat{K} | l''m'' \rangle g_{l'n'l'}(K), \quad (2.46)$$

where the radial integral function

$$g_{l'n'l'}(K) = \int_0^\infty dr \ r^2 \langle n'l' | r \rangle f_{l'}(Kr) \langle r | n'l \rangle; \quad (2.47)$$

is reducible to closed-form with a hypergeometric function. Expressing equation (2.46) in an equivalent form in which $K$ is expressed in the polar coordinates $(K, \Theta, 0)$, the direct potential is also given by

$$V_{nm}'^{ll'}(k', k) = \frac{1}{2\pi^2 K^2} \sum_{l''} i^{l''} (-1)^{l''} \hat{n} \hat{m} \hat{l} \hat{r} \hat{s} \left( \begin{pmatrix} l'' & l' & l \\ m'' & m' & m \end{pmatrix} \right)^{1/2} C_{l''m''l'm} \left( \begin{pmatrix} l'' & l' & l \\ 0 & 0 & 0 \end{pmatrix} \right) P_{l''m''}^m(\cos \Theta) \sum_N g_{l'n'l'}^N(K). \quad (2.48)$$

The partial-wave expansion of (2.48) forms the basis of computing the direct potentials in numerical calculations. The radial integral component of this equation is contained within the function $g_{l'n'l'}^N(K)$, where the summation $\sum_N$ is simply a short-hand notation for the double sum $\sum_{\mu \mu'}$ over the Slater basis functions defining the bound state radial
eigenfunctions. Therefore, this radial integral is given by

\[
N_r^N(K) = C_N \int_0^\infty dr j_{l'}(Kr)r^{n_N} e^{-\alpha_N r}
\]

\[
= K^{-\ell'} \frac{\pi^{1/2} \alpha_N C_N \Gamma(2\beta - 1)}{2^\gamma (\alpha_N^2 + K^2)^\beta \Gamma(\gamma + \frac{1}{2})} \binom{\beta}{\gamma + \frac{1}{2}; \frac{K^2}{\alpha_N^2 + K^2}},
\]

(2.49)

with

\[
n_N = n_\mu + n_\mu',
\]

\[
C_N = c_\mu A_\mu c_\mu' A_\mu',
\]

\[
\alpha_N = \alpha_\mu + \alpha_\mu',
\]

\[
\beta = \frac{l'' + n_N + 2}{2},
\]

\[
\gamma = l'' + 1.
\]

From a computational aspect, the hypergeometric function can always be calculated as a terminating series. Firstly, observe that \(\gamma + \frac{1}{2}\) must be half-integer. Secondly, the 3-\(j\) symbol in equation (2.48) demands that the condition \(l'' \leq l + l'\) be satisfied, and therefore

\[
\beta - n_N = \frac{l'' - n_N + 2}{2} \leq \frac{l + l' - n_N + 2}{2}.
\]

The allowable range for \(n_\mu\) is \(l + 1, \ldots, n\) and so, the right side of the above inequality is maximum when \(n_N\) is minimum, giving

\[
\beta - n_N \leq \frac{l + l' - (l' + 1)(l' + 1) + 2}{2} = \frac{-l' + 1}{2}
\]

\[
\rightarrow \quad \beta - n_N \leq \frac{1}{2}.
\]

Clearly, when \(l'' - n_N\) is even, \(\beta - n_N\) must be either a negative integer or zero, and the hypergeometric series in (2.49) terminates after \(\beta - n_N + 1\) terms. In the other case, when \(l'' - n_N\)
is odd, $\beta - n_N$ is half-integer and less than $\frac{1}{2}$. Applying the hypergeometric transformation

$$2F_1(a, b; c; x) = (1 - x)^c - a - b 2F_1(c - a, c - b; c; x), \quad (2.50)$$

then observe that $c - b = \gamma + \frac{1}{2} - \beta = \frac{l'' - n_N + 1}{2}$, which must be even when $l'' - n_N$ is odd.

Analysing its maximum value also reveals that

$$\gamma + \frac{1}{2} - \beta \leq \frac{l + l' - (l + 1)(l' + 1) + 1}{2} = \frac{-l l'}{2}$$

$$\Rightarrow \gamma + \frac{1}{2} - \beta \leq 0.$$

Therefore, when $l'' - n_N$ is odd, the transformed hypergeometric function (2.50) is also a terminating series consisting of $\gamma + \frac{1}{2} - \beta + 1$ terms and is easily computed numerically.

For the two-electron direct potential, the half-off-shell partial-wave matrix elements are given by the equation

$$V_{n L l}^{Dp L' l'}(j')(k', k) = \frac{1}{2\pi^2} (-1)^{l' + 1} \hat{L} \hat{L} \hat{l} \hat{l} \sum_{l'' l'} l'' A_{p L l l'}^{L' L'' l'}(j') g_{n L l}^{m'} (k', k), \quad (2.51)$$

with the three summation ranges being $l'' = \max(|l - l'|, |L - L'|) \ldots \min(l + l', L + L')$, $\lambda = 0 \ldots l''$, and $l'' = \max(|L - \lambda|, |L' - (l'' - \lambda)|) \ldots \min(L + \lambda, L' + l'' - \lambda)$. The angular and radial contributions in (2.51) are

$$A_{p L l l'}^{L' L'' l'}(j') = \left( \frac{(2l'')!}{(2\lambda)! [2(l'' - \lambda)]!} \right)^{1/2} \hat{l} \hat{l} \hat{l} \hat{l} \left\{ \begin{array}{ccc} l'' & l' & l' \\ 0 & 0 & 0 \end{array} \right\} \left\{ \begin{array}{ccc} L & l'' & L' \\ l' & J & l \end{array} \right\} \left( \begin{array}{ccc} \hat{l} & \hat{l}^m & \hat{l} \\ 0 & 0 & \hat{l} \end{array} \right)$$

$$\times \left( \begin{array}{ccc} L'' & l'' & l'' - \lambda \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} L & l'' & L' \\ 0 & 0 & 0 \end{array} \right) \left\{ \begin{array}{ccc} L & l'' & L' \\ l'' - \lambda & l'' & \lambda \end{array} \right\}, \quad (2.52)$$

$$g_{n L l}^{m'} (k', k) = 2\pi k' (l' - \lambda) k\lambda \int_{-1}^{1} du \frac{P_{l''}(u)}{K^{l'' + 2}} \sum N \mathcal{S}_{l''}^N (K). \quad (2.53)$$
Note that McCarthy and Stelbovics' (1983) paper, equation (63) of, has an error in its phase, which is given as \((-1)^{J^*+l^*+l''-\lambda}\). This phase is incorrect for the transfer momentum defined by (31) of their paper. The correct phase is \((-1)^{J^*+l''+\lambda}\), which reduces to \((-1)^{J^*+L}\) as given in equation (2.51). Despite this small error, the correct phase was coded into the routines that calculate the partial-wave direct potentials in the original FORTRAN software.

In practice, the partial-wave direct potential (2.51) is not usually calculated because it requires the additional overhead associated with complex arithmetic due to the complex factor \(i^r\). Instead, \(i^{L^*-L} \nu D^{n,l'}^{n',l''}(J)(k',k)\) is calculated because it is entirely real. To see why, consider the symmetry properties of the two 3-j symbols in equation (2.52) which have zero magnetic quantum numbers. The angular quantum numbers must satisfy the condition \((-1)^{L^*-l''+l'-\lambda} = (-1)^{L+l'-\lambda} = 1\), which implies that \((-1)^{L'-L} = (-1)^{2\lambda}\).

Therefore, the product

\[ i^{L^*-L} i^r = i^{L^*-L + r} = (-1)^{(L^*-L + r)}/2 = (-1)^{\lambda} \]

is always real, and hence, putting

\[ \tilde{V}^{D^{n,l'}^{n,l''}(J)}_{n,L,l}(k',k) = i^{L^*-L} \nu D^{n,l'}^{n',l''}(J)(k',k) \]

and incorporating the factor \((-1)^{L^*-l''+l'-\lambda}/2\) into the function \(\tilde{A}^{L',L''}_{L,L',\lambda}(J)\) gives

\[ \tilde{V}^{D^{n,l'}^{n,l''}(J)}_{n,L,l}(k',k) = \frac{1}{2\pi^2} (-1)^{J^*+L^*} L^* \hat{l} ^* \hat{j} ^* \sum_{l',l''} \tilde{A}^{L',L''}_{L,L',\lambda} \nu D^{n',l'}^{n'',l''}(J) (k',k), \quad (2.54) \]

with

\[ \tilde{A}^{L',L''}_{L,L',\lambda}(J) = (-1)^{(L^*-L')/2} \left( \frac{(2I'')!}{(2\lambda)! [2(I''-\lambda)]!} \right)^{1/2} (I''\lambda)^2 \begin{pmatrix} I'' & I' & l'' \\ 0 & 0 & 0 \end{pmatrix} \]

\[ \times \begin{pmatrix} L & l'' & L' \\ l' & J & l \end{pmatrix} \begin{pmatrix} L & l'' & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L & l'' & L' \\ l' & J & l \end{pmatrix}. \quad (2.55) \]
Naturally, the additional complex factor $i^{L'-L}$ is removed at a later stage when the computed on-shell T-matrix elements are used to calculate observable quantities such as cross sections.

### 2.4.2 Electron-core direct matrix elements

The electron-core potential $V_1$ is a local, central potential with potential matrix elements given by

$$
\langle \mathbf{k}'; n'l'm' | V_1 | nlm; \mathbf{k} \rangle = \langle \mathbf{k}'; n'l'm' | -\frac{Z}{r_1} | nlm; \mathbf{k} \rangle. \tag{2.56}
$$

This electron-core direct potential has the same symmetry property (2.42) as the T-matrix and evaluates to the trivial solution

$$
\langle \mathbf{k}'; n'l'm' | V_1 | nlm; \mathbf{k} \rangle = -\frac{Z}{2\pi^2 K^2} \delta_{nn'} \delta_{ll'} \delta_{mm'}. \tag{2.57}
$$

However, rather than attempting a partial-wave expansion of this result, which requires evaluating the double integral

$$
\int d\mathbf{\hat{k}}' \int d\mathbf{\hat{k}} \langle L'M' | \mathbf{\hat{k}}' \rangle \frac{1}{K^2} \langle \mathbf{\hat{k}} | L'M \rangle,
$$

an alternative strategy is employed which utilises the expression for the partial-wave two-electron direct-potential matrix. First note that in equation (2.47), whenever $l = l'$, setting $l'' = 0$ and $K = 0$ reduces the expression to

$$
\xi_{n'l}(0) = \int_0^\infty dr r^2 \langle n'l | r \rangle j_0(0) \langle r | nl \rangle = \delta_{nn'}.
$$

Using this result in equation (2.46) and multiplying by $-Z$, gives
\[ -\frac{Z}{2\pi^2 K^2} 4\pi \sum_{l^*} (-1)^m \frac{\hat{l} \hat{l}'}{(4\pi)^{1/2}} \begin{pmatrix} l'' & l' & l \\ m'' & m' & -m \end{pmatrix} \begin{pmatrix} l'' & l' & l \\ 0 & 0 & 0 \end{pmatrix} \langle \hat{\bf K} | l'' m'' \rangle g^r_{n'l'}(0). \]

Considering only the case when \( l'' = 0 \), the summation collapses and

\[ \frac{-Z}{2\pi^2 K^2} 4\pi (-1)^m \frac{\hat{l} \hat{l}'}{(4\pi)^{1/2}} \begin{pmatrix} 0 & l' & l \\ 0 & m' & -m \end{pmatrix} \begin{pmatrix} 0 & l' & l \\ 0 & 0 & 0 \end{pmatrix} \langle \hat{\bf K} | 00 \rangle g^r_{n'l'}(0) \]

\[ = \frac{-Z}{2\pi^2 K^2} 4\pi (-1)^m \frac{\hat{l} \hat{l}'}{(4\pi)^{1/2}} (-1)^{l+m} \delta_{ll'} \delta_{mm'} \frac{1}{(4\pi)^{1/2}} \delta_{nn'} \]

\[ = \frac{-Z}{2\pi^2 K^2} \delta_{nn'} \delta_{ll'} \delta_{mm'}. \]

Comparing this result with (2.57) shows that the two-electron direct potential given by equation (2.46) can be used to calculate the direct potential for the electron-core potential. This relationship only holds under the strict conditions that the matrix elements are diagonal \((n' = n, l' = l, l'' = 0)\), \(l'' = 0\) in (2.46), and \(l'' = 0\) and \(K = 0\) in (2.47). Extending this result to the partial-wave direct potential given by (2.54), then for the diagonal matrix elements with \(l'' = 0\) and putting \(v^N_{l'}(0)\) in (2.53), the expression gives the partial-wave direct-potential matrix elements for the electron-core potential. Hence, the total partial-wave direct potential is given by

\[ \tilde{V}^{n' l' l'}_{n L L'}(k',k) = \frac{1}{2\pi^2} (-1)^{l-L} \hat{L} \hat{L} \hat{l} \hat{l}' \sum_{l'' m''} \tilde{\tilde{A}}^{n' l' l'}_{n L L' l'' m''} \tilde{g}^r_{n'l'l''m''}(k',k), \quad (2.58) \]

with

\[ \tilde{g}^r_{n'l'l''m''}(k',k) = g^r_{n'l'l''m''}(k',k) - Z \delta_{n,n'} \delta_{l,l'} \delta_{m,m'} \tilde{g}^r_{n'l'l''m''}(k',k), \quad (2.59) \]

and

\[ \tilde{g}^r_{n'l'l''m''}(k',k) = 2\pi k' (l'^{- l}) k^l \int_{-1}^{1} du \frac{P_n(u)}{K^{(l'+2)}} \sum_N g^r_{n'u}(0). \quad (2.60) \]
2.4.3 Electron-electron exchange matrix elements

The exchange-potential matrix elements for electron-atom scattering are given by
\[
V^{Xn'lm'}_{nlm}(k', k) = \langle k', n'l'm' | (-1)^S (H - E) P_{12} | nlm; k \rangle,
\]
where \( P_{12} \) is the exchange operator and \( H \) is the full electron-hydrogen atom Hamiltonian
\[
H = -\frac{1}{2} \nabla_1 - \frac{1}{2} \nabla_2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{|r_1 - r_2|}.
\]

In a partial-wave expansion over total angular momentum quantum number \( J \), the partial-wave exchange matrix elements for the two-electron potential \( V_{12} = \frac{1}{|r_1 - r_2|} \) are calculated using the expression
\[
V^{Xn'LL'}_{nn'LL'}(k', k) = (-1)^S \frac{2}{\pi k' k} i^{L-L'} (-1)^{l+l'} \hat{L} \hat{L'} \hat{l} \hat{l'} \times \sum_{\lambda} \begin{pmatrix} l & L & J \\ l' & L' & \lambda \end{pmatrix} \begin{pmatrix} l & L & \lambda \\ 0 & 0 & 0 \end{pmatrix} R^{(3)}_{nn'LL'}(k', k).
\]

The radial information in this equation is given by
\[
R^{(3)}_{nn'LL'}(k', k) = \int_0^\infty dr_1 \int_0^\infty dr_2 u_L(k', r_1) \varphi_{n_1}(r_1) \frac{r_1^\lambda}{r_{\lambda+1}} \varphi_{n'L}(r_2) u_L(k, r_2),
\]
where \( u_L \) is the regular Coulomb function \( kr F_L(Z/k, kr) \) and \( \varphi_{nl} \) is the radial eigenfunction \( r R_{nl}(r) \). As with the direct-potential matrix elements, the complex factor \( i^{L-L'} \) in (2.63) is removed by multiplying by \( i^{L'-L} \), also allowing the exchange-potential matrix elements to be calculated using real arithmetic. The double integration in (2.64) is computed using the equivalent form
\[
\int_0^\infty dr_1 h_c'(k', r_1) \left[ \int_0^{r_1} dr_2 \frac{r_2^\lambda}{r_{\lambda+1}} h_c(k, r_2) + \int_{r_1}^\infty dr_2 \frac{r_2^\lambda}{r_{\lambda+1}} h_c(k, r_2) \right] \int_0^\infty dr_2 \frac{r_2^\lambda}{r_{\lambda+1}} h_c(k, r_2),
\]
where \( h_c'(k', r_1) = u_L(k', r_1) \varphi_{n_1}(r_1) \) and \( h_c(k, r_2) = u_L(k, r_2) \varphi_{n'L}(r_2) \).
2.4.4 Energy-dependent exchange matrix elements

The remaining contribution to the partial-wave exchange potential due to the electron-core interaction is considerably simpler to calculate than the two-electron contribution (2.63) and is given by (for further details, see Appendix B.4)

\[
V_{n'l'm'}^{nlm}(E; k', k) = \frac{2}{\pi k' k} \sum_{L} \delta_{n, n'} (e_n + e_n - E) \delta_{i, i'} \delta_{m, m'} \delta_{l, l'} \delta_{m', M} u_L(k', r_1) \varphi_{n' l'}(r_2) \varphi_{n l}(r_1) u_L(k, r_2).
\]

(2.66)

Note that this equation is derived assuming that the functions \(\varphi_{n l}(r)\) are exact eigenstates of the hydrogen atom. When the hydrogen atom is diagonalized in an \(L^2\) basis, as is done in the CCC formulation, approximate eigenstates or pseudo-states lead to the equivalent form given by

\[
V_{n'l'm'}^{nlm}(E; k', k) = \frac{2}{\pi k' k} \sum_{L} \delta_{n, n'} (e_n + e_n - E) \delta_{i, i'} \delta_{m, m'} \delta_{l, l'} \delta_{m', M} \left[ \left( \frac{3}{2} k' + \frac{1}{2} k - E \right) \varphi_{n l}(r_1) u_L(k, r_2) - \frac{1}{r_1} \frac{1}{r_2} \varphi_{n l}(r_1) u_L(k, r_2) \right].
\]

(2.67)

Returning to the eigenstate form, a partial-wave expansion of (2.66) over total angular momentum quantum number \(J\) gives the partial-wave expression

\[
V_{n'l'm'}^{nlm}(E; k', k) = (-1)^S \frac{2}{\pi k' k} \sum_{L} \delta_{n, n'} (e_n + e_n - E) \delta_{i, i'} \delta_{m, m'} \delta_{l, l'} \delta_{m', M} \Delta_{l, l', J} (r_1 + r_2 - E)
\]

(2.68)

\[
\times \int_0^{\infty} dr_1 \frac{u_L(k', r_1)}{r_1} \varphi_{n' l'}(r_2) \int_0^{\infty} dr_2 \frac{\varphi_{n l}(r_1)}{r_2} u_L(k, r_2).
\]

with \(\Delta_{l, l', J}\) indicating that the triangle condition must be satisfied for the angular momentum quantum numbers \(l, l', J\). Now consider the non-radial part of equation...
(2.63) for the two-electron partial-wave exchange potential and evaluate only the \( \lambda = 0 \) term of the \( \lambda \) summation, giving

\[
(-1)^S \frac{2}{\pi k' k} i^{L-L'} (-1)^{J+J'} \hat{L} \hat{L'} \hat{\iota} \hat{\iota'} \left\{ \begin{array}{ccc} l & L & J \\ l' & L' & 0 \end{array} \right\} \left\{ \begin{array}{ccc} l' & L & 0 \\ 0 & 0 & 0 \end{array} \right\} \left\{ \begin{array}{ccc} l' & L & 0 \\ 0 & 0 & 0 \end{array} \right\}
\]

\[
= (-1)^S \frac{2}{\pi k' k} i^{L-L'} (-1)^{J+J'} \hat{L} \hat{L'} \hat{\iota} \hat{\iota'} \left\{ \begin{array}{ccc} l & l' & J \\ l' & l & 0 \end{array} \right\} \delta_{l,l'} \delta_{J,J'}
\]

\[
= (-1)^S \frac{2}{\pi k' k} i^{L-L'} \hat{\iota} \hat{\iota'} \left\{ (-1)^{J+J'} \frac{\delta_{l,l'} \delta_{J,J'}}{\iota} \right\} \Delta_{l,l'} \delta_{J,J'}
\]

\[
= (-1)^S \frac{2}{\pi k' k} i^{L-L'} (-1)^{J+J'} \delta_{l,l'} \delta_{J,J'} \Delta_{l,l'}
\]

Comparing this result with equation (2.68) shows that the energy-dependent component can be calculated using the non-radial part of the two-electron exchange term. Therefore, the energy-dependent partial-wave exchange matrix elements are calculated by

\[
V_{n L l}^{X_{n L l}}(E; k', k) = (-1)^S \frac{2}{\pi k' k} i^{L-L'} (-1)^{J+J'} \hat{L} \hat{L'} \hat{\iota} \hat{\iota'} \left( \epsilon_{n^+} + \epsilon_{n'} - E \right)
\]

\[
\times \sum_{\lambda} \delta_{\lambda,0} \left\{ \begin{array}{ccc} l & L & J \\ l' & L' & \lambda \end{array} \right\} \left\{ \begin{array}{ccc} l' & L & \lambda \\ 0 & 0 & 0 \end{array} \right\} \left\{ \begin{array}{ccc} l' & L & \lambda \\ 0 & 0 & 0 \end{array} \right\}
\]

\[
\times \int_0^\infty dr_1 u_{l'}(k', r_1) \varphi_{n,l}(r_1) \int_0^\infty dr_2 \varphi_{n',l'}(r_2) u_l(k, r_2).
\]

Stelbovics (1990) points out that alternative exchange potentials can be constructed to give the same on-shell T-matrix elements. The alternative formulation overcomes problems associated with non-uniqueness (Bray & Stelbovics, 1995a) of the T-matrix LS equation.

An optional setting in the numerical software allows T-matrix elements to be calculated using this method, which is also applicable to a rotated-contour solution.
2.5 Calculating Observable Quantities

Fixing the incident momentum direction in the \( z \) direction of the coordinate system simplifies equation (2.35) for the T-matrix, so that in practice, for scattering from incident channel \( i \) to exit channel \( f' \) at angle \( \theta \), the on-shell T-matrix elements are calculated using

\[
T_{n' \ell' i' n m}^{n l m} (k_f', k_i) = \sum_{L L'} (-1)^{L'} \frac{\hat{L} \cdot \hat{L'}}{4\pi} \left( \frac{(L' - M')!}{(L' + M')!} \right) C_{M'M''}^{L L'} \sum_{nm'} C_{0 m m'}^{L L'} \times T_{n \ell \ell'}^{n' \ell' i' (j)} (k_f', k_i') P_{L'}^{M'} (\cos \theta),
\]

(2.70)

where \( M' = m - m' \). Scattering differential cross sections are then calculated from

\[
\frac{d\sigma_{ji}}{d\Omega} = \frac{k_f}{k_i} \frac{\hat{S}^2}{i^2} \sum_{m m'} |T_{n' \ell' i' n m}^{n l m} (k_f', k_i)|^2.
\]

(2.71)

Finally, the total cross section calculated from the on-shell partial-wave T-matrix elements is given by

\[
\sigma_{fi} = (2\pi)^4 \frac{k_f}{k_i} \frac{\hat{S}^2}{i^2} \frac{1}{4\pi} \sum_{L L'} J^2 \left| T_{n \ell \ell'}^{n' \ell' i' (j)} (k_f', k_i') \right|^2.
\]

(2.72)

2.6 Characterisation of the LS Kernels

Solving the coupled-channels equations (2.37) via numerical methods requires a suitable quadrature grid for each of the coupled channels to ensure an accurate evaluation of the integral equations. This task is not difficult for calculations involving only a small number of coupled channels using a fixed integration mesh, as is evident from McCarthy & Stelbovics' (1983) results computed for 1s, 2s and 2p coupled-channels. However, it is clear that the discretised kernels \( K_{ij}(p_{in}, p_{jn}) \) defined in equation (2.40) may still contain singular points if a quadrature point \( p_{in} \) happens to be coincident with the on-shell
momenta $k_j$. Thus, formulating robust forms of discretised LS matrix equations requires careful methodology. In this thesis, computer algebra is extensively used in analysing the analytic behaviour of both the direct potential and the corresponding kernel connecting various low-orbital channels.

### 2.6.1 Partial-wave potentials in closed form

McCarthy and Stelbovics (1983) point out that the partial-wave direct potentials cause the most significant numerical difficulties in forming robust numerical methods of solution, whereas, the exchange potentials are less troublesome. Using Maple, it will be shown that it is now possible to obtain analytic expressions for partial-wave direct potentials and, with greater effort, first-order partial-wave exchange potentials for electron-hydrogen scattering. This is done by evaluating the partial-wave direct potentials (2.58) and the partial-wave exchange potentials (2.68) and (2.63) algebraically, then accurate numerical data can be computed from these analytic expressions. Closed-form partial-wave potentials will be discussed in more detail in Chapters 5 and 7.

As an example, Maple evaluates equation (2.58) to obtain an analytic expression for the 1s-1s first-order ($J=0$) partial-wave direct potential, which is

$$
\hat{V}_{D}^{100(J=0)}(p',p) = \frac{\ln \left( \frac{4 + (p - p')^2}{4 + (p + p')^2} \right)}{2 \pi p' p} - \frac{8}{\pi (4 + (p + p')^2)(4 + (p - p')^2)}, \quad (2.73)
$$

where $p'$ and $p$ are arbitrary momenta (off-shell or on-shell). These analytic expressions allow accurate values to be calculated to any arbitrary precision using Maple and are useful for verifying numerical computations. In fact, all direct partial-wave potentials for coupled-
channels involving 1s, 2s and 2p states can be computed analytically using Maple. It will be shown in Chapter 5 that the natural log function in (2.73) is characteristic of almost all partial-wave direct potentials and always arises whenever the electron-core contribution is present in the direct potential for transitions between the diagonal channels. Only the partial-wave direct potentials for s-orbital off-diagonal transitions, such as 1s-2s, lack such logarithmic terms in their analytic form.

Partial-wave direct potentials computed numerically for \( J = 0 \) by the TCrossWin program (available on the included CDROM) are listed in Table 2.1 and compare very well with values calculated by Maple using the analytic expression (2.73). Other combinations of 1s, 2s and 2p direct potentials also compare with similar accuracy to analytic calculations done with Maple. In fact, all partial-wave direct potentials for any partial wave can be computed in analytic form using Maple, given sufficient memory. Examples of first-order partial-wave potentials for 1s and 2s channels are given in Chapter 5 and for 1s, 2s and 2p channels

Table 2.1: 1s-1s direct-potential matrix elements for e-H scattering computed both numerically (TCrossWin) and analytically (Maple) using a simple four-point momentum grid. The on-shell momenta have indices \( i = i' = 1 \), while the off-shell quadrature points are indexed from 2 to 5. Incident energy is 13.605 eV \( (k_{1s} = 1) \).

<table>
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<tr>
<th>J</th>
<th>n</th>
<th>l</th>
<th>L</th>
<th>i</th>
<th>n'</th>
<th>l'</th>
<th>L'</th>
<th>i'</th>
<th>Vd (TCrossWin)</th>
<th>Vd (Maple)</th>
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<td>5</td>
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</tr>
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</table>

Momentum grid

\[
\begin{array}{cc}
 i & p \\
 1 & 1.00000000e+00 \\
 2 & 1.35794413e+01 \\
 3 & 8.96456339e-01 \\
 4 & 3.69499311e+00 \\
 5 & 2.43927561e+01 \\
\end{array}
\]
in Chapter 7, while higher-order direct potential examples for 1s, 2s, 2p, 3s, 3p and 3d channels are provided on the CDROM.

2.6.2 Real-valued momentum formulations of LS kernels

In order to determine the most effective manner in which to position the quadrature points, knowledge of the kernel's behaviour is needed. As already mentioned, numerical difficulties can be encountered in solving the coupled-channels equations due to a discontinuity in the kernel at any quadrature point equal to the on-shell momentum. The LS kernel is constructed from off-shell potentials and the free Green's function; in discretised form it is

\[
K_{ff}(p_{fn}, p_{jn}) = \frac{p_{jn}^2 w_n V_{fj}(p_{fn}, p_{jn})}{\frac{1}{2} (k_j^2 - p_{jn}^2)},
\]

(2.74)

where \(k_j\) is the on-shell momentum for channel \(j\). Rather than studying the behaviour of this expression as the quadrature grid is varied discretely over \(n'\) and \(n\), it is convenient to use a continuous form that excludes the Gaussian weight \(w_n\):

\[
K_{ff}(p', p) = \frac{p^2 V_{fj}(p', p)}{\frac{1}{2} (k_j^2 - p^2)},
\]

(2.75)

where \(p'\) and \(p\) are now continuous arbitrary momenta. This expression is sufficient for analysing the structure of the kernel as a function of the momenta \(p'\) and \(p\). The analytic structures of both the kernel (2.75) and its numerator \(p^2 V_{fj}(p', p)\) are shown graphically in Figure 2.2 as a function of both real-valued off-shell momenta. Plotting the negative of the numerator in Figure 2.2 (a) is simply for convenience in displaying the 3D surface, as is the graph's' orientation.
The prominent feature observed in the kernel plot Figure 2.2 (b) is the discontinuity occurring along the line \( p = k_{1s} = \frac{1}{2} \) due to the vanishing denominator in the off-shell kernel expression (2.75). Since \( p \) corresponds to the integration variable, and normally translates to a quadrature point, it is now clear that if the selected Gaussian quadrature has points on or very near the kernel's discontinuity, serious numerical difficulties could eventuate. For single-channel calculations, it is not difficult to arrange the quadrature mesh so that mesh points do not fall on or too near the on-shell momentum \( k \). Balancing mesh points symmetrically about the singularity is also used to handle this numerical problem, optimising the Gaussian quadrature of the principal-value integral.

Now consider the kernel that couples the 1s and 2s channels. Plots of the direct potential and the kernel for 1s-2s coupling are shown in Figure 2.3. The direct potential peaks along the diagonal, a characteristic that was noted by McCarthy and Stelbovics (1983) as being common among all non-dipole transitions. Observe that the kernel now has a discontinuity along \( p = k_{2s} = \frac{1}{2} \). Similarly, a 2s-2s transition has a discontinuity in its kernel along the

![Graph](a) \(-p^2 V_{\text{1s}-\text{1s}}^{D}(p', p)\)

![Graph](b) \(K_{\text{1s}-\text{1s}}^{D}(p', p)\)

Figure 2.2: Direct potential and kernel for 1s-1s e-H scattering. Figure (a) shows the direct-potential matrix \(-p^2 V_{\text{1s}-\text{1s}}^{D}(p', p)\) plotted for \( J = 0 \) as a function of the momenta \( p' \) and \( p \). Plot (b) shows the corresponding kernel \(K_{\text{1s}-\text{1s}}^{D}(p', p)\) defined by equation (2.75).
same line. Therefore, coupled-channels calculations coupling $1s$ and $2s$ states have two possible values of momenta at which numerical problems can occur in the kernel. These problems can be avoided when including a few coupled-channels in a calculation by carefully selecting the quadrature mesh to miss the small number of on-shell momenta $k_j$.

Including a $1s$-$2p$ coupling in the calculation introduces the same discontinuity at $p = \frac{1}{2}$ in the kernel that occurs for the $1s$-$2s$ and $2s$-$2s$ transitions, but the structure of the direct potential is radically different. A negative and positive peak can be seen in Figure 2.4 (a) on either side of the diagonal $p' = p$. This introduces more complexity into the kernel’s structure along the diagonal, although it is not visible in Figure 2.4 (b) because the discontinuity feature dominates the amplitude. Couplings involving dipole transitions characteristically exhibit this structure along the diagonal, which becomes more and more sharply defined for higher-order partial waves. Another problem associated with this feature in the dipole transitions is that their first derivative is discontinuous along the diagonal. Moreover, the analytic structure analysis of potentials undertaken later in this

Figure 2.3: Direct potential and kernel for $1s$-$2s$ $e$-$H$ scattering. Figure (a) shows the direct-potential matrix $-p^2 f^{D_{2s0}(0)}_{1s0}(p', p)$ plotted for $J = 0$ as a function of momenta $p'$ and $p$. Plot (b) is the corresponding kernel $K^{D_{2s0}(0)}_{1s0}(p', p)$. 

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thesis reveals that most partial-wave direct potentials are not analytic functions, making it difficult to obtain good convergence using Gaussian quadrature integration in solve the momentum-space T-matrix Lippmann-Schwinger equation (2.37).

Serious problems can occur in large calculations in which many states are coupled. In these cases, selecting a suitable quadrature grid to circumvent undesired encounters with on-shell momenta, and at the same time, accurately representing the kernel, becomes an increasingly difficult task. On-shell momenta for higher and higher states, tend to bunch closer together near zero as the principal quantum number increases, so quadrature mesh points are almost certain to be coincident with one or more on-shell momenta in large calculations. In the present generation of CCC code of Bray, the problem has been addressed by using a different momentum integration mesh for each transition (private communication, Bray). Consequently, potential matrix element calculations are less efficient due to the large arrays of continuum functions that need to be constructed. However, in the largest CCC calculations, it is solving the large set of linear equations that dominates computation time.

Figure 2.4: Direct potential and kernel for $2p-1s$ e-H scattering. Figure (a) shows the direct-potential matrix $-p^2 V_{1s0}^{D2p1(0)}(p', p)$ plotted for $J = 0$ as a function of momenta $p'$ and $p$, while plot (b) shows the associated kernel $K_{1s0}^{D2p1(0)}(p', p)$. 
This dilemma is the underlying motivation for the research undertaken in this thesis into developing a rotated-contour method for solving coupled-channels equations for electron-atom scattering. Under this scheme, an appropriate quadrature mesh is selected in the complex plane of momentum space, rather than along the real axis. Therefore, the complex momentum quadrature points can never be equal to the real-valued on-shell momenta, and hence, the denominator in the kernel never vanishes – rather, it is the discontinuity in the kernel that vanishes.
In computational atomic physics, the one-dimensional momentum-space Lippmann-Schwinger equation (2.15) for partial-wave T-matrix elements is solved by numerical integration techniques. This approach usually involves converting (2.15) to an equivalent integral equation that necessitates evaluating a Cauchy principal-value integral (2.22), which is aided by regularisation, resulting in equation (2.25). However, after transforming this integral equation into a numerical quadrature form (2.29), a singularity associated with the Green’s function $G_0$ in the resulting kernel still remains at $p = k$ where $k$ is the on-shell momentum. Care must be taken when selecting an integration quadrature mesh, particularly the points near $p = k$. Calculations with quadrature points too near the Green’s function singularity at $k$ can potentially introduce serious errors which may render the final answer highly inaccurate.

Complicating the situation further, the singularity’s location on the real axis changes for each channel in a multi-channel computation, at times requiring changes to the integration mesh for each channel (see for example Bray & Stelbovics, 1992). Overcoming these problems associated with the singularity in the kernel of (2.25) requires special programming effort to handle the principal-value integration satisfactorily. This is particularly true for electron-atom scattering calculations involving large numbers of
channels. Transforming the integral into a form that is free of the troublesome singularity potentially simplifies this programming effort and thereby, streamlining the task of computing the T-matrix elements.

Although exploiting complex variable techniques is not new to solving scattering problems (see for example Stelbovics, 1977), it appears from the literature that contour rotation has not been used to solve coupled-channels equations in atomic physics. Integration in the complex plane often facilitates the task of evaluating real valued integrals which are otherwise difficult or even impossible to solve using conventional integration techniques. These methods are used routinely to solve difficult integrals analytically and are described in standard texts on the complex variable (see for example Churchill & Brown, 1990; Ablowitz & Fokas, 1997).

3.1 The Rotated-Contour Method

Complex variable techniques provide useful mathematical tools that are often used in solving problems in engineering and the physical sciences. As an application of the complex variable, this thesis aims to apply a rotated-contour method to solving the Lippmann-Schwinger equation for electron-atom scattering. In particular, the discussion in this section focuses on applying the method to singular integrals of the form

$$\int_0^\infty dx \frac{f(x)}{x_0 - x + i\varepsilon}.$$  \hspace{1cm} (3.1)

In the notation used here, it is understood that a limit $\varepsilon \rightarrow 0^+$ is only taken after evaluating the integral. Employing the residue theorem (Churchill & Brown, 1990) for the complex
variable provides the well-known Cauchy principal-value integral equivalent of (3.1), which is

\[
\int_0^\infty dx \frac{f(x)}{x_0 - x + i\epsilon} = \mathcal{P}\int_0^\infty dx \frac{f(x)}{x_0 - x} - i\pi f(x_0). \tag{3.2}
\]

The relationship expressed by (3.2) is derived by evaluating the integral (3.1) around a closed rectangular contour in the complex plane (see Roman, 1965).

Choosing a different deformed contour which is always arranged so that singular points are avoided in the integrand and lie well away from the contour itself has obvious computational advantages. The rotated-contour method employs just such a contour deformed by a rotation through the negative angle \(-\alpha\) and is illustrated in Figure 3.1.

