ELECTRON – HELIUM SCATTERING USING ANALYTICAL AND NUMERICAL WAVE FUNCTIONS

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Declaration

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

Gurdeep Kaur
Dedicated

To my loving sons, Jasky and Tejveer.
Abstract

Theoretical investigations of electron-inert gas scattering are challenging because of the complex target structure. The electron-Helium system has been the most studied both at low and intermediate energies by sophisticated R-matrix and coupled channels methods. For the other inert gases, few calculations have been attempted at the same level sophistication. One problem is that general target-structure codes provide different forms of wave functions that must be interfaced with the scattering equations. The theoretical work presented in this thesis is based on the momentum-space coupled channels equations. For this formalism only one and two-electron atoms have been studied and purpose-built routines, specific to these atoms, have been developed. For the inert gases however such a task is much more formidable and a more practical approach is to use existing structure codes that have taken several man-years to develop.

The framework of this thesis comprises of two parts. In the first part we discuss the need for, and the way to, modify the existing close-coupling code developed by Berge & Stelbovics in order to interface with other atomic structure packages in the literature. Two mainstream packages, an atomic structure package of Charlotte Froese Fischer and an atomic structure of Alan Hibbert are discussed. Methods to extract the wave functions for Helium and Neon targets using Hibbert's package are given. In the second part, various options and strategies for the calculation of the target structure, including frozen-core and configuration-interaction wave functions, using analytic Slater, Laguerre or numerical orbitals are considered for the Helium target. Hibbert's structure code wave functions are shown to be correctly interfaced into our momentum-space coupled channels code. The pros and cons of the various target structure descriptions are given and applied for low-energy elastic and inelastic scattering of electron from Helium.
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Chapter 1

Introduction

1.1 Motivation and Aim


The thesis work to be described comprises two parts. The first part of this thesis is concerned with the need to modify an existing close-coupling code in order to interface with other atomic structure packages. The existing momentum space coupled channels code LBAS was developed by Berge & Stelbovics (1992) for the special case of a Helium target only. For all but the simplest atoms, the target wave functions for the ground and excited states are provided by complex structure packages. Some atomic structure packages are designed to calculate the wave functions only numerically, particularly for
more complex atoms while others express the states as a sum of analytic Slater functions of the orbitals. In this thesis two mainstream packages, an atomic structure package of Charlotte Froese Fischer (1973) and CIV3 package of Alan Hibbert (1975) are discussed. We also discuss the way the close-coupling code LBAS needs to be modified in order to interface with these packages and implement these modifications.

The second part of the thesis concentrates on the applications of close-coupling model to electron-Helium elastic and inelastic scattering at low energies. Among all the rare gases, electron-Helium scattering has been the subject of extensive theoretical investigation [Fursa & Bray (1995) and Saha (1989,1993)] in recent years because of its relatively simple structure. Similarly because of its inert properties, accurate electron cross sections data for this target has been obtained by experimentalists.

The excitation of Helium by electron impact is of importance in fields as diverse as the interpretation of various types of astrophysical plasmas, rare-gas lasers and fusion plasmas. Much theoretical effort has been put into establishing the behaviour of the electron excitation cross sections with energy, particularly from the 1S ground state of Helium and two relatively long-lived metastable states 2S and 2S.

From the point of view of scattering theory, the electron-Helium system provides a much richer set of models and model calculations than one-electron atomic targets; one may consider the approximation of target states of Helium with a large degree of variation in sophistication. For example single-configuration frozen-core models, configuration-interaction models and Hartree-Fock descriptions have all been used for electron-helium
scattering. Close-coupling equations require target wave functions for the ground and excited states. Our present close-coupling code (LBAS) allows for target states constructed from frozen core, partially frozen core through to full configuration interaction states. Analytical orbitals of Slater or Laguerre type are permitted and used for the evaluation of all radial integrals. For the Helium target the target states were generated by our own Helium structure code. It will be demonstrated that this code leads to excellent scattering results in both configurations-interaction and frozen-core modes.

The modified LBAS close-coupling program was used to search for the lowest-lying resonance for Helium as detailed by Berrington et al (1975). The position of the resonance is well described by experiment but the R-matrix theory calculation uses a frozen-core ground state, which leads to a significant adjustment to its position. We therefore studied the effect that use of more accurate CI ground and low-lying excited state wave functions had on the low energy scattering regime. We will calculate various elastic and inelastic cross sections paying particular attention to resonances and cusps, which dominate the cross sections in this low energy region. All these inelastic cross sections will be compared with theoretical results of Berrington et al (1975), Oberoi & Nesbet (1973) and experimental results of Brongersma et al (1972).

1.2 Electron Scattering Theories for Inert Gas Targets

Electron scattering by atoms is a many-body problem. Although the Helium atom is the simplest inert gas, its structure cannot be analytically described and is much more
complex than for hydrogen. At low energies, the close-coupling formalism has been quite satisfactory; at high energies the Born approximation and distorted-wave Born approximation work extremely well. The most difficult energy region is at intermediate energies. The basic problem in this intermediate energy range is that, there are an infinite number of open channels including the continuum. Therefore, many theoretical efforts of the previous three decades have been directed to treating these open channels and the continuum. These methods fall into two major classes; perturbative and close-coupling methods. We now give a brief summary of the most important techniques and methods applied to the problem.

1.2.1 Perturbative Methods

In the past thirty years, the perturbative methods have been the subject of much activity. A review of these methods has been made by Walters (1984). The main methods in this area are the Born series (first, second and high-order Born approximations) and distorted-wave Born series (first, second and high-order Born approximation). Different distorted-wave Born approximation (DWBA) calculations of electron-Helium scattering gained much attention with works of Madison & Shelton (1973), Thomas et al (1974), Bransden & Winters (1975), Scott & McDowell (1976), Winters (1978) Vanderpoortan & Winters (1978), Beijers et al (1987) and Bartschat & Madison (1988) among others.

All Born-based approximations are described in terms of the $T$-matrix, which may be defined as the solution of $T=V+VG_0T$. Here $V$ is the matrix of potentials coupling to all
channels in the scattering problem, and $G_0$ is the diagonal matrix of free Green’s function coupling to all the channels. The Born approximation is obtained by omitting the kernel term on the right-hand side of the $T$-matrix equation. In the DWBA method the potential $V$ is partitioned into two terms where one term is assumed to be dominant and readily calculable. A comparison of the different types of DWBA calculations has been made by Madison (1979), who found a strong sensitivity to the choice of target wave functions and distorting potentials. Madison & Winters (1983) performed a second-order DWBA calculation, which demonstrated the importance of higher-order terms in the Born series.


First-order DWBA and FOMBT are high-energy approximations and are not expected to be accurate for electron-Helium scattering in the low- and intermediate-energy range (up to 200eV) where polarisation and absorption effects cannot be ignored. Both these methods applied to electron-Helium scattering provide a good description of the optically allowed transitions but disagree with experiment for optically forbidden transitions. For singlet-triplet transitions, which are due to exchange scattering only, the disagreement is largest. The reason the born approximation works so well at high energies is that Green’s
function has inverse energy dependence, so neglecting kernel is increasingly well justified as the energy increases.

The second-order distorted-wave Born approximation (DW2BA) improves on the first-order calculation by adding an additional term that is obtained by iterating the $T$-matrix defining equation once and generating $V+VG_0T$ as a second order approximation. The DW2BA (Kingston & Walters 1980) includes a sum over the complete set of target states in the second order term. It is common to evaluate the DW2BA in the closure approximation (McCarthy & Weigold 1990). An explicit second order approximation (ESOA) of DWBA has been an important development made by Madison (1989). In the ESOA, the total wave function has been represented by the product of an exact target state (discrete or continuum) and a distorted wave calculated in a local central potential. A test of the validity of closure approximation (McCarthy & Weigold 1990) was made possible by the explicit use of target states in ESOA. Madison (1989) concluded that closure approximation was not very accurate.