Evaluating the integral (3.1) around the rotated contours \(C_1\) and \(C_2\) shown in Figure 3.1 (a) and (b), respectively, then summing them gives

![Figure 3.1](image)

Figure 3.1: Complex contours for deriving the rotated-contour method.
3: Solving the LS equation using rotated contours

\[
\int_{C_a} \frac{f(z)}{x_0 - z} + \int_{C_R} \frac{f(z)}{x_0 - z} + \mathcal{P} \int_{R}^{0} \frac{f(x)}{x_0 - x} = -i\pi f(x_0).
\] (3.3)

If \( \frac{f(Re^{-ia})}{(x_0 - Re^{-ia})} \to 0 \) in the limit as \( R \to \infty \), then by Jordan’s Lemma (Ablowitz & Fokas, 1997), the integral along the contour \( C_R \) vanishes and the integral along the rotated contour \( C_a \) then reduces to

\[
\int_{C_a} \frac{f(z)}{x_0 - z} = \mathcal{P} \int_{0}^{\infty} \frac{f(x)}{x_0 - x} - i\pi f(x_0).
\] (3.4)

Comparing this expression with relationship (3.2) shows that integrating along a rotated-contour \( C_a \) is equivalent to the integral (3.1). This result establishes the underlying mathematical basis for a rotated-contour method, which is expressed by the fundamental relationship

\[
\int_{C_a} dz \frac{f(z)}{x_0 - z} = \int_{0}^{\infty} dx \frac{f(x)}{x_0 - x + i\varepsilon}.
\] (3.5)

The procedure for evaluating the complex contour integral on the left side of (3.5) is similar to standard substitution method of integration, except that the lower and upper integration limits effectively remain unchanged. Therefore, since the integration variable \( z \) is the line in the fourth quadrant of the complex plane defined by \( z = re^{-ia} \), then \( dz = e^{-ia} dr \) and rotated-contour integral is

\[
\int_{0}^{\infty} dr \ e^{-ia} \frac{f(re^{-ia})}{x_0 - re^{-ia}} = \int_{0}^{\infty} dx \frac{f(x)}{x_0 - x + i\varepsilon}.
\] (3.6)

An important point to note here is that the deformed contour shown in Figure 3.1 is rotated into the fourth quadrant of the complex plane by a negative rotation angle, \(-\alpha\), and in principle is independent of the actual rotation angle within certain constraints. The function
\( f(x) \) must have a form that allows its analytic continuation into the complex plane. The rotation angle \( \alpha \) is then only dependent upon the singularity structure of \( f(z) \). The sector between the positive real axis and the rotated contour \( z = re^{-i\alpha} \), including along the contour itself, must be free of singular points. Consequently, before a rotated-contour method can be used to solve integrals of the form given by equation (3.1), the singularity structure of \( f(z) \) must be ascertained, allowing a suitable rotation angle to be chosen for the rotated contour. Before proceeding with an outline of the singularity-structure analysis for the momentum-space T-matrix Lippmann-Schwinger equation, the rotated-contour method is first demonstrated with the evaluation of a singular integral with a known analytic solution.

3.1.1 An analytic example of the rotated-contour method

As a simple analytic example of applying a rotated-contour method, consider the integral

\[
\int_{0}^{\infty} dx \frac{1}{a^2 - x^2 + i\varepsilon} = \int_{0}^{\infty} dx \frac{1}{(a + x)(a - x + i\varepsilon)} \tag{3.7}
\]

for \( a > 0 \). Evaluating the integral on the left side using Maple, it is found to have a simple analytic solution

\[
\int_{0}^{\infty} dx \frac{1}{a^2 - x^2 + i\varepsilon} = \lim_{\varepsilon \to 0} \frac{1}{2} \pi + i \ln(1 + \varepsilon^2/a^2) + 2 \arctan(a/\varepsilon) = -\frac{i\pi}{2a}.
\]

Using the rotated-contour method to solve this problem, the contour integral to be evaluated is written as

\[
\oint_{C} \frac{1}{a^2 - z^2} = \oint_{C} \frac{1}{(a + z)(a - z)}.
\]
A rotated contour suitable for this problem is the negative imaginary axis defined by \( z = r e^{-i\pi/2} = -ir \). Since \( z = -ir \) and \( dz = -idr \), then by substitution, the contour integral becomes

\[
-i \int_0^\infty dr \frac{1}{a^2 - (-ir)^2} = -i \int_0^\infty dr \frac{1}{a^2 + r^2} = -i \lim_{r \to \infty} \frac{1}{a} \arctan(r/a) = -\frac{i\pi}{2a}.
\]

Thus, the rotated-contour method furnishes the expected result without needing to evaluate a Cauchy principal-value integral. In this simple example, it should be noted that \( f(z) = (a + z)^{-1} \), which is singular only at one point, namely \( z = -a \). Therefore, the contour-rotation angle \(-\alpha\) can be chosen for any rotation where \( 0 < \alpha < \pi \).

Although the Green's function \( G_0 \) in equation (2.20) has a similar form to the integrand of the integral in equation (3.7), the singularity structure of the momentum-space T-matrix Lippmann-Schwinger equation is far more complicated due to the potential matrix elements, requiring detailed analysis to select an appropriate rotated contour.

It is also noteworthy to mention that although the rotated-contour method outlined here uses a straight line contour in complex-momentum space, this does not preclude the use of other curves in the complex plane, so long as they satisfy the condition that no singularity is crossed or enclosed. The derivation of the contour method makes no assumptions about the actual shape of the deformed contour, only that it forms a closed region in the complex plane and that the positive real axis forms one part of the closed contour. However, using a straight line results in the simplest contour and hence the simplest contour integral.
3.2 Contour Rotation Applied to the LS Equation

Evaluating the principal-value integral in expression (2.15) often involves regularisation to minimise singularity problems before using standard numerical integration techniques. Rotating a contour into the complex plane of momentum space eliminates the troublesome singular point due to the Green’s function $G_0$. Consider a simple one-channel elastic scattering problem and apply the rotated-contour method to the Lippmann-Schwinger equation

$$T_i(z',k) = V_i(z',k) + \frac{2}{\pi} \int_{C_a} dz \, z^2 \frac{V_i(z',z) T_i(z,k)}{E - \frac{1}{2} z^2},$$  \hspace{1cm} (3.8)$$

where it is assumed that the contour $z = pe^{-ia}$ can be used to evaluate the integral in equation (2.15), an assumption that will be justified rigorously later. The fully on-shell T-matrix is computed from the half-off-shell contour-rotated T-matrix amplitudes using

$$T_i(k',k) = V_i(k',k) + \frac{2}{\pi} \int_{C_a} dz \, z^2 \frac{V_i(k',z) T_i(z,k)}{E - \frac{1}{2} z^2},$$ \hspace{1cm} (3.9)$$

Now substituting $dz = e^{-ia} dp$ and the total energy $E = \frac{1}{2} k^2$ into equation (3.8) gives a rotated-contour solution

$$T_i(z',k) = V_i(z',k) + \frac{2}{\pi} \int_{0}^{\infty} dp \, e^{-ia} z^2 \frac{V_i(z',z) T_i(z,k)}{\frac{1}{2} (k^2 - z^2)},$$ \hspace{1cm} (3.10)$$

bearing in mind that $z$ is the rotated contour $pe^{-ia}$. For a numerical solution, the integral may be evaluated using standard $N$-point Gaussian quadrature integration. Equation (3.10) is then written as

$$T_i(z',k) = V_i(z',k) + \frac{2}{\pi} \sum_{n=1}^{N} w_n e^{-ia} z_n^2 \frac{V_i(z',z_n) T_i(z_n,k)}{\frac{1}{2} (k^2 - z_n^2)},$$ \hspace{1cm} (3.11)$$

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where $w_n$ are the Gaussian weights, $z_n = p_n e^{-i\alpha}$ and $p_n$ are the Gaussian mesh points transformed onto the interval $(0, \infty]$. Rewriting (3.11) in a simpler form

$$T_i(z', k) = V_i(z', k) + \sum_{n=1}^{N} W(z_n) V_i(z', z_n) T_i(z_n, k), \quad (3.12)$$

where $W(z_n) = \frac{2 w_n z_n^2 e^{-i\alpha}}{\pi^2 (k^2 - z_n^2)}$ is the super-weight.

This equation contains $N$ unknown half-off-shell T-matrix elements $T_i(z_n, k)$ corresponding to each of the $N$ rotated quadrature points $z_n$. Allowing $z'$ to be any of the $N$ off-shell rotated quadrature points $z_n$, the expression for the T-matrix elements then represents the $N$ equations for $T_i(z_n', k)$

$$T_i(z_n', k) = V_i(z_n', k) + \sum_{n=1}^{N} W_n V_i(z_n', z_n) T_i(z_n, k), \quad n' = 1 \ldots N. \quad (3.13)$$

When solved, the set of $N$ equations (3.13) give the $N$ half-off-shell T-matrix elements $T_i(z_n, k)$ that are necessary to calculate the physical solution, namely the on-shell T-matrix element $T_i(k', k)$. Rewriting (3.13) in matrix form gives

$$\begin{pmatrix} T_i(z_1, k) \\ \vdots \\ T_i(z_N, k) \end{pmatrix} = \begin{pmatrix} V_i(z_1, k) \\ \vdots \\ V_i(z_N, k) \end{pmatrix} + \begin{pmatrix} V_i(z_1, z_1) & \cdots & V_i(z_1, z_N) \\ \vdots & \ddots & \vdots \\ V_i(z_N, z_1) & \cdots & V_i(z_N, z_N) \end{pmatrix} \begin{pmatrix} W_1 \\ \vdots \\ W_N \end{pmatrix} \begin{pmatrix} T_i(z_1, k) \\ \vdots \\ T_i(z_N, k) \end{pmatrix} \quad (3.14)$$

Solving this matrix equation does not explicitly yield the on-shell T-matrix element required for a physical solution. However, the on-shell T-matrix $T_i(k', k)$ can be calculated from the half-off-shell T-matrix elements $T_i(z_n, k)$:

$$T_i(k', k) = V_i(k', k) + \sum_{n=1}^{N} W_n V_i(k', z_n) T_i(z_n, k). \quad (3.15)$$
As a separate calculation, this is an added complication and also unnecessary. A simpler solution is to complete the set of equations in (3.14) with the inclusion of equation (3.15). Then the desired on-shell T-matrix element $T_i(k', k)$ is calculated when this expanded set of $N + 1$ equations is solved. This also requires the associated super-weight $W_0$ be set to zero so that the on-shell momentum $k'$ is not treated as an integration mesh point. The expanded matrix equation is then

$$
\begin{pmatrix}
T_i(k', k) \\
T_i(z_1, k) \\
\vdots \\
T_i(z_N, k)
\end{pmatrix}
= 
\begin{pmatrix}
V_i(k', k) \\
V_i(z_1, k) \\
\vdots \\
V_i(z_N, k)
\end{pmatrix}
\begin{pmatrix}
V_i(k', z_N) \\
V_i(z_1, z_N) \\
\vdots \\
V_i(z_N, z_N)
\end{pmatrix}
\begin{pmatrix}
0 & 0 & \cdots & 0 \\
0 & W_1 & \cdots & 0 \\
\vdots & \vdots & \ddots & \vdots \\
0 & 0 & \cdots & W_N
\end{pmatrix}
\begin{pmatrix}
T_i(k', k) \\
T_i(z_1, k) \\
\vdots \\
T_i(z_N, k)
\end{pmatrix}
$$

(3.16)

Compare this matrix equation with the standard matrix formulation (2.31) resulting from regularisation of the Lippmann-Schwinger equation from section 2.2.3. Aside from the rotated off-shell momenta, the key change to the way in which the Lippmann-Schwinger equation is solved under the rotated-contour method simply reduces to setting the super-weight $W_0$ to zero. Consequently, modifying existing software which solves the Lippmann-Schwinger equation by regularisation to a solution using a rotated-contour method is a relatively simple coding change. Hence, code necessary for solving the momentum-space T-matrix Lippmann-Schwinger equations using either method can easily coexist in the one software package. Naturally, the complex off-shell momenta implicit in the rotated-contour solution introduces additional computational overheads due to the complex arithmetic requirements.
To summarise, the necessary changes to existing codes include: off-shell quadrature mesh
points \( p_n \) are rotated to the complex values \( z_n = p_n e^{-ia} \) for \( n = 1 \ldots N \); the super-weights
\( W_n \) are multiplied by \( \frac{dz}{dp} = e^{-ia} \) for \( n = 1 \ldots N \); and the super-weight \( W_0 \) is set to zero. The
most significant changes needed to implement the rotated-contour method in existing codes
are concerned with calculating potential matrix elements in complex-momentum space.

3.3 Mapping the LS Equation's Singularity Structure

Successfully solving the momentum-space T-matrix Lippmann-Schwinger equation (2.12)
using the method of contour rotation outlined in section 3.1 requires the singularity
structure of the integral's integrand to be established so that an appropriate rotated contour
can be determined. Therefore, the analytic structure of the integrand must be established.

For this analysis, it is convenient to first write the Lippmann-Schwinger equation (2.12) in
its operator representation

\[
T = V + VG_0 T. \tag{3.17}
\]

Through successive substitutions of \( T \),

\[
T = V + VG_0 (V + VG_0 T) \\
= V + VG_0 V + (VG_0)^2 (V + VG_0 V + (VG_0)^2 T) \\
\vdots
\]

the T-matrix LS equation is expanded formally in terms of the Born-series as

\[
T = V + \sum_{n=1}^{\infty} (VG_0)^n V. \tag{3.18}
\]

The analytic structure of \( T \) can then be inferred from that of the Born-series. An analysis
of the singularity structure of a general perturbation-series term, similar to the \( (VG_0)^n V \)
term in equation (3.18), has been discussed in detail by Stelbovics (1977) for integration contours rotated away from energy-dependent singularities. Such an analysis is required to ensure that the rotated contour avoids all singularities in the sector between the positive real axis and the deformed contour.

The \( n \)th term of the Born-series representation of the Lippmann-Schwinger equation (3.18) is defined as the \( 3n \)-dimensional integral \( T_n \) given by

\[
T_n(k', k) = \langle k' | (V G_0)^n V | k \rangle = \int dp_1 ... dp_n \frac{V(k', p_1) V(p_1, p_2) ... V(p_{n-1}, p_n) V(p_n, k)}{(E - \frac{1}{2} p_1^2 + i\epsilon_1)... (E - \frac{1}{2} p_n^2 + i\epsilon_n)}.
\]  

(3.19)

Following the analysis of Stelbovics (1977), a generalised spherical polar coordinate system in \( R^{3n} \) is employed rather than analysing (3.19) in the complex space \( C^{3n} \). The Cartesian coordinates \( p_i = (p_{i1}, p_{i2}, p_{i3}) \) are replaced by the generalised polar coordinates \( P, \theta_i \), \( i = 1, ..., 3n - 1 \) defined by

\[
p_{ij} = P \cos \theta_{3i-j-4} \prod_{k=3i-j-3}^{3n-1} \sin \theta_k, \quad i = 1, ... n; \quad j = 1, 2, 3; \]

(3.20)

\[
P \geq 0; \quad \theta_0 = 0; \quad 0 < \theta_1 < 2\pi; \quad 0 < \theta_k < \pi; \quad i = 1, ... 3n - 1.
\]

A consequence of this definition is that \( p_i^2 \leq P^2 \) and therefore, the magnitudes \( p_i \) can always be written as

\[
p_i = a_i P, \quad 0 \leq a_i \leq 1; \quad i = 1, ... n.
\]  

(3.21)

For a local potential, the potential matrix \( V(k', k) \) is always dependent on the transfer momentum and under this restriction, the integrand of \( T_n \) depends on the magnitudes of momenta \( p_i \) and the direction cosines \( u_i \) defined by
3: Solving the LS equation using rotated contours

\[
\begin{align*}
    u_1 &= \hat{k} \cdot \hat{p}_1, \\
    u_{i+1} &= \hat{p}_i \cdot \hat{p}_{i-1}, \quad i = 1, \ldots, n-1; \\
    u_{n+1} &= \hat{p}_n \cdot \hat{k}.
\end{align*}
\]

(3.22)

Using this scheme, \( T_n \) can then be written in terms of integrations over a single magnitude \( P \) and the directions \( \hat{P} \)

\[
T_n(k', k) = \int_0^\infty dP P^{3n-1} \int_{\Omega_n} d\hat{P} I_n(E; k', k, P, a_1, \ldots, a_n, u_1, \ldots, u_{n+1}),
\]

(3.23)

where the Jacobian has introduced a factor of \( P^{n-1} \) in addition to the \( P^{2n} \) from the radial integrations. When a rotated-contour method is used to evaluate the integral \( T_n \), the integrations over the directions \( \hat{P} \) remain unchanged and only the integration over the magnitude \( P \) is evaluated along a complex rotated contour \( z \). Therefore, a rotated-contour solution of equation (3.23) is expressed as

\[
T_n(k', k) = \int_C dz z^{3n-1} \int_{\Omega_n} d\hat{P} I_n(E; k', k, z, a_1, \ldots, a_n, u_1, \ldots, u_{n+1}).
\]

(3.24)

The singularity structure of each Born term can then be mapped over \( z \) in the complex plane of momentum space as a function of \( a_i \) varying from 0 to 1 and of \( u_i \) varying between -1 and 1. For the \( n \)th term, the integrand \( z^{3n-1} I_n \) becomes

\[
z^{3n-1} I_n = z^{3n-1} \frac{V(k', z, a_1, u_1) V(z, a_1, a_2, u_2) \ldots V(z, k, a_n, u_{n+1})}{(E - \frac{1}{2} a_1^2 z^2) (E - \frac{1}{2} a_2^2 z^2) \ldots (E - \frac{1}{2} a_n^2 z^2)}.
\]

(3.25)

It is clear from (3.25) that the singularity structures of the Green's functions only depend on \( a_i \) and the total energy \( E \), whilst the half-off-shell potential matrix elements have singularity structures dependant on both \( a_i \) and \( u_n \), and either the incident or scattered projectile momenta. Thus, both half-off-shell potentials exhibit similar singularity
structures, which in general, are different from that of the off-shell potentials. For the \( n - 1 \) off-shell potentials, the \( i \)th potential has a singularity structure that depends only on \( a_i, a_{i+1} \) and \( u_{i+1} \). Therefore, all the off-shell potentials feature similar singularity structures. This means that for a singularity-structure analysis of the momentum-space T-matrix Lippmann-Schwinger equation, it is sufficient to examine the structure of only one of the two half-off-shell potential expressions

\[
p_1 V(k', p_1, u_1) = a_1 z V(k', z, a_1, u_1)
\]

or

\[
p_n V(p_n, k, u_{n+1}) = a_n z V(k, z, a_n, u_{n+1}),
\]

and one off-shell potential

\[
p_{i+1} V(p_{i+1}, u_{i+1}) = a_i a_{i+1} z^2 V(z, a_i, a_{i+1}, u_{i+1}), \quad i = 1 \ldots n - 1.
\]

as the coefficients \( a_1, \ldots, a_n \) and direction cosines \( u_1, \ldots, u_n \) vary over their respective ranges. The Green’s functions are evidently singular for values of \( z \) in which

\[
E - \frac{1}{2} a_i^2 z^2 = 0,
\]

resulting in

\[
z = \pm \frac{\sqrt{2 E}}{a_i} = \pm \frac{k}{a_i}.
\]

As expected, singularities associated with the Green’s functions are located only on the real axis and as such, are not critical to the rotated-contour method because their presence is already taken into account. Singularities associated with the potential matrix elements, on the other hand, are most important and ultimately determine which rotated contour is best suited to a particular problem. Therefore, a singularity-structure analysis required by the rotated-contour method can only be completed with detailed knowledge of the potential matrix element’s analytic structure. The singularity-structure analysis outlined in this
3: Solving the LS equation using rotated contours

section is used later in this thesis to perform the necessary detailed analysis for particular scattering problems being solved by a rotated-contour method.

3.3.1 Restrictions on the contour-rotation angle

As already noted, for a rotated-contour method to be applied to solving the momentum-space T-matrix Lippmann-Schwinger equation, the chosen contour must be rotated into the fourth quadrant of the complex momentum plane, i.e. the rotation angle must be a negative angle between zero and $-90^\circ$. The maximum permissible angle will be shown to be inversely proportional to projectile electron’s initial on-shell momentum $k$. Thus, a rotated-contour method of solution is better suited to low energy problems, where relatively large angles of contour rotation can be used. If the maximum angle of rotation is small, the rotated contour passes close to the Green’s function singularity on the real axis, resulting in integration convergence being difficult to obtain. Fortunately, high energy collisions are in the regime where second-Born and unitarised-Born approximations become valid.

The contour-rotation method is also restricted to integral equations in which the integrand has an analytic continuation into the complex plane. This means that the integrand cannot contain functions such as absolute value or complex conjugates, neither of which can be continued analytically into the complex plane. It will be shown that this observation is of critical importance in determining the analytic structure of the T-matrix amplitudes for the full electron-hydrogen problem.
To illustrate the rotated-contour method in preparation for its application to the electron-hydrogen scattering problem, the simple one-channel elastic scattering problem for an electron scattered by a Yukawa potential is first discussed in the next chapter.
Chapter 4  
Yukawa Scattering: Illustration of a Rotated-Contour Approach

Developing the necessary computational methods required to solve the momentum-space T-matrix Lippmann-Schwinger equation using the rotated-contour method is the primary aim of this chapter. For the purpose of illustrating the rotated-contour method, the Yukawa potential is chosen as the scattering potential since it has a simple singularity structure and is a local, central potential. The Yukawa potential also has partial-wave momentum-space potential matrix elements that are readily represented in analytic form, providing an intermediate check for the computation of the partial-wave potentials associated with the partial-wave expansion of the T-matrix.

In this chapter, calculating potential matrix elements in complex-momentum space for the Yukawa scattering problem is discussed. Computing partial-wave potentials using closed-form expressions is considered in detail. Partial-wave calculation by numerical integration is also outlined for potentials since it is relevant to calculating general potentials where closed-form solutions are not available. Requirements for solving the momentum-space T-matrix LS equation are then examined and include a detailed analysis of the analytic structure of the potentials from which the maximum contour-rotation angle can be determined. This is followed by a discussion on the numerical solution, computer software and calculated results for potentials, and for the second-Born and full T-matrix amplitudes.
obtained from the LS equation's solution using a rotated-contour method.

With initial momentum $\mathbf{k}$, the incident free electron is elastically scattered by its interaction with the potential $V(r)$ such that the scattered electron has final momentum $\mathbf{k}'$ directed at an angle $\theta$ from its original direction. Since the electron is scattered elastically, its initial and final momenta are equal in magnitude; $k' = k = \sqrt{2E}$. Hence, in terms of the on-shell partial-wave T-matrix elements $T_i(k, k)$, the on-shell T-matrix element $T(k', k)$ for physical scattering is given by the partial-wave expansion

$$T(k', k) = \frac{1}{2\pi^2} \sum_{l=0}^{\infty} (2l + 1) T_i(k, k) P_l(\hat{k}' \cdot \hat{k}). \quad (4.1)$$

where $\hat{k}' \cdot \hat{k} = \cos \theta$. The potential $V(k', k)$ has an analogous partial-wave expansion with $T$ simply replaced by $V$. For an arbitrary final momentum with magnitude $p'$, which includes both non-physical off-shell and physical on-shell points in momentum space, the half-off-shell partial-wave T-matrix elements $T_i(p', k)$ are calculated by solving the momentum-space Lippmann-Schwinger equation (2.15). Software developed for this thesis to solve the Yukawa scattering problem numerically is designed to handle both a conventional method of solution using regularisation and the new rotated-contour method. Regularisation is performed whenever the rotation angle $\alpha$ is set to zero, the matrix equation (2.31) is solved in the manner outlined in section 2.2.3. A rotated-contour solution is applied whenever the rotation angle $\alpha$ is set to a non-zero value using the matrix equation (3.16).
4.1 Computing Yukawa-Potential Matrix Elements

In this section, calculating momentum-space partial-wave potential matrix elements is discussed for the complex momenta arising from the rotated-contour method. Since the potential $V(k', k)$ for the Yukawa potential can be expressed in a simple closed form, the accuracy of the partial-wave potential calculations can be reliably tested. The scattering potential for the problem is defined by the Yukawa potential

$$V(r) = A \frac{e^{-\mu r}}{r}, \quad (4.2)$$

where $A$ is the potential's strength and $\mu$ is a positive constant. The analytic form of the momentum-space Yukawa-potential matrix elements are well known

$$V(k', k) = \frac{A}{2\pi^2(\mu^2 + K^2)} \quad (4.3)$$

Since physical scattering by this potential is always elastic, the momentum-transfer vector $K$ has a magnitude given by

$$K = k \sqrt{2(1 - \cos \theta)} = 2k \sin \frac{\theta}{2} \quad (4.4)$$

4.1.1 Partial-wave expansion of the potential matrix

The partial-wave momentum-space potential matrix elements $V_i(p', p)$ for a local potential $V(r)$ may be written as a coordinate-space integral (Landau, 1996)

$$V_i(p', p) = \int_0^\infty dr \, r^2 j_i(p'r) \, V(r) j_i(pr), \quad (4.5)$$

where $j_i$ are spherical Bessel functions of the first kind. Examining the integral in equation (4.5) is also pertinent to the potentials required for the full electron-hydrogen problem,
although in the latter case a complete general closed-form solution is not available. However, a useful closed-form expression does exist for the Born partial-waves for the Yukawa potential (4.2). This analytic approach to calculating partial-wave momentum-space potentials is now considered for the Yukawa scattering problem.

### 4.1.2 Analytic approach to evaluating potentials

Expressing the spherical Bessel functions \( j_1(kr) \) appearing in equation (4.5) in terms of Bessel functions of the first kind gives

\[
V_l(k',k) = A \int_0^\infty dr \ r^2 \left( \frac{\pi}{2k' r} \right)^{1/2} J_{l+1/2}(k' r) e^{-\mu r} \left( \frac{\pi}{2k r} \right)^{1/2} J_{l+1/2}(k r)
\]

\[
= \frac{\pi A}{2 \sqrt{k' k}} \int_0^\infty dr \ e^{-\mu r} J_{l+1/2}(k' r) J_{l+1/2}(k r).
\]

The integral in this last expression is a standard integral (Erdélyi, Magnus, Oberhettinger & Tricomi, 1954), and the resulting partial-wave Yukawa potential is given by

\[
V_l(k',k) = \frac{A}{2k' k} Q_l \left( \frac{\mu^2 + k'^2 + k^2}{2k' k} \right),
\]

where \( Q_l \) is the Legendre polynomial of the second kind. Note that expressing the argument of \( Q_l \) in equation (4.7) in the form

\[
\frac{\mu^2 + (k' - k)^2}{2k' k} + i
\]

reveals that the argument’s value is never less than unity. This property is useful for selecting an appropriate method for numerically calculating \( Q_l \) and hence, for computing partial-wave potential matrix elements for the Yukawa potential via equation (4.7).
Computer algebra is convenient for analysing the Legendre polynomials of the second kind, which can be calculated in a number of ways (Abramowitz & Stegun, 1965), not all of which are computationally viable. Firstly, Legendre polynomials of the first kind \( P_l \) and of the second kind \( Q_l \), both satisfy the same recurrence relation. Since Legendre polynomials of the first kind are already required to calculate the three-dimensional potential matrix elements using equation (4.1), employing the recurrence relation

\[
(l + 1) Q_{l+1}(z) = (2l + 1) z Q_l(z) - l Q_{l-1}(z)
\]

(4.8)
is one possibility for computing \( Q_l \). Although \( P_l \) can be computed using the recurrence relation for increasing \( l \), the same is not true for \( Q_l(z) \) when \(|z| > 1\). Downward recurrence must be used to avoid the loss of significant digits, so another method must first be used to calculate the highest order polynomial required.

A second possibility, which initially appears attractive, expresses \( Q_l \) in terms of \( P_l \)'s

\[
Q_0(z) = \frac{1}{2} \ln \left( \frac{z+1}{z-1} \right),
\]

\[
Q_l(z) = \frac{1}{2} P_l(z) \ln \left( \frac{z+1}{z-1} \right) - \sum_{n=1}^{l} \frac{1}{n} P_{n-1}(z) P_{l-n}(z), \quad l \geq 1.
\]

However, this method is found to be numerically unstable, particularly for computing high-order polynomials, where round-off errors associated with the subtraction of two very large, almost equal numbers produces erroneous results. For example, for \( l = 20 \) and \( z = 2 \), Maple calculates the exact answer as

\[
Q_{20}(2) = \frac{9382052284364629}{524288} \ln(3) - \frac{147025018679086655521}{7478575104}.
\]
When this result is evaluated to a precision of 15 digits using Maple's floating-point arithmetic, the computed answer is

\[ Q_{20}(2) = 19659496178.6837 - 19659496178.6836 = 0.0001 \]

Extending the precision to 24 digits produces quite a different result, with

\[ Q_{20}(2) = 4 \times 10^{-13}, \]

while a 40-digit precision calculation gives the value

\[ Q_{20}(2) = 3.9349643970593549 \times 10^{-13}. \]

Clearly, the rounding errors in typical double-precision floating-point computations render this method grossly inaccurate for large-order polynomials. In addition, the overhead of calculating three \( P_i \)'s makes this method unattractive from the perspective of computational efficiency.

One method that is numerically stable expresses \( Q_i \) in terms of the hypergeometric function \( _2F_1 \), which tends to converge rapidly for \( |z| > 1 \). The relationship is given by

\[ Q_i(z) = \frac{\sqrt{\pi} \Gamma(l+1)}{(2z)^{l+1} \Gamma(l+3/2)} \ _2F_1 \left( \frac{l+1}{2}, \frac{l+2}{2}; \frac{l+3}{2}; \frac{1}{z^2} \right), \quad |z| > 1. \quad (4.9) \]

A drawback in using this expression for numerical computations is that the hypergeometric function is non-terminating, and neither can it be transformed into a terminating series. However, in most cases the rapid convergence of the series gives accurate results after calculating relatively few terms. Returning to the example above, evaluating \( Q_{20}(2) \) with Maple using equation (4.9) gives

\[ Q_{20}(2) = \frac{1}{11303415363240} \ _2F_1 \left( \frac{21}{2}, 11; \frac{43}{2}; \frac{1}{4} \right). \]
Evaluating this result to 10-digit floating-point precision using Maple gives the answer

\[ Q_{20}(2) = 3.934964397 \times 10^{-13}, \]

while to 15-digit precision, Maple obtains

\[ Q_{20}(2) = 3.93496439705935 \times 10^{-13}. \]

For the practical numerical computation of equation (4.9), the required hypergeometric function is expressed as the sum of terms \( T_k \)

\[ F_1(a, b; c; z) = \sum_{k=0}^{N} T_k, \]  

where

\[ T_0 = 1, \]

\[ T_k = \frac{(a+k)(b+k)}{(c+k)(k+1)} z T_{k-1}, \quad k \geq 1. \]  

The number of terms required in the summation is determined by the numerical accuracy needed in the calculation. Typically, the summation can be terminated when \( T_k \) becomes smaller than some predetermined value or smaller than some fraction of the current sum.

The computational performance of an algorithm calculating \( Q_l \) can be assessed in a simple manner using the relationship

\[ (l + 1) \left( P_{l+1}(z) Q_l(z) - P_l(z) Q_{l+1}(z) \right) = 1. \]  

Calculating the required potential matrix elements for the Yukawa potential using the \( Q_l \) representation (4.9) is also suitable for use with complex values of momenta since it can be continued analytically into the complex plane.
4.1.3 Numerical integration for evaluating potentials

For completeness, a generalised approach is now discussed for computing the partial-wave potential matrix elements $V_i (k', k)$. The problem involves evaluating the integral in equation (4.5) using standard numerical quadrature integration in coordinate-space. This approach has been examined with the view that the method may be used with potentials other than the Yukawa potential where analytic forms of momentum-space potentials are generally unknown. However, it must be kept in mind that both $z_n$ and $z_n'$ in equation (3.13) are typically off-shell and under the contour-rotation scheme, such off-shell momenta have complex values. Whilst the behaviour of spherical Bessel functions of the first kind is well known, at least for real arguments, any numerical computation of these functions associated with a rotated-contour solution must handle them with complex arguments. It is clear from equation (4.5) that the partial-wave potentials required for a rotated-contour solution are calculated by

$$V_i(z_n, z_n') = \int_0^\infty dr \ r^2 j_i(z_n', r) V(r) j_i(z_n, r)$$

(4.13)

for all combinations of real on-shell and complex off-shell momenta $z_n'$ and $z_n$. Although calculating spherical Bessel functions of the first kind numerically is a routine calculation (Barnett, 1996; Thomson & Barnett, 1985) when the argument is complex, computation can be done using simple upward or downward recursion algorithms based on the recurrence relation,

$$j_{i-1}(z) - \frac{2n + 1}{z} j_i(z) + j_{i+1}(z) = 0.$$  

(4.14)
However, serious problems soon become apparent because in the complex plane these functions can exponentially increase in amplitude. The behaviour of the real and imaginary parts of $j_0(z)$ in the complex plane $z = x + iy$ is graphically illustrated in Figure 4.1.

For any complex contour $z$ with a fixed imaginary part $y$, the oscillations steadily decay as the real part $x$ increases, just as it does along the real axis. However, under the rotated-contour scheme, both the real and imaginary parts of the contour increase in magnitude, the real part in the positive direction and the imaginary part in the negative direction. Basic analysis of even the lowest-order spherical Bessel function $j_0(z)$ reveals that as $z$ follows a complex contour in which the magnitude of the imaginary part $y$ increases towards infinity, the spherical Bessel function’s amplitude also increases – at an exponential rate. Using double-precision arithmetic, the imaginary part of $z$ must be limited in magnitude to less than about 700, otherwise floating-point overflow errors occur. This imposes severe limitations on the numerical evaluation of partial-wave potential matrix elements using equation (4.13) under the rotated-contour scheme.

![Re($j_0(z)$) and Im($j_0(z)$)](image)

Figure 4.1: Real and imaginary parts of spherical Bessel $j_0(z)$ plotted over a small region of the complex plane $z = x + iy$. 
Davies, Strayer & White (1988) and Davies (1988) developed a complex plane contour method to evaluate integrals of highly oscillatory functions like spherical Bessel functions. Their solution, although designed for real valued oscillatory functions, provides some insight into a possible method that may overcome the numerical difficulty outlined previously in computing complex-valued partial-wave potential matrix elements via equation (4.13). The basic idea involves expressing the spherical Bessel functions of the first kind in terms of the spherical Bessel functions of the third kind, otherwise known as spherical Hankel functions, \( h_i^{(1)}(z) \) and \( h_i^{(2)}(z) \) (Abramowitz and Stegun, 1965).

\[
j_i(z) = \frac{h_i^{(1)}(z) + h_i^{(2)}(z)}{2}.
\]  

(4.15)

These functions behave in a similar manner to spherical Bessel functions of the first kind in either the upper or lower half of the complex plane, but exponentially diminish in the opposite half of the plane. This property is illustrated in Figure 4.2. With suitably chosen complex contours for the integration variable \( r \), integrals involving spherical Bessel functions can be evaluated in the regions where the spherical Hankel functions decay.

However, an important issue to note is that the Hankel functions are singular at the origin and so, if they are used at all, equation (4.13) must first be integrated from zero to some positive \( R \) before considering evaluating the remainder of the integration from \( R \) to infinity using a complex contour in \( r \)-space. The concepts employed by Davies, et al (1988) are certainly tantalizing, but suitable \( r \)-space contours for evaluating equation (4.13) in the half-off-shell case are very difficult to find.
Consider equation (4.13) and the four possible situations involving on-shell and off-shell momenta under the rotated-contour scheme. Firstly, if both momenta are on-shell, they are both real and the potential matrix element can be evaluated as an integral of real-valued oscillating functions. In the second case, where both momenta are off-shell, they are both complex and have been rotated away from the real axis into the fourth quadrant of complex-momentum space by the angle \( \alpha \). If the \( r \) integration is evaluated by contour rotation along the contour \( z = r e^{i\alpha} \), then the arguments of the spherical Bessel functions will be real because the complex parts of the \( p e^{-i\alpha} \) and \( r e^{i\alpha} \) rotations cancel and once

Figure 4.2: Real and imaginary parts of spherical Hankels \( h_0^{(1,2)}(z) \) plotted over a small region of the complex plane \( z = x + iy \). With \( h_0^{(1)}(z) \), oscillations rapidly decay in the upper half of the complex plane (positive \( y \)), while \( h_0^{(2)}(z) \) decays in the lower half (negative \( y \)).
again, the integrals can be evaluated. However, difficulties do arise when one momentum value is on-shell and the other is off-shell. Counter-rotating $r$ simply shifts the complex argument from one spherical Bessel function to the other and does not help evaluate the integral in equation (4.13). Under the rotated-contour scheme, this difficulty represents a significant numerical impediment to calculating partial-wave potential matrix elements by numerically evaluating the integral (4.13). However, it will be shown in chapter 5 that the counter-rotation concept is useful in the electron-hydrogen problem for numerically computing the exchange contribution to the partial-wave potential.