Flannery & McCann (1975) and Mansky & Flannery (1987, 1990 and 1992) applied multichannel eikonal theory (MET) to the calculations of electron-Helium scattering. They obtained description of Helium singlet excitation for a limited angular range but not able to describe the excitation of Helium triplet states. MET applies a small angle approximation to the solutions of close-coupling equations at high energies and neglecting electron exchange effects.
While the thesis calculations are concerned with Helium targets our evaluation of target structure packages also included tests on Neon, so we briefly mention scattering calculations for Neon as well. The experimental results for the electron-impact excitations of the $2p^53p$, $J = 2$ and $J = 3$ states of Neon are reported by Baerveldt et al (1994). They have taken an incident energy of 80eV in the electron scattering angular range $22^0–70^0$ and 50eV for the angle of $22^0$ for the calculations of integral cross-section (ICS) and differential cross-section (DCS). Baerveldt et al (1997) also reported theoretical results using non-relativistic distorted-wave approximation (DWA) at 50eV and 80eV for the excitations of the $2p^53p$, $J = 2$ and $J = 3$ states. At 50 eV, for the excitation of the $2p^53p$, $J = 2$ states only, Gorelenkova and Grum-Grzhimailo (1995) reported non-relativistic distorted-wave Born approximation (DWBA) calculations over the entire scattering-angle range. They also used the multichannel-diffraction approximation (MCDA) for scattering angles in the range $(0–50^0)$.

An extensive amount of theoretical results for the scattering parameters associated with the excitation of the $2p^53p$, $J=1$, 2 and 3 states of Neon at both 50 and 80eV using relativistic distorted-wave approximation (RDW) have been performed by Kaur et al (1998) and compared with the experimental and theoretical calculations of Baerveldt et al (1994, 1997) and. For $J = 1$ states no comparison has been done because of non-availability of the data. There is a good agreement for the cross-sections and for some of the Stokes parameters but less satisfactory agreement for other Stokes parameters. More experimental data on one hand and the implementation of more sophisticated models that include channel coupling, on the other hand, are highly desirable.
1.2.2 Close-Coupling Methods

One of the most successful approaches to electron-atom scattering has been the momentum space formulation of the close-coupling method. This method describes the electron-atom system by means of a complete antisymmetric wave function, which fully treats the different scattering channels and the polarisation of the atom by the external electron. In the close-coupling formalism one way of treating the continuum is by means of the Intermediate-Energy $R$-matrix method (IERM).

1.2.2.1 Intermediate-Energy $R$-Matrix Method

The $R$-matrix method was first introduced by Wigner & Eisenbud (1947), but general reviews of $R$-matrix approaches to the electron-atom problems have been presented by Burke & Robb (1975) and Burke et al (1987). The continuum was not included in the standard $R$-matrix approach until Burke et al (1987) introduced a new method suitable for intermediate energy electron scattering, called the intermediate-energy $R$-matrix method.

In the $R$-matrix method the three body wave function in co-ordinate space is divided into an internal and external region, the boundaries of which intersect at a specified radial distance $r = a$. In the internal region, $r < a$, electron exchange and correlation between the scattered electron and the N-electron target are considered to be important; in the external region, $r > a$, exchange between the scattered electron and the target is neglected.
Investigators including, Berrington et al (1975), Freitas et al (1984), Berrington et al (1985), Berrington & Kingston (1987) and Fon et al (1989, 1994 and 1994a) performed electron-Helium inelastic transition calculations at small energies (under the ionisation threshold) and at intermediate energies (above the ionisation threshold), by treating many discrete target states (up to 19) using R-matrix method. These calculations do not include the target continuum and therefore may be inaccurate above the ionisation threshold. Fon et al (1989) included pseudo states in the application of R-matrix theory and gave good elastic cross sections as well.

Fon et al (1989) used a 19-state R-matrix calculation to investigate the resonance structure in the low-energy electron-Helium cross sections. Berrington & Kingston (1987) and Sawey et al (1990) used 19 and 29 states for R-matrix calculations to search for resonances in this energy range. The method has been applied by Fon et al (1988, 1991 and 1994) at 30 eV to calculate excitations of the n = 2 to n = 3 (19-states only) states. None of the above calculations was able to achieve agreement with experiment for optically forbidden transitions at 30 eV.

A review of R-matrix theory as well as examples of its use to inert gases are given by Burke & Berrington (1993), while a description of the code is given by Burke & Noble (1995). Taylor et al (1985) performed a non-relativistic nine-state R-matrix calculation including the (2p^6) \(^1\)S, (2p^53s) \(^1\)P and (2p^53p) \(^1\)S, \(^1\)P and \(^1\)D states for electron-Neon cross-sections. Zeman & Bartschat (1997) have performed a 31-state semi-relativistic Breit-Pauli R-matrix calculation for electron-impact excitation of Neon. The incident energies are taken from threshold to 30eV. The angle-integrated cross-sections for
(2p\(^3\)3p) states are in reasonable agreement with the small amount of available experimental data. The comparison of both the integrated and differential calculations for the two different methods of optimisation of the 3p orbital shows that the R-matrix calculation is very sensitive to such changes.

We take the opportunity to mention the J-matrix method. According to Broad & Reinhardt (1976) the philosophy of the J-matrix method is very similar to R-matrix method and it relies on the use of a set of square integrable \((L^2)\) functions, which span the target space. The full Hamiltonian is diagonalized in a finite subset of this basis and the scattering information is extracted from matching at the boundary of the asymptotic forms of the scattering wave functions expanded in the \(L^2\) basis. The method was studied extensively during the early 1980’s but limited calculations were performed. This method has been applied to the calculation of low-energy electron-helium scattering by Konovalov & McCarthy (1994). A close-coupling formalism for both discrete and continuum excitation of the helium atom has been used by them. Excitation cross-sections are in good agreement with the results of Fon et al (1994). Resonance structure in \(n = 2\) and \(n = 3\) excitation cross section has been calculated and checked for convergence. These cross sections agree with the R-matrix calculations of Fon et al (1993).
1.2.2.2 Coupled Channels Optical Method

There are many versions of this coupled channel optical potential method, which have various approximations; one of the most successful is the CCO method of Bray et al (1991) applied to electron-Hydrogen scattering. Their method uses $P$ and $Q$ projection operators (introduced by the formalism of Feshbach 1962) that are symmetric in the two-electrons scattering problem by Bray (1992), Bray & McCarthy (1993). The CCO method divides the target space into two orthogonal spaces, $P$ and $Q$. McCarthy & Stelbovics (1983) introduced this method and suggested the direct solution of a set of coupled integral Lippmann-Schwinger equation for the $T$-matrix by treating the chosen reaction channels ($P$ space) in the close-coupling method, while all other channels ($Q$ space) are included through a complex polarization potential.

The half-on-shell optical model developed by McCarthy & Stelbovics (1980) has been widely used in electron-atom scattering problems. This polarization potential produces total ionisation cross section that compare well with experiment at all energies (McCarthy & Stelbovics 1983). This method has been successfully applied to electron-Hydrogen scattering by Bray et al (1991, 1991a) and one-electron atoms in general by Bray et al (1991b, 1991c), Bray (1992) and Bray & McCarthy (1993) by Bray et al (1993).

The CCO model with CI wave functions was applied to calculate the cross sections of Helium at intermediate energies by Brunger et al (1990 and 1992), McCarthy et al (1990) and electron-magnesium scattering by McCarthy et al (1989). Their results showed good
agreement with experimental data for both differential and total cross sections, but only for singlet electron-Helium transitions. The results were less satisfactory for triplet transitions. A number of approximations in the CCO theory make it less reliable for the triplet Helium transitions.

1.2.2.3 Convergent Close-Coupling Method

We concentrate in the rest of the thesis on one of the latest electron scattering methods, the convergent close-coupling (CCC) method developed by Bray & Stelbovics (1992a). It takes the close-coupling (CC) formalism to completeness, and satisfies the requirement of a general, reliable and practical scattering theory. The CCC method was developed by including the target continuum consistently in the close-coupling formalism. In the coupled channels formalism one must in principle sum over the complete set of target states including the continuum. This problem has been addressed in a general way by Bray & Stelbovics (1992) where it was shown that the sum could be replaced by the set of target states constructed from a basis of square integrable Laguerre functions. This method relies on including square integrable pseudo states with positive energy to represent the target continuum in the close-coupling formalism. The target states are obtained by diagonalising the target Hamiltonian in a complete square-integrable Laguerre/Slater basis. The orthogonality of the basis ensures that the "completeness" of the expansion is approached as the basis size is increased. Convergence is achieved whenever a further increase in basis size does not have a significant effect on the results of interest. The square-integrability of the basis ensures that both the negative and
positive energy states are square integrable and take into account both the discrete and continuum part of the target space. The CCC method is general in its application and independent of the projectile energy or transition of interest.