4.2 Solving the Lippmann-Schwinger Equation

Having resolved the problem of calculating the potentials for electron-Yukawa potential scattering with complex momenta using an analytic approach, the momentum-space T-matrix elements must be calculated. The rotated-contour method of solution for the one-channel scattering problem described in section 3.2 is used to calculate the on-shell partial-wave T-matrix elements. On-shell partial-wave T-matrix amplitudes are then summed in equation (2.16) to obtain the amplitude $T(k', k)$ at any desired scattering angle $\theta$. Before this can be done, the contour-rotation angle must be determined by analysing the singularity structure of the potential matrix elements.

4.2.1 Singularity-structure analysis for the Yukawa potential

Mapping the singularity structure of the momentum-space Lippmann-Schwinger T-matrix equation for the Yukawa potential is accomplished using the procedures outlined in section 3.3. Starting with the analytic closed-form Yukawa-potential matrix element given by
equation (4.3), the magnitude \( K \) of an arbitrary momentum-transfer vector \( \mathbf{K} = \mathbf{p} - \mathbf{p}' \) is expressed in terms of arbitrary initial and final momenta magnitudes, \( p \) and \( p' \), respectively, and the direction cosine \( u = \hat{\mathbf{p}} \cdot \hat{\mathbf{p}}' \). The off-shell potential matrix element for the Yukawa potential is then given by

\[
V(\mathbf{p}', \mathbf{p}) \equiv V(p', p, u) = \frac{A}{2\pi^2 (\mu^2 + p^2 + p'^2 - 2pp'u)}.
\]  

(4.16)

First considering the off-shell potential expression, \( p_i, p_{i+1}, V(p_i, p_{i+1}, u_{i+1}) \), the generalised polar coordinate system (3.20) is used to analyse its singularity structure. Off-shell momenta \( p_i \) and \( p_{i+1} \) are replaced by \( ap \) and \( bp \), respectively, where the coefficients \( a \) and \( b \) can vary independently between 0 and 1. To apply the rotated-contour solution, the Born-series singularity structure must be investigated as \( P \) is continued into the complex plane. Denoting the complex continuation of \( P \) by \( z \), and with \( u = \hat{\mathbf{p}}_i \cdot \hat{\mathbf{p}}_{i+1} \), the generalised off-shell potential expression is

\[
ab z^2 V(z, a, b, u) = \frac{abz^2 A}{2\pi^2 (\mu^2 + a^2 z^2 + b^2 z^2 - 2ab z^2 u)}, \quad \text{with} \quad \begin{cases} 0 \leq a, b \leq 1 \\ -1 \leq u \leq 1 \end{cases} \quad (4.17)
\]

This function is singular when

\[
\mu^2 + a^2 z^2 + b^2 z^2 - 2ab z^2 u = 0. \quad (4.18)
\]

Solving for \( z \), the singularities for the off-shell potentials are described by

\[
z(\mu, a, b, u) = \pm i \frac{\mu}{\sqrt{a^2 + b^2 - 2abu}}. \quad (4.19)
\]

Thus, all the singularities associated with the off-shell potentials lie along the imaginary axis. The minimum distance between these singular points and the origin is \( \frac{\mu}{2} \) in either
the positive or negative direction on the imaginary axis. A plot of this singularity structure in the complex momentum plane is shown in Figure 4.3 (a) as \( b \) and \( u \) are varied over their respective ranges for \( \mu = 1 \) and \( a = 1 \). Next the half-off-shell potentials are considered.

Since elastic scattering only occurs in this problem, both half-off-shell matrix potentials have identical singularity structures, so it is sufficient to analyse only \( p V(k, p, u) \). Continuing the generalised polar coordinate magnitude \( P \) into the complex plane and denoting it by \( z \), and with \( u = \hat{k} \cdot \hat{p} \), the half-off-shell potential expression is

\[
az V(z, k, a, u) = \frac{az A}{2\pi^2(\mu^2 + k^2 + a^2 z^2 - 2 k a z u)}, \quad \text{with} \quad \begin{cases} 
0 \leq a \leq 1 \\
-1 \leq u \leq 1
\end{cases}
\] (4.20)

which is singular when

\[
\mu^2 + k^2 + a^2 z^2 - 2 k a z u = 0.
\] (4.21)

Figure 4.3: Singularity structure of potential matrix elements. (a) is the singularity structure of the off-shell Yukawa-potential matrix elements with \( \mu = 1 \) and \( a = 1 \). (b) is the singularity structure of the half-off-shell Yukawa-potential matrix elements with \( \mu = 1 \) and \( p' = k = 1 \).
Therefore, the singularity structure for the half-off-shell potential expressed in terms of $\mu$, $k$, $a$ and $u$ is

$$z(\mu, k, a, u) = \frac{ku}{a} \pm i \frac{\sqrt{\mu^2 + (1-u^2)k^2}}{a}.$$ \hspace{1cm} (4.22)

Figure 4.3 (b) shows this singularity structure mapped onto the complex plane for $\mu = 1$ and $k = 1$ as $a$ and $u$ are varied over their respective ranges.

It is immediately evident that a region exists around the origin that is free of singular points and that there are also sectors in the complex momentum plane devoid of singularities. The plot shown in Figure 4.3 (b) is better understood if $z$ is expressed as the complex value $x + iy$, then the singularity structure described by (4.22) for the half-off-shell potential has real and imaginary components

$$x = \frac{ku}{a} \hspace{1cm} \text{and} \hspace{1cm} y = \pm \frac{\sqrt{\mu^2 + (1-u^2)k^2}}{a}.$$ 

Fixing $u$ and substituting for $a$ in $y$, the imaginary part can be written as function of the real part $x$, which itself, varies as a function of $a$. This gives the equation

$$y = \pm \frac{\sqrt{\mu^2 + (1-u^2)k^2}}{ku} x.$$ 

The expression above shows that for particular values of $\mu$, $k$ and $u$, singularities appear in the complex plane along straight lines radiating outwards from the origin as the real part $x$ increases, i.e. as $a$ is varied from one to zero. These lines have a minimum slope of $\pm \frac{1}{k}$ when $u = \pm 1$. 

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Now consider fixing $a$, then substituting for $u$ in $y$, so that the imaginary part is expressed as a function $x$, which in turn, varies as a function of $u$. This yields the relationship

$$y = \pm \sqrt{\frac{\mu^2 + k^2 - a^2 x^2}{a}}.$$

A little rearranging gives $y^2 + x^2 = \frac{\mu^2 + k^2}{a^2}$, which is recognised as the equation of a circle of radius $\sqrt{\frac{\mu^2 + k^2}{a}}$. Singular points are closest to origin when $a$ is one and in this case, lie on two arcs at a distance of $\sqrt{\mu^2 + k^2}$ from the origin, subject to the constraints imposed by the range of $u$.

This analysis shows that the singularities associated with the half-off-shell potentials for the Yukawa potential are distributed in two regions bounded by an arc of radius $\sqrt{\mu^2 + k^2}$ and lines of slope $\pm \frac{\mu}{k}$. Such a distribution imposes a restriction on the maximum angle of rotation that can be used in solving the momentum-space Lippmann-Schwinger T-matrix equation for scattering by the Yukawa potential.

### 4.2.2 Contour-rotation angle constraints

From the preceding Born-series singularity-structure analysis for the T-matrix, the angle of rotation $\alpha$ allowed for a complex contour in the solution of the momentum-space Lippmann-Schwinger T-matrix equation for the Yukawa potential evidently must lie within the range

$$0 < \alpha < \tan^{-1} \frac{\mu}{k}.$$

(4.23)
Choosing an angle close to the extremes of this range is a poor selection, since such rotated contours pass too near the singular points on the real axis and in the complex-momentum plane. It will be demonstrated that the best strategy for choosing a rotation angle is to select the angle midway in the range given by (4.23) which maximises the rotated-contour’s angular distance from these singular points. This will be called the “optimum” contour-rotation angle and denoted by $\alpha_0$. Hence,

$$\alpha_0 = \frac{1}{2} \tan^{-1} \frac{\mu}{k}. \tag{4.24}$$

For high energy scattering, $k$ is large and $\alpha_0$ will be small, making the rotated-contour method more difficult to use. However, at low and intermediate energies, the optimum-rotation angle $\alpha_0$ is large and so the integrand along such a contour should be smooth, allowing an efficient numerical solution to the LS equation.

### 4.3 Numerical Solution

A Windows-based software package was developed in C++ to compute momentum-space potentials, second-Born T-matrix and full T-matrix elements for electron scattering from the Yukawa potential. The program called TMatrix is provided on the accompanying CDROM (see appendix C) and provides a flexible testing environment for the rotated-contour method. It allows the user to set various parameters including the incident electron energy in either atomic units or electron-volts, the Yukawa potential’s strength and range, a range of scattering angles and a Gaussian quadrature integration mesh from 2 to 512 points in either a linear mapping scheme from zero to any user-defined upper limit or a zero to infinity mapping with a selectable mid-point. Second-Born and full T-matrix elements
can be calculated either using the conventional regularisation method or a rotated-contour method. Setting the contour-rotation angle to zero selects the standard regularisation method of solution while a non-zero contour-rotation angle selects a rotated-contour method of solution. Users can set the rotation angle either manually to any angle or automatically to $\alpha_0$ defined by equation (4.24). Settings can be changed without exiting and restarting the program so that calculations can be done for different parameters, allowing various calculated data to be easily compared directly on-screen. Users may choose from the program's menu to calculate partial waves for on-shell, half-off-shell and off-shell potentials, $V G_0 V$ matrix elements, second-Born and full T-matrix amplitudes.

### 4.3.1 Potential matrix elements

TMatrix calculates on-shell, half-off-shell and off-shell partial-wave potential matrix elements using equation (4.7). $Q_l$ Legendre polynomials are calculated by numerically evaluating equation (4.9) to an accuracy specified by the user via a program setting. The number of partial waves summed is also an option selected by the user. Memory is allocated by the program to store computed partial-wave potentials for use in other calculations, recalculating them automatically if settings such as the contour-rotation angle or quadrature mesh size are changed. Potentials can be calculated from computed partial-wave potentials using the $V$-matrix form of equation (4.1) for a selected range of scattering angles $\theta$. Analytic potentials are also calculated using the closed-form expression (4.3), providing an accurate error check for those calculated from the partial-wave sum (4.1).
4: Yukawa-potential scattering: illustrating a rotated-contour approach

Table 4.1 lists a sample output of on-shell potentials calculated by TMatrix using 20 partial waves for an electron energy of 54.42 eV incident on an attractive Yukawa potential with strength $A = -1$ and range parameter $\mu = 1$. The last column shows an error figure which is defined by

$$\text{error} = \frac{|V_{\text{partial}}| - |V_{\text{analytic}}|}{|V_{\text{analytic}}|},$$

(4.25)

and represents the error in the magnitude of the partial-wave calculated potentials. The partial-wave potentials were calculated numerically using equation (4.7) with the $Q_t$ accuracy parameter set to $10^{-6}$. The small errors indicate that the partial waves are sufficiently accurate to be used in the computation of the T-matrix elements. Errors in the order of $10^{-8}$ percent can be obtained by increasing the potential accuracy parameter to $10^{-10}$ and the number of summed partial waves to 40.

Table 4.1: Potentials for electron-Yukawa scattering computed by the partial-wave sum (4.1) and the closed form expression (4.3) for scattering angles $0$ to $180^\circ$. The Yukawa potential's strength is $A = -1$, its range parameter is $\mu = 1$, while the incident electron energy is 54.42 eV ($k = 2$).

| $\theta$ | On-shell $V(k,\theta)|k = 2$ | (analytic $V(k,\theta)$) | error |
|---------|-----------------------------|--------------------------|------|
| 0       | -5.06501744974499e-02       | (-5.06605918211689e-02) | -2.06e-02 |
| 10      | -4.51746497323854e-02       | (-4.51706432681513e-02) | +8.47e-03 |
| 20      | -3.41711743967209e-02       | (-3.4173350270946e-02)  | -6.37e-03 |
| 30      | -2.44532710223890e-02       | (-2.44524909785943e-02) | +3.19e-03 |
| 40      | -1.76416886227294e-02       | (-1.7641658169888e-02)  | +1.29e-04 |
| 50      | -1.31328794754912e-02       | (-1.3132336041400e-02)  | -3.46e-03 |
| 60      | -1.01327970847819e-02       | (-1.01321183642338e-02) | +6.70e-03 |
| 70      | -8.08710366398042e-03       | (-8.08778658054297e-03) | -8.44e-03 |
| 80      | -6.65704134613338e-03       | (-6.65639548796604e-03) | +9.70e-03 |
| 90      | -5.62846794143405e-03       | (-5.62895464679654e-03) | -8.65e-03 |
| 100     | -4.87661348208431e-03       | (-4.87628141828437e-03) | +6.81e-03 |
| 110     | -4.31649496592674e-03       | (-4.31662373993751e-03) | +2.98e-03 |
| 120     | -3.89690166365203e-03       | (-3.89696860162838e-03) | +1.72e-03 |
| 130     | -3.58245385299767e-03       | (-3.58220294278960e-03) | +7.00e-03 |
| 140     | -3.34827590689591e-03       | (-3.34871768915253e-03) | +1.32e-02 |
| 150     | -3.18113426653186e-03       | (-3.18055910567966e-03) | +1.81e-02 |
| 160     | -3.06632606482889e-03       | (-3.06707832143831e-03) | -2.45e-02 |
| 170     | -3.0023877777787675e-03     | (-3.00149336763266e-03) | +2.98e-02 |
| 180     | -2.97762518530111e-03       | (-2.98003481300993e-03) | -8.09e-02 |
4.3.2 Second-Born T-matrix elements

The on-shell second-Born T-matrix approximation

\[ T^{(2)}(k',k) = V(k',k) + \int dp \ V(k',p) \ G_0(p) \ V(p,k), \]

is a useful predictor of quality for the quadrature mesh applied to the full T-matrix LS equation. As with the potential matrix elements, the second-Born amplitudes (4.26) are calculated via a partial-wave expansion, requiring the partial-wave representation of the VG_0V integral. The on-shell partial-wave second-Born matrix elements are

\[ T_i^{(2)}(k',k) = V_i(k',k) + \frac{2}{\pi} \int_0^\infty dp \ p^2 \ \frac{V_i(k',p) \ V_i(p,k)}{E - \frac{1}{2} p^2 + i\varepsilon}. \]

(4.27)

Using these partial waves, the second-Born T-matrix is then calculated in the usual manner from the partial-wave sum (4.1). Equation (4.27) provides the first test for the application of the rotated-contour method to solving a scattering problem. For the Yukawa potential given by (4.2), VG_0V matrix elements can be calculated using the closed-form solution given by Lewis (1956):

\[ \int dp \ V(k',p) \ G_0(p) \ V(p,k) = \begin{cases} \frac{-A^2}{2\pi^2 s} \ln\left(\frac{b+s}{b-s}\right), & s \neq 0 \\ -\frac{A^2}{\pi^2 b}, & s = 0 \end{cases} \]

(4.28)

where

\[ s = \sqrt{b^2 - c \ a^2}, \]

\[ a = \mu (\mu - 2 i k), \]

\[ b = 2\mu^3 - i k c, \]

\[ c = K^2 + 4\mu^2, \]

(4.29)
and \( K \) is the magnitude of the momentum transfer given by (4.4). An alternative expression for the \( V_{G_0}V \) amplitude (4.28) is given by Newton (1982):

\[
\int dp \ V(k',p) \ G_0(p) \ V(p,k) = \begin{cases} 
-\frac{A^2}{2\pi^2 K f} \left[ 2\tan^{-1}\left( \frac{K\mu}{2f} \right) + i\ln\left( \frac{f + kK}{f - kK} \right) \right], & K \neq 0 \\
-\frac{A^2}{2\pi^2 f^2} (\mu + i2\kappa), & K = 0 
\end{cases}
\]  

(4.30)

where \( f^2 = \mu^4 + 4\mu^2k^2 + k^2K^2 \). It was verified that the two solutions are equivalent. TMATRIX employs equation (4.28) to calculate \( V_{G_0}V \) analytically for comparison with values calculated numerically by a partial wave sum. Combining the on-shell \( V_{G_0}V \) with on-shell potentials gives the second-Born T-matrix (4.26).

Sample data for the on-shell \( V_{G_0}V \) contributions calculated by TMATRIX are listed in Table 4.2 for an incident energy of 54.42 eV summing 20 partial-waves. The first set of results (a) are calculated using a non-rotated contour, i.e. conventional regularisation has been used to evaluate the \( V_{G_0}V \) partial-wave integral

\[
\frac{2}{\pi} \int_0^\infty dp \ p^2 \frac{V_i(k',p) \ V_i(p,k)}{E - \frac{1}{2}p^2 + i\epsilon}.
\]

(4.31)

Results listed in the second set (b) were calculated using the rotated-contour method described for single-channel potential scattering in section 3.2. The rotation angle was auto-selected according to the Yukawa potential’s range parameter \( \mu \) and the incident projectile’s momentum \( k \) using equation (4.24). Gaussian quadrature was used for the momentum-space integration mesh, with the standard Gaussian points \( \xi_i \) and weights \( \omega_i \).
on the interval [-1, 1] being mapped onto the interval [0, ∞] by the Gauss-rational rule 
(Delves & Mohamed, 1988) given by

\[ p_i = \frac{2\gamma}{1 - \xi_i} - \gamma, \quad w_i = \frac{2\gamma \omega_i}{(1 - \xi_i)^2}. \]  \hspace{1cm} (4.32)

Using this simple quadrature scheme, \( \gamma \) is a compression factor defining the mesh mid-point 
such that half the mapped quadrature points reside in the interval [0, \( \gamma \)]. Results shown in 
Table 4.2 were calculated using a Gaussian mesh mapped with a compression factor \( \gamma = 2 \).

It was found that setting \( \gamma = k \), the on-shell momentum, optimises the convergence of \( VG_0V \) 
on the rotated contour, particularly for the real part. Decreasing the quadrature grid size to 
48 points increases the error figure by three orders of magnitude, while increasing to a 128-
point mesh decreases the error by one to two orders of magnitude. Increasing the number 
of partial waves has no effect on the calculation's accuracy, while summing only 10 partial 
waves increases the error by three orders of magnitude. Increasing the accuracy of the 
partial-wave potentials improves the error figure marginally.

These calculated results show that convergence of \( VG_0V \) is excellent in both the non-
rotated and rotated calculations, with the rotated-contour method achieving slightly smaller 
errors. When sufficient partial waves are included, the accuracy of \( VG_0V \) is determined by 
how accurately the partial waves are computed, which is controlled by the convergence of 
the hypergeometric function in equation (4.9) and moreover, by the size and distribution 
of the momentum-space quadrature mesh.
Table 4.2: \( V_{G,V} \) for electron-Yukawa potential scattering computed by a 20 partial-wave sum (4.1) and by the closed form expression (4.28) for scattering angles 0 to 180°. In (a), results have been calculated with no rotation, while (b) lists results obtained using a rotated contour. The Yukawa potential’s strength \( A = -1 \), range \( \mu = 1 \), incident electron energy is 54.42eV (\( k' = k = 2 \)). The 72-point mesh used a compression factor \( \gamma = 2 \).

(a) Contour rotation angle \( \alpha = 0° \), 72 point quadrature mesh

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<th>On-shell ( V_{G,V}(k',k) \mid k'=k=2 )</th>
<th>(analytic ( V_{G,V}(k',k) ) )</th>
<th>error</th>
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(b) Contour rotation angle \( \alpha = 13.282526° \), 72 quadrature mesh

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<th>(analytic ( V_{G,V}(k',k) ) )</th>
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</tbody>
</table>
Figure 4.4: Contour-rotation angle convergence of $V_{\nu}V$ for $\mu/k = 5$ Yukawa scattering. Potential strength $A = -1$, range $\mu = 1$; incident energy $E = 0.5442\text{eV}$ ($k = 0.2$, $\alpha_0 = 39.3^\circ$); scattering angle $\theta = 0$ with 20 partial waves; compression factor of quadrature mesh, $\gamma = 0.2$. 

4: Yukawa-potential scattering: Illustrating a rotated-contour approach
Next, a study of $V G_0 V$ convergence as a function of incident energy, quadrature mesh size and contour-rotation angle $\alpha$ is presented. TMatrix program options provide for convergence testing with varying quadrature mesh size, compression factor, contour-rotation angle and number of partial waves. Figure 4.4 shows plots of on-shell $V G_0 V$ matrix elements calculated using three quadrature mesh sizes, each summing 20 partial waves for an attractive Yukawa potential ($A = -1$) with a range parameter $\mu = 1$, an incident on-shell momentum $k = 0.2$ and scattering angle $\theta = 0$. The graphs show the convergence of $V G_0 V$ as the contour-rotation angle $\alpha$ is varied between zero and $2\alpha_0$ (≈ 78º), the upper limit of allowed contour rotation.

The curves plotted in Figure 4.4 indicate that convergence with a small quadrature mesh is only achieved over a narrow range of rotation angles near the optimum $\alpha_0$ (≈39º). Larger mesh sizes are needed to obtain satisfactory convergence over a wider range of rotation angles. Note that setting the quadrature compression factor $\gamma$ to the on-shell momentum of 0.2 produces excellent convergence in the real part of $V G_0 V$ for all three mesh sizes and rotation angles up to about 48º. Similar curves to those in Figure 4.4 are obtained for scattering angles $\theta$ other than zero – the scattering direction does not significantly influence the convergence of $V G_0 V$. This is to be expected due to the partial waves being independent of the scattering direction.

The convergence in the real part of $V G_0 V$ is maintained for small rotation angles because the compression factor $\gamma$ defines the value to which the mid-point of quadrature mesh is mapped. Consequently, the integration points are distributed symmetrically about the
singular point occurring at the on-shell momentum on the real axis. Such a balanced Gaussian quadrature distribution produces the best results when evaluating the real part of the integral at small rotation angles, where the real part more closely approximates the principal-value integral as the rotation angle decreases. However, the imaginary part becomes more sharply peaked at the on-shell momentum as the rotation angle is reduced and hence, its convergence deteriorates at small angles of rotation. Other values of $\gamma$ can be used, but they produce an unbalanced quadrature mesh distribution and result in poor convergence in the real part of $V_{G_0}V$ for small rotation angles.

For a moderate sized ratio $\mu/k = 1$, with $\mu = 1$ and incident energy $E = 13.605$eV, Figure 4.5 shows similar convergence characteristics as the contour-rotation angle $\alpha$ is varied over its allowed range for a 20 partial-wave sum and scattering angle $\theta = 180^\circ$. As with the 0.54eV plots in Figure 4.4, curves are plotted in Figure 4.5 for 16, 48 and 72-point quadrature grids, but the compression factor is now set to the new on-shell momentum so that $\gamma = 1$. Sufficient convergence is achieved in the real part for rotation angles between zero and the optimum $\alpha_0 = 22.5^\circ$, independently of the quadrature mesh size used. For rotation angles greater than $\alpha_0$, convergence is attained up to $\alpha \approx 40^\circ$ for the 72-point quadrature mesh, while the 48-point mesh exhibits good convergence up to $\alpha \approx 36^\circ$. However, convergence is poor for the 16-point mesh with rotations larger $\alpha_0$. Convergence of $V_{G_0}V$'s imaginary part is very weak at the extremes of the contour-rotation range, but good for the larger mesh sizes over a $30^\circ$ range about the optimum-rotation angle $\alpha_0$. 
Figure 4.5: Rotation convergence of \( VG_0V \) amplitudes for \( \mu/k = 1 \) Yukawa scattering. Potential: strength \( A = -1 \), range \( \mu = 1 \); incident energy \( E = 13.605 \text{eV} \) (\( k = 1 \)); scattering angle \( \theta = 180^\circ \) with 20 partial-waves; compression factor for quadrature mesh, \( \gamma = 1 \).
Figure 4.6: Contour-rotation angle convergence of $\text{VG}_\alpha V$ for $\mu/k = 1/5$ Yukawa scattering. Potential strength $A = -1$, range $\mu = 1$; incident energy $E = 340.125\text{eV}$ ($k = 5$); scattering angle $\theta = 0$ with 20 partial waves; compression factor of quadrature mesh $\gamma = 5$. 
Finally, when the ratio $\mu/k$ is small, the range of allowed rotation angles is limited. Figure 4.6 shows contour-rotation angle $\Gamma_{\mu}V$ convergence tests with $\mu/k = 1/5$ for incident energy 340.125 eV, where $k = 5$, where the maximum rotation angle is reduced to $2\alpha_0 \approx 11^\circ$. Obtaining adequate convergence also requires larger grid sizes than employed in the previous two tests at 0.54 eV and 13.6 eV, and hence the curves shown are for 48, 72, 128 and 164-point meshes. The quadrature compression factor is also set to $\gamma = 5$, the on-shell momentum. Despite the higher energy, the smaller range of rotation angles and using only 20 partial waves, these curves still show good convergence at least for the larger quadrature mesh sizes. Convergence of these high-energy matrix elements is sensitive to the quadrature distribution controlled by the compression factor $\gamma$. Setting $\gamma$ to values other than the on-shell momentum results in a rapid decay in convergence for the small mesh sizes. Note that the curves plotted in Figure 4.6 are not smooth because the TMatrix program’s minimum rotation angle step size is one degree, limiting the number of data points that can be sampled for a small range of contour-rotation angles.

Maintaining a symmetric quadrature point distribution about the on-shell momentum appears to be a sound strategy for obtaining convergence. The convergence tests for $\Gamma_{\mu}V$ demonstrate that the contour rotation can accurately compute the integrals containing the singular kernel originating from the Green’s function $G_0$. Clearly, contour rotation near the optimum-rotation angle $\alpha_0$ defined by (4.24) gives the best convergence. Contour-rotation is increasingly restricted for high energy calculations, where increased quadrature mesh sizes compensate for the small rotation angle. These considerations are also applicable to the full T-matrix calculation presented in the next section.
4.3.3 Full T-matrix elements

On-shell momentum-space T-matrix elements for Yukawa-potential scattering are also calculated by the TMatrix program using the methods of either regularisation when the contour rotation is set to zero, or a rotated-contour method otherwise. Naturally, a closed-form solution is not available to check results computed for the full T-matrix amplitudes. Convergence testing is used as a guide to select an appropriate quadrature mesh and number of partial waves required to obtain valid data for the on-shell T-matrix elements. Full T-matrix amplitudes calculated for low energy scattering using a rotated-contour method are listed in Table 4.3, column (a). These results required summing only 15 partial waves since higher-order partial waves became insignificant due to the small on-shell momentum. There is a strong indication that convergence has been achieved to at least six significant figures on a 100-point quadrature mesh in both the real and imaginary parts. These amplitudes compare very well with those listed in column (b), which have been calculated using the standard regularisation method. Computation times are considerably longer for this convergence test, taking about 10 minutes on a 733MHz machine to obtain the T-matrix amplitudes listed in column (a) of Table 4.3 and likewise for column (b).
Table 4.3: T-matrix convergence for electron-Yukawa scattering computed by a 15 partial-wave sum for scattering angle $\theta = 0$. Amplitudes in column (a) are calculated as a function of quadrature mesh size $N$, using a compression factor $\gamma = 4$ at the optimum-rotation angle $\alpha_0$. The Yukawa potential's strength is $A = -1$ and has a range parameter $\mu = 1$. Amplitudes for incident electron energies 0.5442eV ($k = 0.2$, $\alpha_0 = 39.34^\circ$) 13.605eV ($k = 1$, $\alpha_0 = 22.5^\circ$) and 54.42eV ($k = 2$, $\alpha_0 = 13.28^\circ$) are given.

(a) rotated-contour method

| $N$  | $T(k,k) | k = 0.2$                | $T(k,k) | k = 0.2$                |
|------|--------------------------------|--------------------------------|
| 20   | 4.44073714e-02 -1.03210526e-011 | 4.47648773e-02 -1.03632512e-011 |
| 40   | 4.47512903e-02 -1.03649652e-011 | 4.47504825e-02 -1.03649981e-011 |
| 60   | 4.47495114e-02 -1.03650846e-011 | 4.47497400e-02 -1.03650882e-011 |
| 80   | 4.47495257e-02 -1.03651025e-011 | 4.47496098e-02 -1.03651040e-011 |
| 100  | 4.47495332e-02 -1.03651079e-011 | 4.47495722e-02 -1.03651086e-011 |
| 120  | 4.47495370e-02 -1.03651099e-011 | 4.47495578e-02 -1.03651103e-011 |

(b) standard regularisation

| $N$  | $T(k,k) | k = 1$                | $T(k,k) | k = 1$                |
|------|--------------------------------|--------------------------------|
| 20   | -4.32750859e-02 -2.49818334e-021 | -4.32305954e-02 -2.50382811e-021 |
| 40   | -4.32319546e-02 -2.50359296e-021 | -4.32320578e-02 -2.50360374e-021 |
| 60   | -4.32321257e-02 -2.50359195e-021 | -4.32321330e-02 -2.50359296e-021 |
| 80   | -4.32321448e-02 -2.50359082e-021 | -4.32321460e-02 -2.50359110e-021 |
| 100  | -4.32321504e-02 -2.50359053e-021 | -4.32321502e-02 -2.50359057e-021 |
| 120  | -4.32321526e-02 -2.50359040e-021 | -4.32321516e-02 -2.50359036e-021 |

| $N$  | $T(k,k) | k = 2$                | $T(k,k) | k = 2$                |
|------|--------------------------------|--------------------------------|
| 20   | -4.85422652e-02 -1.22804262e-021 | -4.87446900e-02 -1.25906181e-021 |
| 40   | -4.87416989e-02 -1.25901738e-021 | -4.87462689e-02 -1.25897257e-021 |
| 60   | -4.87462452e-02 -1.25897223e-021 | -4.87462551e-02 -1.25896519e-021 |
| 80   | -4.87462703e-02 -1.25896608e-021 | -4.87462617e-02 -1.25896409e-021 |
| 100  | -4.87462706e-02 -1.25896568e-021 | -4.87462618e-02 -1.25896376e-021 |
| 120  | -4.87462712e-02 -1.25896559e-021 | -4.87462649e-02 -1.25896372e-021 |
Chapter

5

Analytic Structure of Potentials for
s-Wave Model e-H Scattering

The rotated-contour method developed and then applied to the single-channel Yukawa-
potential scattering problem in Chapters 3 and 4, respectively, demonstrates that contour
rotation can be employed successfully to solve a momentum-space T-matrix Lippmann-
Schwinger equation. However, atomic targets introduce additional complexity to the
scattering problem, in that, coupled potentials connect an infinite number of channels which
have direct and exchange contributions, with exchange also having an energy-dependent
component. The momentum space representation of these potentials is normally obtained
by numerical computation. It is therefore a considerable challenge to obtain the analytic
properties of these potentials needed to ensure that their analytic continuation to complex-
momentum space is appropriately formulated for the application of the rotated-contour
method. In this chapter, as a prelude to studying the full e-H scattering problem, the
simpler problem obtained by restricting the coupled-channels expansions to coupling only
s-orbital target states is considered. This subset of the full problem will be referred to in
this thesis as the “s-wave model” and serves to illustrate the general procedures needed to
study the analytic structures of the direct and exchange potentials.

Maple is used extensively to study the analytic structure of direct potentials for transitions
between s-orbital channels and also for checking the numerical computation of these
potentials with real and complex momenta. Closed-form expressions for partial-wave direct potentials are algebraically computed using Maple. Analytic results primarily calculated for the first-order partial waves are presented for the first time in this thesis. In this chapter, first-order partial-waves are explicitly given for the 1s-1s, 1s-2s (2s-1s) and 2s-2s transitions. Maple can also readily evaluate higher-order partial-wave direct potentials for these and other channel transitions, although expressions quickly become very large with increasing order (total angular momentum $J$) and principle quantum numbers. Partial-wave exchange potentials proved considerably more difficult to compute algebraically, with only the first-order partial-wave potentials for 1s-1s, 1s-2s and 2s-2s transitions being easily evaluated in closed-form. Maple has been an invaluable tool for investigating discrepancies between numerical and analytic results, allowing computational problems to be isolated quickly. Computer algebra has also aided algorithm development for numerical calculations on a rotated contour. The discussion in this chapter begins by considering the Born-series singularity structures for the direct-potentials and analysing them using Maple's computer algebra system.

### 5.1 s-Wave Model Born-Series' Singularity Structures

In this section, the singularity structures for direct potentials involving transitions between initial and final s-orbital channels are discussed in detail. Closed-form expressions for electron-hydrogen Born scattering amplitudes $f_B(K)$ are easily evaluated as a function of the momentum-transfer vector $K = (k, \Theta, \Phi) = k - k'$ using computer algebra (Blackett & Stelbovics, 1999). Expressions for the potential matrix elements are then given by

$$V(K) = -\frac{1}{4\pi^2} f_B(K).$$  (5.1)
The standard practice of adopting a coordinate system in which $\Phi = 0$ simplifies the analysis so that the incident, scattered and transfer momenta have the orientations shown in Figure 5.1. Using the sine and cosine rules for triangles, the momentum-transfer vector is then related to the incident and scattered momenta by the equations

\[ K = \sqrt{k^2 + k'^2 - 2kk'\cos\theta} = \sqrt{k^2 + k'^2 - 2kk'u} \]

\[ \cos\Theta = \frac{k - k'\cos\theta}{K} = \frac{k - k'u}{K} \]

(5.2)

\[ \sin\Theta = \frac{k'\sqrt{1 - \cos^2\theta}}{K} = \frac{k'\sqrt{1 - u^2}}{K} , \]

where $\theta$ is the scattering angle between $k$ and $k'$. The singularity-structure analysis can then be carried out using the methods described in sections 3.3 and 4.2.1 by examining the analytic structures of the half-off-shell and off-shell potentials.

![Figure 5.1: Orientation of the momentum-transfer vector $K$ with respect to the incident momentum $k$ and scattered momentum $k'$.](image)
5.1.1 Singularity structure for the direct 1s-1s kernel

In terms of the momentum-transfer vector \( \mathbf{K} \), the full direct potential for 1s-1s electron-hydrogen scattering is

\[
V_{1s1s}(\mathbf{K}) = -\frac{1}{2\pi^2} \frac{8 + K^2}{(4 + K^2)^2}. \tag{5.3}
\]

The singularity structure of this potential is fully determined by the factor appearing in the denominator. It is found that all direct potentials have a similar factor of the form

\[
\frac{1}{(\xi^2 + K^2)^{n + n'}} \tag{5.4}
\]

where \( \xi = \frac{1}{n} + \frac{1}{n'} \). This is similar to the \( \frac{1}{(\mu^2 + K^2)} \) factor occurring in the denominator of the Yukawa potential (4.3). Therefore, it is expected that singularity structures for direct potentials exhibit some similarities to the singularity structure of the Yukawa potential.

Substituting for the transfer momentum magnitude \( K \) given by (5.2), the potential (5.3) is expressed in terms of general initial and final off-shell momenta, \( p \) and \( p' \) and the direction cosine \( u = \cos \theta \), by

\[
V_{1s1s}(p', p, u) = -\frac{1}{2\pi^2} \frac{8 + p^2 + p'^2 - 2pp'u}{(4 + p^2 + p'^2 - 2pp'u)^2}. \tag{5.5}
\]

Singularity structures associated with the Green's function \( G_0(E, p) \), the half-off-shell and the fully off-shell potentials are analysed with the aid of the generalised polar coordinate system (3.20) in which \( p = aP \) and \( p' = bP \) for \( 0 < a, b < 1 \). Using the off-shell form of the potential for terms in the Born-series expansion of the T-matrix given by (3.27) and allowing the complex continuation of \( P \) to be denoted by \( z \), the off-shell potential for the
1s-1s transition is

\[ abz^2 V_{1s1s}(z,a,b,u) = -\frac{1}{2\pi^2} \frac{abz^2(8 + a^2z^2 + b^2z^2 - 2abz^2u)}{(4 + a^2z^2 + b^2z^2 - 2abz^2u)^2} \]  

(5.6)

Clearly, singularities are found to occur in the complex plane whenever the Yukawa-like factor in the denominator vanishes and this occurs in regions defined by

\[ z = \frac{\pm 2i}{\sqrt{a^2 + b^2 - 2abu}}. \]  

(5.7)

Thus, the singularity regions due to the off-shell potentials lie entirely on the imaginary axis, excluding the segment between \( \pm i \). Analogous to the singularity structure of the off-shell Yukawa potential, singularities on the imaginary axis always exclude the segment between \( \pm i \frac{\xi}{2} \) with \( \xi = \frac{1}{n} + \frac{1}{n'} \). It should also be noted here that this implies that the off-shell direct potentials can be rotated through any angle \( -\alpha \) with \( 0 < \alpha < \frac{\pi}{2} \), a feature that is demonstrated in section 6.2.3 of the next chapter.

For the half-off-shell potentials in the Born-series expansion of the T-matrix, it is sufficient to analyse the expression \( pV(k, p) \), where \( k \) denotes the on-shell momentum for the 1s channel. Again using the generalised polar coordinate system and allowing the analytic continuation of \( P \) to be denoted by \( z \), the half-off-shell expression for analysis is

\[ az V_{1s1s}(k,z,a,u) = -\frac{1}{2\pi^2} \frac{az(8 + k^2 + a^2z^2 - 2akzu)}{(4 + k^2 + a^2z^2 - 2akzu)^2}, \]  

(5.8)

which is singular for

\[ z = \frac{k}{a} \pm \frac{i}{a} \sqrt{k^2(1 - u^2) + 4}. \]  

(5.9)
This singularity region is of particular interest for the rotated-contour method since it dictates the maximum rotation angle allowed for this transition in so far as the direct potential in concerned. Plots of these two singularity regions, (5.7) and (5.9), over the complex-momentum plane for an on-shell momentum $k = 1$ are shown in Figure 5.2. Note the similarity of these plots to the singularity-structure plots for the Yukawa-potential scattering problem shown in Figure 4.3. This structure is common among all the $s$-orbital transitions.

Of particular interest is the singularity region in the lower half of the complex $z$ plane originating from the half-off-shell direct potential corresponding to

![Diagram](image)

Figure 5.2: e-H Born-series 1s-1s singularity structure plotted over the complex off-shell momentum $z$ plane for an on-shell momentum $k_{1s} = 1$. 

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\[
    z = \frac{ku}{a} - \frac{i}{a} \sqrt{k^2(1-u^2) + 4}.
\] (5.10)

Figure 5.2 shows that a deformed contour rotated into the fourth quadrant must lie between the positive real axis and the singularity region defined by equation (5.10) in the lower half of the complex-momentum plane along the boundary with \( a = u = 1 \). The maximum contour-rotation angle that can be used for the 1s-1s transition is then found to reduce to the argument of \( z = k - i2 \), and therefore
\[
    \alpha_{1s1s} = \tan^{-1} \frac{2}{k_{1s}}.
\] (5.11)

For example, at an incident kinetic energy of 0.5, where the 1s on-shell momentum \( k_{1s} = 1 \), the maximum allowed contour-rotation angle \( \alpha \) is 63.4°. Computed results for single-channel scattering in the 1s-1s transition are presented and discussed in section 6.2. They demonstrate that consistent results can be obtained over a range of rotation angles about the optimum rotation angle \( \alpha_0 = 31.7° \), subject to the constraints imposed by the maximum rotation angle (5.11).

### 5.1.2 Singularity structure for the direct 1s-2s (2s-1s) kernel

The procedure used for analysing the 1s-1s singularity structure is now repeated for the 1s-2s (2s-1s) direct potential, which in terms of the momentum-transfer vector \( \mathbf{K} \), is
\[
    V_{2s1s}(\mathbf{K}) = V_{1s2s}(\mathbf{K}) = \frac{1}{2\pi^2} \frac{\sqrt{2}}{\left(\frac{9}{4} + K^2\right)^{3/2}}.
\] (5.12)

It is sufficient to consider only one of these transitions due to the potential's symmetry
under the exchange of initial and final channels. Choosing the 1s-2s transition, first substituting for the magnitude of the momentum transfer $K$, then using the generalised polar coordinate scheme (3.20), the off-shell 1s-2s direct-potential expression is

$$ abP^2 V_{2s1s}(P, a, b, u) = \frac{1}{2\pi^2} \sqrt{2 \frac{abP^2}{9 + b^2P^2 + a^2P^2 - 2abP^2u^2}}. $$

(5.13)

For the half-off-shell 1s-2s direct-potential, consideration must be given to whether the on-shell momentum $k$ is in the 1s channel or the 2s channel. Denoting the on-shell momentum for channel $j$ by $k_j$, the direct potential expression is

$$ aP V_{2s1s}(P, k_j, a, u) = \frac{1}{2\pi^2} \sqrt{2 \frac{aP}{9 + k_j^2 + a^2P^2 - 2k_jau^2}}. $$

(5.14)

The singularity structure for the Born-series in the 1s-2s transition when $P$ is continued into the complex $z$ plane is shown in Figure 5.3. Again, off-shell potentials have singularities only on the imaginary axis. Since the contour-rotation angle depends only on the half-off-shell potential, only its singularity structure needs consideration to determine the contour-rotation angle $\alpha$. The singularity region of interest in the lower $z$-plane is defined by

$$ z = \frac{k_ju}{a} - \frac{i}{a} \sqrt{k_j^2(1 - u^2) + \frac{9}{4}}. $$

(5.15)

This region has a boundary in the fourth quadrant along the line $z = k_j - i \frac{3}{2}$. Consequently, the maximum contour-rotation angle allowed for the 1s-2s transition is

$$ \alpha_{2s1s} = \tan^{-1} \frac{3}{2k_j}. $$

(5.16)
Since this transition is inelastic, the magnitudes of the initial and final on-shell momenta are different, begging the question – which on-shell momenta should be used to calculate the rotation angle? Clearly, (5.16) must give different maximum rotation angles depending on whether the on-shell momentum \( k_j \) is in the 1s or in the 2s channel. Selecting the smallest maximum rotation angle is an appropriate strategy to take, and therefore, the larger on-shell momenta must be used in calculating the contour-rotation angle. In this particular case, the momenta corresponding to the 1s-channel is the appropriate on-shell momentum to use. For the 1s-2s transition, the example with \( k_{1s} = 1 \) gives a maximum contour-rotation angle of 56.3° and the optimum rotation angle \( \alpha_0 \) is then approximately 28.2°.

![Diagram](image)

**Figure 5.3:** e-H Born-series 1s-2s singularity structure plotted over the complex off-shell momentum \( z \) plane for an on-shell momentum \( k_{1s} = 1 \).
5.1.3 Singularity structure for the direct 2s-2s kernel

The full direct potential for the 2s-2s transition is

\[
V_{2s2s}(K) = -\frac{1}{2\pi^2} \frac{7 + 4K^2 + 4K^4 + K^6}{(1 + K^2)^4}. \tag{5.17}
\]

Analysing the off-shell and half-off-shell singularity structure reveals that the Born-series terms have singularities in regions of the momentum z-plane shown in Figure 5.4. The singularity region relevant to the rotated-contour method is associated with the half-off-shell potentials and is defined by

\[
z = \frac{k_u}{a} - \frac{i}{a} \sqrt{k_u^2 (1 - u^2) + 1}. \tag{5.18}
\]

![Figure 5.4: e-H Born-series 2s-2s singularity structure plotted over the complex off-shell momentum z plane for an on-shell momentum $k_{2s} = 1/2$.](image)
This expression gives a maximum contour-rotation angle for the 2s-2s transition

$$\alpha_{2s2s} = \tan^{-1} \frac{1}{k_{2s}}.$$  \hspace{1cm} (5.19)

For an on-shell momentum $k_{2s} = 1/2$, the maximum contour-rotation angle for the 2s-2s transition is therefore $63.4^\circ$, giving an optimum contour-rotation angle $\alpha_o = 31.7^\circ$.

### 5.2 Contour-Rotation Angle Constraints

After analysing the kernel singularity structures of many $s$-orbital transitions with higher principal quantum numbers, a clear pattern emerges for calculating the maximum allowed contour-rotation angle $\alpha$. The analysis reveals that the maximum allowed contour-rotation angle depends only on the principal quantum numbers, $n$ and $n'$, and the on-shell momenta, $k_n$ and $k_{n'}$, of the initial and final channels, respectively. The maximum contour-rotation angle allowed for a given $ns - n's$ direct potential is given by

$$\alpha_{(nn')} = \tan^{-1} \frac{1 + \frac{1}{n}}{k_{>}},$$ \hspace{1cm} (5.20)

where $k_{>} = \max(k_n, k_{n'})$ is the greater of the two on-shell momenta for the particular channels involved. Half the maximum rotation angle is defined as the optimum rotation angle $\alpha_o$ given by

$$\alpha_{0(\langle nn\rangle')} = \frac{1}{2} \tan^{-1} \frac{1 + \frac{1}{n}}{k_{>}}.$$ \hspace{1cm} (5.21)

Equation (5.21) explicitly shows that for high-energy collisions in which $k_{>}$ is large, the optimum rotation angle $\alpha_o$ can be very small, so small that it may render the rotated-contour method impractical for solving the momentum-space T-matrix Lippmann-Schwinger
equation at such energies. Similar restrictions on the rotated-contour method apply for high energy target eigenstates in which principal quantum numbers are large (small eigenstate momenta). These considerations impose limitations upon the applicability of the rotated-contour method to the electron-hydrogen scattering problem.

5.3 Analytic Continuation of Direct Potentials

The momentum space partial-wave direct potentials \( \tilde{\Psi}^{DnLl}_{nl} (k', k) \) for e-H scattering given by equations (2.54), (2.55) and (2.53) have been computed algebraically by developing a set of Maple procedures. In this section, closed form expressions are given for the first-order partial-wave direct potentials for e-H scattering transitions 1s-1s, 1s-2s and 2s-2s. Closed-form expressions for higher-order partial-wave direct potentials for these and other transitions are also readily evaluated using Maple, although they rapidly become very large expressions. An integration over the cosine direction \( u \) is required to evaluate the partial-wave direct potentials. This is made easier by a change of variable so that the integral is evaluated over the magnitude of momentum transfer squared \( K^2 \). Maple\textregistered worksheets for the partial-wave direct potential are provided on the accompanying CDROM.

5.3.1 1s-1s partial-wave direct potential in closed form

The first-order partial-wave of the 1s-1s direct potential is given by the integral

\[
\tilde{\Psi}^{D1s0 (0)}_{1s0} (k', k) = -\frac{1}{\pi} \int_{-1}^{1} du \frac{8 + K^2}{(4 + K^2)^2}. \tag{5.22}
\]

where \( K \) is the transfer momentum's magnitude given by \( K^2 = k^2 + k'^2 - 2kk' u \). With a
change of variable, putting \( x = K^2 = k^2 + k'^2 - 2kk' u \), this integral becomes

\[
\tilde{\mathcal{D}}_{1s0}^{1s0(0)}(k', k) = -\frac{1}{2\pi k'k} \int_{K_1^2}^{k^2} \frac{dx}{x} \left( \frac{4}{(4 + x)^2} + \frac{1}{4 + x} \right),
\]

(5.23)

where \( K_1^2 = (k - k')^2 \) and \( K_2^2 = (k + k')^2 \). Evaluating this integral gives

\[
\tilde{\mathcal{D}}_{1s0}^{1s0(0)}(k', k) = \frac{1}{2\pi k'k} \ln \left( \frac{4 + K_1^2}{4 + K_2^2} \right) - \frac{8}{\pi \left( 4 + K_1^2 \right) \left( 4 + K_2^2 \right)},
\]

(5.24)

for the \( J = 0 \) partial-wave of the \( 1s-1s \) direct potential of e-H scattering. Analysing the singularities associated with equation (5.24) in the complex momentum plane for the half-off-shell direct potential, it is found that singular points occur at \( z = k_{1s} \pm i2 \) and \( z = -k_{1s} \pm i2 \). Consequently, the maximum contour-rotation angle \( \alpha \) that can be used is equal to \( \tan^{-1} \frac{2}{k_{1s}} \), which, as expected, is the same maximum rotation angle obtained previously in section 5.1.1 for the full \( 1s-1s \) direct potential.

### 5.3.2 1s-2s partial-wave direct potential in closed form

The analytic partial-wave potential evaluated using Maple for the \( 1s-2s \) \((2s-1s)\) direct potential is

\[
\tilde{\mathcal{D}}_{1s0}^{2s0(0)}(k', k) = \frac{1}{\pi} \int_{-1}^{1} du \frac{256\sqrt{2}}{(9 + 4K^2)^3} = \tilde{\mathcal{D}}_{2s0}^{1s0(0)}(k, k'),
\]

(5.25)

which evaluates to

\[
\tilde{\mathcal{D}}_{1s0}^{2s0(0)}(k', k) = \frac{8\sqrt{2}}{\pi} \frac{9}{4} + \left( k^2 + k'^2 \right) \frac{\left( \frac{9}{4} + K_1^2 \right)}{\left( \frac{9}{4} + K_2^2 \right)^2},
\]

(5.26)
Examining the singularity structure of the 1s-2s half-off-shell partial-wave direct potential reveals that singular points are located at $z = k_{1s} \pm i \frac{3}{2}$ and $z = -k_{1s} \pm i \frac{3}{2}$. This translates to a maximum contour-rotation angle $\alpha$ being equal to $\tan^{-1} \frac{3}{2k_{1s}}$. Once again, the result agrees with the singularity analysis of the full 1s-2s direct potential in section 5.1.2.

### 5.3.3 2s-2s partial-wave direct potential in closed form

For the 2s-2s transition, the first-order partial-wave direct potential is given by the integral

$$
\tilde{V}^{D_{2s0}(0)}_{2s0}(k', k) = \frac{1}{\pi} \int_{-1}^{1} du \frac{1 - 3K^2 + 2K^4}{(1 + K^2)^4 K^2} - \frac{1}{K^2}.
$$

(5.27)

Setting $K^2 = (k - k')^2$ and $K^2 = (k + k')^2$, this integral simplifies to

$$
\tilde{V}^{D_{2s0}(0)}_{2s0}(k', k) = \frac{1}{2\pi k' k} \ln \left( \frac{1 + K^2}{1 + K^2} \right) - \frac{(K^2 - K^2)}{2 \pi k' k (1 + K^2)^3 (1 + K^2)^3} \times \frac{1}{2} \left[ 12 + K^2(5K^2 + 13) + \left( 13 + (8 + 3K^2)K^2 + [5 + (3 + 2K^2)K^2]K^2 \right)K^2 \right] + \frac{1}{K^2}.
$$

(5.28)

Although the closed-form expression for the 2s-2s partial wave ($J = 0$) direct potential is more complicated than the 1s-1s and 1s-2s expressions, a singularity analysis of the half-off-shell 2s-2s direct partial-wave potential reveals that singular points occur at $z = k_{2s} \pm i$ and $z = -k_{2s} \pm i$. Therefore, the maximum contour-rotation angle $\alpha$ cannot exceed $\tan^{-1} \frac{1}{k_{2s}}$, again in agreement with the full 2s-2s direct-potential singularity analysis given in section 5.1.3.

Only a small sample of closed-form partial-wave direct potentials for the e-H scattering problem in the $s$-wave model has been given here. Although Maple is capable of calculating closed-form expressions for practically any partial-wave direct potential in the
s-wave model of e-H scattering, the resulting expressions are generally large and difficult to simplify. For example, fully expanded, the $J=5$ partial-wave direct potential for the 1s-5s transition consists of 658 terms, whereas the 5s-5s transition has 1972 terms.

The preceding analysis of s-wave model direct potentials for e-H scattering shows that their closed-form expressions are suitable to be continued analytically into complex-momentum space, as required by a rotated-contour method of solving the T-matrix Lippmann-Schwinger equation. This analytic continuation to a rotated contour in the complex plane is subject to the conditions imposed by equation (5.20) on the contour-rotation angle $\alpha$. However, there is also the contribution from the exchange potential to consider, and its analytic structure needs to be examined before the rules for the rotated-contour angle can be firmly established.

5.4 Analytic Continuation of Exchange Potentials

Unlike the direct potential, a closed-form solution for the full exchange potential is not readily available, even for transitions between s-states in e-H scattering. Although it is easy to evaluate a closed-form energy-dependent exchange term, it will be shown that this is not the case for the electron-electron contribution. Therefore, the singularity-structure analysis performed for the direct potential cannot be repeated in the same detail for the exchange potential. While the exchange potentials are more complicated to evaluate algebraically, Maple is still able to provide closed-form expressions for a few of the first-order partial-wave exchange potentials between low-orbital initial and final s-states. It was shown in section 5.3.1 that the singularity-structure analysis of the first-order partial waves for direct
potentials gave the same upper limit for the allowable contour-rotation angle as given by analysing the full direct potential. The same partial-wave analysis technique will be used in this section to infer the exchange potentials’ maximum contour-rotation angle.

5.4.1 1s-1s partial-wave exchange potential in closed form

The simplest of the partial-wave exchange potentials and easiest to evaluate is the $J = 0$ partial-wave 1s-1s exchange potential given by the equation

$$
\tilde{V}^{X_{1s 0}(0)}_{1s 0 S}(E; k', k) = (-1)^{s} \frac{16}{\pi} \left[ \frac{-2(1 + E)}{(1 + k'^{2})^{2}(1 + k^{2})^{2}} + \frac{10 + k^{2} + k'^{2}}{(1 + k'^{2})(1 + k^{2})(4 + k_{1s}^{2})(4 + K_{1s}^{2})} \right],
$$

(5.29)

where $E$ is the total energy incident electron energy given in terms of the incident momentum $k_{1s}$ by $E = \frac{1}{2}(k_{1s}^{2} - 1)$. In the absence of a full singularity-structure analysis of the 1s-1s exchange potential, it is sufficient to analyse the partial-wave singularity structure so that the conditions for contour rotation can be inferred. Analysis of the half-off-shell exchange potentials $\tilde{V}^{X_{1s 0}(0)}_{1s 9 S}(E; k_{1s}, z)$ and $\tilde{V}^{X_{1s 0}(0)}_{1s 0 S}(E; z, k_{1s})$ show that singularities occur at the points $z = \{ \pm i, k_{1s} \pm i2, -k_{1s} \pm i2 \}$. Therefore, the contour-rotation angle $\alpha$ is limited to a maximum $\tan^{-1} \frac{2}{k_{1s}}$, the same maximum contour-rotation angle obtained for the 1s-1s direct potential given in section 5.1.1 and also consistent with equation (5.20).
5.4.2 1s-2s partial-wave exchange potential in closed form

For the 1s-2s transition, Maple evaluates the $J = 0$ partial-wave exchange potential as

$$
\tilde{V}^{X2s0(0)}_{1s0S}(E; k', k) = (-1)^S \frac{16 \sqrt{2}}{\pi} \left[ \frac{-(4k^2 - 1)(5 + 8E)}{(1 + k^2)^2 (1 + 4k^2)^3} \right.
+ \frac{4P(k', k)}{(1 + k^2)(1 + 4k^2)^2(9 + 4K^2)(9 + 4K^2)^2},
\right]
$$

(5.30)

where the polynomial $P$ is

$$
P(k', k) = 256k^2(k'^2 + k^2)K^2K^2 - 64k^6 - 464k^4 + 2688k^2k'^4 - 3264k^4k'^2
- 1476k'^2 + 5584k^2k'^2 + 2952k^2 + 2944k^6 + 6976k^4 - 1701.
$$

(5.31)

This expression also gives the partial-wave exchange potential for the 2s-1s transition using the equivalent symmetry relationship (2.42) for potentials. Singularities for the half-off-shell partial-wave exchange potentials are summarized by

$$
\tilde{V}^{X2s0(0)}_{1s0S}(E; k_{2s}, z), \quad z = \left\{ \pm i \frac{1}{2}, \frac{k_{2s} \pm i}{2}, \frac{3}{2}, \frac{-k_{2s} \pm i}{2}, \frac{3}{2} \right\};
$$

$$
\tilde{V}^{X2s0(0)}_{1s0S}(E; z, k_{1s}), \quad z = \left\{ \pm i, \frac{k_{1s} \pm i}{2}, \frac{3}{2}, \frac{-k_{1s} \pm i}{2}, \frac{3}{2} \right\}.
$$

(5.32)

Similar singularities exist for the 2s-1s exchange potential due to the symmetry property of potentials. Hence, since $k_{1s}$ has the larger momentum, the contour-rotation angle $\alpha$ must not exceed $\tan^{-1} \frac{3}{2k_{1s}}$. These results yield the same as the maximum contour-rotation angle derived from the 1s-2s full direct-potential.
5.4.3 2s-2s partial-wave exchange potential in closed form

Although maple6 calculates the closed-form expression for the 2s-2s $J = 0$ partial-wave exchange potential, it is a large expression needing manual simplification to reduce it to a more readable form. The simplified result is

\[
\hat{v}^{X2s0(0)}_{2s0S}(E; k', k) = (-1)^s \frac{8}{\pi} \left[ \frac{-32 (1 + 4E) (4k^2 - 1) (4k'^2 - 1)}{(1 + 4k^2)^3 (1 + 4k'^2)^3} \right] P(k', k) \\
+ \frac{P(k', k)}{(1 + 4k'^2)^2 (1 + 4k^2)^2 (1 + k'^2)^3 (1 + k^2)^3}
\]

(5.33)

with the polynomial

\[
P(k', k) = 13 - 121k^4 - 121k'^4 - 273k^6 + 64k^2k'^12 + 13k'^2 - 273k^6 + 13k^2 \\
+ 177k'^4k^2 + 177k'^2k^4 - 46k'^2k^2 - 1904k^8k^4 - 192k'^10k^4 \\
+ 544k^8k'^2 - 192k'^10k^4 + 128k^8k'^4 + 544k'^10k^2 + 2752k^6k'^6 \\
+ 128k^6k'^8 - 1904k^4k'^4 + 488k^6k'^4 + 820k^6k'^2 + 820k^8k'^2 \\
+ 488k^6k^4 + 1720k^4k'^4 + 504k^6k'^2 - 76k^10 - 16k'^12 - 76k'^10 \\
- 212k^8 - 212k^8 - 16k'^12 + 64k^12k'^2 + 504k^6k^2.
\]

(5.34)

The singularity-structure analysis of the half-off-shell 2s-2s first-order partial-wave exchange potentials $\hat{v}^{X2s0(0)}_{2s0S}(E; k, z)$ and $\hat{v}^{X2s0(0)}_{2s0S}(E; z, k)$ yields singular points at $z = \left\{ \pm i \frac{1}{2}, k_{2s}, -k_{2s}, -i \right\}$, and therefore, the contour rotation is restricted to angles less than $\tan^{-1} \frac{1}{k_{2s}}$. This is also the same result obtained for the full 2s-2s direct potential.

Analysing the first-order partial-wave exchange-potential singularity structures for other s-orbital transitions gives similar results to those presented in the preceding discussion, but the closed-form expressions become very large as the principal quantum numbers increase. Unfortunately, Maple cannot complete the outer integration to evaluate higher-order partial
waves for the e-H exchange potential without intervention. The reason is simply due to the explosive growth in the number of integrals and maple6's inability to simplify the generated expressions prior to evaluation. The expression resulting from the inner integration suggests that the partial-wave exchange potential grows rapidly in size with increasing partial-wave order \( J \) and target excitation.

These observations indicate that the singularity structures of exchange potentials impose the same limitations on the contour-rotation angle as the direct potentials. Therefore, the exchange potentials are also expressed in an appropriate form for their analytic continuation into complex-momentum space under a rotated-contour scheme. However, it is shown in section 5.5.2 that in order to compute numerically half-off-shell partial-wave exchange potentials for e-H scattering, a more restrictive condition must be imposed on the contour-rotation angle \( \alpha \) than that imposed by the direct and exchange-potentials' singularity structures.

### 5.5 Evaluating Partial-Wave Exchange Integrals

Since it is not possible to give generalised analytic forms for the exchange potentials for use in practical calculations, the integrals must be evaluated numerically. Choosing complex momentum as required for a rotated-contour method requires considerable care. This section is devoted to describing strategies for evaluating partial-wave exchange potentials under the rotated-contour scheme for the \( s \)-wave model e-H scattering problem. Calculating exchange potentials consists of two parts. Firstly, there is an energy-dependent contribution resulting from the electron-core interaction which is relatively easy to calculate.
using numerical methods. It is also possible for maple6 to evaluate the energy-dependent contribution in closed form. However, this option has not been implemented in the numerical software since the energy-dependent term only contributes under special conditions ($\lambda = 0$, see equation (2.69)) and the efficiency gain would be small. The second contribution to the exchange potential arises from the electron-electron interaction and is a considerably more involved problem to solve. The numerical calculation of the partial-wave direct matrix elements is a simpler procedure which is discussed in section 6.1.1.

5.5.1 Integrals for the energy-dependent exchange potential

The focus in this section is on evaluating the pair of coordinate-space integrals in equation (2.69) for the s-wave model of e-H scattering with real and complex momenta. Containing the simplest integrals in the exchange potential, this energy-dependent term is the easiest to implement an appropriate numerical method of solution for a rotated-contour scheme. Equation (2.69) shows that the energy-dependent term consists of two separable coordinate-space integrals. Numerical computation of these uncoupled integrals can be handled in a relatively simple manner under a contour-rotation scheme. Three cases must be considered:

(i) the on-shell case, in which both momenta, $k$ and $k'$, are the real valued physical momenta of the incident and scattered electron;

(ii) the off-shell case, where both momenta are quadrature mesh points that have been rotated into the complex plane;

(iii) the half-off-shell case, with one of the momenta being a complex-valued quadrature point, while the other is a real-valued physical momenta.
Typically, the exchange integrals are evaluated for real values of momenta using standard numerical integration techniques. However, for the complex values of momenta inherent in the off-shell and half-off-shell rotated-contour calculations, serious numerical difficulties can arise in handling the numerical computation of regular Coulomb functions with complex arguments. In the case of a neutral atomic target, these Coulomb functions reduce to spherical Bessel functions, and as shown in section 4.1.3, these functions oscillate with an exponentially increasing amplitude in the complex plane if the imaginary part of their argument increases in magnitude without limit, leading to wildly inaccurate results or numerical overflow of the floating-point arithmetic.

The approach taken to solve this difficulty is to apply an appropriate counter-rotation to the coordinate-space variables, $r_1$ and $r_2$, so that the products $kr_1$ and $kr_2$ are always real-valued for off-shell momenta. This idea was proposed in Chapter 4 for calculating general potentials which do not have closed-form solutions. For a local potential like the Yukawa potential, there are problems in using the counter-rotation approach to evaluate half-off-shell potentials, as was discussed in section 4.1.3 on page 72. However, applying a counter-rotation method to evaluate the $e$-$H$ exchange integrals for complex momenta has the advantage that the exchange operator acts to ensure that the Coulomb functions have different coordinate-space variables. These variables can be independently counter-rotated without encountering the difficulties described for local potentials in section 4.1.3.
On-shell energy-dependent exchange potential

In the on-shell case, both momenta are real and therefore the integrals are evaluated along the real axis without resorting to a counter-rotation. This involves evaluating the integrals

\[ \int_0^\infty dr_1 \ h_e'(k',r_1) \int_0^\infty dr_2 \ h_e(k,r_2) \]  \hspace{1cm} (5.35)

via standard quadrature methods, where the function \( h_e(k,r) \) is defined in equation (2.65).

Off-shell energy-dependent exchange potential

In the off-shell case, the solution to the problem with complex-valued momenta is to counter-rotate the coordinate-space variables through the same angle of rotation that has been applied to both momenta, but with the rotation applied in the opposite direction. This is possible because the integrands, \( h_e'(k',r_1) \) and \( h_e(k,r_2) \), are composed of analytic functions (sinusoids and exponentials) which are not singular in the complex coordinate-space. Counter-rotations in coordinate-space effectively compensate for the complex valued, rotated off-shell momenta, \( k' = |k'| e^{-i\alpha} \) and \( k = |k| e^{-i\alpha} \), which arise naturally in the Coulomb functions under a rotated-contour scheme. After applying a counter rotation in coordinate-space, the energy-dependent integral for the off-shell momenta becomes

\[ \int_0^\infty dr_1 \ e^{i\alpha} h_e'(k',r_1 e^{i\alpha}) \int_0^\infty dr_2 \ e^{i\alpha} h_e(k,r_2 e^{i\alpha}) . \]  \hspace{1cm} (5.36)

Writing \( h_e(k,r) = e^{i\alpha} h_e(k,r e^{i\alpha}) \) identifies the counter-rotated integrand and allows this integral to be written more compactly as

\[ \int_0^\infty dr_1 \ h_e'(k',r_1) \int_0^\infty dr_2 \ h_e(k,r_2) . \]  \hspace{1cm} (5.37)
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Half-off-shell energy-dependent exchange potential

In the two half-off-shell cases, a coordinate-space counter-rotation is applied only to the respective integral containing the complex off-shell momenta. Therefore, if \( k' \) is the off-shell momenta, then the energy-dependent integral is calculated by evaluating

\[
\int_0^\infty dr_1 \ h^i_\sigma(k',r_1) \int_0^\infty dr_2 \ h_t(k,r_2). \tag{5.38}
\]

Similarly, when \( k \) is the off-shell momenta, the energy dependent exchange integral is calculated from

\[
\int_0^\infty dr_1 \ h^c_\sigma(k',r_1) \int_0^\infty dr_2 \ h_a(k,r_2). \tag{5.39}
\]

Counter rotating in coordinate-space guarantees that in each of the integral equations (5.37) to (5.39), the Coulomb functions always have real arguments, allowing the computation to be done using standard numerical quadrature integration without encountering floating-point overflow problems. Thus, the energy dependent term of the exchange integral is easily calculated numerically under a rotated-contour scheme by applying an appropriate counter-rotation in coordinate-space. However, evaluating the double integral in equation (2.64) for the two-electron contribution to the exchange potential using a rotated-contour method is a considerably more challenging numerical problem to solve.

5.5.2 Integrals for the two-electron exchange potential

The double integral in the second term of equation (2.64) cannot be evaluated as two independent single-dimensional integrals, as was the case for the energy-dependent term. The existence of the min \((r_c)\) and max \((r_a)\) functions within the double integral
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\[
\int_0^\infty dr_1 \int_0^\infty dr_2 \ h_c^\prime(k', r_1) \ \frac{r_<^\lambda}{r_>^\lambda+1} \ h_c(k, r_2),
\]

(5.40)

make it impossible to completely disentangle the two integrations. A common technique employed to handle this type of double integration also produces an efficient algorithm for numerically evaluating the integrals. Consider the integral having the general form

\[
I = \int_0^\infty dr_1 \int_0^\infty dr_2 \ f(r_1) \ \frac{r_<^\lambda}{r_>^\lambda+1} \ g(r_2).
\]

(5.41)

Such a double integral can also be evaluated using the equivalent expression

\[
I = \int_0^\infty dr_1 \ \frac{f(r_1)}{r_1^\lambda+1} \ \int_0^{r_1} dr_2 \ r_2^\lambda g(r_2) + \int_0^\infty dr_2 \ \frac{g(r_2)}{r_2^\lambda+1} \ \int_0^{r_2} dr_1 \ r_1^\lambda f(r_1).
\]

(5.42)

Swapping the coordinate variable labels in the second term allows this expression to be written as

\[
I = \int_0^\infty dr_1 \ \frac{f(r_1)}{r_1^\lambda+1} \ \int_0^{r_1} dr_2 \ r_2^\lambda g(r_2) + g(r_1) \ \int_0^{r_1} dr_2 \ r_2^\lambda f(r_2)
\]

(5.43)

Transforming (5.43) into its corresponding numerical quadrature integrations, the double integral is numerically evaluated using

\[
I \approx \sum_{n=1}^N w_n f(r_n) \left( T_n^{(l)}(g, r) - w_n g(r_n) \frac{r_n^\lambda}{r_n^{\lambda+1}} \right) + w_n g(r_n) T_n^{(h)}(f, r).
\]

(5.44)

where \( T_n^{(l)}(t, r) \) is the numerical quadrature integral

\[
T_n^{(l)}(t, r) = \sum_{m=1}^n w_m r_m^\lambda t(r_m).
\]

(5.45)
These equations provide the numerical integration techniques for efficiently evaluating
equation (5.40). As with the energy dependent term, the on-shell, off-shell and half-off-
shell cases need to be treated separately.

**On-shell two-electron exchange potential**

Considering the on-shell case first, as both values of momenta are real, counter-rotation in
coordinate-space is not required to evaluate (5.40) numerically. Therefore, the two-electron
integral for on-shell momenta is calculated by numerically evaluating

\[
\int_0^\infty dr_1 \, h_c^*(k', r_1) \int_0^{r_1} dr_2 \, r_2^\lambda \, h_c(k, r_2) + h_c(k, r_1) \int_0^{r_1} dr_2 \, r_2^\lambda \, h_c^*(k', r_2)
\]

\( r_1^{\lambda+1} \) \hspace{1cm} (5.46)

**Off-shell two-electron exchange potential**

In the off-shell case, both values of momenta are complex and counter-rotating both \( r_1 \) and
\( r_2 \) provides an integral form for the two-electron exchange potential that can be computed
numerically. Precisely how to apply this counter-rotation requires some care, especially
with respect to the min and max functions. The potential between the free and bound
electrons is

\[
V_{12} = \frac{1}{|r_1 - r_2|}.
\]

\( 5.47 \)

However, before introducing the rotated coordinate variables, the absolute value function
must be expressed in a form that allows the analytic continuation of the \( r \)'s into the
complex plane. A suitable form for the two-electron potential is given by
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\[
\frac{1}{|r_1 - r_2|} = \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \hat{r}_1 \cdot \hat{r}_2}}. \tag{5.48}
\]

To make it clear why this is necessary, consider counter-rotating the coordinate vectors' magnitudes in the absolute function, giving

\[
\frac{1}{|r_1 e^{i\alpha} - r_2 e^{i\alpha}|} = \frac{1}{|\left(r_1 - r_2\right) e^{i\alpha}|} = \frac{1}{|r_1 - r_2| |e^{i\alpha}|} = \frac{1}{|r_1 - r_2|}. \tag{5.49}
\]

This result suggests that the counter-rotated potential has the same form as no rotation at all, a situation that intuitively must be incorrect. Hence, the two-electron potential must be expressed in another form.

For this purpose, a useful expansion for any \(|t| \leq 1\) and \(|u| \leq 1\) is given by

\[
\frac{1}{\sqrt{1 + t^2 - 2 tu}} = \sum_{\lambda=0}^{\infty} t^\lambda P_\lambda(u). \tag{5.50}
\]

To apply this relationship in the expansion of the two-electron potential (5.48), two cases require consideration: when \(r_1 > r_2\); and when \(r_2 > r_1\). The appropriate expansion for real \(r_1, r_2\) is

\[
\frac{1}{|r_1 - r_2|} = \frac{1}{r_<} \sum_{\lambda=0}^{\infty} \left( \frac{r_<}{r_>} \right)^\lambda P_\lambda(\hat{r}_1 \cdot \hat{r}_2). \tag{5.51}
\]

If both magnitudes, \(r_1\) and \(r_2\), are counter-rotated by the same rotation, \(e^{i\alpha}\), then the generalisation of (5.51) is

\[
\frac{1}{r_< e^{i\alpha}} \sum_{\lambda=0}^{\infty} \left( \frac{r_<}{r_>} \right)^\lambda P_\lambda(\hat{r}_1 \cdot \hat{r}_2). \tag{5.52}
\]

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As an intuitive check, taking the limit \( r_1 \to r_{22} \) in the expressions (5.52) gives a consistent result in both cases. This partial-wave expansion is the origin of the min and max functions in equation (5.40). Since equation (5.40) only deals with the magnitudes of the coordinate-space vectors, the angular part of (5.52) contained in the Legendre polynomials can be ignored at this stage. The result expressed by (5.52) shows that the counter-rotation applied to the coordinate-space double integral (5.40) for the off-shell momenta case can be written simply as

\[
\int_0^\infty dr_1 \ e^{i\alpha} h_c'(k', r_1 e^{i\alpha}) \int_0^\infty dr_2 \ e^{i\alpha} \frac{r_2^\lambda}{r_{12}^{\lambda+1}} h_c(k, r_2 e^{i\alpha}).
\]  

(5.53)

Converting this expression to a form similar to (5.43) gives the integral equation

\[
\int_0^\infty dr_1 \ e^{i\alpha} \frac{h_c'(k', r_1 e^{i\alpha})}{r_1^{\lambda+1} e^{i\alpha}} \int_0^{r_1} dr_2 \ e^{i\alpha} r_2^\lambda h_c(k, r_2 e^{i\alpha}) + \int_0^\infty dr_1 \ e^{i\alpha} \frac{h_c(k, r_1 e^{i\alpha})}{r_1^{\lambda+1} e^{i\alpha}} \int_0^{r_1} dr_2 \ e^{i\alpha} r_2^\lambda h_c'(k', r_2 e^{i\alpha}).
\]  

(5.54)

Simplifying the notation again by inserting \( h_a(k, r) = e^{i\alpha} h_c(k, r e^{i\alpha}) \) allows this result to be written in a form similar to the on-shell expression (5.46), i.e.

\[
\int_0^\infty dr_1 \ \frac{h_a'(k', r_1)}{r_1^{\lambda+1} e^{i\alpha}} \int_0^{r_1} dr_2 \ r_2^\lambda h_a(k, r_2) + h_a(k, r_1) \int_0^{r_1} dr_2 \ r_2^\lambda h_a'(k', r_2).
\]  

(5.55)

When the double integrals are converted to a numerical quadrature, tests confirm that expression (5.55) gives the correct results for the off-shell calculation compared to analytic calculations done with the aid of computer algebra and Maple.
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Half-off-shell two-electron exchange potential

Finally, the half-off-shell case is considered. Initially, the approach taken was similar to that taken in the off-shell case, noting that only one value of momenta will be complex. To be specific, let $k'$ be the off-shell momenta, such that $k' = |k'| e^{-i\alpha}$. Therefore, only a counter-rotation of $r_1$ is required, in which case, the expanded two-electron potential is

\[
\frac{1}{r_1} \sum_{\lambda=0}^{\infty} \left( \frac{r_2}{r_1} \right)^{\lambda} P_{\lambda}(\hat{r}_1 \cdot \hat{r}_2), \quad r_1 > r_2
\]

and

\[
\frac{1}{r_2} \sum_{\lambda=0}^{\infty} \left( \frac{r_1}{r_2} \right)^{\lambda} P_{\lambda}(\hat{r}_1 \cdot \hat{r}_2), \quad r_2 > r_1.
\]

(5.56)

Repeating the intuitive check for consistency in these expressions by taking the limit $r_1 \rightarrow r_2e^{i\alpha}$ reveals an obvious inconsistency in the complex exponential's sign. It appears that the simple technique used to apply the counter-rotations for the off-shell case is not applicable in the half-off-shell case, where only one counter-rotation is applied.