A review of the CCC applications has been presented by Bray & Stelbovics (1995) using Laguerre basis states, which demonstrates that the CCC method solves the electron-Hydrogen scattering problem in a convergent manner. The most accurate tests the convergence with basis sizes were carried out for the Temkin-Poet model (Temkin (1962), Kyle & Temkin (1964) and Poet (1978, 1980 and 1981)), which is a simplified model of electron-hydrogen scattering. Bray & Stelbovics (1992) demonstrated that the CCC method yielded convergent results as the basis size was increased. The pseudo resonances, typically associated with square-integrable expansions of the target continuum diminished and disappeared with increasing basis size. They also showed that convergence was to the correct result (Poet 1978, 1980), independent of the projectile energy or the transition studied. They calculated convergent elastic 2s and 2p differential cross sections spin asymmetries and angular correlation parameters for the 2p excitation at 35.5 eV, 54.4 eV and 100 eV energies. Their results show excellent convergence, with excellent agreement between calculations with 52 and 72 basis states.

The calculation of the total ionisation cross-section for the electron impact of atomic hydrogen by Bray & Stelbovics (1993) is in excellent agreement with the experimental data of Shah et al (1987). Furthermore, the measurements of the total ionisation spin asymmetries are also in excellent agreement with the CCC predictions. These results indicate that CCC method apportions the correct amount of electron flux in both the
singlet and triplet ionisation channels in contrast to the IERM method of Scholz et al (1990) and the pseudo state method of Callaway & Oza (1979). The CCC method also permits the calculation of ionisation from excited states.

Fursa (1995) and Fursa & Bray (1995) extended the formalism of the CCC method to the helium target in the frozen-core (FC) model with considerable success. Excellent agreement with measured differential cross-section and angular correlation parameters has been obtained. Their implementation focused on a FC model but they noted that the method worked for the full CI target states as well. Their calculations were directed mainly to energies above the ionisation threshold.

The electron-atom close-coupling equations may not have a unique solution. Burke & Seaton (1971) reviewed the formalism and method of solution in the coordinate space. In electron-atomic Hydrogen scattering, Stelbovics (1990) demonstrated the non-uniqueness of the equation in standard form is a consequence of the incomplete application of Pauli principle in constructing the electron-hydrogen wave function. For very large calculations this non-uniqueness causes numerical instabilities. He also showed a general prescription to obtain well-defined unique-solution equations.

The CCC calculations of Fursa & Bray (1995) for electron-Helium scattering have used these methods to guarantee a unique solution and obtain good agreement with experiment. For electron-Helium scattering also, Stelbovics & Berge (1997) have shown that the non-uniqueness of the coupled channels equations depends on the scattering system and model (CI or FC) used. By a minor modification of the exchange term they
have developed new CC equations, which have a unique solution. A subtle difference between FC and CI models, with respect to the manner in which anti-symmetrisation is incorporated has been noted. It has been proved by them that CI wave functions give a consistent system of CC equations in contrast to FC wave functions. The code developed by Berge & Stelbovics provided the starting point for the numerical work reported in this thesis.

1.3 Wave Functions from General Packages used in Close-Coupling Equations

For electron-inert gas scattering, the close-coupling equations require target wave functions for the ground and excited states. For electron-helium scattering we had our own CI/FC target structure code but this was specialised to this system. A decision was made for all other inert gas targets to calculate target wave functions from complex atomic structure code packages available in the literature. Some atomic structure packages such as the atomic structure package of Fischer (1973), are designed to calculate the wave functions only numerically. Other packages such as the CIV3 package of Hibbert (1975), express the target states as a sum of analytic Slater functions for the orbitals. Our close-coupling-equation formulation uses analytical orbitals in the Slater/Laguerre form. In order to adapt these packages to our close-coupling formalism, it became necessary to modify the existing close-coupling codes to incorporate the standard packages. This task formed a major part of this thesis work. We discuss here these two mainstream packages and the way our close-coupling packages needed to be modified in order to interface with them.
1.3.1 Fischer’s Numerical Packages

In order to assess Fischer’s numerical package for inert gas atoms such as Neon, we decided to use Helium first as our test example. It is a ‘simple’ target with states well described by LS coupling scheme and there are several good theoretical studies with which to compare. Moreover for electron-Helium scattering we have a sophisticated close-coupling code, which uses analytical orbitals for the evaluation of radial integrals. In the remainder of this thesis we will refer to this version of our close-coupling package as the “analytic orbital code”. From the point of view of scattering theory, the electron-Helium system provides the opportunity to test a rich set of models and model calculations since one may consider the target states of the Helium atom constructed with a large degree of variation in sophistication. We can approximate the target-Helium atom by a simple frozen-core model up to a full configuration-interaction representation in which both the electrons are described by a large set of $L^2$ functions, which can be extended to completeness in one-particle Hilbert space.

Fischer’s package was used to provide orbitals for the Helium target by solving the Hartree-Fock (HF) equations and multi-configuration Hartree-Fock (MCHF) equations. The total wave function in MCHF method is an atomic state function that describes a many-electron system. The radial functions in the total wave function are evaluated by using the numerical radial functions. This code produces orbitals only in a numerical form.
To incorporate these numerical orbitals in our present CC analytical packages we had to substantially modify the code. We used Slaters as basis functions as it is simple to express analytical Slaters in the numerical form. The analytic orbital CC code of Berge & Stelbovics was re-written. A number of routines, which relied on use of analytic orbitals in the radial integral computations, were replaced by new routines using numerical orbitals as input to perform the numerical integration of these integrals. As a result a new code has evolved that permits the use of analytical Slater orbitals as before and in addition the option of a numerical set of orbitals and numerical integration of radial integrals. We will present in chapter three, the tests on the Helium atom showing the implementation was successfully carried out.

The modified numerical orbital CC model was forced to use Fischer’s numerical orbitals, CI coefficients and total energy for a particular state. The scattering results were convincing only for a one-target-state CC calculation using the ground state. The reason why calculations using ground and excited states calculated from Fischer’s package proved impractical is to do with orthogonality issues which we discuss now.

For the present scattering calculations all target states use a common set of orbitals. Each general potential matrix element will be formed as a sum over various CI coefficients multiplied by common numerical radial integrals computed from the designated common orbitals The complete set of potentials connecting all initial and final target states only have their CI coefficients varying. The common set of orbitals ensures that a basis set can be orthogonalised easily and extended to completeness in a systematic manner. Unfortunately in Fischer’s code to generate a wave function an optimisation of orbitals is
carried out internally in the code separately for each target state whose CI wave function is desired. This leads to severe problems with the orthogonality of the target states. For the CC calculations involving two or more states, it is well known that the orthogonality of the states is an essential condition for numerical stability where as for Fischer's wave functions it is not guaranteed. Indeed in all our tests, using her target states beyond the one-state CC model the lack of orthogonality lead to extremely disappointing results. For these reasons it was concluded that Fischer's numerical orbitals could not be used as a successful basis for generalising the existing CC code to other inert gas targets.

1.3.2 Configuration-Interaction Method of Alan Hibbert

Fortunately the problems encountered with the Fischer code were overcome with the adoption of a second atomic structure package, CIV3 package of Hibbert (1975) which provides the option of using the same set of orbitals to generate the ground state and excited states which suits the basic requirement of our CC code and is therefore preferable to Fischer's package.

The total wave functions formed by Hibbert's package have the same general form as Fischer's. The radial wave functions are expressed in the analytical form, not numerical as in Fischer's package. These radial functions can be expressed as a sum of Slater-type-orbitals. The orbitals are assumed to form an orthonormal set. Each orbital in Hibbert's package can be optimised over more than one state/symmetry. The flexibility with this package is that different optimisation procedures can be adopted to achieve a good set of
orbitals and CI coefficients needed for a particular type of scattering calculation. A great deal of effort was expended to use Hibbert’s package and to extract the best basis for a target adopting various optimisation procedures. These different methods of optimisation are detailed in chapter three.

To use Hibbert’s package in our numerical orbital version of the CC code, we developed a direct relation between CC analytic Slaters and Hibbert’s Slaters for a particular state as detailed in chapter three, section 3.1.5. Each CC orbital in the analytic orbital CC code was replaced by a sum of Hibbert’s Slaters and then converted to numerical orbital form. The numerical orbitals and CI expansion coefficients of Hibbert were used as a sophisticated basis in the modified numerical CC code to perform scattering calculations. The reason we adopted the numerical version of our CC code was, that after having made the changes to add the numerical option in addition to the analytic one, the numerical option proved to be more efficient in terms of computation time without loss of accuracy in the calculated scattering information.

With the modifications to the program it was possible to use a limited number of high quality CI wave functions to describe the target. Such expansion sets are adequate at low energies. In the final chapters, studies of CI target expansions were carried out for the Helium target. A number of illustrations to this application of electron-Helium scattering are detailed in chapter four, where we have compared the phase shifts at a range of low energies with Nesbet (1979) and Saha’s (1989) results. For these applications we have used both the analytical orbital as well as numerical orbital CC codes. Inelastic scattering calculations are detailed in chapter five.
The modified numerical orbital close-coupling electron-Helium program forms the basis of a general scattering code for complex targets. An important interface of the coupled-channel package has been developed using Hibbert’s wave functions and tested successfully for Helium targets.