A solution to this problem may be found by expanding the double integral in the more conventional way such that the exchange integral has the form

\[
\int_0^{\infty} dr_1 \ e^{i\alpha} h_c'(k', r_1) \left[ \frac{1}{r_1^{\lambda+1}} \int_0^{r_1} dr_2 \ r_2^\lambda h_c(k, r_2) + r_1^\lambda \int_0^{\infty} dr_2 \ h_c(k, r_2) \right].
\]

(5.57)

Proceeding with a counter-rotation applied to the $r_1$ variable, this double integral becomes

\[
\int_0^{\infty} dr_1 \ e^{i\alpha} h_c'(k', r_1 e^{i\alpha})
\]

\[
\times \left[ \frac{1}{(r_1 e^{i\alpha})^{\lambda+1}} \int_0^{r_1 e^{i\alpha}} dr_2 \ r_2^\lambda h_c(k, r_2) + (r_1 e^{i\alpha})^\lambda \int_0^{\infty} dr_2 \ h_c(k, r_2) \right].
\]

(5.58)
Now the inner integrals must be evaluated over complex ranges, so although the counter-rotation eliminates the undesirable effect of the complex momentum $k'$, the problem is simply transferred to the inner $r_2$ integrals. At this stage it should be noted that this difficulty is only a numerical problem associated with evaluating the Coulomb function with a complex argument. For the special case of neutral targets like hydrogen, the Coulomb functions reduce to spherical Bessel functions, which in turn can be expressed as linear combinations of spherical Hankel functions.

The spherical Hankel functions $h^{(1)}$ and $h^{(2)}$ contain exponential factors $e^{ikr}$ and $e^{-ikr}$, respectively, which produce the oscillating characteristics of the spherical Bessel function. These exponential factors are the root of the problem when dealing with rotated complex momenta. If the product $kr$ is complex, then one of these exponentials grows rapidly and causes problems in the floating-point arithmetic of any numerical calculation. On the other hand the magnitude of the bound-state eigenfunction $\varphi_{n'l'}(r)$ eventually it decays exponentially as $e^{-r/l'}$ for sufficiently large $r$. When the spherical Bessel function and bound state eigenfunction are combined in $h_c(k,r)$ for real values of $r$, the exponentially decreasing factor $e^{-r/l'}$ ultimately damps the spherical Bessel oscillations as $r$ becomes large. This observation can be used to prevent numerical problems arising in evaluating the two-electron partial-wave exchange potential in the half-off-shell case, as is now demonstrated.
First consider defining the function $h_c(k,r)$ as

$$h_c(k,r) = \frac{1}{2} \left[ \tilde{u}_L^{(1)}(kr) e^{ikr} + \tilde{u}_L^{(2)}(kr) e^{-ikr} \right] \tilde{\phi}_{n'k}(r) e^{-r/n'}.$$

(5.59)

where $\tilde{\phi}_{n'k}(r) = \phi_{n'k}(r) e^{r/n'}$. The modified functions $\tilde{u}_L^{(1,2)}(kr)$ are related to the spherical Hankel functions by $\tilde{u}_L^{(1)}(kr) = \tilde{h}_L^{(1)}(kr) e^{-ikr}$ and $\tilde{u}_L^{(2)}(kr) = \tilde{h}_L^{(2)}(kr) e^{ikr}$. Now suppose variable $r$ is replaced by the complex value $z = r(\cos \alpha + i \sin \alpha)$ resulting from a counter-rotation through a positive rotation angle $\alpha$. Equation (5.59) then becomes

$$h_c(k,z) = \frac{1}{2} \left[ \tilde{u}_L^{(1)}(kz) e^{ikz - z/n'} + \tilde{u}_L^{(2)}(kz) e^{-ikz - z/n'} \right] \tilde{\phi}_{n'k}(z).$$

(5.60)

The conditions needed for this expression to be numerically computable at large magnitudes of $z$ (large $r$) are that the exponentials must always produce damping of the oscillatory terms, i.e. $\text{Re}(\pm ikz - z/n') < 0 \to -r \sin \alpha - \frac{r}{n'} \cos \alpha < 0$. Therefore, the counter-rotation angle is restricted to the range defined by

$$-\frac{1}{n'k} < \tan \alpha < \frac{1}{n'k}.$$  

(5.61)

Since the counter-rotation angle must be positive, the negative values of $\alpha$ are discarded.

The smaller the rotation angle $\alpha$, the more rapidly the exponential damps the oscillations; a safe choice of rotation angle adopted for the numerical calculations in this thesis was

$$\alpha \leq \frac{1}{2} \tan^{-1} \frac{1}{n'k}.$$  

(5.62)

If $\alpha$ is chosen to be too large (close to the upper limit), then numerical problems may occur before $r$ is sufficiently large to bring about damping. Obviously, this restriction imposes a similar condition upon the allowed contour-rotation angle that can be applied to the off-
shell momenta.

There still remains a numerical difficulty in using equation (5.60). The two functions \( u_{l}^{(1,2)}(kz) \) are irregular at the origin, so numerical problems can occur when the magnitude of \( kz \) is small, leading to a divergent result, particularly for the higher-order partial waves. This is overcome by first integrating a short distance along the complex contour, evaluating the function \( h_{c}(k,z) \) in its normal form,

\[
h_{c}(k,z) = u_{L}(kz) \varphi_{n_{l}l_{l}}(z),
\]

then switching to equation (5.60) as the magnitude of \( kz \) increases. The switch over point must increase with the partial-wave order \( J = L \) and has been selected in this application to be the point given by

\[
|kz| = \frac{1}{2}(L + 1).
\]

Although employing this strategy requires calculating \( u_{L}(kz) \) for a complex argument, using (5.64) ensures that the function can be calculated numerically without arithmetic problems. This procedure then allows equation (5.58) to be evaluated for the half-off-shell case under the condition imposed by (5.62). For the other half-off-shell case in which \( k \) is the contour rotated off-shell momenta, \( r_{2} \) is counter-rotated and the double integral is evaluated by

\[
\int_{0}^{\infty} dr_{2} \; e^{i\alpha} h_{c}(k,r_{2}e^{i\alpha}) \times \left[ \frac{1}{(r_{2}e^{i\alpha})^{\lambda + 1}} \int_{0}^{r_{2}e^{i\alpha}} dr_{1} r_{1}^{\lambda} h_{c}^{*}(k',r_{1}) + (r_{2}e^{i\alpha})^{\lambda} \int_{r_{2}e^{i\alpha}}^{\infty} dr_{1} \frac{h_{c}^{*}(k',r_{1})}{r_{1}^{\lambda + 1}} \right].
\]
and the suitable contour-rotation angle is limited to

\[ \alpha \leq \frac{1}{2} \tan^{-1} \frac{1}{n\,k'} \]  \hspace{1cm} (5.66)

Hence, numerically evaluating the e-e exchange potentials in the half-off-shell case imposes further limitations (5.61) on the maximum contour-rotation angle (5.20) derived for the remaining portion of the full potential. This condition is purely the result of numerical calculations being limited in practice to the finite set of numbers that can be represented in floating-point arithmetic. For a typical scattering energy of 54.42eV, a 1s-4s transition can utilise an optimum contour-rotation angle of 16° if the exchange potential is not included. If exchange is included, then (5.62) limits the optimum contour rotation to no more than 3.5°, and with such a small rotation angle, convergence of the T-matrix solution will be difficult to obtain. In the next chapter, analytic and numeric results for potential matrix elements, second Born T-matrix elements and full T-matrix elements calculated on a rotated contour are given for the s-wave model of the electron-hydrogen scattering problem using the numerical software developed to implement the methods described in this chapter.
Chapter 6
Rotated-Contour CC(ns) Electron-Hydrogen Scattering Results

In this chapter, analytic and numerical results for partial-wave direct and exchange potentials, second-Born T-matrix amplitudes, full T-matrix elements and differential cross sections calculated using a rotated-contour method are presented and assessed for the s-wave model of electron-hydrogen scattering. First, a brief overview of the changes made in the numerical software to accommodate a rotated-contour method is presented with an emphasis on calculating the direct and exchange potentials for real and complex momenta. Results are then furnished for a one-channel calculation involving only the elastic 1s-1s transition for electron-hydrogen scattering. Following this, the calculation is extended to a basic coupled-channels calculation that includes 1s and 2s target states for which results are given for a rotated-contour calculation. Finally, differential cross section data for a three-state coupled-channels calculation are presented with 1s, 2s, and 3s target states.

6.1 Program Structure and Methodology

A significant proportion of time during this thesis was devoted to writing and modifying software source code. With the vast number of modifications made to the C++ code derived from the original FORTRAN program that ultimately produced the TCrossWin software, extensive testing had to be performed to ensure that the modified program calculated V-matrix and T-matrix elements correctly on a rotated contour. The new
program, which is provided on the included CDROM, has also been designed to calculate T-matrix amplitudes on a non-rotated contour using the standard regularisation method for principal-value integration. Consequently, throughout the entire modification process, testing was performed using the calculated results from the original FORTRAN program as a benchmark. This process, coupled with modifications made in incremental steps, reduced the incidence of coding errors, and any problems that did emerge were quickly identified and corrected.

Many options have been designed into the TCrossWin software. Settings can be changed without rerunning the program and are optionally saved when the program is closed, ready for reloading when the program is next executed. Figure 6.1 shows the interaction setting panel of the computation setting dialog box from TCrossWin. Of these options, three
provide for studying the potential matrix elements, allowing the selection of the direct potential only, the exchange potential only or both the direct and exchange potentials. This option permits the direct and exchange contributions to the potentials to be studied in isolation if required.

6.1.1 Calculating s-wave direct potentials on a rotated contour

An initial examination of the near closed-form expressions (2.54), (2.55) and (2.53) developed by McCarthy and Stelbovics (1983) to calculate the phase-modified momentum-space partial-wave direct matrix elements indicates that these equations should be adaptable to handling the complex momenta required under a rotated-contour scheme. The analytic structure of the s-orbital direct potentials was discussed in the previous chapter and reveals that they are in a suitable form for their analytic continuation into complex momentum-space. Hence, numerically computing s-wave partial-wave direct potentials on a rotated contour is a reasonably straightforward complex arithmetic calculation. Based on this observation, the implementation in the C++ code that was derived from the original FORTRAN program simply involved minor modifications so that the magnitudes of momenta were treated as complex values, rather than the usual real values. Naturally, complex arithmetic calculations are done only where necessary, keeping computation overheads as low as possible. The angular contributions contained in the expressions (2.54) and (2.55) are unaffected by the rotated-contour method; it is only the momentum radial contribution from (2.53) that needs to be considered.
The main difficulty in calculating direct potentials with complex momenta in the new C++ code is that the original FORTRAN program used the adaptive Romberg integration routine QA05AD to evaluate the polar integral whenever the direct matrix element is calculated on the diagonal. A program option also allows adaptive Romberg integration to be carried out for the full angular integration, rather than using Gaussian quadrature for off-diagonal points. The QA05AD routine is designed specifically for integrating real-valued functions only. In the conversion to C++, the original FORTRAN adaptive Romberg algorithm has not been altered, and rather than attempting a complete rewrite or modifying the routine so that it integrates the required complex-valued functions arising from the rotated-contour method, a simpler approach is taken.

Each complex-valued function $w(t)$ of a real independent variable $t$ can be written as the sum of real and imaginary parts: $w(t) = \text{Re}w(t) + i\text{Im}w(t)$. Evaluating the integral of such a complex-valued function with respect to the real independent variable can be accomplished by observing that

$$\int dt \ w(t) = \int dt \ \text{Re}w(t) + i \int dt \ \text{Im}w(t). \quad (6.1)$$

Applying this technique to evaluate the partial-wave direct matrix elements, the integral (2.53) is written in the form

$$g_{l',l}^{N}(k',k) = 2\pi (k')^{l'-\lambda} k^{\lambda} \left( \int_{-1}^{1} du \ \text{Re}f(K,u) + i \int_{-1}^{1} du \ \text{Im}f(K,u) \right), \quad (6.2)$$

where $f(K,u) = P_{l''}(u) K^{-(l''+2)} g_{l''}^{N}(K)$. Clearly, both integrals in (6.2) have integrands that are real-valued functions and therefore, the numerical evaluation of this expression can
be performed using an integration routine that only integrates real functions. The penalty for employing such a solution is that the complex-valued function \( f(K, u_i) \) is evaluated twice at each quadrature point \( u_i \), doubling the computation time that is already increased by the need for complex arithmetic. If computation speed were a serious problem, then storing the intermediate values \( f(K, u_i) \) during the first integration allows their reuse in the second integration without needing to recompute them. At present, there is little advantage in such added complications, although, computation speeds for calculations with large integration grids would improve with intermediate storage of \( f(K, u_i) \).

Since the electron-core contribution to the direct potentials are computed using the same basic algorithm that calculates the two-electron contribution, once the appropriate coding modifications are made to compute the two-electron matrix elements on the rotated contour, the electron-core component should also be calculated correctly.

### 6.1.2 Calculating exchange potentials on a rotated contour

Calculating partial-wave exchange potentials under a rotated-contour scheme requires special treatment, as discussed for each of the four cases of on-shell, off-shell and two half-off-shell potentials in section 5.5. Apart from modification of the original code to handle complex momenta, the key area of the exchange-potential algorithm that needs significant changes is in evaluating the coordinate-space integrals for the two-electron term, given by equation (2.64) and for the energy-dependent term in equation (2.68). The counter-rotation method described in section 5.5 for evaluating these integrals numerically with various combinations of real and complex momenta has been implemented in the software, with
the appropriate counter-rotation applied. Evaluating the half-off-shell exchange potentials is more complicated than the on-shell and off-shell potentials, as it requires spherical Bessel functions of the first kind with complex arguments.

The original FORTRAN code also implemented various options for overcoming the non-uniqueness problem associated with the matrix solution of the momentum-space T-matrix Lippmann-Schwinger equation (Bray & Stelbovics, 1995a). Some segments of the algorithm were modified implicitly as a consequence of the changes needed to implement a rotated-contour calculation of the exchange energy-depended term coordinate-space integrals. Other areas of code were modified such that each case of real and complex momenta combinations were evaluated separately, as required for the exchange coordinate-space integrals.

6.2 Single-Channel e-H Elastic Scattering – CC(1s)

Benchmark results are provided by solving the Lippmann-Schwinger equation along the real momentum axis for the second-Born and the full T-matrix. Computer algebra and maple6 provide a convenient means of testing numerical methods for the potential calculations by giving closed-form expressions for the partial-wave direct potentials and for a number of first-order partial-wave exchange potentials. Further, the second-Born T-matrix can be evaluated from the analytic potentials to any desired precision using Maple. Thus, all aspects of the rotated-contour method may be tested by comparing numerical results against these benchmarks.
6.2.1 Direct potential for the 1s-1s transition

Since the 1s-1s direct potential is quite simple, it is natural to examine it in detail and to compare numerically-calculated partial-wave direct matrix elements for \( J = 0 \) with the analytic expression derived with Maple. A low energy collision in which the electron energy is 13.6eV (0.5 au) is chosen to allow a reasonably large contour-rotation angle. The on-shell momentum is \( k_s = 1 \). In this case, equation (5.21) gives \( \alpha = 63.4^\circ \) as the maximum contour-rotation angle that can be used to calculate the 1s-1s direct potential on a rotated contour. The direct potential is calculated numerically by the TCrossWin program using equation (2.58), evaluating the integration over the direction cosine \( u \) in equation (2.53) as the last step in the calculation. In Chapter 2, expression (5.24) was used to check the numerical 1s-1s direct-potential calculations on a small 4-point non-rotated momentum-space quadrature mesh. This same expression is used here to verify the numerical 1s-1s direct potentials calculated on a four-point contour, rotated by an angle of 30\(^\circ\), which is

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Table 6.1: 1s-1s partial-wave \((J = 0)\) direct potentials for 13.6eV \((k_s = 1)\) e-H scattering computed numerically and analytically for a four-point momentum grid contour-rotated by \( \alpha = 30^\circ \). On-shell momenta have indices \( i = i' = 1 \), while for off-shell rotated quadrature indices are 2-5.
very near the optimum rotation angle for this transition and on-shell momentum.

Results for the numerical calculation using the TCrossWin software for the $J = 0$ partial-wave $1s-1s$ direct-potential matrix elements are listed in Table 6.1. This data has been computed using identical computation settings (integration mesh sizes, etc.) to those used in calculating the data listed in Table 2.1 for the non-rotated calculation. The analytic calculations using Maple are also shown for comparison in the right-hand column, and indicate excellent agreement with the numerical results. In this thesis, it has been found

![Graph](Image)

**Figure 6.2:** $1s-1s$ half-off-shell partial-wave ($J = 0$) direct potential for e-H scattering at 13.6eV. These graphs show the real and imaginary parts of the direct potential for analytic and numerical calculations with a contour-rotation angle $\alpha = 30^\circ$. 
that half-off-shell potentials present the greatest difficulties for their numerical computation on a rotated contour. In light of this, plots of the half-off-shell 1s-1s direct potentials with on-shell \( k_{1s} = 1 \) are shown in Figure 6.2. These plots show curves for the real and imaginary parts of the analytic equation (5.24) and also discrete points for the real and imaginary parts of the 1s-1s partial-wave \( J = 0 \) direct potential calculated numerically by TCrossWin at the off-shell contour-rotated momentum quadrature points for a 48-point mesh. These numerical and analytic data are in very good agreement, suggesting that the direct-potential's analytic continuation into the complex momentum-space plane has been correctly implemented in TCrossWin.

Another feature of the rotated-contour method is that, in principle, the on-shell second-Born and full T-matrix elements must be independent of the selected contour-rotation angle, subject to the constraints imposed by the maximum allowed rotation angle. Listed in Table 6.2 are 1s-1s on-shell potentials and second-Born T-matrix first-order \( (J = 0) \) partial-wave results for a single-channel direct-potential calculation (without exchange) at various contour-rotation angles between 10° and 80°. The coordinate-space integration mesh consisted of 199 intervals, each with six Gaussian quadrature points. Results for no rotation (0°) are also shown for comparison. The second-Born T-matrix amplitudes clearly show consistent results over a wide range of rotation angle, even within about 10° of the maximum allowed rotation of 63.4°. Above the maximum allowed angle of rotation, there is a complete breakdown in the rotated-contour calculation of the second-Born T-matrix resulting from the crossing of singularities in the half-off-shell potentials in complex momentum-space.
Table 6.2: 1s-1s on-shell direct potential and second-Born T-matrix for 13.6eV ($k_b = 1$) e-H scattering computed numerically (no exchange) for a range of contour-rotation angles $\alpha$, including zero rotation. These are partial-wave ($J = 0$) potentials for even parity, singlet/triplet spin states.

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<th>T-matrix (2nd Born)</th>
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6.2.2 Exchange potential for the 1s-1s transition

Calculating partial-wave exchange potential on a rotated contour numerically requires a smaller rotation angle than is needed for direct potentials. For this case, with the on-shell momentum being $k = k' = k_b = 1$, the rotation must be less than 45°; 22.5° is used as the contour-rotation angle for these calculations. On-shell, off-shell and half-off-shell exchange potentials numerically calculated on a rotated contour by TCrossWin are listed in Table 6.3 for a small four-point momentum-space integration grid. Also listed for comparison in this table are the same exchange potentials calculated analytically by Maple using equation (5.29). Of the numerical potentials listed below, those with relatively large magnitudes are in good agreement with the Maple values, although the accuracy for the numerical calculation deteriorates for potentials with small magnitudes. Errors in such potentials of negligible magnitude do not impact on the overall accuracy of the T-matrix calculations.
Table 6.3: 1s-1s partial-wave \((J = 0)\) exchange potentials for 13.6eV \((k = 1)\) e-H scattering computed numerically and analytically for a four-point momentum grid, contour-rotated by \(\alpha = 22.5^\circ\). On-shell momenta have indices \(i = i' = 1\), while indices for off-shell quadrature points are 2-5.

<table>
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<td>-4.1475e-09 +1.8025e-06</td>
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Since the half-off-shell potentials are the most difficult to calculate numerically on a rotated contour, numerical and analytic results are compared graphically in Figure 6.3 for a 48-point integration mesh in momentum-space. The curves and plotted data shown have been calculated for the contour-rotation angle of 30°, larger than that used to calculate the data listed in Table 6.3. However, Figure 6.3 clearly demonstrates that agreement is still very good between the numerical and analytic calculation of half-off-shell 1s-1s exchange potentials. These results indicate that the 1s-1s exchange potentials are being calculated correctly by the numerical software.

Amplitudes for the second-Born T-matrix with both direct and exchange contributions are listed in Table 6.4 for a range of rotated-contour angles. Inclusion of the exchange potential forces a reduced range of allowed contour-rotation angles due to the counter-rotation
Figure 6.3: 1s-1s half-off-shell partial-wave ($J = 0$) exchange potential 13.6 eV e-H scattering showing the real and imaginary part for analytic and numerical calculations with a contour-rotation angle $\alpha = 30^\circ$.

method of evaluating the half-off-shell exchange potentials. The results show that good convergence is maintained over almost the entire range of rotation, again to within $10^\circ$ of the maximum allowable rotation angle $\alpha = 45^\circ$.

6.2.3 CC(1s) T-matrix elements and differential cross sections

Satisfied that the direct and exchange-potential matrix elements are being calculated by the numerical software with sufficient accuracy under a rotated-contour scheme and having calculated consistent on-shell second-Born T-matrix amplitudes over a range of allowed contour-rotation angles, the results for a full T-matrix calculation are now shown. The
Table 6.4: 1s-1s on-shell potential and second-Born T-matrix for 13.6eV \((k_1 = 1)\) e-H scattering computed numerically for a range of contour-rotation angles \(\alpha\), including no rotation. The partial-wave potentials listed include exchange potentials modified to handle the non-uniqueness problem and are for \(J = 0\), even parity, singlet/triplet spin states.

<table>
<thead>
<tr>
<th>(\alpha (\degree))</th>
<th>V-matrix</th>
<th>T-matrix (2nd Born)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s-1s Singlet spin states</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>5.8686e-02</td>
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First-order \((J = 0)\) partial-wave T-matrix amplitudes calculated at various angles of contour rotation, including the standard regularisation-method calculation for zero rotation, are listed in Table 6.5. Also listed are the first-order partial-wave potentials and determinants of the kernel matrix \(\text{Det}(1-VG_0)\). This determinant is dependent only on the off-shell potentials and therefore, is independent of the chosen contour-rotation angle in the range \([0, \frac{\pi}{2}]\). The reason for this is in the singularity structure of the off-shell potentials, where the analysis in section 5.1 showed that singularities associated with the off-shell potentials only occur on the imaginary axis in complex momentum-space. Therefore, a kernel containing only off-shell potentials can be contour-rotated at any angle in the fourth quadrant of complex momentum-space. The determinants and T-matrix amplitudes listed here in Table 6.5 show satisfactory convergence, indicating that the rotated-contour method is working over the allowed range of contour-rotation angles. Default settings were used in calculating the data listed in Table 6.5 (a), with the exception of the momentum-space
and coordinate-space quadrature meshes. The momentum-space mesh used in the LS equation momentum integrations (2.37) was set to 72 quadrature points, while the coordinate-space mesh used in the exchange potential integrations (2.64) and (2.69) was

Table 6.5: 1s-1s on-shell T-matrix and V-matrix for e-H scattering at 13.6eV ($k_e = 1$) computed for a range of contour-rotation angles $\alpha$, including no rotation. The partial-wave potentials listed include direct and exchange terms for $J = 0$, even parity, singlet/triplet spin states. (a) lists calculations in which the potentials are calculated by numerical integration, while (b) lists results for potentials calculated from the 1s-1s analytic forms (5.24) and (5.29). Also shown are the determinants of the kernel matrix (1-VG0).

(a) Results with V-matrix computed by numerical integration

<table>
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<th>$\alpha$ (°)</th>
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<th>T-matrix</th>
<th>V-matrix</th>
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(b) Results with V-matrix computed from analytic expressions

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<th>T-matrix</th>
<th>V-matrix</th>
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constructed from 199 intervals, each having 8 quadrature points. A large number of coordinate-space mesh points are necessary to obtain reasonably accurate integrations of the oscillatory functions that occur in the exchange integrals. The data listed in Table 6.5 (b) show the results for the same calculation with the first-order partial-wave potentials being computed by the analytic forms (5.24) and (5.29). This is an option in the TCrossWin software for the first-order 1s-1s partial-wave potential. These results demonstrate that highly accurate potentials produce excellent convergence in the T-matrix over a wide range of contour-rotation angles. Similar quality results are obtained for higher-order partial waves.

Lastly, differential cross sections have been calculated using the calculated partial-wave V-matrix and T-matrix elements. Differential cross sections for 1s-1s single-channel e-H scattering are plotted as a function of scattering angle in Figure 6.4 and compared with data supplied by Bray (private communication, October 2001) for the same coupled-channels calculation. Amplitudes computed using the rotated-contour method and those of Bray, are calculated from 10 partial waves and include exchange potentials calculated using a modified form to overcome uniqueness problems associated with the momentum-space coupled-channels equations (Stelbovics, 1990; see also Stelbovics & Berge, 1996). This is an option in the numerical software associated with the exchange-potential computation. The differential cross sections plotted in Figure 6.4 give a very clear indication that the rotated-contour method successfully solved the momentum-space T-matrix Lippmann-Schwinger equation for this simple problem.
Figure 6.4: \(1s-1s\) differential cross section for e-H scattering calculated using a rotated-contour method. The contour-rotation angle was set at \(\alpha = 30^\circ\) with an incident energy of 13.6 eV \((k_{1s} = 1)\).

### 6.3 Two-State Coupling e-H Scattering – CC(1s,2s)

Following the success of the single-channel elastic scattering example, the next simplest case to consider is a coupled-channels calculation involving two channels corresponding to the \(1s\) and \(2s\) target states. Once again, an incident energy of 13.6 eV is chosen to allow a large contour-rotation angle. The on-shell momenta are \(k_{1s} = 1\) and \(k_{2s} = 0.5\), respectively.

With the larger on-shell momentum corresponding to the \(1s\) channel, the maximum contour-rotation angle is \(\alpha = \tan^{-1}(3/2) = 56.31^\circ\) and therefore, the optimum rotation angle is approximately 28°. This angle is sufficiently close to the rotation used for the \(1s-1s\)
single-channel calculation, that the same rotation angle $\alpha = 30^\circ$ is used for the $1s$, $2s$ coupling calculation.

6.3.1 Direct potentials for $2s$-$2s$, $1s$-$2s$ and $2s$-$1s$ transitions

Using equations (5.28) and (5.26), the analytic $2s$-$2s$, $1s$-$2s$ and $2s$-$1s$ half-off-shell direct potentials are plotted in Figure 6.5, Figure 6.6 and Figure 6.7 from numerical results calculated on a rotated contour by the TCrossWin program. It is clear that the numerical data for the half-off-shell direct potentials is in complete agreement with the analytic data.

![Graph of 2s0-2s0 Half-off-shell Partial-wave ($J = 0$) Direct Potential](image)

Figure 6.5: 2s-$2s$ half-off-shell partial-wave ($J = 0$) direct potential for e-H scattering at 13.6eV. The curves illustrate the real and imaginary parts for analytic results, while the points indicate numerically calculated values at off-shell grid points contour-rotated at $\alpha \approx 30^\circ$. 

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6: Results for s-wave model e-H scattering on a rotated contour

![Graph](image_url)

Figure 6.6: 1s-2s half-off-shell partial-wave \((J = 0)\) direct potential.

![Graph](image_url)

Figure 6.7: 2s-1s half-off-shell partial-wave \((J = 0)\) direct potential.
6.3.2 Exchange potentials for 2s-2s, 1s-2s and 2s-1s transitions

Continuing with the 13.6 eV e-H scattering example, the critical counter-rotation angle for numerically calculating the 1s-2s and 2s-1s exchange potentials on a rotated contour is found to be $\tan^{-1}\frac{1}{2} = 26.6^\circ$. Therefore, a safe contour-rotation angle to use is $\alpha = 15^\circ$, as evident from Figure 6.9 and Figure 6.10, which show numerical potentials calculated for the 1s-2s and 2s-1s half-off-shell partial-wave exchange potentials on a 48-point quadrature mesh plotted against exact values calculated from the analytic equation (5.30). The half-off-shell 2s-2s partial-wave ($J = 0$) exchange potential is plotted in Figure 6.8 along with the potentials calculated numerically on the mesh contour-rotated by an angle of $15^\circ$.

![Graph showing 2s-2s half-off-shell partial-wave (J = 0) exchange potential for 13.6 eV (k = 1) e-H scattering calculated on 48-point mesh contour rotated by an angle $\alpha = 15^\circ$.](image)

Figure 6.8: 2s-2s half-off-shell partial-wave ($J = 0$) exchange potential for 13.6 eV ($k = 1$) e-H scattering calculated on 48-point mesh contour rotated by an angle $\alpha = 15^\circ$. 
6. Results for s-wave model e-H scattering on a rotated contour

Figure 6.9: 1s-2s half-off-shell J = 0 partial-wave exchange potential.

Figure 6.10: 2s-1s half-off-shell J = 0 partial-wave exchange potential.
6.3.3 CC(1s,2s) T-matrix and differential cross sections

For a full coupled-channels calculation of the on-shell T-matrix elements using a rotated-contour method, the contour-rotation angle is determined by the constraints imposed on the numerical calculation of exchange potentials. Differential cross sections for a rotated-contour coupled-channels calculation for 1s and 2s target states are plotted in Figure 6.11 for 13.6eV e-H scattering.

![Differential Cross Section for 1s-1s, 1s-2s e-H Scattering](image)

Figure 6.11: 1s-1s and 1s-2s differential cross sections for e-H scattering calculated using a rotated-contour method. The contour-rotation angle was set at $\alpha = 15^\circ$ with an incident energy of 13.6eV.
6.4 Three-State Coupling e-H Scattering – CC(1s,2s,3s)

Lastly, differential cross section results for a rotated-contour calculation are plotted in Figure 6.12 and are compared with the same calculation done using TCrossWin without rotation. Inclusion of the 3s target state requires the rotation angle to be reduced to a value of 7° so that the exchange potentials can be numerically calculated. As with the 1s, 2s coupled-channels cross section results, the three-state coupling calculation on a rotated contour also compares very well with data calculated using a standard CC method. For higher states, convergence is more difficult to obtain due to the small contour-rotation angle involved and it also becomes very difficult to calculate the exchange potentials.

Differential Cross Section for 1s-1s, 1s-2s and 1s-3s e-H Scattering
CC(1s,2s,3s) 13.6eV (rotated-contour α = 7°)

Figure 6.12: 1s-1s, 1s-2s and 1s-3s differential cross sections for 13.6eV e-H scattering calculated using a rotated-contour method at α = 7°.
The results calculated using the TCrossWin software and presented in this chapter demonstrate that the contour-rotation method can be applied to solving the T-matrix Lippmann-Schwinger equation for the simpler s-wave model of the e-H scattering problem. Agreement between rotated-contour and conventional calculations is particularly good in the case of differential cross section results, which when plotted, cannot be distinguished from each other. The incident electron energy used was deliberately low (13.6 eV) so as to allow the use of a large contour-rotation angle. However, similar results are obtained for higher energies such as 54.42 eV and 100 eV, although the rotation angle must be reduced to less than 20°.

Extending the rotated-contour calculation to excitation channels beyond 3s has problems due to the difficult numerical calculation of the half-off-shell exchange potential for complex-valued momentum, which restricts the contour-rotation angle to a smaller value that would otherwise be the case – typically less than 5° for a 13.6eV calculation. Reducing the energy certainly allows use of larger contour-rotation angles, but the maximum rotation angle must always be less than 90° due to the off-shell potential singularity structure.

In the next chapter, the analytic properties for general channels other than those in the s-wave model of e-H scattering are studied.
Chapter 7

Analytic Structure of General Potentials for e-H Scattering

This final chapter is concerned with exploring the analytic properties of general direct and exchange potentials for the electron-hydrogen scattering problem, bearing in mind their suitability for analytic continuation into complex momentum-space under a rotated-contour scheme. Despite the successful application of a rotated-contour method in solving the T-matrix Lippmann-Schwinger equation for the $s$-wave model of electron-hydrogen scattering, it will be demonstrated in this chapter that the situation is quite different when the method is applied to problems involving general target states. In particular, all direct potentials, with the exception of the $s$-wave direct potentials, exhibit singularity structures across the entire plane of complex momentum-space.

The analysis focuses first on the dipole transitions $1s-2p$ and $2p-1s$, since their direct potentials have a simple form that is representative of this class of problem. Computer algebra is used to evaluate direct potentials in closed form for these transitions, allowing the kernel singularity structures for the Born-series expansion of the T-matrix to be studied in detail. Although general exchange potentials are not obtainable as closed-form expressions, their singularity structures can be deduced by exploring the analytic structure of the few closed-form partial-wave exchange potentials which can be obtained using Maple.
7: Analytic structure of general potentials for e-H scattering

7.1 Singularity Structures of Direct 1s-2p Kernels

The singularity-structure analysis discussed in this section for the 1s-2p dipole transition follows the same procedure adopted for analysing the potentials for the Yukawa and s-wave model of e-H scattering problems previously discussed in Chapters 4 and 5. There are three cases associated with the 1s-2p dipole transition, one for each possible value of the magnetic quantum number, i.e. \( m = 0, \pm 1 \). Analytic forms of the direct potentials for the 1s-2p, and 1s-2p, transitions are identical. It will be shown that the rotated-contour method of solving the T-matrix LS equation cannot be applied in its current form when these potentials are included in the electron-hydrogen scattering problem.

7.1.1 Analytic properties of the 1s-2p, direct potential

Beginning with the simplest dipole transition 1s-2p, the direct potential is given as a function of the transfer momentum vector \( K \) by

\[
V_{1s2p_0}(K) = \frac{i}{2\pi^2} \frac{6 \sqrt{2} \cos \Theta}{K^{\left(\frac{9}{4} + K^2\right)^{3}}}. \tag{7.1}
\]

Substituting for the \( \cos \Theta \) using (5.2) with \( K^2 = |p - p'|^2 \) gives the arbitrary off-shell potential

\[
V_{1s2p_0}(K, p', p, u) = \frac{i}{2\pi^2} \frac{6 \sqrt{2} (p - p'u)}{K^{\left(\frac{9}{4} + K^2\right)^{3}}}. \tag{7.2}
\]

This direct potential has two factors in its denominator which determine the nature of its singularity structure. As with the s-wave direct potentials, this dipole potential has the
Yukawa-like factor (5.4). However, it also has a $K^2$ factor in its denominator, a feature common in all non-s-wave direct potentials. In analysing the singularity structure of the Born-series expansion of the s-wave T-matrix, singularities for the off-shell direct potentials only occurred on the imaginary axis, with the exception of a small region either side of the origin. These are due to a denominator factor having the form $(\xi^2 + K^2)^{n'*n'}$. The same factor also appears in equation (7.1) and therefore it is expected that the singularity analysis of the $1s-2p_0$ off-shell potential will also reveal similar singularity structure on the imaginary axis of the complex $z$-plane. The off-shell potential expression to be analysed is

$$pp' V_{1s2p_0} (p', p, u) = \frac{i}{2 \pi^2} \frac{6 \sqrt{2} \ pp' (p - p'u)}{(p^2 + p'^2 - 2pp'u) \left( \frac{9}{4} + (p^2 + p'^2 - 2pp'u) \right)^3}. \tag{7.3}$$

Again, the generalised polar coordinate system (3.20) is used in which $p = aP$ and $p' = bP$ for $0 \leq a, b \leq 1$ and allowing the complex continuation of $P$ to be denoted by $z$, the off-shell potential expression to be analysed is

$$abz^2 V_{1s2p_0} (z, a, b, u) = \frac{i}{2 \pi^2} \frac{6 \sqrt{2} \ ab (a - bu) z}{(a^2 + b^2 - 2abu) \left( \frac{9}{4} + (a^2 + b^2 - 2abu) z^2 \right)^3}. \tag{7.4}$$

Note that the $z^2$ factor from the $K^2$ in the denominator cancels with the $z^2$ from the $pp'$ in the numerator and so there is no singularity associated with the $K^2$ factor for the off-shell potential expression. Singularities in the $z$-plane only arise from the Yukawa-like factor and are given by

$$z = \frac{\pm i \ 3}{2 \sqrt{a^2 + b^2 - 2abu}}. \tag{7.5}$$
7: Analytic structure of general potentials for e-H scattering

These lie on the imaginary axis for \( z \geq \frac{i3}{4} \) and \( z \leq -\frac{i3}{4} \), as shown in Figure 7.1 (a). Consequently, these singularities permit rotation of the contour into the fourth quadrant of complex momentum-space. However, as with the s-wave e-H scattering problem, the kernel singularity structures originating from half-off-shell potentials in the Born-series expansion of the T-matrix are very important for the application of a rotated-contour method and therefore, the half-off-shell potential's structure is the main focus of this discussion.

Although in any term \( T_n(k', k) \) of the Born-series T-matrix expansion there are two half-off-shell potentials, \( V(k', p_1) \) and \( V(p_n, k) \), it is sufficient for the purpose of the singularity analysis to consider only one of these, say \( V(p_n, k) \), because both have the similar analytic structure. Analysis begins with the half-off-shell momentum-transfer vector defined as \( K = k - p \), where \( k \) is the on-shell momentum vector and \( p \) is the arbitrary off-shell momentum vector. In terms of the generalised polar coordinate system (3.20) in which \( p = a P \) with \( 0 \leq a \leq 1 \), then continuing \( P \) into the complex plane and denoting this by \( z \), the half-off-shell 1s-2p\(_0\) direct potential expression to be analysed is

\[
V_{1s2p_0}(a z, k, u) = \frac{i6\sqrt{2}}{2\pi^2} \frac{(k - az u)}{k^2 + a^2 z^2 - 2k a z u} \left( \frac{9}{4} + k^2 + a^2 z^2 - 2k a z u \right)^{-3/2}.
\] (7.6)

In this expression there are two factors in the denominator that can lead to singularities in the complex plane. As in the case of s-wave potentials, a Yukawa-like singularity structure exists which is associated with the right-hand factor in the denominator of (7.6). The singularities of interest are located in the lower half-plane of complex momentum-space.
and are given by

\[ z = \frac{ku - i \sqrt{\frac{k^2(1 - u^2)}{4} + \frac{9}{4}}}{a}, \quad \text{with} \quad \begin{cases} 0 \leq a \leq 1, \\ -1 \leq u \leq 1. \end{cases} \] (7.7)

This is the same type of singularity structure found for the 1s-2s transition in the s-wave e-H scattering problem given by equation (5.15). The singularity region is plotted as a set of arcs in Figure 7.1 (a) along with the off-shell direct potential singularity region for \( k = 1 \).

The second singularity region is associated with the complex-valued transfer momentum vanishing in the left-hand denominator factor of (7.6). In the numerator, \( (k - azu) \) can only vanish for real values of \( z (= k/au) \) and therefore a second singularity region exists in the lower half-plane and is defined by

Figure 7.1: Singularity structure of 1s-2p_0 e-H direct potentials. (a) shows singularities on the imaginary axis due to the off-shell 1s-2p_0 direct potential. Also shown are singularity regions for the half-off-shell potentials given by equation (7.7) with \( k_{1s} = 1 \). (b) maps the singularity regions of the 1s-2p_0 half-off-shell potentials with \( k_{1s} = 1 \) associated with equation (7.8).
7: Analytic structure of general potentials for e-H scattering

\[ z = \frac{k u - i k \sqrt{1 - u^2}}{a}. \]  \hspace{1cm} (7.8)

Writing this equation in the form

\[ z = \frac{k \cos \theta - i k \sin \theta}{a} = \frac{k}{a} e^{-i\theta} \]  \hspace{1cm} (7.9)

for \(0 \leq \theta \leq 2\pi\), it is then obvious that singularities must lie on circles of radius \(\frac{k}{a}\) in the entire complex-momentum plane. Hence, a singularity will always be encountered by a rotated contour regardless of the chosen rotation angle. This singularity region is shown in Figure 7.1 (b) for an on-shell momentum \(k = k_s = 1\) and clearly indicates that no region exists for a rotated contour that is free of singularities. Examining the problem from another perspective, consider where singularities occur due to the denominator's \(K^2\) factor as a function of \(u\), rather than \(z\). Since \(z\) is actually a rotated contour which is defined by \(z = Pe^{-ia}\), then singularities occur for values of \(u\) given by

\[ u = \frac{k^2 e^{ia} + a^2 P^2 e^{-ia}}{2aP k} = \frac{k^2 + a^2 P^2}{2aP k} \cos \alpha + i \frac{k^2 - a^2 P^2}{2aP k} \sin \alpha \]  \hspace{1cm} (7.10)

Since \(u\) must be real, the imaginary part must be zero which imposes the condition \(P = \frac{k}{a}\) \((P \geq 0)\) and therefore, (7.10) reduces to

\[ u = \cos \alpha \]  \hspace{1cm} (7.11)

Thus, irrespective of the chosen contour-rotation angle \(\alpha\), a singularity will always be encountered on the contour as \(u\) varies over its range \((-1, 1)\). Thus, the half-off-shell direct potentials cannot be analytically continued into complex momentum-space, a necessary requirement for the application of the rotated-contour method described in Chapter 3. Consequently, a rotated-contour method cannot be used in the form outlined previously to
solve the T-matrix Lippmann-Schwinger equations in this case. It is important to note that in the usual case of zero rotation \((\alpha = 0)\) where \(z\) is real and positive, then the denominator vanishes at \(z = \frac{k}{a}\) when \(u = 1\). This is not normally a problem because the numerator also vanishes at this point, and therefore the potential is a smooth function that can be integrated.

### 7.1.2 Analytic properties of the 1s-2p\(_{\pm 1}\) direct potential

Direct potentials for 1s-2p transitions with non-zero magnetic quantum numbers are now studied. In terms of transfer momentum \(\mathbf{K}\), the dipole 1s-2p\(_{\pm 1}\) direct potentials are

\[
V_{1s2p_{\pm 1}}(\mathbf{K}) = \frac{ze^i}{2\pi^2} \frac{3 \sin \Theta}{K \left( \frac{9}{4} + K^2 \right)^3},
\]

and the generalised half-off-shell potential expression continued into complex momentum-space is therefore

\[
az V_{1s2p_{\pm 1}}(k,az,u) = \frac{ze^i 6a^2z^2 \sqrt{1 - u^2}}{2\pi^2 \left( k^2 + a^2 z^2 - 2ka z u \right) \left( \frac{9}{4} + k^2 + a^2 z^2 - 2ka z u \right)^3}.
\]

Note that the denominator in this expression has exactly the same form as the 1s-2p\(_0\) potential (7.6) and once again, the transfer momentum term in the denominator vanishes when \(z\) satisfies equation (7.8). Hence, there are no regions in the lower half-plane of complex momentum-space that are free of singularities and the rotated-contour method in its current form cannot be used with this potential either. Thus, both forms of the 1s-2p direct potentials, equations (7.6) and (7.13), contain a \(K^2\) factor in their denominators which result in poles being distributed throughout the complex plane of momentum-space.
7.1.3 Analytic properties of general direct potentials

Analysis of other \( n l - n' l' \) direct potentials with \( l \neq 0 \) and/or \( l' \neq 0 \) reveals that they all exhibit this same structure, which originates either from the explicit appearance of the isolated factors \( K \) or \( K^2 \) in the denominator and/or through some form of \( \Theta \) angular dependence in the numerator. Regardless of the mechanism, an isolated \( K^2 \) factor always appears in the denominator, with the exception of \( s \)-wave channels. For example, the \( 2p_1-2p_0 \) direct potential for e-H scattering is

\[
V_{2p_1,2p_0}(K) = \frac{1}{2\pi^2} \frac{3\sqrt{2}}{(1 + K^2)^4} \sin\Theta \cos\Theta,
\]

(7.14)

After substituting for the \( \sin\Theta \) and \( \cos\Theta \) factors (5.2), the half-off-shell potential expression becomes

\[
pV_{2p_1,2p_0}(p, k, u) = \frac{1}{2\pi^2} \frac{3\sqrt{2}}{K^2(1 + K^2)^4} \frac{p^2 \sqrt{1 - u^2} (k - pu)}{K^2(1 + K^2)^4}.
\]

(7.15)

A transfer momentum factor \( K^2 \) now appears in the denominator, as it does in the case of the \( 1s-2p \) transitions. Continuing the generalised half-off-shell potential expression into the complex plane gives

\[
a zV_{2p_1,2p_0}(k, z, u) = \frac{1}{2\pi^2} \frac{3\sqrt{2}}{(k^2 + a^2 z^2 - 2kazu)(1 + k^2 + a^2 z^2 - 2kazu)^3} \sqrt{1 - u^2} (k - azu).
\]

(7.16)

Once again, on a rotated contour the \( K^2 \) factor in the denominator vanishes when \( z = \frac{k}{a} \) and \( u = \cos\alpha \), leading to singularity problems on the deformed contour. Since all direct potentials, other than the \( s \)-orbital potentials, have some form of \( \Theta \) dependence through the spherical harmonics, the singularity structures associated with the transfer momentum factor \( K \) are common to general direct potentials. Since partial-wave expansions are
actually used in practice to compute T-matrix elements, the analytic structures of the 1s-2p and 2p-1s partial-wave direct potentials are now investigated to determine how the singularity structure manifests problems in calculating the half-off-shell direct potential partial-waves on a rotated contour.

7.2 Analytic Structure of Partial-Wave Direct Potentials

In this section, it is shown that a large class of partial-wave direct potentials have a logarithmic singularity on the real momentum axis. In all cases the potentials are continuous functions of momenta, but at some value of higher-order derivatives the derivative ceases to exist. Therefore, they are not analytic functions in the strict sense in that they cannot be expressed as a convergent infinite Taylor-series expansion. The partial-wave expansion of the direct potentials for the e-H scattering problem weakens the singularity occurring in the half-off-shell direct potentials, converting the pole to a logarithmic singularity in the partial waves. However, the presence of this logarithmic singularity in almost all half-off-shell partial-wave direct potentials has a severe impact on their numerical calculation under the rotated-contour scheme. With closed-form expressions now readily available for partial-wave direct potentials, definitive testing can be carried out on the numerical calculation of these potentials, particularly on a complex rotated-contour. It must be emphasized that Maple has been an invaluable tool for investigating the nature of this problem by providing the analytic closed-form expressions for these potentials.
Naturally, the difficulties encountered with the analytic forms of the half-off-shell partial-wave direct potentials on a rotated contour are also reflected in the corresponding numerical calculations. The need to test partial-wave potentials calculated numerically on a rotated contour provided the impetus to develop Maple solutions in closed-form. Numerical problems were first noticed during software testing, but the true nature and extent of the difficulties were only revealed after developing closed-form expressions in Maple for the partial-wave direct potentials. In this section, closed-form expressions for partial-wave direct potentials are given for $1s-2p$ and $2p-1s$ transitions along with analytic and numerical data illustrating the problem in calculating the half-off-shell potentials using a rotated-contour method. It should also be stressed that calculating off-shell partial-wave direct potentials for these transitions is not a problem on a rotated contour; the difficulties encountered here are only in calculating the half-off-shell partial-wave direct potentials.

### 7.2.1 Analytic structure of $1s-2p$ partial-wave direct potential

Insights into the nature of this problem begin with the closed-form partial-wave direct potentials. Although the focus of this discussion is on the first-order partial-wave direct potential with $J=0$, the results are equally valid for the higher-order partial waves. For the $1s-2p$ transition, the $J=0$ half-off-shell partial-wave direct potential is

$$
\hat{\mathcal{V}}^{D_{2p}^{(0)}}_{1s0}(p, k) = \frac{384 \sqrt{2}}{\pi} \int_{-1}^{1} du \frac{uk - p}{(9 + 4K^2)^3 K^2}.
$$

(Eq. 7.17)

Evaluating (7.17) is made easier with a change of variable, making the substitution $x = K^2$. The integral is then evaluated over $x$, from $K^2 = (k - p)^2$ to $K^2 = (k + p)^2$. This results in the transformed integral
\[ \tilde{V}_{1s0}^{D2p1(0)}(p, k) = -\frac{192}{\pi \sqrt{2} p^2 k} \int_{k^2}^{K^2} dx \frac{(p^2 - k^2 + x)}{(9 + 4x)^3 x}, \] (7.18)

and when evaluated gives

\[
\tilde{V}_{1s0}^{D2p1(0)}(p, k) = \frac{32}{243} \frac{\sqrt{2} (k^2 - p^2)}{\pi k^2 p} \left[ \ln \left( \frac{K^2}{K^2} \right) + \ln \left( \frac{9 + 4K^2}{9 + 4K^2} \right) \right] \\
+ \frac{32}{27} \frac{\sqrt{2} (K^2 - K^2)}{\pi k^2 p (9 + 4K^2)} (9 + 4K^2) \\
\times \left( 4 (k^2 + p^2) + 9 \left[ 4(k^2 - p^2) - 9 \left[ 2(K^2 + K^2) + 9 \right] \right] (9 + 4K^2) \right). \] (7.19)

The analogous 2p-1s transition potential has a similar analytic form, and is easily calculated from (7.19) via the symmetry relation (2.42) for potentials, so that

\[ \tilde{V}_{2p1}^{D1s0(0)}(p, k) = \tilde{V}_{1s0}^{D2p1(0)}(k, p). \] (7.20)

Note that equation (7.19) contains a natural logarithm term of the form

\[ f(p, k) = \frac{k^2 - p^2}{k^2 p} \ln \left( \frac{(k - p)^2}{(k + p)^2} \right). \] (7.21)

The logarithm has a logarithmic branch point singularity and is undefined at \( p = k \). However, the logarithm is multiplied by the factor \( (k^2 - p^2) \), which also vanishes when \( p = k \), resulting in \( f(p, k) \) being the smooth function of \( p \) shown in Figure 7.2 (a). The origin of this term is the \( K^2 \) factor in the integrand’s denominator of equation (7.17). Since \( s \)-wave direct potentials do not have such \( K^2 \) factors in their denominators, their partial-wave expansions do not possess this logarithmic singularity. The derivative of \( f(p, k) \) is

\[ \frac{d}{dp} f(p, k) = -\frac{(k^2 + p^2) \ln \left( \frac{(k + p)^2}{(k - p)^2} \right) + 4kp}{k^2 p^2}, \] (7.22)

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Figure 7.2: Direct potential log function and its derivative. (a) shows a plot of the log function $f(p, 1)$ defined by (7.21). In (b), the derivative of this function is plotted, demonstrating that the derivative is undefined at the point $p = 1$.

which is also shown plotted as a function of the off-shell $p$ in Figure 7.2 (b), with the on-shell $k = 1$. The derivative of $f(p, k)$ is undefined at $p = k$ and therefore, since all orders of derivatives must exist for a function to be analytic, the partial-wave direct potential for the 1s-2p transition is not an analytic function. This observation explains why the electron-hydrogen scattering problem is so difficult to solve numerically. Gaussian quadrature methods are generally used for the numerical integrations needed to solve the T-matrix Lippmann-Schwinger equation and these numerical techniques are best suited to integrals with analytic integrands in which all their derivatives are defined. The reason for this is that the integration error using an $N$-point Gaussian quadrature method is proportional to the $(2N + 1)^{th}$ derivative (Delves & Mohamed, 1985). For the rotated-contour method, the existence of the logarithmic term (7.21) in the 1s-2p partial-wave ($J = 0$) direct potential presents a different class of problem.
Under the rotated-contour scheme, the logarithm term (7.21) has the form

\[ f(z, k) = \frac{k^2 - p^2 e^{-i2\alpha}}{k^2 p e^{-i\alpha}} \ln \left( \frac{(k - p e^{-i\alpha})^2}{(k + p e^{-i\alpha})^2} \right). \]  

(7.23)

Although the log function in expression (7.23) is defined for all values of \( p \), including \( p = k \), another problem exists which adversely affects both the analytic results calculated using Maple and the numerical results computed using TCrossWin. The logarithmic function \( f(z, k) = f(p e^{-i\alpha}, k) \) is plotted in Figure 7.3 (a) as a function of \( p \) with \( k = 1 \) for a contour angle \( \alpha = 30^\circ \) and clearly shows a significant problem. A serious discontinuity arises in the 1s-2p partial-wave direct potential on the rotated contour as a consequence of the branch point of this logarithm term.

![Figure 7.3: Direct potential log function on rotated contour.](image)

The plots in (a) show the real and imaginary parts of \( f(z, k) = f(p e^{-i\alpha}, k) \), also for \( k = 1 \) and a contour-rotation angle \( \alpha = 30^\circ \). In (b), the factor \((k - p e^{-i\alpha})^2/(k + p e^{-i\alpha})^2\) is plotted in the complex plane as a function of \( p \) varying from zero to 3 with \( k = 1 \) and a contour-rotation angle \( \alpha = 30^\circ \). The curve crosses the negative real axis when \( p = k \) (= 1). If \( p \) is continued to infinity, the curve closes itself at the starting point \( x = i \) and \( y = 0 \).
Both Maple and the complex arithmetic routines in C++ (and FORTRAN) define the principal branch of the argument for complex numbers as an angle in the range \((-\pi, \pi)\), and as such, a branch cut is defined along the negative real axis. Therefore, Maple and C++ define their log function as the principal logarithm function. As the magnitude of the off-shell momentum \(p\) increases, the value of \(\frac{(k - pe^{-i\alpha})^2}{(k + pe^{-i\alpha})^2}\) when \(p = k\) is

\[
\frac{(k - ke^{-i\alpha})^2}{(k + ke^{-i\alpha})^2} = \frac{\cos \alpha - 1}{\cos \alpha + 1} < 0, \quad \text{for } 0 < \alpha < \frac{\pi}{2}.
\] (7.24)

Hence, the branch cut on the negative real axis is crossed when \(p\) passes through the value \(k\), as shown in Figure 7.3 (b). Consequently, discontinuities occur in the real and imaginary parts of \(f(z, k)\), which are shown in Figure 7.3 (a) when \(p\) is equal to the on-shell momentum \(k\).

The presence of the logarithm term (7.21) in the 1-2\(p\) and 2\(p\)-1\(s\) partial-wave direct potentials means that the integration along a rotated-contour, as applied thus far in this thesis, is invalid because it crosses a branch cut. Although the branch cut defined on the negative real axis is arbitrary and alternatives can be used, they must always run from 0 to infinity in some direction. Hence, any chosen branch cut will be crossed by the curve shown in Figure 7.3 (b) and cannot overcome the problem.

### 7.2.2 Numerical 1\(s\)-2\(p\) and 2\(p\)-1\(s\) partial-wave direct potential

Some initial testing of the numerical software on a rotated contour was actually done for various combinations of 1\(s\), 2\(s\) and 2\(p\) states before the potentials' analytic-structure analysis was completed. This preliminary testing revealed discrepancies between the
contour-rotated and standard calculations of on-shell T-matrix amplitudes only when 2p states were included. In the first instance, this was thought to be due to an inadequate quadrature mesh and that the problem would be resolved with improved quadrature meshes for the radial and polar momentum integrations. However, the true nature and extent of the problem were only uncovered by comparing numerically computed direct potentials on a rotated contour with the analytic forms computed by Maple. On completing a thorough investigation of the partial-wave direct potentials’ analytic and singularity structures, it was realised that numerical and analytic difficulties always exist for a rotated-contour scheme.

For example, consider the partial-wave \((J = 0)\) direct potentials for the 2p-1s transition listed in Table 7.1. These show reasonable agreement with Maple results, except for one glaring disparity in the half-off-shell potential at \(i = 3, i' = 1\) (shown highlighted), where the magnitude of the off-shell momentum magnitude \(p \approx 0.9\), i.e. in the vicinity of the on-shell momentum \(k = 1\). Although these are encouraging results for a rotated-contour calculation, they are somewhat misleading. Plotting half-off-shell \(J = 0\) partial-wave direct potentials for the analytic expression and the numerical results with complex off-shell momenta, the flaw becomes much clearer. The plot shown in Figure 7.4 reveals the problem’s source. Both the analytic and calculated numerical results for the 2p-1s transition have distinct discontinuities in their real and imaginary parts occurring precisely where the off-shell momentum’s magnitude is equal to the on-shell momentum, i.e. \(p = k' (= 1)\). Similarly, the first-order partial-wave direct potentials for the 1s-2p transition shown plotted in Figure 7.5 also exhibit analogous discontinuities where the off-shell momentum magnitude coincides with the on-shell momentum, namely \(p = k' (= 0.5)\).
The deviation in the numerically computed potentials near the on-shell value of momentum compared with the analytic form is simply a manifestation of numerical difficulties associated with numerical computations in the vicinity of the branch point revealed in the analytic form of the potential. It confirms that the continuation of the partial-wave direct potentials into complex momentum-space is not as simple as originally believed, but is actually quite an involved problem for the rotated-contour method and its application to the atomic scattering problem.

Table 7.1: 2p-1s partial-wave (J=0) direct potentials for e-H scattering at 13.6eV (k_{ls}=1) computed numerically and analytically for a four-point momentum grid contour-rotated by α = 30°. On-shell momenta indices are i = i' = 1, while off-shell rotated quadrature points indices are 2-5. The highlighted potential is the half-off-shell potential at which the off-shell momentum’s magnitude is near the on-shell momentum (see text).

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<td>0</td>
<td>2p</td>
<td>1</td>
<td>5</td>
<td>ls</td>
<td>0</td>
<td>4</td>
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<tr>
<td>0</td>
<td>2p</td>
<td>1</td>
<td>5</td>
<td>ls</td>
<td>0</td>
<td>5</td>
</tr>
</tbody>
</table>
2p1-1s0 Half-off-shell Partial-wave ($J = 0$) Direct Potential
13.6 eV (on-shell $k' = k_s - 1$), rotated-contour $\alpha = 30^\circ$

Figure 7.4: 2p-1s half-off-shell partial-wave ($J = 0$) direct potential for 13.6 eV e-H scattering.

1s0-2p1 Half-off-shell Partial-wave ($J = 0$) Direct Potential
13.6 eV (on-shell $k' \approx k_s = 0.5$), rotated-contour $\alpha = 30^\circ$

Figure 7.5: 1s-2p half-off-shell partial-wave ($J = 0$) direct potential for 13.6 eV e-H scattering.
7.2.3 Analytic structure of 2p-2p partial-wave direct potential

To complete this section, the integral for the e-H scattering 2p-2p partial-wave \((J=0)\) direct potential is given by

\[
\hat{\tilde{V}}^{D2p1(0)}_{2p1}(p, k) = \int_{-1}^{1} du \frac{6pk - 2u(2p^2 + 2k^2 - pku) - uK^2(K^4 + 4K^4 + 6K^2 + 5)}{\pi (1 + K^2)^4 K^2}.
\] (7.25)

This potential is not of the “dipole class”. Its result can be computed analytically with the help of Maple and the resultant form is

\[
\hat{\tilde{V}}^{D2p1(0)}_{2p1}(p, k) = \frac{-3(p^2 - k^2)^2}{4\pi p^2 k^2} \ln \left( \frac{(p + k)^2}{(p - k)^2} \right) - \frac{3(p^2 + k^2 - 3(p^2 - k^2)^2)}{4\pi p^2 k^2} \ln \left( \frac{1 + (p + k)^2}{1 + (p - k)^2} \right)
\] (7.26)

\[
\frac{S(p, k)}{4\pi p^2 k^2 (1 + (p - k)^2)^3 (1 + (p - k)^2)^3},
\]

where \(S(p, k)\) is a polynomial given by

\[
S(p, k) = -16p^3k - 16k^3p + 80p^3k^3 - 80p^5k - 80k^5p + 128p^3k^5 + 128p^5k^3 - 160pk^7 - 160p^7k
\]
\[-160k^9p - 160p^9k + 176p^3k^7 + 176k^7p^3
\]
\[-80p^{11}k - 160p^9k^7 + 240p^9k^3 - 240p^3k^9
\]
\[-32p^5k^5 - 160k^5p^7 - 80k^{11}p + 96p^{11}k^3
\]
\[-240p^5k^9 - 240p^9k^5 + 96p^3k^{11} + 320p^7k^7
\]
\[-16pk^{13} - 16p^{13}k.
\] (7.27)

The \(K^2\) factor in (7.25) produces a natural log term of the form

\[
f(p, k) = \frac{(p^2 - k^2)^2}{p^2 k^2} \ln \left( \frac{(k + p)^2}{(k - p)^2} \right),
\] (7.28)

which is similar to (7.21). Interestingly, the first derivative of the 2p1-2p1 partial-wave...
potential is defined for all values of real off-shell momenta, unlike the 1s0-2p1 dipole potential whose first derivative is singular at \( p = k = 1 \). However, the second derivative of the 2p1-2p1 potential produces a singularity at \( p = k = 1 \) and therefore, it is also a non-analytic function at that point.

Figure 7.6: 2p-2p direct potential log function and its derivatives. (a) shows a plot of the log function \( f(p, 1) \) defined by (7.28). In (b), the derivative of this function is plotted. The second derivative is plotted in (c), showing that the second derivative is undefined at \( p = 1 \).

7.2.4 Numerical 2p-2p partial-wave direct potential

Similar branch cut effects encountered in the 1s-2p dipole transition are also evident in the 2p-2p transition, as can be seen from the analytic and numerical data plots shown in Figure 7.7. All other non s-wave partial-wave direct potentials exhibit this same fundamental problem, with the exception of one particular sub-class. For example, the analytic forms for all combinations of \( 1 \leq n, n' \leq 3 \) and \( 1 \leq l, l' \leq 3 \) have been explicitly checked and the
Figure 7.7: 2p-2p half-off-shell partial-wave ($J = 0$) direct potential for 13.6 eV e-H scattering. Numerical and analytic calculations are for a rotated contour with rotation angle $\alpha = 30^\circ$.

only $n l L - n' l' L'$ transitions that do not have a logarithmic term with a branch point singularity are the $J^{th}$ partial waves of transitions in which $l = l' = J$ and $L = L' = 0$, i.e. $n J 0 \sim n' J 0$. These partial waves have analytic forms that are similar to the s-wave direct partial-wave potentials. The simplest example of this well-behaved sub-class of direct potentials is the $J = 1$ partial wave for 2p0-2p0, as evidenced by the plot of the numerical and analytic half-off-shell calculations shown in Figure 7.8 for e-H scattering at 13.6eV on a 30° rotated contour.
7. Analytic structure of general potentials for e-H scattering

Figure 7.8: $2p-2p$ half-off-shell partial-wave ($J = 1$) direct potential for 13.6 eV e-H scattering. Numerical and analytic calculations are for a rotated contour with rotation angle $\alpha = 30^\circ$.

7.3 Partial-Wave Exchange Potentials

General partial-wave exchange potentials for e-H scattering do not have the problematic analytic structure that plagues most direct potentials when they continued into complex momentum-space. Therefore, their numerical computation is accomplished using the counter-rotation technique that was applied to calculating the $s$-wave exchange potentials in the previous chapter. Limitations imposed on the counter-rotation angle $\alpha$ by equation (5.62) also applies in calculating general partial-wave exchange potentials. In this section the partial-wave exchange potentials for the dipole transitions $1s-2p$ and $2p-1s$ are

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discussed in detail since they are the simplest examples of more the general exchange potentials. Attention is directed to the half-off-shell exchange potentials because they are the most difficult to calculate numerically under a rotated-contour scheme. It will be shown that the $1s$-$2p$ and $2p$-$1s$ partial-wave ($J = 0$) exchange potentials can be calculated numerically on a rotated contour with a satisfactory degree of accuracy when compared to the analytic calculations.

### 7.3.1 Analytic structure for $1s$-$2p$ exchange potential

Although maple6 has been successfully used in algebraically computing partial-wave ($J=0$) exchange potentials for electron-Hydrogen scattering in the $s$-wave model, it is not as successful in evaluating the more complicated integrals required to obtain a closed-form expression for the $1s$-$2p$ first-order partial-wave exchange potential. It is anticipated that within a few years this limitation will be surmounted as future refinements are made to computer algebra systems like Maple. At present, Maple fails to recognise divergent integral terms which cancel to give a bounded solution.

The $1s$-$2p$ partial-wave ($J = 0$) exchange potential for e-H scattering is given by the double integral expression

$$
\hat{\nu}^E_{1s0}^{2p1} (k', k) = \frac{\sqrt{2}}{3} \frac{(-1)^5}{\pi k k'^2} \int_0^\infty dr' e^{-r'} \frac{k'r' \cos(k'r') - \sin(k'r')}{r'^2} \\
\times \left[ \int_0^r dr' r'^3 \sin(kr') e^{-r'/2} + r'^3 \int_r^\infty dr' \sin(kr') e^{-r'/2} \right].
$$

(7.29)
Maple6 cannot evaluate the double integral in this form. An attempt was made to use a parametric differentiation technique, so that the expression could be formed from simpler integrals. For example, the expression above can be also written as

\[
\hat{V}^{E2p1(0)}_{1s0}(k',k) = \frac{\sqrt{2}}{3} \frac{(-1)^5}{\pi k k'^2} \int_0^\infty dr' \ e^{-r'} \ \frac{k' r' \cos(k' r') - \sin(k' r')}{r'^2} \times \left( \left[ \frac{(-\partial)^3}{\partial \beta^3} \int_0^{r'} dr \ \sin(kr) e^{-\beta r} \right]_{\beta = \frac{1}{2}}^{r'^2} + r'^2 \int_0^\infty dr' \ \sin(kr) e^{-r'^2/2} \right).
\] (7.30)

Maple6 will evaluate these forms, but the technique illustrates the degree of intervention that is needed to force the evaluation of complicated integrals. Fortunately, at the time of writing this section, a copy of the newly released maple7 was purchased and this new version can evaluate the 1s-2p first-order partial-wave exchange potential to produce a closed form solution, although the resulting expression was very large, with 238 terms when expanded (see the accompanying CDROM). Although this expression is probably not in its simplest form, it does allow data for the half-off-shell partial-wave exchange potential to be calculated from the analytic form and compared with its numerical counterpart on a rotated contour.

Having the closed-form solution for the 1s-2p first-order partial-wave exchange potential also allows its singularity structure to be examined. Like the s-wave exchange potentials, a closed-form solution for the full exchange potential is not available. However, examining the singularity structure of the half-off-shell first-order partial wave reveals that relevant singularities occur on the imaginary axis at \(-i\) and in the complex plane at \(k - \frac{3}{2} i\). This implies a maximum contour-rotation angle \(\alpha = \tan^{-1} \frac{3}{2k}\), which is recognised as the same
rotation angle applying to the 1s-2s and 2s-1s direct potentials. The restriction on rotation imposed by the half-off-shell numerical exchange calculation reduces the practical rotation to a smaller angle of contour rotation than would otherwise be allowed. From this result it can be inferred that the singularity structure of the exchange potential permits the application of a rotated-contour method in the form applied in this thesis.

For 13.6eV e-H scattering, results from numerical calculations and the analytic form are plotted in Figure 7.9 and clearly demonstrate that the numerical calculation for a 15° ($\frac{1}{2} \tan^{-1} \frac{1}{2} = 13.28°$) contour-rotation angle agrees very well with the analytic form.

![Figure 7.9: 1s-2p half-off-shell partial-wave (J = 0) exchange potential for 13.6 eV e-H scattering. Numerical and analytic calculations are for a rotated contour with rotation angle $\alpha = 15°$.](image)
calculated using mapl7. The numerical data and analytic curve are smooth functions in both their real and imaginary parts, indicating that the continuation into complex momentum-space is analytic for the exchange potentials. Attempting to evaluate the integrals in equation (7.29) in the reverse order, as in the case of the 2p-1s transition, it is found that mapl7 cannot evaluate a solution. With some degree of intervention in rearranging the integrals, it may be possible to coerce mapl7 into completing the evaluation. However, since the potential’s symmetry property (2.42) allows 2p-1s potentials to be calculated analytically from the 1s-2p closed-form expression, the computation has not been pursued with mapl7. The analytic form and computed

![Graph of 2p-1s0 Half-off-shell Partial-wave (J = 0) Exchange Potential](image)

**Figure 7.10:** 2p-1s half-off-shell partial-wave (J = 0) exchange potential for 13.6 eV e-H scattering. Numerical and analytic calculations are for a rotated contour with rotation angle α = 15°.
numerical data are plotted in Figure 7.10 and also indicate very good agreement in the 2p-1s exchange calculation for the half-off-shell potential. Maple7 can also evaluate closed-form expressions for other dipole transitions in which the initial channel is an s-state. For example, see the accompanying CDROM for 2s-2p, 1s-3p, 2s-3p and 3s-3p transitions.

Maple7 fails to evaluate the J = 0 partial-wave exchange potential in closed form for either the 2s-2p or the 2p-2p first-order partial-wave exchange potentials. It appears that the present limits of Maple’s integration capabilities have been reached with these complicated double integrals. It should be emphasised that it may be possible to evaluate these integrals.

Differential Cross Section for 1s-1s, 1s-2s and 1s-2p e-H Scattering
CC(1s,2s,2p) 13.6eV (exchange only, rotated-contour α = 15°)

Figure 7.11: 1s, 2s, 2p differential cross sections (exchange only) for 13.6 eV e-H scattering. Data are plotted for a contour-rotation angle α = 15° against data calculated using standard subtraction methods.
using the parametric differentiation technique and that it is the explosion of terms from the more complicated nodal structures of the excited states that make evaluation difficult.

Differential cross sections for a 15° rotated-contour calculation with exchange only are shown plotted in Figure 7.11 against data for the same calculation using the standard subtraction method. These results for the exchange-only T-matrix confirm the viability of a rotated-contour method to solve the momentum-space T-matrix Lippmann-Schwinger equation for exchange potentials. However, due to the analytic nature of the partial-wave direct potentials, contour rotation cannot be applied to the full electron-hydrogen scattering problem in practice.

7.4 Consideration of Modified Contours

The question naturally arises whether it is possible to modify the rotated-contour procedure to avoid the logarithmic branch cuts in the partial-wave direct potentials that are the source of difficulty? Examining the 1s-2p_0 direct potential’s singularity-structure map shown in Figure 7.1 (b) again suggests that the answer is to this question no. It will be shown here that this answer is correct and that such a procedure applied to solving the momentum-space partial-wave T-matrix is not possible. Since the expanded T-matrix (3.18) contains the second-Born T-matrix, it is sufficient to examine this approximation. As a simplified example to illustrate the problem, consider the second-Born T-matrix for the elastic 1s-1s transition given by

\[ T_{1s0}^{1s0}(k,k) = V_{1s0}^{1s0}(k,k) + \sum_j \int_0^\infty dp \ p^2 \frac{V_j^{1s0}(k,p) V_j^{1s0}(p,k)}{E_j - \frac{1}{2} p^2 + i\varepsilon}, \]  

(7.31)
where the channel energy $E_j$ is defined by (2.39) and the potentials are for the $J=0$ partial wave. The second-order term is computed using the half-off-shell potentials and in view of the discussions so far, it is clear that the general nature of the continuation difficulties experienced are encapsulated in the second-order term. Choosing just one of these terms for convenience, consider only

$$
\int_0^\infty dp\ p^2 \frac{V_{1s0}^{2p1(0)}(p,k)^2}{E_{2p} - \frac{1}{2} p^2 + i\varepsilon},
$$

(7.32)

where the symmetry relation (2.42) for potentials has been used to express it in a simpler form. Now it is known that the partial wave $V_{1s0}^{2p1(0)}(p,k)$ has a logarithmic branch point singularity at $p = k$ on the real axis. This point can be moved either above or below the real axis by adding or subtracting a small imaginary part $i\eta$ to the on-shell momentum $k$. The half-off-shell potential can then be written as

$$
V(p,k) = \frac{1}{2} V(p,k+i\eta) + \frac{1}{2} V(p,k-i\eta).
$$

(7.33)

Thus, the integral (7.32) is equivalent to

$$
\frac{1}{4} \int_0^\infty dp\ p^2 \frac{V_{1s0}^{2p1}(p,k+i\eta)^2}{E_{2p} - \frac{1}{2} p^2 + i\varepsilon} + \frac{1}{4} \int_0^\infty dp\ p^2 \frac{V_{1s0}^{2p1}(p,k-i\eta)^2}{E_{2p} - \frac{1}{2} p^2 + i\varepsilon} + \frac{1}{2} \int_0^\infty dp\ p^2 \frac{V_{1s0}^{2p1}(p,k+i\eta) V_{1s0}^{2p1}(p,k-i\eta)}{E_{2p} - \frac{1}{2} p^2 + i\varepsilon}.
$$

(7.34)

Is it now possible to deform a contour such that it avoids the logarithmic branch point singularities occurring at $k \pm i\eta$ for each of the terms in (7.34)? Clearly for the first term, the logarithmic branch point is located above the real axis at $k + i\eta$ and is in the same quadrant of the complex plane as the free Green's function singularity. This means that the
rotated-contour method can be applied to evaluate the integral of this first term. The second term has a logarithmic branch point below the real axis at \( k - i \eta \), with the free Green's function singularity still being above the real axis. Therefore, there is nowhere to deform a contour without enclosing the logarithmic branch point. The same can be said for the third term which also has a logarithmic branch point below the real axis at \( k - i \eta \).