The numerical coupled-channels code can be extended for use in other inert gas targets such as Neon. The more complex targets will require more complicated manifolds of target states and larger orbital basis sets but in principle the final channel potentials apart from more complicated CI wave functions and Clebsch-Gordan algebra will use the same radial integral routines for overlaps involving the orbitals. Due to insufficient time, we could not develop the potential matrix equations for Neon Target. However we have already been able to construct a set of orbitals for Neon using radial wave functions from CIV3 package of Hibbert (chapter three, section 3.2). An optimisation procedure as outlined by Zeman & Batschat (1997) has been adopted to produce these orbitals. The electron-Neon scattering with numerical CC code can be taken up as a future work using this best set of seven orbitals and thirty-one jLS coupled target states.

1.4 Inelastic Electron-Helium Scattering

As a final application, the close-coupling equations are solved for inelastic scattering of electrons from Helium target. An investigation of resonances has been done in the energy range 18 – 23 eV. This work is unique in its form, as CC equations with first five target states of Helium using high quality CI wave functions, have not been reported in the
literature for inelastic scattering. The Belfast group has performed a vast amount of work on inelastic cross sections but using R-matrix method only and the quality of wave functions describing the ground and excited states is not as good as the CI states used in our calculations.

The CC packages for this application have been used in both forms, numerical orbital as well as analytical orbital. As a test, numerical orbital CC code was used to locate the position of the lowest resonance employing the same set of basis as used by Berrington et al (1975). The analytical orbital CC code using target states from our own Helium structure code gave the position of the lowest resonance close to the value as claimed by others [Berrington et al (1975) and Oberoi & Nesbet (1973)]. Other theorists and experimentalists [Cvejanovic & Read (1973), Sanche & Schulz (1972) and Cvejanovic et al (1974)], while publishing their results have adopted a number of renormalization procedures of incident energy and rescaling of other thresholds, whereas no such rescaling was needed because of our use of high-quality CI wave functions for the low-lying states. Illustrations of this application are detailed in chapter five and a results comparison of inelastic cross sections with theoretical results of Berrington et al (1975), Oberoi & Nesbet (1973) and experimental results of Brongersma et al (1972) are presented in this chapter. The low energy electron-Helium inelastic work can be extended to search for resonances with positions \( n > 2 \), using both analytical and numerical orbital CC codes, as the basis developed for our Helium target states is well suited to these applications.
Chapter 2

Coupled-Channels Equations for Electron-Helium Scattering

A description of the momentum-space convergent close-coupling method for electron-Helium scattering using CI wave functions will be given in this chapter. An important feature of the coupled-channel formalism is that the derivation of the coupled equations and method of their solution are essentially independent of the choice of the target. The procedures for solving these equations are similar to those for hydrogenic targets given by Bray (1994), the major difference being the calculation of potential matrix elements for the Helium target which involve more complicated derivations than those for hydrogenic targets detailed by Bray & Stelbovics (1995). Fursa & Bray (1995) have successfully solved these equations for electron-Helium scattering.

2.1 Coupled Channels Formalism

The target states are labelled as $\Psi_{\gamma \pi l m s m_s} (\vec{x}_1, \vec{x}_2)$ where $l, s$ are the orbital and spin angular momenta and $m, m_s$ their magnetic quantum numbers, $\pi$ is the parity of the state, $\gamma$ labels the energy and

$$\vec{x}_i = (\sigma_i, \vec{r}_i), \quad i = 1, 2.$$  

The target states are fully antisymmetric under the interchange of electrons, so that

$$P_{12} \Psi_{\gamma \pi l m s m_s} (\vec{x}_1, \vec{x}_2) = - \Psi_{\gamma \pi l m s m_s} (\vec{x}_2, \vec{x}_1) \tag{2.01}$$

and the wave function over spin and space coordinates can be written as a product of a spin wave function and a coordinate wave function:
\[ \Psi_{\gamma \pi l m_{s} m_{l}} (\vec{x}_1, \vec{x}_2) = \chi_{s m_{s}} (\sigma_1, \sigma_2) \Psi_{\gamma \pi l m_{s}} (\vec{r}_1, \vec{r}_2). \] (2.02)

For convenience we will often abbreviate \( \Psi (\vec{x}_1, \vec{x}_2) \) by \( \Psi (1, 2) \) and set \( j = \gamma \pi l \) for simplicity of notation. Here
\[ \chi_{s m_{s}} (\sigma_1, \sigma_2) = \sum_{\mu_1, \mu_2} C^{\frac{1}{2} \frac{1}{2}}_{\mu_1 \mu_2} \chi^{\frac{1}{2}}_{\frac{1}{2} \mu_1} (\sigma_1) \chi^{\frac{1}{2}}_{\frac{1}{2} \mu_2} (\sigma_2). \]

where \( \chi^{\frac{1}{2}}_{\frac{1}{2} \mu} (\sigma) \) is the spin function for a single electron.

The target states are constructed by means of a configuration-interaction expansion as
\[ \Psi_{\gamma \pi l m_{s} m_{l}} (1, 2) = \sum_{a b} C^{ab}_{\gamma \pi l s} \Phi^{a b}_{l m s m_{l}} (1, 2) \] (2.03)

where
\[ \Phi^{a b}_{l m s m_{l}} (1, 2) = \chi_{s m_{s}} (1, 2) \varphi^{a b}_{l m} (1, 2) \] (2.04)

and
\[ \varphi^{a b}_{l m} (1, 2) \equiv \varphi^{a b}_{l m} (\vec{r}_1, \vec{r}_2) = \frac{\varphi^{a b}_{n_{a} l_{a}} (r_1)}{r_1} \frac{\varphi^{a b}_{n_{b} \ell_{b}} (r_2)}{r_2} \mathcal{Y}_{(l_{a} l_{b}) l m} (\hat{r}_1, \hat{r}_2). \] (2.05)

Thus \( a = n_{a} l_{a} \) and \( \sum_{a b} \) means a sum over all allowed \( n_{a}, l_{a}, n_{b}, l_{b} \) i.e., over all configurations. The \( \mathcal{Y}_{(l_{a} l_{b}) l m} \) are the bipolar spherical harmonics defined by
\[ \mathcal{Y}_{(l_{a} l_{b}) l m} (\hat{r}_1, \hat{r}_2) \equiv \langle \hat{r}_1, \hat{r}_2 | (l_{a} l_{b}) l m \rangle = \sum_{m_{a} m_{b} m} C^{l_{a} l_{b} l}_{m_{a} m_{b} m} Y_{l_{a} m_{a}} (\hat{r}_1) Y_{l_{b} m_{b}} (\hat{r}_2) \] (2.06)

and satisfy the orthogonality property
\[ \langle (l_{a} l_{b}) l m | (l'_{a} l'_{b}) l' m' \rangle = \delta_{l_{a} l'} \delta_{l_{b} l'} \delta_{m m'}. \] (2.07)
The radial orbitals are normalized according to

$$
\int_0^\infty dr \, \varphi_n^2 (r) = 1.
$$  \tag{2.08}

From the Pauli Principle (2.01) it follows that the CI coefficients satisfy the symmetry property

$$
C_{\gamma \pi \lambda s}^{ab} = (-1)^{s_i + s_k + l} C_{\gamma \pi \lambda s}^{ba}.
$$  \tag{2.09}

If the target states are normalized to unity and if for a fixed \( l \) we also assume the \( \varphi_{nl} \) are orthogonal in \( n \), it also follows from equations (2.02-2.08) that

$$
\sum_{ab} \left( C_{\gamma \pi \lambda s}^{ab} \right)^2 = 1.
$$  \tag{2.10}

Often in practice we relax the assumption of orthogonality for the \( \varphi_{nl} \).

The non-relativistic Hamiltonian for the electron-Helium scattering problem may be written as

$$
H = H_0 + H_1 + H_2 + V_{01} + V_{02} + V_{12} = H_T + H_0 + V_{01} + V_{02}
$$  \tag{2.11}

where the incident electron is labelled 0 and the target electrons are labelled as 1 and 2. The one-body Hamiltonian for each electron in the electrostatic potential of the static nucleus is

$$
H_i = K_i + V_i = -\frac{1}{2} \nabla_i^2 - \frac{2}{r_i}, \quad i = 0, 1, 2
$$  \tag{2.12}

and the two-body potential for each electron pair is

$$
V_{ij} = \frac{1}{\left| r_i - r_j \right|}.
$$  \tag{2.13}

The target Hamiltonian is

$$
H_T = H_1 + H_2 + V_{12}
$$  \tag{2.14}

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and the target states satisfy the eigenvalue equation

$$H_T \Psi_{j m z m_z} (12) = \varepsilon_{j z} \Psi_{j m z m_z} (12). \quad (2.15)$$

The total energy is related to the projectile kinetic energy and the bound state energy by

$$E = \frac{1}{2} k^2 + \varepsilon_{j z} \quad (2.16)$$

The three-electron wave function satisfies the equation

$$(E - H_T - H_0 - V_{01} - V_{02}) \Psi^{(+)}_{S M_z} (012) = 0. \quad (2.17)$$

The total spin $S$ and its magnetic quantum number $M_S$ are conserved quantities and so we construct our electron Helium-atom three-body scattering functions labelled by these quantities.

A fully antisymmetric close-coupling multi-channel expansion of the three-electron wave function is then given by

$$\Psi^{(+)}_{S M_z N r} (012) = (1 - P_{01} - P_{02}) \sum_{s=0}^{N_r} \sum_{j=1}^{N_r} C_{\mu m_z M_z}^{1 S} \sum_{m} F^{(+)}_{S M_z u s j m} (0) \Psi_{s m_z j m} (12) \quad (2.18)$$

where $N_T = \sum_{s=0}^{N_r}$ is the total number of target states and $\mu$ is the spin projection of the electron labelled 0 and $C_{\mu m_z M_z}^{1 S}$ is the Clebsch-Gordan coefficient coupling the incident electron and target spins. The target wave functions are assumed fully antisymmetric in writing equation (2.18). We used the abbreviation $j \equiv \gamma n l$ for the target state labels excluding spin. The $F^{(+)}_{S M_z u s j m}$ can be regarded as distorted waves in a single coordinate with incoming plane wave and outgoing scattered waves.
Since the Clebsch-Gordan coefficient only couples the spins, the expansion is simplified somewhat by separating out the space and spin parts of the three-body wave function by writing

\[
\sum_{\mu, m, m_s} C_{\mu, m_s}^{1/2} \Phi_{S, m, m_s} \Psi_{S, m, m_s}(x_0, x_1, x_2) = \chi_{S}^{1/2} \Phi_{S, m, m_s} \psi_{S, m, m_s}(r_0, r_1, r_2).
\]  \hspace{1cm} (2.19)

Inserting (2.18) into (2.17) and using (2.19) leads to

\[
(E - H_0 - H_T) \sum_{s=0}^{N_T} \chi_{S}^{1/2} \Phi_{S, m, m_s} \psi_{S, m, m_s}(r_0, r_1, r_2) = \left[ (V_0 + V_{01} + V_{02}) + (E - H)(P_{01} + P_{02}) \right] \sum_{s=0}^{N_T} \chi_{S}^{1/2} \Phi_{S, m, m_s} \psi_{S, m, m_s}(r_0, r_1, r_2).
\]  \hspace{1cm} (2.20)

For simplicity in notation in the sequel we will not write the subscript \(N_T\) unless we specifically wish to refer to a particular basis expansion over target states. The equation (2.20) can be written explicitly as a set of coupled equations for the distorted waves by projecting out and integrating over the radial target state functions and total spin functions (using their orthogonality properties) on the left:

\[
(E + \frac{1}{2} V_0^2 - \varepsilon_{s, s'}) \Phi_{S, m, m_s}^{(+)}(r_0) = \sum_{s'=0}^{N_T} \sum_{m'} \int d^3 r_1 d^3 r_2 \psi_{S, m, m_s}^{(+)}(r_1, r_2) \times \left[ (V_0 + V_{01} + V_{02}) \delta_{s, s'} + (E - H)(X_{S, s}^{01} P_{01} + X_{S, s}^{02} P_{02}) \right] \times \psi_{S, m, m_s}^{(+)}(r_1, r_2) \hspace{1cm} (2.21)
\]
In deriving this equation we have denoted the spin recoupling matrix elements by $X_{S^x S^x'}^{01}$. For example $X_{S^x S^x'}^{01}$ is obtained by writing,

\[
\begin{align*}
\left\langle X_{\frac{1}{2}S}^{\frac{1}{2}S} (012) \middle| P_{01} \right| X_{\frac{1}{2}S}^{\frac{1}{2}S} (012) \right\rangle \\
= \left\langle X_{\frac{1}{2}S}^{\frac{1}{2}S} (012) \middle| P_{01} \right| \Psi_{S^x f} (r_1, r_2) f_{S^x f}^{(s)} (r_0) \right\rangle
\end{align*}
\]

and similarly for $X_{S^x S^x'}^{02}$. The operator $P_{01}$ exchanges coordinates in spin and coordinate space. The explicit form of these matrix elements for spin recouplings is

\[
X_{S^x S^x'}^{01} = (-1)^{s + s'} \begin{pmatrix} \frac{1}{2} & 1 & s \\ 2 & 2 & s' \end{pmatrix}
\]

\[
(2.23)
\]

\[
X_{S^x S^x'}^{02} = (-1)^{s + s'} X_{S^x S^x'}^{01}.
\]

\[
(2.24)
\]

The scattering boundary conditions for $f^{(s)}$ will be

\[
f_{S^x S^x f}^{(s)} (r) \approx \exp(i k_{j_0} \cdot r) \delta_{j_0 j_0} \delta_{m_m_0} \\
+ A_s^{S} (k_{j_0}, k_{j_0}) \cdot \frac{e^{i k_{j_0} \cdot r}}{r}.
\]

\[
(2.25)
\]

Here $\delta_{j_0 j_0} = \delta_{\gamma_0, \gamma_0} \delta_{s_0, s_0} \delta_{l_0, l_0}$, where $\gamma_0, \pi_0, l_0, s_0$ and $k_{j_0}$ are the labels for the incident channel. The $A$'s are the complex scattering amplitudes.
2.2 T-Matrix Equations

In order to write down a T-matrix formulation of equation (2.20), we write (2.20) more compactly as

$$ G_0^{-1}(E - \varepsilon_{s j}) \langle f^{(s)}_{i s', i'm'} \rangle = \sum_{s' j'm'} \langle s j m | V_{D}^S + V_{E}^S | s' j'm' \rangle \langle f^{(s)}_{i s', i'm'} \rangle $$  \hspace{1cm} (2.26)

$V_{D,E}^S$ are the direct and exchange potentials written as

$$ \langle s j m | V_{D}^S | s' j'm' \rangle = \langle s j m | V_0 + V_{01} + V_{02} | s' j'm' \rangle \delta_{s's'} $$ \hspace{1cm} (2.27)

$$ \langle s j m | V_{E}^S | s' j'm' \rangle = \langle s j m | (E - H)(X_{s s's'}^0P_{01} + X_{s s's'}^2P_{02}) | s' j'm' \rangle $$
$$ = X_{s s's'}^0 \langle j m | (E - H)(P_{01} + (-1)^{s s's'}P_{02}) | j m \rangle. $$ \hspace{1cm} (2.28)

Now the coupled equations for the $| f^{(s)} \rangle$ can be rewritten in the standard manner as integral equations for T-matrix operators by defining

$$ \langle f^{(s)}_{i s', i'm'} \rangle = | s_0 j_0 m_0 \rangle + G_0(E - \varepsilon_{s j}) \langle s j m | T^S | s_0 j_0 m_0 \rangle $$ \hspace{1cm} (2.29)

and where $| s_0 j_0 m_0 \rangle$ is the incident state defined as the solution of

$$ G_0^{-1}(E - \varepsilon_{s j}) | s_0 j_0 m_0 \rangle = 0. $$ \hspace{1cm} (2.30)

Then the T-matrix equations are formed from equation (2.24) and satisfy

$$ \langle s j m | T^S | s_0 j_0 m_0 \rangle = \langle s j m | V^S | s_0 j_0 m_0 \rangle $$
$$ + \sum_{s' j'm'} \langle s j m | V^S | s' j'm' \rangle G_0(E - \varepsilon_{s j}) \langle s' j'm' | T^S | s_0 j_0 m_0 \rangle. $$ \hspace{1cm} (2.31)
This set of equations will be solved in the momentum representation. There is a simple relation between the scattering amplitudes $A$'s and the momentum-space T-matrix elements:

$$A^s_{jj_{0},j_{0}}(\vec{k},\vec{k}_{0}) = -4\pi^2 \left\langle \vec{k}_{1} ; s_{j_{0}} m \bigg| T^s \bigg| \vec{k}_{0} ; s_{0} j_{0} m_{0} \right\rangle. \quad (2.32)$$

In writing this relation we have assumed atomic units and that the plane waves are normalised to delta functions in momentum space.