The conclusion drawn from this argument is that it is not possible to deform a contour that can be used to evaluate the second-order term of the second-Born T-matrix for the e-H scattering problem. Since all higher-order terms of the T-matrix Born-series expansion (3.18) also contain half-off-shell potentials, a rotated-contour method cannot be applied in general to solve the momentum-space T-matrix Lippmann-Schwinger equation.

It is also interesting to note that in the standard real-axis integration formulations, the fact that equation (7.33) results in direct potentials that are bounded and continuous must account for the reasonable success achieved by the present methods. However, as noted throughout section 7.2, in most cases higher-order derivatives for direct potentials fail to exist at the on-shell momentum. This is possibly one reason why the accurate solution of the coupled-channels equations appears to require large numbers of quadrature points when the Gaussian rules are applied.
Chapter 8

Conclusions

The work presented in this thesis was concerned with describing and applying a new technique for solving the coupled-channels equations based on reformulating the momentum-space integrals from the real axis into the complex-momentum plane. This rotated-contour method has the appealing benefit of eliminating the singularities arising from the free Green’s functions, which otherwise result in the Lippmann-Schwinger equations having singular kernels when solved by conventional principle-value methods. To some degree, this advantage may be offset by the necessity for complex arithmetic to handle the complex-valued momentum quadrature integrations. However, modern computers now operate at exceptionally high speeds, have large memory capacities and can handle the demanding processing requirements for these computationally intensive operations with relative ease, so this is no longer a significant drawback.

8.1 Rotated-Contour Method

Application of a rotated-contour solution to solve the momentum-space Lippmann-Schwinger equation was found to be a surprisingly simple procedure for short-range potentials. Aside from the complex arithmetic requirements, the matrix equations normally used to solve the momentum-space on-shell T-matrix elements were easily modified to accommodate a rotated-contour method. This required rotating the real momentum
quadrature points into the fourth quadrant of the complex momentum plane, calculating potentials as appropriate for real on-shell and complex off-shell momenta, and setting the super-weights for the on-shell potentials to zero. Ensuring that the potentials have a form that allows their analytic continuation into the complex momentum plane was vital for the successful application of a rotated-contour method.

A Yukawa-potential scattering problem provided an ideal single-channel example for illustrating the application of a rotated-contour solution. Yukawa potential matrix elements have simple analytic structures that are appropriate for their analytic continuation into the complex momentum plane. The closed-form solution for the Yukawa-potential facilitated the singularity-structure analysis necessary for a rotated-contour solution. This involved investigating the singularity structures of generalised half-off-shell and fully-off-shell potentials arising from the Born-series expansion of the T-matrix. It was revealed from this analysis that the maximum useable contour angle was determined by the singularity structure of the half-off-shell potentials, and yielded a simple expression relating the incident particle’s momentum and the Yukawa potential’s range. Therefore, a deformed contour can be chosen so that it is quite removed from singularities in the complex momentum plane that are associated with the half-off-shell potentials and from the free Green’s function singularity on the real axis.

The numerical results presented in this thesis for the Yukawa second-Born and the full T-matrix amplitudes, demonstrated that a rotated-contour solution offers a viable alternative for solving the momentum-space LS equation. Convergence was shown to be independent
of the chosen contour-rotation angle and only degrades appreciably near the extremes of the rotation angle’s range, where the contour approaches singular points.

Extending contour rotation to a simple atomic scattering problem, e-H scattering in the s-wave model, also gave excellent results when compared to conventional subtraction method calculations. Differential cross-sections calculated from the on-shell T-matrix amplitudes computed using contour-rotation methods, compared favourably with the couple-channels solution using principle-value integrals. However, the rotation angle’s dependence on channel principal quantum numbers meant that relatively large angles (>5°) can only be used effectively for low incident energy problems. Numerical considerations in calculating exchange potentials under the counter-rotation scheme also impacted on the maximum rotation angle, reducing it further from that defined by the half-off-shell potential. Therefore, a rotated-contour method for solving atomic scattering problems using actual eigenfunctions was best suited to low energy problems coupling low principle quantum number excitation channels. This restriction could be alleviated by using alternative basis functions, such as a Laguerre basis, for the target states, where the exponential factor $e^{-r/n}$ in the Slater basis is replaced by $e^{-\lambda r}$ for an arbitrarily chosen $\lambda > 0$.

When extended to more general potentials other than s-orbital potentials, the analytic structure of most direct potentials was found to be more complicated, due to singularities in higher-order derivatives on the real axis. This difficulty prevented selection of suitable rotated contour that did not enclose or cross a singularity. For half-off-shell partial-wave direct potentials, any chosen contour always crossed a logarithmic branch-cut, producing
a discontinuity in the contour-rotated form of these potentials. This effect was clearly illustrated in, but not restricted to, the dipole transitions $1s-2p$ and $2p-1s$, where both the analytic form and numerical data for half-off-shell partial-wave potentials were in agreement and showed the same discontinuity on a rotated contour. This problem only applied to the calculation of half-off-shell partial-wave direct potentials on a rotated contour. Off-shell direct potentials did not present any problems and neither did the partial-wave exchange potentials. The latter case was clearly demonstrated by the comparison between calculations of exchange only differential cross sections using a rotated-contour method and a conventional regularised principle-value method.

Unfortunately, the major conclusion of this thesis was that a rotated-contour method of solving the coupled-channels momentum-space T-matrix LS equations for general electron-atom scattering problems does not appear to be practical. For the $s$-wave model of e-H scattering, a rotated-contour method has been shown to be viable. However, the non-analytic structures of most other partial-wave direct potentials prevent the method from being applied generally.

### 8.2 Computer Algebra Systems

Maple, the symbolic computation system used in this thesis illustrated the value of computer algebra as a worthy research tool. For the first time, the ability to easily calculate any desired partial-wave direct potential in closed form has allowed a detailed analytic-structure analysis of these functions. This analysis has confirmed the well established, difficult nature of solving scattering problems involving the long-range Coulomb
interaction. The realisation that almost all momentum-space partial-wave direct potentials for e-H scattering are not strictly analytic functions, even on the real momentum axis, explains why numerical integrations of these functions using Gaussian quadrature methods often have difficulties in obtaining convergent solutions. Rather than there being the two distinct profiles of partial-wave direct potentials suggested by McCarthy and Stelbovics (1983), there appears to be a small analytic class encompassing the s-orbital potentials only; almost all other partial-wave direct potentials are non-analytic functions due to logarithmic branch-point singularities along the real momentum axis. The dipole transitions, such as 1s0-2p1, not only have complicated structures along their diagonal, but their first derivatives are singular on the diagonal. Although some partial-wave direct potentials appear to be well behaved with continuous first derivatives, such as 2p1-2p1, their second derivatives are not and therefore these are not analytic functions either.

Partial-wave exchange potentials have been found to be considerably more difficult to evaluate in closed form. Maple can only compute a few simple first-order partial waves for exchange potentials, but these are sufficient to indicate that they are analytic functions and can be analytically continued into the complex plane of momentum-space. Although maple6 failed to compute the 1s-2p first partial-wave for the exchange potential, the latest release of maple7 succeeded in evaluating this expression. As computer algebra systems continue to improve, it is anticipated that in the near future, many more exchange potentials will be able to be calculated in closed form.

A significant issue with the Maple computer algebra system was simplification of large
expressions. Most closed-form expressions obtained for partial-wave potentials required additional simplification which was done with specially written Maple simplification procedures. Forcing Maple to do this form of simplification required considerable effort in developing functions that break long expressions down into smaller component terms and factors, simplifying these sub-expressions and then reassembling them to obtain the simplified complete expression.

It should also be acknowledged that Maple can convert expressions directly into FORTRAN or C code, ready for inclusion in programme source code. This lends itself to using the closed-form partial-wave expressions to numerically calculate potentials without the need for evaluating quadrature integrations. This was done for the first-order 1s-1s partial-wave potential (direct and exchange) to illustrate that highly accurate potentials gave consistent on-shell T-matrix amplitudes and kernel determinants over a wide range of contour-rotation angles. However, at present the practicalities of implementing this in general are prohibitive, due to the enormous number of very large expressions that would be required to obtain a sufficient number of partial waves and coupled-channels for a practical calculation.

8.3 Numerical Software Development in C++

FORTRAN has clearly been the dominant language used in physics problem solving. However, there are other choices which can perform just as well for a particular application. Using C++ in this thesis to develop the numerical software implementing a rotated-contour method of solving the momentum-space LS equations, has produced modern software
packages that can be easily run on any PC under the Windows operating system. The C++
development system used in this thesis was Borland’s C++ Builder 5, which has an
integrated development environment offering rapid Windows application development.
The system also has an integrated debugging facility which provides an extremely flexible
environment for locating software errors quickly. Many of the library routines available
for FORTRAN are now also available for C++ (for example, the Template Numerical
Toolkit; math.nist.gov/tnt and LAPACK++; math.nist.gov/lapack++). Complex arithmetic
in C++ is comprehensive, and although its efficiency may not be as strong as FORTRAN,
the ability to mix real and complex data types in standard arithmetic expressions and
functions allowed much simpler and more readable code to be written. Object oriented
programming techniques also offer advanced methods of software development which can
result in better code reusability and maintainability. The success of the numerical
calculations presented in this thesis has demonstrated the value of C++ as a useable and
viable programming language for the scientific community.
Appendix

A

Selected Useful Formulae

A selection of formulae useful in solving and simplifying atomic physics problems is provided in this appendix.

A.1 Wigner 3-j and 6-j Symbols

Wigner 3-j symbols are invariant under the rotation of columns, but differ by a phase $(-1)^{j_1+j_2+j_3}$ under the exchange of adjacent columns or under a sign change of all the magnetic quantum numbers.

$$
\begin{pmatrix}
  j_1 & j_2 & j_3 \\
  m_1 & m_2 & m_3
\end{pmatrix}
= \begin{pmatrix}
  j_3 & j_1 & j_2 \\
  m_3 & m_1 & m_2
\end{pmatrix}
$$

(A.1)

$$
\begin{pmatrix}
  j_1 & j_2 & j_3 \\
  m_1 & m_2 & m_3
\end{pmatrix}
= (-1)^{j_1+j_2+j_3}
\begin{pmatrix}
  j_2 & j_1 & j_3 \\
  m_2 & m_1 & m_3
\end{pmatrix}
= (-1)^{j_1+j_2+j_3}
\begin{pmatrix}
  j_1 & j_2 & j_3 \\
  -m_1 & -m_2 & -m_3
\end{pmatrix}
$$

(A.2)

Orthogonality of 3-j symbols

$$
\sum_{m_1,m_2,m_3}
\begin{pmatrix}
  j_1 & j_2 & j_3 \\
  m_1 & m_2 & m_3
\end{pmatrix}
\begin{pmatrix}
  j_1 & j_2 & j_3' \\
  m_1 & m_2 & m_3'
\end{pmatrix}
= \frac{1}{2j_3+1}
\delta_{j_1,j_3'}\delta_{m,m'}
$$

(A.3)
Appendix A: Useful formulae

Contraction of 3-j symbols

\[
\sum_{m_1,m_2,m_3} (-1)^{j_1+j_2+j_3-m_1-m_2} \begin{pmatrix}
J_1 & J_2 & J_3 \\
M_1 & m_2 & -m_3 \\
-\ell_1 & M_2 & m_3 \\
\end{pmatrix} \begin{pmatrix}
J_1 & J_2 & J_3 \\
M_1 & M_2 & M_3 \\
\ell_1 & \ell_2 & \ell_3 \\
\end{pmatrix} = \begin{pmatrix}
J_1 & J_2 & J_3 \\
M_1 & M_2 & M_3 \\
\ell_1 & \ell_2 & \ell_3 \\
\end{pmatrix} \begin{pmatrix}
J_1 & J_2 & J_3 \\
M_1 & m_2 & -m_3 \\
-\ell_1 & M_2 & m_3 \\
\end{pmatrix} \] (A.4)

A.2 Clebsch-Gordan Coefficients

\[
\langle j_1 j_2 m_1 m_2 | j_3 m_3 \rangle = C_{j_1 j_2 j_3}^{j_1 j_2 j_3} = (-1)^{j_1-j_2-m_3} (2j_3+1)^{1/2} \begin{pmatrix}
j_1 & j_2 & j_3 \\
m_1 & m_2 & -m_3 \\
\end{pmatrix} \] (A.5)

A.3 Legendre and Associated Legendre Polynomials

Expansion of Legendre polynomial

\[
P_l(\hat{r} \cdot \hat{x}) = \frac{4\pi}{2l+1} \sum_m Y_{lm}^*(\hat{r}) Y_{lm}(\hat{x}) \] (A.6)

Associated Legendre polynomial for \(-m\)

\[
P_{l-m}(x) = (-1)^m \frac{(l-m)!}{(l+m)!} P_l^m(x) \] (A.7)

A.4 Spherical Harmonics

\[
\langle \hat{r} | l m \rangle = Y_{lm}(\hat{r}) = Y_{lm}(\theta, \varphi) = (-1)^m \left( \frac{(2l+1)(l-m)!}{4\pi(l+m)!} \right)^{1/2} P_l^m(\cos\theta) e^{im\varphi} \] (A.8)

Conjugate

\[
\langle l m | \hat{r} \rangle = Y_{lm}^*(\hat{r}) = (-1)^m Y_{l-m}(\hat{r}) \] (A.9)
Reflection

\[ Y_{lm}(-\hat{r}) = (-1)^l Y_{lm}(\hat{r}) \]  
(A.10)

Orthogonality

\[ \int d\hat{r} \ Y_{l'm'}^*(\hat{r}) Y_{lm}(\hat{r}) = \delta_{l,l'} \delta_{m,m'} \]  
(A.11)

Integrals

\[ \int d\hat{r} \ Y_{lm}(\hat{r}) Y_{l'm'}(\hat{r}) Y_{LM}(\hat{r}) = \int d\hat{r} \ Y_{lm}^*(\hat{r}) Y_{l'm'}^*(\hat{r}) Y_{LM}^*(\hat{r}) \]
\[ = \frac{i L L}{(4\pi)^{1/2}} \begin{pmatrix} l & l' & L \\ m & m' & M \end{pmatrix} \begin{pmatrix} l & l' & L \\ 0 & 0 & 0 \end{pmatrix} \]  
(A.12)

\[ \int d\hat{r} \ Y_{lm}(\hat{r}) Y_{l'm'}(\hat{r}) Y_{LM}(\hat{r}) = \int d\hat{r} \ Y_{lm}^*(\hat{r}) Y_{l'm'}^*(\hat{r}) Y_{LM}^*(\hat{r}) \]
\[ = (-1)^M \frac{i L L}{(4\pi)^{1/2}} \begin{pmatrix} l & l' & L \\ m & m' & -M \end{pmatrix} \begin{pmatrix} l & l' & L \\ 0 & 0 & 0 \end{pmatrix} \]  
(A.13)

Expansion

If \( r = r_1 - r_2 \), then

\[ Y_{lm}(\hat{r}) = \frac{(4\pi)^{1/2}}{r l} \sum_{\lambda,\mu} (-1)^{l+m+\lambda} \left( \frac{(2l+1)(2l+1)!}{(2\lambda+1)(2(l-\lambda)+1)!} \right)^{1/2} \frac{1}{r_1^{l-\lambda}} \frac{1}{r_2^{\lambda}} \]
\[ \times Y_{l-\lambda,m-\mu}(\hat{r}_1) Y_{\lambda\mu}(\hat{r}_2) \]
\[ \begin{pmatrix} l-\lambda & \lambda & l \\ m-\mu & \mu & -m \end{pmatrix} \]  
(A.14)

Special case

\[ Y_{lm}(\hat{z}) = Y_{lm}(0,\varphi) = \left( \frac{2l+1}{4\pi} \right)^{1/2} \delta_{0,m} \]  
(A.15)

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A.5 Integrals

\[ \int_0^\infty dr \, r e^{-ar} f_i(b,r) f_i(c,r) = \frac{1}{2bc} Q_i \left( \frac{a^2 + b^2 + c^2}{2bc} \right) \]  \hspace{1cm} (A.16)

A.6 Hypergeometric Functions

\[ _2F_1(a,b;c;z) = \sum_{k=0} \frac{(a)_k (b)_k}{(c)_k} \frac{z^k}{k!}, \quad (a)_k = \frac{\Gamma(a+k)}{\Gamma(a)} \]  \hspace{1cm} (A.17)

Transformation

\[ _2F_1(a,b;c;z) = (1-z)^{c-a-b} _2F_1(c-a,c-b;c;z) \]
\[ = (1-z)^{-b} _2F_1 \left( a,c-b;c; \frac{z}{z-1} \right) \]  \hspace{1cm} (A.18)
Appendix B

Potential Matrix Elements for Electron-Atom Scattering

Calculating the transition matrix for any scattering problem first requires the computation of potential matrix elements. Since the transition matrix is numerically calculated via a partial-wave expansion, partial-wave potential matrix elements are needed, rather than the full potential matrix. This appendix describes the details for deriving the expressions necessary to calculate momentum-space partial-wave potential matrix elements for electron scattering from one-electron atoms. Although these equations were given almost twenty years ago by McCarthy & Stelbovics (1983), a full account of their derivation has not been provided in explicit detail.

Some equations derived in this appendix differ slightly from those given by McCarthy & Stelbovics. The generalised expression for the partial-wave potential matrix element derived in the discussion that follows has a summation over total angular momentum magnetic quantum number $M_p$, whereas, McCarthy & Stelbovics’ equation (54) does not. Although these expressions are essentially equivalent, it is necessary to do the summation over $M_j$ in deriving the two-electron direct matrix elements so that the expression can be simplified to form that is reasonably efficient for numerical calculations.
Appendix B: Direct and exchange potentials for e-H scattering

An error in the phase is also present in McCarthy & Stelbovics' equation (62) for the two-electron direct-potential matrix elements. This expression has been derived for the momentum transfer defined as \( K = k' - k \), which is opposite to the convention specified by (31). The incorrect phase appearing in (62) of their 1983 paper is \((-1)^{j'+r' + r + \lambda}\). It should read \((-1)^{j'+r'}\). Checking the Fortran code of McCarthy & Stelbovics shows that the correct phase was used in their numerical work.

B.1 Potential Matrix as a Partial-Wave Expansion

The three-body system consisting of an electron projectile and a single-electron target atom with nuclear charge \( Z \), have initial and final quantum states defined by \( |i\rangle = |nlm; k\rangle \) and \( |f\rangle = |n'l'm'; k'\rangle \), respectively. The momentum-transfer vector \( K \) is defined by the difference between initial and final projectile momenta, i.e. \( K = k - k' \). This system has potential matrix elements given by

\[
|f\rangle \langle V| i\rangle = \langle k'; n'l'm'| V|nlm; k\rangle
\]

(B.1)

For the numerical computation of these matrix elements, it is necessary to express (B.1) as a momentum-space partial-wave sum over the total angular momentum \( J \). This partial-wave representation of the potential matrix element is established by the following procedure. Start by inserting two complete sets of angular momentum states for the incident and scattered electron into equation (B.1), which is then

\[
|f\rangle \langle V| i\rangle = \sum_{L' M' L M} \langle \hat{k}'| L'M' \rangle \langle L'M'| V |n'l'm'| \langle k'n'l'm'| V |nlm k\rangle \langle LM|LM| \hat{k}\rangle
\]

\[
= \sum_{L' M' L M} \langle \hat{k}'| L'M' \rangle \langle L'M'| I'm'| \langle k'n'| V |nk\rangle \langle LMIm \rangle \langle LM| \hat{k}\rangle
\]

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Now expanding $|LMlm\rangle$ and $|L'M'l'm'\rangle$ over complete sets of total angular momentum states for $J$ and $J'$, respectively

$$
|f\rangle \langle V| i \rangle = \sum_{L'M'MJM_JJ'M'_J} \langle \hat{k}'| L'M' \rangle \langle L'M'I'm'| L'I'J'M'_J \rangle \langle L'I'J'M_J | k'n'| V \rangle \langle n \rangle \langle k \rangle 
\times | LMJM_J \rangle \langle LMJM_J | LMlm \rangle \langle LM| \hat{k} \rangle 
\times \sum_{L'M'MJM_JJ'M'_J} \langle \hat{k}'| L'M' \rangle C^{L'I'_J}_{M'm'M'_J} \langle J'M'_J | k'n'l'| V \rangle \langle n \rangle \langle l \rangle \langle k \rangle | JM_J \rangle 
\times C^{L_IJ}_{mM_J} \langle LM| \hat{k} \rangle
$$

Defining $V^{n'L'I'_I}_{nL} (k', k) = \langle k' L'n'l'| V \rangle \langle n \rangle \langle l \rangle \langle k \rangle$, then by the Wigner-Eckart theorem (Brink & Satchler, 1999), the matrix element $\langle J'M'_J | \langle k' L'n'l'| V \rangle \langle n \rangle \langle l \rangle \langle k \rangle | JM_J \rangle$ becomes

$$
\langle J'M'_J | \langle k' L'n'l'| V \rangle \langle n \rangle \langle l \rangle \langle k \rangle | JM_J \rangle = \langle J| \langle V^{n'L'I'_I}_{nL} (k', k) \rangle \langle J \rangle | J'M_J \rangle | J'0M_J 0 \rangle 
= \langle J| \langle V^{n'L'I'_I}_{nL} (k', k) \rangle \langle J \rangle \delta_{JJ'} \delta_{M_J M'_J} \rangle \quad (B.2)
$$

The potential matrix element of interest is therefore

$$
|f\rangle \langle V| i \rangle = \sum_{L'M'MJM_JJ'M'_J} \langle \hat{k}'| L'M' \rangle C^{L'I'_J}_{m'm'M'_J} \delta_{JJ'} \delta_{M_J M'_J} \langle J| \langle V^{n'L'I'_I}_{nL} (k', k) \rangle \langle J \rangle \rangle 
\times C^{L_IJ}_{mM_J} \langle LM| \hat{k} \rangle
$$

Summing this expression over $J$ and $M_J$ gives

$$
|f\rangle \langle V| i \rangle = \sum_{L'M'MJM_J} \langle \hat{k}'| L'M' \rangle C^{L'I'_J}_{m'M'_J} \langle J| \langle V^{n'L'I'_I}_{nL} (k', k) \rangle \langle J \rangle \rangle C^{L_IJ}_{mM_J} \langle LM| \hat{k} \rangle
$$

Writing the reduced matrix element as $V^{n'L'I'_I}_{nL} (J') (k', k)$, the partial-wave representation of the potential matrix element expanded over total angular momentum $J$ is given by

$$
\langle k'; n'l'm'| V \rangle \langle nlm; k \rangle 
= \sum_{L'M'MJM_J} \langle \hat{k}'| L'M' \rangle C^{L'I'_J}_{m'M'_J} V^{n'L'I'_I}_{nL} (J) (k', k) C^{L_IJ}_{mM_J} \langle LM| \hat{k} \rangle \quad (B.3)
$$
Appendix B: Direct and exchange potentials for e-H scattering

An important point to note here is that the partial-wave matrix element in (B.2) is independent of the total angular momentum magnetic quantum number $M_f$ and consequently, summing over $M_f$ simply results in

$$\sum_{M_f} V_{n L}^{l_1 l_2 l_3 l_4} (k', k) = (2J + 1) V_{n L}^{l_1 l_2 l_3 l_4} (k', k)$$  \hspace{1cm} (B.4)

B.2 Partial-Wave Potential Matrix Elements

Now an expression for the momentum-space partial-wave matrix element $V_{n L}^{l_1 l_2 l_3 l_4} (k', k)$ is required. To determine this, consider the following double integral.

$$\int d\mathbf{k}' \int d\mathbf{k} \sum_{M_M m_M', m_M} \langle L' M' | \mathbf{k}' \rangle \langle \mathbf{k}' | n l m \rangle \langle \mathbf{k} | L M \rangle C_{M_M m_M'}^{l_1 l_2 l_3 l_4} \langle \mathbf{k}' | L M \rangle$$

Inserting the partial-wave expansion of the potential matrix element gives

$$\int d\mathbf{k}' \int d\mathbf{k} \sum_{M_M m_M', m_M} \langle L' M' | \mathbf{k}' \rangle \langle \mathbf{k}' | L M \rangle C_{M_M m_M'}^{l_1 l_2 l_3 l_4} \times \sum_{L' M' L M} \langle \mathbf{k}' | L M \rangle \langle L' M' | k' \rangle \langle k' | n l m \rangle \langle n l m | L M \rangle \langle L M | \mathbf{k} \rangle$$

EValuating the integrals yields

$$\sum_{M_M m_M', m_M} \delta_{L' L} \delta_{M' M} \delta_{l_1 l} \delta_{l_2 l_3} \delta_{l_4 l_4} C_{M_M m_M'}^{l_1 l_2 l_3 l_4} \langle \mathbf{k}' | L M \rangle \langle L' M' | k' \rangle \langle k' | n l m \rangle \langle n l m | L M \rangle \langle L M | \mathbf{k} \rangle$$

Now summing over $L'$, $M'$, $L$ and $M$ reduces the expression to

$$\sum_{M_M m_M', m_M} C_{M_M m_M'}^{l_1 l_2 l_3 l_4} C_{M_M m_M'}^{l_1 l_2 l_3 l_4} \langle \mathbf{k}' | L M \rangle \langle L' M' | k' \rangle \langle k' | n l m \rangle \langle n l m | L M \rangle \langle L M | \mathbf{k} \rangle$$
Using the orthogonality properties of the Clebsch-Gordan coefficients, summing over \( M, m, M', m' \) gives

\[
\sum_{M,J,M,J} \delta_{J,J} \delta_{M,M} \sum_{n,L,L'} V_{n,L,L}^{n',L',L'(J)}(k', k) \delta_{J,J} \delta_{M,M} = (2J + 1) V_{n,L,L}^{n',L',L'(J)}(k', k)
\]

This result shows that the momentum-space representation of the partial-wave potential matrix element is given by

\[
V_{n,L,L}^{n',L',L'(J)}(k', k) = \frac{1}{j^2} \int d\hat{k}' \int d\hat{k} \sum_{M,m,M',m',M,J} \langle L'M' | \hat{k}' \rangle C_{M,m,M,J}^{L',L,J} \langle f | V | i \rangle C_{M,m,M,J}^{L,L,J} \langle \hat{k} | L M \rangle
\]

where the notation \( \hat{J} \) means \((2J + 1)^{1/2}\). Writing the Clebsch-Gordan coefficients in terms of 3-j symbols, equation (B.5) becomes

\[
V_{n,L,L}^{n',L',L'(J)}(k', k) = \sum_{M,m,M',m',M,J} (-1)^{L+L'+L'} \left( \begin{array}{ccc} L' & L & J \\ M' & m' & M,J \end{array} \right) \left( \begin{array}{ccc} L & I & J \\ M & m & -M,J \end{array} \right) \int d\hat{k}' \int d\hat{k} \langle L'M' | \hat{k}' \rangle \langle f | V | i \rangle \langle \hat{k} | L M \rangle
\]

This expression is the common starting point for both the direct and exchange-potential matrix elements.

### B.3 Direct-Potential Matrix Elements

The direct potential consists of two contributions: the electron-core potential \((V_1)\) due to the projectile’s interaction with the target’s nucleus; and the two-electron \((V_{12})\) potential due to the free electron’s interaction with the target’s bound electron. Subscript labels 1 and 2 refer to the free and bound electrons, respectively. These two components will be treated separately in the following discussion.
Appendix B: Direct and exchange potentials for e-H scattering

B.3.1 Electron-core direct-potential matrix elements

The electron-core potential $V_1$ is a local, central potential with potential matrix elements given by

$$\langle k'; n'l'm' \mid V_1 \mid nlm \mid k \rangle = \langle k'; n'l'm' \mid -\frac{Z}{r_1} \mid nlm \mid k \rangle$$  \hspace{1cm} (B.7)

Inserting the usual expansions gives

$$\langle k'; n'l'm' \mid V_1 \mid nlm \mid k \rangle = -Z \int dr_1 \langle k' \mid r_1 \rangle \frac{1}{r_1} \langle r_1 \mid k \rangle \int dr_2 \langle n'l'm' \mid r_2 \rangle \langle r_2 \mid nlm \rangle$$

which, when evaluated gives the trivial solution

$$\langle k'; n'l'm' \mid V_1 \mid nlm \mid k \rangle = -\frac{Z}{2\pi^2 K^2} \delta_{nn'} \delta_{ll'} \delta_{mm'}$$  \hspace{1cm} (B.8)

Although this expression is not in a partial-wave form, an alternative strategy can be employed utilising the expression for the partial-wave expansion of the two-electron direct-potential matrix element. This method is discussed in section 2.4.2.

B.3.2 Electron-electron direct-potential matrix elements

Consider the two-electron interaction having the potential operator $V_{12}$, for which, the direct-potential matrix is given by

$$V_{n'l'm'}^{n'l'm'}(k', k) = \langle k'; n'l'm' \mid V_{12} \mid nlm \mid k \rangle$$

$$= \langle k'; n'l'm' \mid \frac{1}{r_1 - r_2} \mid nlm \mid k \rangle$$  \hspace{1cm} (B.9)

When this expression is evaluated, the result is (Blackett & Steibovics, 1999)
\[ V_{n' l' m'}^{n l m} (K) = \frac{1}{2\pi^2 K^2} 4\pi \sum_{l'' m''} i^{l''} (-1)^m i^n i^{l'} \left( \frac{i^{l''} i^{l'} \binom{l'' \ l' \ l}{m'' \ m' \ -m} \binom{l'' \ l' \ l}{0 \ 0 \ 0}}{(4\pi)^{1/2}} \right) \times \langle \hat{\mathbf{K}} | l'' m'' \rangle g_{l'' n' l'}^{n' l'} (K) \] (B.10)

with the radial contribution being

\[ g_{l'' n' l'}^{n' l'} (K) = \int_0^\infty dr \ r^2 \langle n' l' | r \rangle j_{l'} (Kr) \langle r | n l \rangle \] (B.11)

Equation (B.10) gives the two-electron direct-potential matrix purely in terms of the momentum transfer \( \mathbf{K} \). However, an expression is required that gives the matrix element mainly in terms of the components \( \mathbf{k}' \) and \( \mathbf{k} \). Reference to the momentum-transfer direction \( \mathbf{K} \) is first removed from (B.10) by observing that the spherical harmonic \( \langle \hat{\mathbf{K}} | l'' m'' \rangle \) can be written in terms of \( \mathbf{K}' \)’s components (Brink & Satchler, 1999) as

\[ \langle \hat{\mathbf{K}} | l'' m'' \rangle = \sum_{\nu, \mu} (-1)^{m'' + \lambda} i^n \left( \frac{4\pi (2l'' + 1)!}{(2\lambda + 1)! (2\lambda' + 1)!} \right)^{1/2} \frac{k^{\lambda'} k^{\lambda}}{K^{l''}} \langle \hat{\mathbf{K}}' | \lambda' \mu' \rangle \langle \hat{\mathbf{K}} | \lambda \mu \rangle \left( \begin{array}{c} \lambda' \\ \mu' \\ \lambda \\ \mu \end{array} \right) \] (B.12)

where \( \lambda' = l'' - \lambda \) and \( \mu' = m'' - \mu \). Now defining the auxiliary function

\[ g_{l'' n' l \lambda}^{n' l'} (K) = g_{l'' n' l}^{n' l'} (K) \frac{k^{\lambda'} k^{\lambda}}{K^{l''+2}} \] (B.13)

and then combining this with (B.12), the product \( \langle \hat{\mathbf{K}} | l'' m'' \rangle g_{l'' n' l}^{n' l'} (K) \) becomes

\[ \langle \hat{\mathbf{K}} | l'' m'' \rangle g_{l'' n' l}^{n' l'} (K) = K^2 \sum_{\lambda, \mu} (-1)^{m'' + \lambda} i^n \left( \frac{4\pi (2l'' + 1)!}{(2\lambda + 1)! (2\lambda' + 1)!} \right)^{1/2} \times \langle \hat{\mathbf{K}}' | \lambda' \mu' \rangle \langle \hat{\mathbf{K}} | \lambda \mu \rangle g_{l'' n' l \lambda}^{n' l'} (K) \] (B.14)

Introducing a partial-wave expansion of \( g_{l'' n' l \lambda}^{n' l'} (K) \) defined by

\[ g_{l'' n' l \lambda}^{n' l'} (K) = \sum_{l'' m''} \langle \hat{\mathbf{K}}' | l'' m'' \rangle \langle l'' m'' | \hat{\mathbf{K}} \rangle g_{l' n' l \lambda}^{n' l'} (k', k) \] (B.15)
where, with \( u = \hat{k}' \cdot \hat{k} \)

\[
g_{l^{'n'}l^{'m'}}(k', k) = 2\pi \int_{-1}^{1} du \quad P_{l^{'n'}}(u) \quad g_{l^{'n'}l^{'m'}}(k') \tag{B.16}
\]

almost eliminates the momentum-transfer magnitude \( K \) from equation (B.14), yielding

\[
\langle \hat{k}' | l^{'n'}m'' \rangle g_{l^{'n'}l^{'m'}}(K) = K^{2} \sum_{l^{'m'}m'' \lambda \mu} (-1)^{m''-\lambda} \hat{f}_{l} \left( \frac{4\pi (2l''+1)!}{(2\lambda+1)!(2\lambda'+1)!} \right)^{1/2} \\
\times \langle \hat{k}' | \lambda' \mu' \rangle \langle \hat{k} | \lambda \mu \rangle \left( \begin{array}{cc}
\lambda' & \lambda \\
\mu' & -m''
\end{array} \right) \\
\times \langle \hat{k}' | l''m'' \rangle \langle l''m'' | \hat{k} \rangle \quad g_{l^{'n'}l^{'m'}}(k', k) \tag{B.17}
\]

Substituting (B.17) into equation (B.10) then gives the two-electron direct-potential matrix elements in terms of \( k' \) and \( k \)

\[
V_{l^{'n'}l^{'m'}}(k', k) = \frac{1}{2\pi^{2}} 4\pi \sum_{l^{'m'}m''l^{'m''} \lambda \mu} i^{l''} (-1)^{m''+\lambda} \hat{f}_{l} \hat{f}_{l'} \left( \frac{(2l''+1)!}{(2\lambda+1)!(2\lambda'+1)!} \right)^{1/2} \\
\times \left( \begin{array}{cc}
l'' & l' \\
m'' & m' -m''
\end{array} \right) \left( \begin{array}{cc}
\lambda' & \lambda \\
\mu' & -m''
\end{array} \right) \\
\times \langle \hat{k}' | \lambda' \mu' \rangle \langle \hat{k} | \lambda \mu \rangle \langle \hat{k}' | l''m'' \rangle \langle l''m'' | \hat{k} \rangle \\
\times g_{l^{'n'}l^{'m'}}(k', k)
\]

Inserting this expression into equation (B.6), the partial-wave direct-potential matrix elements are given by

\[
V_{l^{'n'}l^{'m'}}^{(j)}(k', k) = \frac{1}{2\pi^{2}} 4\pi \int d\hat{k} \int d\hat{k}' \sum_{MmM'M'j} i^{l''} (-1)^{L + L' + l + m + m'' + \lambda} \\
\times \hat{f}_{l} \hat{f}_{l'} \left( \frac{(2l''+1)!}{(2\lambda+1)!(2\lambda'+1)!} \right)^{1/2} \left( \begin{array}{cc}
L' & J \\
M' & m' -M_j
\end{array} \right) \\
\times \left( \begin{array}{cc}
L & J \\
M & -M_j
\end{array} \right) \left( \begin{array}{cc}
l'' & l' \\
m'' & m' -m''
\end{array} \right) \left( \begin{array}{cc}
\lambda' & \lambda \\
\mu' & -m''
\end{array} \right) \\
\times \langle \hat{k}' | \lambda' \mu' \rangle \langle \hat{k} | \lambda \mu \rangle \langle \hat{k}' | l''m'' \rangle \langle l''m'' | \hat{k} \rangle \\
\times \langle L'M' | \hat{k}' \rangle \langle \hat{k} | LM \rangle \quad g_{l^{'n'}l^{'m'}}(k', k) \tag{B.18}
\]

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Evaluating the angular integrations in equation (B.18) yields

\[
\int d\hat{k} \langle \hat{k} | L M \rangle \langle L'' m'' | \hat{k} \rangle \langle \hat{k} | \lambda, \mu \rangle \int d\hat{k}' \langle L' M' | \hat{k}' \rangle \langle \hat{k}' | l'' m'' \rangle \langle \hat{k}' | \lambda', \mu' \rangle \\
= (-1)^{m'' + M'} \frac{\hat{L} \hat{L} (\hat{L}')^2 \lambda \lambda'}{4\pi} \left( \begin{array}{ccc} L & l'' & \lambda \\ M & -m'' & \mu \end{array} \right) \left( \begin{array}{ccc} L' & i'' & \lambda' \\ -M' & m'' & \mu' \end{array} \right) \left( \begin{array}{ccc} L & i'' & \lambda \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} L' & i'' & \lambda' \\ 0 & 0 & 0 \end{array} \right)
\]