The T-matrix equations have been developed in a form where the spins of the target and incoming electron have been coupled into total spin states. We now turn to the problem of coupling the angular momenta of the target and incoming electron in order to form states of total angular momentum. It is only after this is done that partial-wave analysed T-matrix equations can be developed in a form suitable for numerical solution.

We expand the momentum-space T-matrix amplitude in terms of complete sets of spherical harmonics and use the fact that the total orbital angular momentum is conserved.

### 2.3 Partial-Wave Expansion for T-Matrix

The coupled Lippmann-Schwinger equations for the $T$-matrices are solved by first reducing the equations to partial-wave form. Then we form a set of coupled equations for the reduced matrix elements of $V$ and $T$. The construction of these reduced matrix elements proceeds as follows:
Consider the general element for scattering from an initial state \( |\vec{k}_i; s\ i\ m\rangle\) to a final state \( |\vec{k}_f; s' j\ m'\rangle\). We begin by forming a partial-wave expansion of the momentum states:

\[
|\vec{k}\rangle = \sum_{LM} Y_{LM}^*(\hat{k}) \ |kLM\rangle
\]

where

\[
\langle r | kLM \rangle = \sqrt{\frac{2}{\pi}} \ i^L j_L(kr) \ Y_{LM}(\hat{r})
\]

assuming the normalization \( \langle \vec{k}' | \vec{k} \rangle = \delta(\vec{k}' - \vec{k}) \).

Then

\[
\langle \vec{k}_j; s' j m' | T^S | \vec{k}_i; s i m \rangle = \sum_{LL'M'M'} \ Y_{LM}(\hat{k}_j) \ Y_{LM'}^*(\hat{k}_i)
\times \langle k_j; s' j L'M' m' | T^S | k_i; s i L M m \rangle.
\]

The partial-wave \( T \)-matrix elements are still in an uncoupled angular momentum representation. We label the total angular momentum and its magnetic quantum number by \( \mathcal{L}, \mathcal{M} \) and form partial-wave states in the total angular momentum using

\[
| (L \ell) \mathcal{L} \mathcal{M} \rangle = \sum_{Mm} C_{Mm}^{L\ell\mathcal{L}\mathcal{M}} |LMm\rangle
\]

In terms of these states, using the Wigner-Eckart theorem the reduced matrix elements are defined by

\[
\langle k_j; s' j (L' \ell') \mathcal{L}' \mathcal{M}' | T^S | k_i; s i (L \ell) \mathcal{L} \mathcal{M} \rangle
= \delta_{\mathcal{L}\mathcal{L}'} \delta_{\mathcal{M}\mathcal{M}'} \langle k_j; s' j L' \ell' | T^S \mathcal{M} \rangle \langle k_i; s i L \ell \rangle
\]

Here \( \Pi \) is the total parity, which is also conserved.
Using equations (2.35 - 2.37) our required partial wave expansion leading to reduced

\[ T\text{-matrix elements is} \]

\[
\left\langle \vec{k}_j; s' j m' \left| T^S \right| \vec{k}_i; s i m \right\rangle = \sum_{L' M' M'' M'''} Y_{L' M'}^{*}(\hat{k}_j) Y_{L M}^{*}(\hat{k}_i) \\
\times C_{M m''}^{L L} C_{M' M''}^{L'' L''} \left\langle k_j; s' j L' l' \left| T^{S \cdot L' \cdot \Pi} \right| k_i; s i L l \right\rangle
\]

(2.38)

We note, the inverse relation for computing the reduced matrix elements is

\[
\left\langle k_j; s' j L' l' \left| T^{S \cdot L \cdot \Pi} \right| k_i; s i L l \right\rangle = \sum_{\pi \pi'} \int d\vec{k}_j d\vec{k}_i Y_{L'' M'}^{*}(\hat{k}_j) Y_{L M}^{*}(\hat{k}_i) \\
\times C_{M m''}^{L L} C_{M' M''}^{L'' L''} \left\langle k_j; s' j l' m' \left| T^{S} \right| k_i; s i l m \right\rangle
\]

(2.39)

The partial wave Lippmann-Schwinger equation for the reduced \( T \) matrix elements is,

\[
\left\langle k'; s' j L' l' \left| T^{S \cdot L \cdot \Pi} \right| k; s i L l \right\rangle = \left\langle k'; s' j L' l' \left| V^{S \cdot L \cdot \Pi} \right| k; s i L l \right\rangle + \sum_{r, r', l''} \int dp \left( \frac{1}{E - \epsilon_r - \frac{1}{2}p^2} \right) \\
\left\langle p; s'' r L'' l'' \left| T^{S \cdot L \cdot \Pi} \right| k; s i L l \right\rangle
\]

(2.40)

This set of equations is formally similar to the hydrogenic case (McCarthy & Stelbovics 1983).

### 2.4 Potential Matrix Elements

The potential is of the form

\[
\left\langle \vec{k}'; s' j' l' m' \left| V^S \right| \vec{k}; s i l m \right\rangle = \left( k'(0); s' j' l' m' (12) \left| V^S \right| k(0); s j i l m (12) \right) \\
= \sum_{abcd} C_{j l s}^{a b} C_{j' l' s'}^{c d} \\
\times \left\langle k'(0); \varphi_c (1) \varphi_d (2) (l_a l_b) l' m' (12) \left| V^S \right| k(0); \varphi_d (1) \varphi_b (2) (l_a l_b) l m (12) \right\rangle
\]

(2.41)
The most general structure we need consider in detail, are the matrix elements

\[
\left\langle \vec{k'}; \varphi_c \varphi_d (l_c l_d) l'm' \right| V^S \left| \vec{k}; \varphi_a \varphi_b (l_a l_b) l m \right\rangle
\]

(2.42)

whose reduced matrix elements are

\[
\left\langle \vec{k}'L'(l_c l_d) l'\pi' s' \right| V^{S,\mathcal{Q}} \left| \vec{k} L (l_a l_b) l \pi \right\rangle = \frac{2}{\pi k' k} \delta_{s,s'} \left\langle d \mid b \right\rangle \hat{L} \hat{L}' \hat{i} \hat{i}' \hat{l}_c \hat{l}_a
\]

\[
\times \sum \left( -1 \right)^{l + l' + r + r' + l_c + l_a + k} \begin{pmatrix} L & \lambda & L' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_d & \lambda & l_c \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & \lambda & l' \\ l & l_a & l' \end{pmatrix} \begin{pmatrix} L' & l' & \mathcal{Q} \\ l & L & \lambda \end{pmatrix}
\]

(2.44)

\[
\times V_D (L k a ; L' k' c)
\]

where

\[
V_D (L k a ; L' k' c) = \int d r_0 \, d r_1 u_L (k r_0) \varphi_c (r_1) u_L (k r_0) \varphi_a (r_1) \left[ -\delta_{k_0} \frac{2}{r_0} + \frac{2 r_0^2}{r_{k+1}^2} \right].
\]

(2.45)

We remind the reader that we are using the abbreviation \( a = n_a l_a \), \( c = n_c l_c \) and similarly for \( b \) and \( d \).
Here we have used
\[ \langle r | k \rangle \equiv \frac{1}{(2\pi)^{\frac{3}{2}}} e^{i\vec{k} \cdot \vec{r}} = \sqrt{\frac{2}{\pi}} \sum_{LM} Y_{LM}^*(\hat{k}) Y_{LM}(\hat{r}) \ i^L \frac{u_L(kr)}{kr} \]  
\[ u_L(kr) \equiv kr \ j_L(kr). \]  
(2.46)

(2.47)

\( V_D^S \) is the direct potential involving the overlap between the projectile wave function and the two-electron orbitals and \( \langle d | b \rangle \) represents the overlap integral between the single particle functions

\[ \langle d | b \rangle = \delta_{l_d l_b} \int_0^\infty dr \ \varphi_d(r) \ \varphi_b(r) \]  
(2.48)

The allowed values of \( \lambda \) are determined by triangle rules for angular momenta \((l', \lambda, l), \ (L', \lambda, L) \) and \((l_a, \lambda, l_c)\).

### 2.6 Exchange Matrix Elements

The exchange matrix elements that need to be calculated are defined by equation (2.28). There are several classes of terms contributing and we now give expressions for each term. Similar to the direct matrix elements we construct reduced matrix elements (equation 2.43) from the defining expressions (equations 2.41 - 2.42).

In all the formulae given subsequently the reduced matrix elements include the spin recoupling coefficients present in equation (2.28) and given by equations (2.24 – 2.25).
First we consider all terms containing the $P_{0l}$ operator:

$$
\langle k' L' (l' a) \mid l' \pi' s' \mid (V_{01} P_{01})^S \Pi \rangle \langle k L (l a) \mid l \pi s \rangle
\begin{align*}
\frac{2}{\pi k' k} & \langle d \mid b \rangle \hat{L} \hat{L}' \hat{I} \hat{I}' \hat{s} \hat{s}' \hat{l}_a \hat{I}_a \sum_{\lambda j} (-1)^{l + l' + l_a + l_a + \lambda + s + s' + 1} (2j + 1) \\
\times & \left( \begin{array}{cccc}
L & \lambda & l & a \\
0 & 0 & 0 & 0
\end{array} \right)
\left( \begin{array}{cccc}
L & l & b & j \\
1/2 & 1/2 & s & j
\end{array} \right)
\left( \begin{array}{cccc}
l_d & l_c & l' & L' \\
1/2 & s & j & L
\end{array} \right)
\times V^A (k k a ; L' k' c)
\end{align*}
\tag{2.49}
$$

where $V^A$ is the radial exchange potential integral and is written as

$$
V^A_{01} ([L k] a ; [L' k'] c)
= \int \int d r_0 d r_1 u_L (k r_0) \varphi_a (r_1) \varphi_a (r_0) u_L (k r_1) \frac{r_a}{r_{a + 1}}
\tag{2.50}
$$

Next we consider the contributions from $V_{02} P_{01}$:

$$
\langle k' L' (l' a) \mid l' \pi' s' \mid (V_{02} P_{01})^S \Pi \rangle \langle k L (l a) \mid l \pi s \rangle
\begin{align*}
\frac{2}{\pi k' k} & \langle c \mid k L \rangle \hat{L} \hat{I} \hat{l} \hat{I} \hat{s} \hat{s}' \hat{l}_a \hat{I}_a \sum_{\lambda j} (-1)^{l' + l + l_a + l_a + \lambda + s + s' + 1} \\
\times & \left( \begin{array}{cccc}
L & l & a \\
0 & 0 & 0
\end{array} \right)
\left( \begin{array}{cccc}
l_d & l & d & l' \\
1/2 & 1/2 & s & j
\end{array} \right)
\left( \begin{array}{cccc}
l_c & L & \lambda & l' \\
1/2 & s & j & L
\end{array} \right)
\times V^A (b a ; [L' k'] d)
\end{align*}
\tag{2.51}
$$

Where $V^A$ is the integral defined by equation (2.50) with $u_L (k r)$ replaced by $\varphi_d$ and $\varphi_c$ by $\varphi_d$:

$$
V^A (b a ; [L' k'] d)
= \int \int d r_0 d r_2 u_L (k r_0) \varphi_d (r_2) \varphi_a (r_0) \varphi_a (r_2) \frac{r_a^d}{r_{a + 1}^d}
\tag{2.52}
$$

and $\langle c \mid k L \rangle$ is the overlap integral between the projectile wave function and the one-electron orbital

$$
\langle c \mid k L \rangle = \delta_{c L} \int \varphi_c (r) u_L (k r).
\tag{2.53}
$$
The calculation of exchange matrix elements for the two-electron potential $V_{12} P_{01}$ involves the re-coupling of angular momenta on the right-hand side and we obtain,

$$\langle k' L'(l_c l_d) \ell' \pi' s' \parallel (V_{12} P_{01})^{s, \ell, \pi} \parallel k L(l_a l_b) l \pi s \rangle$$

$$= \frac{2}{\pi k' k} \left\langle k' L' \mid \phi_a \right\rangle \hat{L} \hat{\ell} \hat{s} \hat{s'} \hat{l}_c \hat{l}_d \sum_{\lambda} (-1)^{l+\ell+l'+\ell'+s+s'+1} \left( \begin{array}{ccc} L & l_c & \ell' \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} l_b & \lambda & l_d \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} l_a & \ell & \ell' \\ 1/2 & 1/2 & s \end{array} \right) \left( \begin{array}{ccc} 1/2 & 1/2 & s' \end{array} \right)$$

$$\times V^\lambda \left( b [Lk]; c d \right)$$

(2.54)

where

$$V^\lambda \left( b [Lk]; c d \right) = \int d r_1 d r_2 \varphi_c (r_1) \varphi_d (r_2) u_{L}(kr_1) \varphi_b (r_2) \frac{r^\lambda}{r^{s+1}} \ .$$

(2.55)

The remaining terms with $P_{01}$ operators are

$$\langle k' L'(l_c l_d) \ell' \pi' s' \parallel [(E - H_0 - H_1 - H_2) P_{01}]^{s, \ell, \pi} \parallel k L(l_a l_b) l \pi s \rangle$$

$$= \frac{2}{\pi k' k} (-1)^{l+\ell+l'+\ell'+s+s'+1} \left( \begin{array}{ccc} L & l_b & \ell' \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} l_a & \ell & \ell' \\ 1/2 & 1/2 & s \end{array} \right) \left( \begin{array}{ccc} 1/2 & 1/2 & s' \end{array} \right)$$

$$\times \left[ \langle c \mid Lk \rangle \langle d \mid b \rangle \langle L'k' \mid a \rangle (E - \varepsilon_{k'} - \varepsilon_b) - \langle c \mid Lk \rangle \langle d \mid b \rangle \langle L'k' \mid V \rangle \right]$$

$$- \langle c \mid V \mid Lk \rangle \langle d \mid b \rangle \langle L'k' \mid a \rangle - \langle c \mid Lk \rangle \langle d \mid H_2 b \rangle \langle L'k' \mid a \rangle$$

(2.56)

$E$ is the total three-body energy given by equation (2.16).

The overlap integral between the projectile wave function, the one-electron potential and the one-electron orbital is,

$$\langle c \mid V \mid Lk \rangle = -Z \delta_{\ell, L} \int_0^\infty dr \varphi_c (r) \frac{u_{L}(kr)}{r}$$

(2.57)

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and one-body Hamiltonian overlap is,

$$
\langle d | H_2 | b \rangle = \int_0^\infty dr \varphi_d(r) \left( -\frac{1}{2} \frac{d^2}{dr^2} - \frac{2}{r} \right) \varphi_b(r).
$$

(2.58)

For higher partial waves the two-electron exchange matrix elements in equations (2.51) and (2.54) and one-electron exchange matrix elements in (2.56) do not appear due to the overlap between the one-electron orbitals and projectile wave functions. These overlaps will vanish whenever $L' \neq l_a$ and $L \neq l_c$ since $l_a$ and $l_c$ are typically limited to be $\leq 3$ in our CI target expansions.

The exchange terms containing the operators $P_{02}$ can all be related by symmetry considerations to an equivalent $P_{01}$ term and hence we do not give separate formulae for them. The complete reduced matrix element for a particular $\mathcal{L}$ and $\mathbf{S}$ in the partial wave expansion (equation 2.56) is the sum of direct potential matrix element in (equation 2.44) and exchange potential matrix elements in equations (2.49), (2.51), (2.54) and (2.56).

### 2.7 Numerical Methods in Close-Coupling Programs

The calculation of direct/exchange potential matrix elements in the above section in equations (2.44), (2.49), (2.51) and (2.54) involves the direct/exchange potential sums over $\lambda$. Each of these potentials $V_D$ and $V^x$'s is calculated by performing the analytic overlap integration while using analytical close-coupling form of the equations.
These potential matrix elements also involve the overlap integrals as, \( \langle d \mid b \rangle \) in equation (2.48) and \( \langle c \mid k L \rangle \) in equation (2.53), which are again calculated in the analytic integration form in analytical CC program.

In the numerical form of close-coupling method of solving these equations, the routines involving the analytic overlap integrations for the calculations of the potentials such as \( V_p \) and \( V^k \)'s were completely replaced by new routines. These new routines calculate these potentials by performing the sum of the overlap of projectile wave functions with the numerical form of radial one/two-electron orbital potentials. The sums are performed over a grid that can have up to \( N = 8000 \) radial integration points. For example equation (2.57) in numerical sum form appears as

\[
\langle c \mid V \mid L_k \rangle = -Z \delta_{l_c l} \sum_{n=1}^{N} \phi_c(r_n) \frac{u_L(kr_n)}{r_n}
\]  

(2.59)

All routines involving analytic overlap integrals between single particle functions and projectile wave functions with one-electron radial orbitals were completely dropped in numerical CC program. The new routines were written, which again perform the sum of the overlap of numerical form of wave function such as

\[
\langle d \mid b \rangle = \delta_{l_d l} \sum_{n=1}^{N} \phi_d(r_n) \phi_b(r_n)
\]  

(2.60)

In the remainder of the thesis while using numerical CC program, we sometimes refer to these sums in (2.59) and (2.60) as "numerical integrations" corresponding to analytical integrations in analytic CC program. A major part of the thesis concentrates on the numerical calculations of close-coupling equations as this modification in fact simplified the calculations and improved the time efficiency to a great deal. By
adopting this numerical method of calculations, we have been able to develop an interface with other atomic structure packages to be used in our close-coupling code.