Using these results in equation (B.18) gives

\[
V_{n L L'}^{n' L' L''}(k', k) = \frac{1}{2\pi^2} \sum_{M M' m' M'} \frac{i l''}{(2l'')! (2\lambda')!} \left( \frac{(2l'')!}{(2\lambda)!} \right)^{1/2} \\
\times \hat{L} \hat{L} (\hat{L}')^2 (\hat{l}')^3 \hat{l} \hat{l'} \left( \begin{array}{ccc} L & l'' & \lambda \\ -M' & m'' & \mu' \end{array} \right) \left( \begin{array}{ccc} L & l'' & \lambda \\ M & -m'' & \mu \end{array} \right) \left( \begin{array}{ccc} L' & i'' & \lambda' \\ M & m & M'_j \end{array} \right) \left( \begin{array}{ccc} L' & i'' & \lambda' \\ M & m & M'_j \end{array} \right) \left( \begin{array}{ccc} 0 & 0 & 0 \end{array} \right)
\]

The six 3-j symbols with non-zero \( m \) values can be simplified to two 6-j symbols. In order to do this, it is convenient to rewrite the magnetic quantum number sums in (B.19) in a standard form that makes simplification easier using formulae for contraction of 3-j symbols given by Blum (1981). Introducing the unit factors \( 1 = (-1)^{J} \) and \( 1 = (-1)^{2l''} \), and making the phase substitutions \( (-1)^m = (-1)^{M + \mu} \) and \( (-1)^M = (-1)^{M_\mu + M_j} \) assists in the simplification process. Applying these changes and rearranging the result, \( V_{n L L'}^{n' L' L''}(k', k) \) becomes
\[
\frac{1}{2\pi^2} \sum \left( -1 \right)^{l''+l'+l''} \hat{L} \hat{L}' (\hat{l}'')^2 (\hat{I}'')^3 \hat{l} \hat{l}' \left( \frac{(2l'')!}{(2\lambda)! (2\lambda')!} \right)^{1/2} \\
\times \left( \begin{array}{cc} L' & \lambda' \\ 0 & 0 \end{array} \right) \left( \begin{array}{ccc} L & I'' & \lambda \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} I'' & I' & l' \\ 0 & 0 & 0 \end{array} \right) g_{I'' I' I \lambda} (k', k) \\
\times \sum_{M'' \mu'' m'' M} (-1)^{\lambda l'' + l'' + l' + m'' + M} \left( \begin{array}{ccc} L' & I'' & \lambda' \\ -M' & m'' & \mu' \end{array} \right) \left( \begin{array}{ccc} \lambda & I'' & \lambda' \\ -\mu & m'' & \mu' \end{array} \right) \\
\times \sum_{M_j, m} (-1)^{l'' + l' + l'' + m_j + m} \left( \begin{array}{ccc} I' & J' & L' \\ m' & -M_j & M' \end{array} \right) \left( \begin{array}{ccc} J & I & L \\ m & -M & -M \end{array} \right) \left( \begin{array}{ccc} I & I' & I'' \\ m & -m' & -m'' \end{array} \right)
\]

The summation over the magnetic quantum numbers \( m', M_j, m \) is evaluated (Brink & Satchler, 1999) as

\[
\sum_{m, M_j, m} (-1)^{l'' + l' + l'' + m_j + m} \left( \begin{array}{ccc} I' & J' & L' \\ m' & -M_j & M' \end{array} \right) \left( \begin{array}{ccc} J & I & L \\ m & -M & -M \end{array} \right) \left( \begin{array}{ccc} I & I' & I'' \\ m & -m' & -m'' \end{array} \right)
\]

\[
= \left( \begin{array}{ccc} L & I'' & L' \\ -M & m'' & M' \end{array} \right) \left( \begin{array}{ccc} \lambda & I'' & \lambda' \\ -\mu & m'' & \mu' \end{array} \right) \\
= \left( \begin{array}{ccc} L & I'' & L' \\ -M & m'' & M' \end{array} \right) \left( \begin{array}{ccc} \lambda & I'' & \lambda' \\ -\mu & m'' & \mu' \end{array} \right)
\]

The 3-j symbol from this result is now included in the summation over the remaining magnetic quantum numbers. Summing over \( \mu' \) can be introduced since, by its definition, it can only contribute one value to the sum, i.e. \( m'' - \mu' \). Also note that the signs of \( M \) and \( M' \) have been changed, which is allowed because for any magnetic quantum number \( m \) being summed over, \( \sum_m f(m) = \sum_m f(-m) \). The result is then

\[
\sum_{M'' \mu'' m'' M} (-1)^{\lambda l'' + l'' + l' + m'' + M} \left( \begin{array}{ccc} L' & I'' & \lambda' \\ M' & m'' & \mu' \end{array} \right) \left( \begin{array}{ccc} L' & I'' & L \\ M' & m'' & -M \end{array} \right) \\
\times \left( \begin{array}{ccc} \lambda & I'' & \lambda' \\ -\mu & m'' & \mu' \end{array} \right) \left( \begin{array}{ccc} \lambda & I'' & \lambda' \\ -\mu & m'' & \mu' \end{array} \right)
\]

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Therefore, after replacing \( \lambda' \) and \( \mu' \), equation (B.19) simplifies to

\[
V_{n' L' l' \lambda'}^{(j)}(k', k) = \frac{1}{2\pi^2} \sum_{l'' l'''} l'' l''' (-1)^{J''+L''+l''} \left( \frac{(2l'')!}{(2\lambda'')! [2(l''-\lambda'')!]} \right)^{1/2} \\
\times \hat{L} \hat{L} \hat{l} \hat{r} (\hat{l}'')^2 (\hat{l}'')^3 \left\{ \begin{array}{c} L' \ l'' \ l''-\lambda' \\ \lambda' \ l'' \ L' \end{array} \right\} \left\{ \begin{array}{c} L \ l'' \ \lambda' \\ \lambda \ \ l'' \ l' \end{array} \right\} \\
\times \left( \begin{array}{c} L' \ l'' \ \lambda' \\ 0 \ 0 \ 0 \end{array} \right) \left( \begin{array}{c} L \ l'' \ \lambda \\ 0 \ 0 \ 0 \end{array} \right) g_{L'' l'' l''\lambda'}^{n'' l'' l''}(k', k)
\]

From the symmetry properties of the 3-\( j \) symbols, \((-1)^{J''+L''+l''} = (-1)^{J+L}\) and using the symmetry properties of the 6-\( j \) symbols, the expression for the two-electron momentum-space partial-wave direct-potential matrix elements is rearranged for improved computational efficiency as

\[
V_{n' L' l' \lambda'}^{(j)}(k', k) = \frac{1}{2\pi^2} (-1)^{J+L} \hat{L} \hat{L} \hat{l} \hat{r} \sum_{l'' l'''} l'' l''' \left( \frac{(2l'')!}{(2\lambda'')! [2(l''-\lambda'')!]} \right)^{1/2} \\
\times (\hat{l}'')^3 (\hat{l}'')^2 \left( \begin{array}{c} l'' \ l' \ l' \\ 0 \ 0 \ 0 \end{array} \right) \left\{ \begin{array}{c} L \ l'' \ L' \\ \lambda \ \ l'' \ \lambda' \end{array} \right\} \\
\times \left( \begin{array}{c} L \ l'' \ \lambda \\ 0 \ 0 \ 0 \end{array} \right) \left( \begin{array}{c} L \ l'' \ \lambda \\ 0 \ 0 \ 0 \end{array} \right) g_{L'' l'' l''\lambda'}^{n'' l'' l''}(k', k)
\]

Substituting for (B.13) into equation (B.16) gives the partial-wave function containing the momenta magnitudes

\[
g_{n'' l'' l''\lambda'}^{n' l' l'}(k', k) = 2\pi \int_{-1}^{1} du P_{l'}(u) k'((l''-\lambda') k \lambda g_{n'' l'' l''\lambda'}^{n' l'' l''}(K) K \lambda k''^{2n''+1} e^{-a_n r}
\]

Writing the one-electron radial bound state as the Slater expansion

\[
\langle r | n l \rangle = \sum_{\mu=1}^{v} c_\mu A_\mu r^{n_{\mu}-1} e^{-a_\mu r}
\]

where \( A_\mu = \left[ (2a_\mu)^{2n_{\mu}-1} / (2n_{\mu})! \right]^{1/2} \), allows equation (B.11) to be expressed as

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\[ g_{\Gamma n \lambda}^{n'\Gamma'}(K) = \sum_{N=1}^{\infty} g_{\Gamma}^{N}(K) \]  

(B.24)

where

\[ g_{\Gamma}^{N}(K) = C_{N} \int_{0}^{\infty} dr \ j_{\Gamma}(Kr) \ r^{n_{N}} e^{-a_{N}r} \]  

(B.25)

and

\[ n_{N} = n_{\mu} + n_{\nu}, \]

\[ C_{N} = c_{\mu} c_{\mu} c_{\nu} A_{\mu}, \]

\[ a_{N} = a_{\mu} + a_{\nu}. \]

Evaluating this integral to its closed form solution gives

\[ g_{\Gamma}^{N}(K) = K^{l_{n}} \frac{\pi^{1/2} \alpha_{N}^{2} C_{N} \Gamma(2 \ b - 1)}{2^{\gamma} \ (\alpha_{N}^{2} + K^{2})^{\frac{3}{2}} \ (\gamma + \frac{1}{2})} \ 2F_{1} \left( b - n_{N}, b; \gamma + \frac{1}{2}; \frac{K^{2}}{\alpha_{N}^{2} + K^{2}} \right) \]  

(B.26)

where \( 2F_{1} \) is the hypergeometric function, \( b = \frac{l_{n} + n_{N} + 2}{2} \) and \( \gamma = l_{n} + 1 \). The two-electron partial-wave direct-potential matrix elements are then given by

\[ V_{n L}^{n' L'}(k', k) = \frac{1}{2 \pi^{2}} (-1)^{l_{n} + l'_{n}} \hat{L} \hat{L'} \hat{l} \hat{l'} \sum_{l_{n}, l_{n}'} i^{l_{n}} A_{\Gamma L L' \lambda}^{L' \Gamma' \lambda'}(j) \ g_{\Gamma n l \lambda}^{n' \Gamma' l'}(k', k) \]  

(B.27)

\[ A_{\Gamma L L' \lambda}^{L' \Gamma' \lambda'}(j) = \left( \frac{(2l_{n})!}{(2\lambda)! \ [2(l_{n} - \lambda)!]!} \right)^{1/2} \ (\hat{j})^{3} \ (\hat{j}')^{3} \ \left( \begin{array}{ccc} l_{n} & l'_{n} & l \noalign{\hrule} 0 & 0 & 0 \noalign{\hrule} L & l_{n'}^{-} & L' \end{array} \right) \left( \begin{array}{ccc} l_{n} & l'_{n} & l \noalign{\hrule} 0 & 0 & 0 \noalign{\hrule} L_{n} & l_{n'} & L' \end{array} \right) \]  

(B.28)

\[ g_{\Gamma n l \lambda}^{n' \Gamma' l'}(k', k) = 2 \pi \ k'(l_{n} - \lambda) k^{\lambda} \int_{-1}^{1} du \ P_{l'}(u) \sum_{N} \ g_{\Gamma}^{N}(K) \frac{K^{l_{n} + 2}}{K(l_{n} + 2)} \]  

(B.29)
An alternative form of the two-electron direct-potential matrix elements requiring a double \( r \)-space integration is also given by McCarthy and Stelbovics (1983), however, it and far is less appealing from a computational perspective. However, a similar double \( r \)-space formulation is used to calculate the exchange-potential matrix elements.

### B.4 Exchange-Potential Matrix Elements

In this section, an expression for calculating the momentum-space partial-wave exchange matrix elements necessary for the electron scattering from a one electron atom target is derived. McCarthy and Stelbovics (1983) define the exchange-potential operator as

\[
V = (-1)^S (H - E) P_{12},
\]

where \( S \) is the total spin, \( P_{12} \) is the space exchange operator, \( E \) the total energy and \( H \) is the Hamiltonian for electron scattering from a one-electron atom. In terms of the kinetic and potential energy operators, \( K \) and \( V \), the Hamiltonian \( H \) is given by

\[
H = K_1 + K_2 + V_1 + V_2 + V_{12}
\]

where the subscript labels 1 and 2 refer to the electron-core interactions for each of the two electrons and \( V_{12} \) is the electron-electron potential. It is assumed that the unbound electron is designated by the subscript 1. The exchange-potential matrix elements are then given by the expression

\[
V_{n l m}^{n' l' m'} (k', k) = \langle k'; n' l' m' | (-1)^S (H - E) P_{12} | n l m; k \rangle
\]

At this early stage, it is convenient to factor the \((-1)^S\) out of the expression and temporarily ignore it until the partial-wave exchange matrix element is determined. Expanding over two complete sets in coordinate-space, one for the free electron \( (r_1) \) and one for the bound electron \( (r_2) \), gives

\[
V_{n l m}^{n' l' m'} (k', k) = \int dr_1 dr_2 \langle k'; n' l' m' | (H - E) P_{12} | r_2 \rangle \langle r_2 | n l m \rangle \langle r_1 | k \rangle
\]
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Now, allowing the space exchange operator $P_{12}$ to act to the right, which simply exchanges the coordinate-space variables on the right. Since the Hamiltonian is a function of the coordinate variables $\mathbf{r}_1$ and $\mathbf{r}_2$, the exchange matrix element can be written as

\[
V^{n'l'm'}_{n'l'm'}(\mathbf{k}',\mathbf{k}) = \int d\mathbf{r}_1 d\mathbf{r}_2 \langle \mathbf{k}' | \mathbf{r}_1 \rangle \langle n'l'm' | \mathbf{r}_2 \rangle (H - E) \langle \mathbf{r}_1 | n'l'm \rangle \langle \mathbf{r}_2 | \mathbf{k} \rangle \tag{B.33}
\]

The partial-wave exchange matrix element is obtained by inserting this expression into equation (B.6), yielding

\[
V^{n'L'J}(nL)(\mathbf{k}',\mathbf{k}) = \sum_{MM'M'M_J} (-1)^{L'+L+J} \left( \begin{array}{ccc}
L' & L & J \\
M' & m' & -M_J \\
M & m & -M_J 
\end{array} \right) \int d\mathbf{k}' d\mathbf{k} \langle L'M' | \mathbf{k}' \rangle \int d\mathbf{r}_1 d\mathbf{r}_2 \langle \mathbf{k}' | \mathbf{r}_1 \rangle \langle n'l'm' | \mathbf{r}_2 \rangle (H - E) \langle \mathbf{r}_1 | n'l'm \rangle \langle \mathbf{r}_2 | \mathbf{k} \rangle \langle \mathbf{k} | LM \rangle \tag{B.34}
\]

Rather than writing out the full expression each time, just the integration parts of this expression will be considered at this stage. Expanding the plane waves gives

\[
\int d\mathbf{r}_1 d\mathbf{r}_2 \int d\mathbf{k}' d\mathbf{k} \langle L'M' | \mathbf{k}' \rangle \frac{4\pi}{(2\pi)^{3/2}} \sum_{\tilde{L} \tilde{M}} i^{-\tilde{L}} j_{\tilde{L}}(k'r_1) \langle \mathbf{k}' | \tilde{L}' \tilde{M}' \rangle \langle \tilde{L}' \tilde{M}' | \mathbf{r}_1 \rangle \times \langle n'l'm' | \mathbf{r}_2 \rangle (H - E) \langle \mathbf{r}_1 | n'l'm \rangle \frac{4\pi}{(2\pi)^{3/2}} \sum_{\tilde{L} \tilde{M}} i^{-\tilde{L}} j_{\tilde{L}}(kr_2) \langle \mathbf{r}_2 | \tilde{L} \tilde{M} \rangle \langle \tilde{L} \tilde{M} | \mathbf{k} \rangle \langle \mathbf{k} | LM \rangle
\]

Carrying out the momentum direction integrations and simplifying results in

\[
\frac{2}{\pi} \sum_{\tilde{L} \tilde{M} \tilde{M}' \tilde{M}} i^{-\tilde{L}} \int d\mathbf{r}_1 d\mathbf{r}_2 \delta_{\tilde{L} \tilde{M}' \tilde{M}} \delta_{M' \tilde{M}} j_{\tilde{L}}(k'r_1) \langle \tilde{L}' \tilde{M}' | \mathbf{r}_1 \rangle \langle n'l'm' | \mathbf{r}_2 \rangle (H - E) \langle \mathbf{r}_1 | n'l'm \rangle j_{\tilde{L}}(kr_2) \langle \mathbf{r}_2 | \tilde{L} \tilde{M} \rangle \delta_{\tilde{L} \tilde{L}} \delta_{\tilde{M} \tilde{M}}
\]

Therefore, the summations reduce the expression to

\[
\frac{2}{\pi} i^{-L'} \int d\mathbf{r}_1 d\mathbf{r}_2 j_{L}(k'r_1) \langle L'M' | \mathbf{r}_1 \rangle \langle n'l'm' | \mathbf{r}_2 \rangle (H - E) \langle \mathbf{r}_1 | n'l'm \rangle j_{L}(kr_2) \langle \mathbf{r}_2 | L \tilde{M} \rangle
\]

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Replacing the Hamiltonian gives

\[ \frac{2}{\pi} i^{L-L'} \int dr_1 \, dr_2 \, j_L(k'r_1) \langle L'M' \mid \hat{r}_1 \rangle \langle n'l'm' \mid r_2 \rangle \times \left( -\frac{1}{2} \nabla_1^2 + V_1 - \frac{1}{2} \nabla_2^2 + V_2 + V_{12} - E \right) \langle r_1 \mid nlm \rangle j_L(kr_2) \langle \hat{r}_2 \mid LM \rangle \] (B.35)

Separating the two-electron potential from the rest of the expression, splits it into two terms, which are dealt with separately.

### B.4.1 Energy-dependent exchange-potential matrix elements

Assuming \( \langle r_1 \mid nlm \rangle \) and \( \langle n'l'm' \mid r_2 \rangle \) are eigenfunctions of the \( -\frac{1}{2} \nabla_1^2 + V_1 \) and \( -\frac{1}{2} \nabla_2^2 + V_2 \) operators with eigenvalues of \( \varepsilon_n \) and \( \varepsilon_{n'} \), respectively, then the energy-dependent exchange term can be written simply as

\[ \frac{2}{\pi} i^{L-L'} (\varepsilon_n + \varepsilon_{n'} - E) \int dr_1 \, dr_2 \, j_L(k'r_1) \langle L'M' \mid \hat{r}_1 \rangle \langle n'l'm' \mid r_2 \rangle \times \langle r_1 \mid nlm \rangle j_L(kr_2) \langle \hat{r}_2 \mid LM \rangle \]

Now the angular parts are separated from the radial parts of this expression, so that

\[ \frac{2}{\pi} i^{L-L'} (\varepsilon_n + \varepsilon_{n'} - E) \int d\hat{r}_1 \, d\hat{r}_2 \, \langle L'M' \mid \hat{r}_1 \rangle \langle l'm' \mid \hat{r}_2 \rangle \langle \hat{r}_1 \mid l \rangle \langle \hat{r}_2 \mid L \rangle \]

\[ \times \int_0^\infty dr_1 \, r_1^2 \int_0^\infty dr_2 \, r_2^2 \, j_L(k'r_1) \langle n'l' \mid r_2 \rangle \langle r_1 \mid n \rangle j_L(kr_2) \]

Defining \( r \langle r \mid n \rangle = \varphi_{n}(r) \) and putting \( kr j_L(kr) = u_L(k,r) \), then evaluating the angular integrations finally gives the result

\[ \frac{2}{\pi k'k} i^{L-L'} (\varepsilon_n + \varepsilon_{n'} - E) \delta_{(l,L')} \delta_{(m,M')} \delta_{(l',L)} \delta_{(m',M)} \times \int_0^\infty dr_1 \, \int_0^\infty dr_2 \, u_L(k',r_1) \varphi_{n'}(r_2) \varphi_{n}(r_1) u_L(k,r_2) \]

(B.36)
Inserting this expression into equation (B.6) gives the energy-dependent exchange partial-wave matrix element.

\[
V_{n l}^{n' L' J}(k', k) = \sum_{M m' M'} (-1)^{L + L' + l + l'} \begin{pmatrix} L' & l' & J \\ M' & m' & -M_j \end{pmatrix} \begin{pmatrix} L & l & J \\ M & m & -M_j \end{pmatrix} \\
\times \frac{2}{\pi k' k} i^{L - L'} (\varepsilon_n + \varepsilon_{n'} - E) \delta_{(l, l')} \delta_{(m, M')} \delta_{(l', L)} \delta_{(m', M)} \\
\times \int_0^\infty dr_1 \int_0^\infty dr_2 u_{L'}(k', r_1) \varphi_{n' l'}(r_2) \varphi_{n l}(r_1) u_L(k, r_2)
\]

Rearranging this expression, exchanging the first two columns of the second 3-\(j\) symbol and then evaluating the summations over \(M\) and \(M'\) reduces the matrix element to

\[
V_{n l}^{n' L' J}(k', k) = \frac{2}{\pi k' k} i^{L - L'} (\varepsilon_n + \varepsilon_{n'} - E) \sum_{M_j} \delta_{(l, l')} \delta_{(l', L)} \\
\times (-1)^{L + L' + j} \sum_{m m'} \begin{pmatrix} L' & l' & J \\ m & m' & -M_j \end{pmatrix} \begin{pmatrix} l & L & J \\ m & m' & -M_j \end{pmatrix} \\
\times \int_0^\infty dr_1 u_{L'}(k', r_1) \varphi_{n' l'}(r_2) \int_0^\infty dr_2 \varphi_{n l}(r_1) u_L(k, r_2)
\]

The two remaining Kronecker delta functions allow \(L'\) and \(L\) to be replaced by \(l\) and \(l'\), respectively.

\[
V_{n l}^{n' L' J}(k', k) = \frac{2}{\pi k' k} i^{L - L'} (\varepsilon_n + \varepsilon_{n'} - E) \sum_{M_j} \delta_{(l, l')} \delta_{(l', L)} \\
\times (-1)^{L + L' + j} \frac{1}{j^2} \sum_{m m'} \begin{pmatrix} l & l' & J \\ m & m' & -M_j \end{pmatrix} \begin{pmatrix} l & l' & J \\ m & m' & -M_j \end{pmatrix} \\
\times \int_0^\infty dr_1 u_{L'}(k', r_1) \varphi_{n' l'}(r_2) \int_0^\infty dr_2 \varphi_{n l}(r_1) u_L(k, r_2)
\]

Now, the orthogonality properties of the 3-\(j\) symbols reduce the summations over the remaining \(m\) and \(m'\) quantum numbers to unity, so, after summing over \(M_j\) and restoring the
spin phase factor, the energy-dependent momentum-space exchange-potential matrix element is

\[
V_{n L l}^{n' L' l'}(k', k) = (-1)^S \frac{2}{\pi k' k} i^{l-L'} (-1)^{l'-l} \delta_{L L'} \delta_{l l'} \Delta(l, l', J) \\
\times (\epsilon_n + \epsilon_{n'} - E) \int_0^\infty dr_1 u_L(k', r_1) \varphi_{n l}(r_1) \int_0^\infty dr_2 \varphi_{n' l'}(r_2) u_L(k, r_2)
\]  

(B.37)

where \(\Delta(l, l', J)\) signifies the triangle condition that must be satisfied by the angular momentum quantum numbers \(l, l'\) and \(J\).

### B.4.2 Electron-electron exchange-potential matrix elements

Now consider the two-electron exchange term in equation (B.35), which, using some of the simplification that has already been done to obtain (B.36), is written as

\[
\frac{2}{\pi k' k} i^{l-L'} \int d\hat{r}_1 d\hat{r}_2 \langle L' M' | \hat{r}_1 \rangle \langle l' m' | \hat{r}_2 \rangle \langle \hat{r}_1 | l m \rangle \langle \hat{r}_2 | L M \rangle \\
\times \int_0^\infty dr_1 \int_0^\infty dr_2 u_L(k', r_1) \varphi_{n' l'}(r_2) \frac{1}{|r_1 - r_2|} \varphi_{n l}(r_1) u_L(k, r_2)
\]

Inserting the expansion

\[
\frac{1}{|r_1 - r_2|} = \sum_{\lambda=0}^\infty \sum_{\lambda=0}^\lambda \frac{r_<^\lambda}{r_>^{\lambda+1}} P_\lambda(\hat{r}_1 \cdot \hat{r}_2) = \sum_{\lambda\mu} \frac{4\pi}{2\lambda + 1} \frac{r_<^\lambda}{r_>^{\lambda+1}} \langle \hat{r}_2 | \lambda \mu \rangle \langle \lambda \mu | \hat{r}_1 \rangle
\]

gives

\[
\frac{2}{\pi k' k} i^{l-L'} \sum_{\lambda\mu} \frac{4\pi}{2\lambda + 1} \int d\hat{r}_1 \langle L' M' | \hat{r}_1 \rangle \langle \hat{r}_1 | l m \rangle \langle \lambda \mu | \hat{r}_1 \rangle \\
\times \int d\hat{r}_2 \langle l' m' | \hat{r}_2 \rangle \langle \hat{r}_2 | L M \rangle \langle \hat{r}_2 | \lambda \mu \rangle \\
\times \int_0^\infty dr_1 \int_0^\infty dr_2 u_L(k', r_1) \varphi_{n' l'}(r_2) \frac{r_<^\lambda}{r_>^{\lambda+1}} \varphi_{n l}(r_1) u_L(k, r_2)
\]

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Evaluating the angular integrals yields

\[
\frac{2}{\pi k'k} i^{L-L'} \sum_{\lambda \mu} \frac{4\pi}{\lambda^2} \frac{1}{(4\pi)^{1/2}} \frac{\hat{L} \hat{\lambda} \hat{l}}{M \mu - m} \left( \begin{array}{ccc} L' & \lambda & l' \\ M' & \mu & -m' \end{array} \right) \left( \begin{array}{ccc} L & \lambda & l \\ 0 & 0 & 0 \end{array} \right) \\
\times (-1)^{m'} \frac{\hat{L} \hat{\lambda} \hat{l}}{(4\pi)^{1/2}} \left( \begin{array}{ccc} L & \lambda & l' \\ M & \mu & -m' \end{array} \right) \left( \begin{array}{ccc} L & \lambda & l \\ 0 & 0 & 0 \end{array} \right) \\
\times \int_0^\infty \int_0^\infty dr_1 dr_2 u_{L'}(k', r_1) \varphi_{n'l'}(r_2) \frac{r_2^\lambda}{r_{1+1}^\lambda} \varphi_{n'l}(r_1) u_L(k, r_2)
\]

A little simplification and rearranging allowed by the 3-j symbols’ symmetry properties results in the expression

\[
\frac{2}{\pi k'k} i^{L-L'} \sum_{\lambda \mu} (-1)^{m+m'} \hat{L} \hat{L'} \hat{\lambda} \hat{l} \hat{l}' \left( \begin{array}{ccc} L' & \lambda & l' \\ M' & \mu & -m' \end{array} \right) \left( \begin{array}{ccc} L & \lambda & l \\ 0 & 0 & 0 \end{array} \right) R^{(\lambda)}_{nn' L' L L'}(k', k) \tag{B.38}
\]

where the radial integral function is

\[
R^{(\lambda)}_{nn' L' L L'}(k', k) = \int_0^\infty \int_0^\infty dr_1 dr_2 u_{L'}(k', r_1) \varphi_{n'l'}(r_2) \frac{r_2^\lambda}{r_{1+1}^\lambda} \varphi_{n'l}(r_1) u_L(k, r_2) \tag{B.39}
\]

Inserting this result back into equation gives the partial-wave exchange matrix element for the two-electron potential.

\[
\hat{V}_{n L}^{n' L' J}(k', k) = \sum_{M M' m' M_j} (-1)^{L'+1+J} \left( \begin{array}{ccc} L' & l' & J \\ M' & m' & -M_j \end{array} \right) \left( \begin{array}{ccc} L & l & J \\ M & m & -M_j \end{array} \right) \\
\times \frac{2}{\pi k'k} i^{L-L'} \sum_{\lambda \mu} (-1)^{m+m'} \hat{L} \hat{L'} \hat{\lambda} \hat{l} \hat{l}' \left( \begin{array}{ccc} L' & \lambda & l' \\ M' & \mu & -m' \end{array} \right) \left( \begin{array}{ccc} L & \lambda & l \\ 0 & 0 & 0 \end{array} \right) R^{(\lambda)}_{nn' L' L L'}(k', k)
\]
Using symmetry properties of the 3-j symbols, this expression can be written as

\[
V_{n' L' L'}^{n L L}(k', k) = \frac{2}{\pi k' k} \sum \varepsilon_{\lambda M M'} M' M_{j} \mu \sum \varepsilon_{L L' L' M' M_{j} \mu} (-1)^{L + L' + \ell + \ell' + m + m'} \hat{L} \hat{L}' \hat{\ell} \hat{\ell}' \hat{\mu} \hat{\mu}' R_{nn'LL'LL}(k', k) \\
\times (-1)^{l + L + J + \ell + L + L} \begin{pmatrix} l & L & J \\ m & M & -M_{j} \end{pmatrix} \begin{pmatrix} l' & L' & \ell' \\ m' & M' & -M_{j}' \end{pmatrix} \begin{pmatrix} l & L & \lambda \\ m & M & -\mu \end{pmatrix} \begin{pmatrix} l' & L' & \lambda' \\ m' & M' & -\mu' \end{pmatrix}
\]

To assist in its simplification, the symmetry properties of a 3-j symbol are used to make the substitution \((-1)^{m} = (-1)^{M' + \mu}\) in the expression above. Since there are summations over all the magnetic quantum numbers, \(M'\) and \(M_{j}\) can change signs in the 3-j symbols without affecting the expression. Making these changes gives

\[
V_{n' L' L'}^{n L L}(k', k) = \frac{2}{\pi k' k} \sum \varepsilon_{\lambda M M'} M' M_{j} \mu \sum \varepsilon_{L L' L' M' M_{j} \mu} (-1)^{l + L + \ell + \ell' + m + m'} \hat{L} \hat{L}' \hat{\ell} \hat{\ell}' \hat{\mu} \hat{\mu}' R_{nn'LL'LL}(k', k) \\
\times \sum_{M m M' m' M_{j} \mu} (-1)^{l' + L + \ell' + m' + M' + \mu} \begin{pmatrix} l & L & J \\ m & M & -M_{j} \end{pmatrix} \begin{pmatrix} l' & L' & \ell' \\ m' & M' & -M_{j}' \end{pmatrix} \begin{pmatrix} l & L & \lambda \\ m & M & -\mu \end{pmatrix} \begin{pmatrix} l' & L' & \lambda' \\ m' & M' & -\mu' \end{pmatrix}
\]

Evaluating the summations over the \(m\) quantum numbers simplifies the four 3-j symbols to a single 6-j symbol (Brink & Satchler, 1999), and reinserting the spin phase, gives the final expression for the two-electron partial-wave exchange matrix elements as defined by McCarthy & Stelbovics (1983)

\[
V_{n' L' L'}^{n L L}(k', k) = (-1)^{S} \frac{2}{\pi k' k} (-1)^{l + L + \ell + \ell'} \hat{L} \hat{L}' \hat{\ell} \hat{\ell}' R_{nn'LL'LL}(k', k)
\]

\[\text{(B.40)}\]
Appendix C

Content of the CDROM

The accompanying CDROM contains examples of direct and exchange e-H potentials calculated in closed form by maple7. The maple worksheets have been converted to HTML format and can be viewed with any standard web browser.

Also included on the CDROM are the executable programs TMATRIX.exe and TCROSSWIN.exe which run under Windows on a standard PC. The first program, TMATRIX, solves the Lippmann-Schwinger equation for the Yukawa potential scattering problem, while the second program, TCROSSWIN, solves the coupled-channels equations for electron-hydrogen scattering problem. These programs can be executed directly from the CDROM or they can be launched from the main contents page index.html.

C.1 CDROM Overview

index.html index to the CDROM contents.

potentials directory containing examples of direct and exchange potentials.

Maple worksheets calculate direct and exchange partial-waves in closed-form.

TMATRIX.exe solves the LS equation for the Yukawa potential scattering problem.

TCROSSWIN.exe solves the LS equation for the electron-hydrogen scattering problem.
C.2 CDROM Contents

This CDROM contains examples of direct and exchange e-H potentials calculated in closed form by maple7. The maple worksheets have been converted to HTML format for viewing with any standard web browser.

**HTML Format Maple Worksheets**

- Potential matrix elements (analytic examples)
- Direct potential maple worksheet (integrating with respect to \( u \))
- Direct potential maple worksheet (integrating with respect to \( K \))
- Exchange potential maple worksheet (integrating in coordinate-space)

**Maple Worksheets**

- Direct potential maple worksheet (integrating with respect to \( u \)) *directV.mws*
- Direct potential maple worksheet (integrating with respect to \( K \)) *directV_K.mws*
- Exchange potential maple worksheet (integrating in coordinate-space) *exchangeV.mws*

**Program Files**

Also included on the CDROM are the executable programs TMatrix.exe and TCrossWin.exe which run under Windows on a standard PC. The first program, TMatrix solves the Lippmann-Schwinger equation for the Yukawa-potential scattering problem, while the second program, TCrossWin, solves the coupled-channels equations for electron-hydrogen scattering problem.

- TMatrix.exe solves the LS equation for the Yukawa-potential scattering problem.
- TCrossWin.exe solves the LS equation for the electron-hydrogen scattering problem.

**Note:** Although these programs can be executed directly from the CDROM, it is recommended that they are copied to a suitable directory on the hard disc.
C.3 Computed Analytic Potentials

Analytic Momentum-Space Partial-Wave Potentials

for Electron-Hydrogen Scattering

Direct Potentials

The following examples of e-H momentum-space partial-wave direct potentials have been evaluated using Maple7.

For each transition \( n l L \rightarrow n' l' L' \), the first 6 partial waves are given.

**s-wave model potentials**

1s-1s \((J = 0.5)\)

1s-2s \((J = 0.5)\)  2s-2s \((J = 0.5)\)

1s-3s \((J = 0.5)\)  2s-3s \((J = 0.5)\)  3s-3s \((J = 0.5)\)

**General potentials**

1s-2p \((J = 0.3)\)  2s-2p \((J = 0.3)\)  3s-2p \((J = 0.3)\)

1s-2p \((J = 4.5)\)  2s-2p \((J = 4.5)\)  3s-2p \((J = 4.5)\)

1s-3p \((J = 0.3)\)  2s-3p \((J = 0.3)\)  3s-3p \((J = 0.3)\)

1s-3p \((J = 4.5)\)  2s-3p \((J = 4.5)\)  3s-3p \((J = 4.5)\)

1s-3d \((J = 0.1)\)  2s-3d \((J = 0.1)\)  3s-3d \((J = 0.1)\)

1s-3d \((J = 2.3)\)  2s-3d \((J = 2.3)\)  3s-3d \((J = 2.3)\)

1s-3d \((J = 4.5)\)  2s-3d \((J = 4.5)\)  3s-3d \((J = 4.5)\)

2p-2p \((J = 0.1)\)

2p-2p \((J = 2.3)\)

2p-2p \((J = 4.5)\)
<table>
<thead>
<tr>
<th>Energy Level</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2p-3p (J = 0..1)</td>
<td>3p-3p (J = 0..1)</td>
</tr>
<tr>
<td>2p-3p (J = 2..3)</td>
<td>3p-3p (J = 2..3)</td>
</tr>
<tr>
<td>2p-3p (J = 4..5)</td>
<td>3p-3p (J = 4..5)</td>
</tr>
<tr>
<td>2p-3d (J = 0..1)</td>
<td>3p-3d (J = 0..1)</td>
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<td>3p-3d (J = 2..3)</td>
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<tr>
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<td>3p-3d (J = 5)</td>
</tr>
<tr>
<td>3d-3d (J = 0..1)</td>
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</tr>
<tr>
<td>3d-3d (J = 2)</td>
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<tr>
<td>3d-3d (J = 3)</td>
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</tr>
<tr>
<td>3d-3d (J = 4)</td>
<td></td>
</tr>
<tr>
<td>3d-3d (J = 5)</td>
<td></td>
</tr>
</tbody>
</table>
Exchange Potentials

The following examples of e-H momentum-space partial-wave exchange potentials have been evaluated using Maple7.

Only the first-order partial wave can be calculated. The s-wave potentials are given for transitions from 1s-1s to 3s-3s, whereas only the 1s-2p, 2s-2p, 3s-2p, 1s-3p, 2s-3p and 3s-3p are calculated for the dipole transitions.

**s-wave model potentials**

1s-1s to 3s-3s \((J = 0)\)

**Dipole potentials**

1s-2p to 3s-3p \((J = 0)\)
References and Bibliography


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