2.8 Differential and Total Cross Sections

The general differential cross section for scattering from an initial state $i$ to a final state $f$, where

$$ |i⟩ = \left| k_i, \mu_{i0}, \gamma_i, \pi_i, l_i, m_i, s_i, \mu_i \right⟩, \quad (2.61) $$

and similarly for $f$ the differential cross section is,

$$ \frac{dσ_{fi}}{dΩ} = \frac{k_f}{k_i} \left| \left\langle f \left| A \right| i \right\rangle \right|^2. \quad (2.62) $$

In this thesis we will be concerned with scattering processes where the magnetic sublevels for the initial and final states are not resolved experimentally, either for spin or orbital angular momentum. In this case the observed scattering cross section is obtained by averaging over the initial target spin and orbital angular magnetic quantum numbers and initial projectile electron spin magnetic quantum numbers, where it is assumed each possible quantum state has equal probability of population.

For the final state we sum over all corresponding magnetic quantum numbers:

$$ \frac{dσ_{fi}}{dΩ} = \frac{k_f}{k_i} \frac{(2π)^4}{2 \left(2S_i + 1 \right) \left(2l_i + 1 \right)} \times \sum_{m_i, \mu_{i0}, \mu_{i0}} \left| \left\langle k_f, \mu_{f0}, s_f, \mu_f, γ_f, l_f, m_f \right| T \left| k_i, \mu_{i0}, s_i, \mu_i, γ_i, l_i, m_i \right⟩ \right|^2 \quad (2.63) $$

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Now we utilize the fact that total spin of the electron-target system is conserved to expand in complete sets of coupled states $\left| \left( \frac{1}{2}, s \right) S \mathcal{M}_S \right\rangle$ and by using the Wigner-Eckart theorem perform the sums over the spin magnetic quantum numbers to yield

$$\frac{d\sigma_{f_i}}{d\Omega} = \frac{k_f}{k_i} \frac{(2\pi)^4}{2 (2s_i + 1)(2l_i + 1)} \times \sum_{s_f, m_f} (2S + 1) \left| \left\langle \vec{k}_f ; s_f, \gamma_f l_f m_f \right| T^S \left| \vec{k}_i ; s_i, \gamma_i l_i m_i \right\rangle \right|^2$$

(2.64)

The $T$-matrices in this expression are computed from the reduced matrix elements through equation (2.38).

To summarise, this chapter details the theory of solving momentum-space close-coupling equations using both the forms of Helium target wave functions, analytical as well as numerical. These equations will need to be modified to enable them to be used for Neon and other inert gases, which can be taken up as a future work. The description of the structure of Helium target states from other packages, to be used in our existing CC program is detailed in the next chapter; chapter three.
Chapter 3

Analytical and Numerical Procedures for Calculations of Target States of Inert Gases

A description of the calculation of target states for both Helium and Neon using configuration-interaction approach will be discussed in this chapter. We present here the successful modification of our present close-coupling electron-Helium analytic code into a numerical close-coupling electron-Helium program, which forms the basis of a general scattering code. Note that as discussed in chapter one, the terminology "analytic" or "numerical" close-coupling code refers only to the type of orbitals employed, either Slater/Laguerre analytic functions or numerical orbitals.

In this chapter, two mainstream packages, the atomic structure package of Charlotte Froese Fischer (1973) and CIV3 package of Alan Hibbert (1975) are described, and the way an existing close-coupling code (LBAS) must be modified in order to interface with them.

3.1 Calculation of Helium Target States

In this section we will outline the discussion of target structure in the configuration-Interaction (CI) representation only, for the simplest inert gas, Helium. Both analytical as well as numerical wave functions are described. The radial functions can be Slater or Laguerre basis functions for the analytical calculations, whereas only Slater orbitals can be used in the numerical orbital solutions of the coupled channels equations. The reason for this will be made clear later.
3.1.1 Target States for Close-Coupling Equations

In chapter two, a CI expansion of the target states was given in equation (2.03). The configurations $\Phi^{ab}$ defined through equation (2.04) were unsymmetrized, but the antisymmetrization of the target wave functions follows from the symmetry (equation 2.09) of the CI coefficients. For completeness and to relate this expansion to others’ works that use explicitly antisymmetrized configurations we note the following relations:

We define an antisymmetrized configuration by $\tilde{\Phi}^{ab}$ and express it in the usual determinantal form as

$$\tilde{\Phi}^{ab}_{l_{s m m_s}}(12) = \sum_{m_0 \mu_0} C^{l_s}_{m_0, m} C^{l_s}_{\mu_0, \mu} \left| \begin{array}{cc} \Phi_a(\vec{x}_1) & \Phi_a(\vec{x}_2) \\ \Phi_b(\vec{x}_1) & \Phi_b(\vec{x}_2) \end{array} \right|$$

(3.01)

where

$$\Phi_a(\vec{x}) = \frac{\varphi_a(r)}{r} Y_{l_s m_s}(\hat{r}) \chi_{\frac{l_s}{2} \mu_s}^{\pm} (\sigma).$$

(3.02)

It is straightforward to show the relationship with the configurations of equation (2.04) as

$$\tilde{\Phi}^{ab}_{l_{s m m_s}}(12) = \Phi^{ab}_{l_{s m m_s}}(12) - \Phi^{ab}_{l_{s m m_s}}(21)$$

$$= \Phi^{ab}_{l_{s m m_s}}(12) + (-1)^{l_s + l_b} \Phi^{ba}_{l_{s m m_s}}(21).$$

(3.03)

In terms of these antisymmetrized configurations the general CI expansion for $\Psi_{r,l,m_s}$ may be written as

$$\Psi_{r,l,m_s m_m}(12) = \sum_{ab, a \neq b} \tilde{C}^{ab}_{r,l,m_s} \tilde{\Phi}^{ab}_{l_{s m m_s}}(12),$$

(3.04)
with
\[ \tilde{C}_{\gamma l \pi s}^{ab} = C_{\gamma l \pi s}^{ab}, \quad a \neq b \]
\[ = \frac{1}{4} (1 + (-1)^{s+l}) C_{\gamma l \pi s}^{aa}, \quad a = b. \]  

(3.05)

Note that the diagonal CI coefficients are present only for \( s + l \) an even integer and also that the sum is now restricted to configurations such that \( a \geq b \).

The overlap for any two configurations \( \Phi^{ab}, \Phi^{cd} \) is
\[ \langle \Phi^{cd}_{l \ell s l', m s' \mu} | \Phi^{ab}_{\ell \ell s m \mu} \rangle = \delta_{\ell'l} \delta_{m'm} \delta_{s's} \delta_{\mu'\mu} B_{n' l}^{(cd)(ab)} \]  

(3.06)

where
\[ B_{n' l}^{(cd)(ab)} = \delta_{\ell l} \delta_{m's} \langle c \mid a \rangle \langle d \mid b \rangle. \]

(3.07)

Similarly for the antisymmetric configurations:
\[ \langle \tilde{\Phi}^{cd}_{l \ell s l', m m' \mu} | \tilde{\Phi}^{ab}_{\ell \ell s m \mu} \rangle = \delta_{\ell'l} \delta_{m'm} \delta_{s's} \delta_{\mu'\mu} \tilde{B}_{n' l}^{(cd)(ab)} \]

(3.08)

where
\[ \tilde{B}_{n' l}^{(cd)(ab)} = 2 B_{n' l}^{(cd)(ab)} + (-1)^{s+l+l'+s} B_{n' l}^{(cd)(ab)}. \]  

(3.09)

The radial functions \( \varphi_{a}(r) \) or \( \varphi_{b}(r) \) may either be Slater or Laguerre basis functions.

The Slater functions are given as
\[ \varphi_{a}(r) = \left( \frac{(2 \mu_{a})^{2n_{a}+1}}{(2n_{a})!} \right)^{1/2} r^{n_{a}} e^{-\mu_{a} r}, \quad n_{a} = 1, 2, \ldots \ldots \]  

(3.10)

while the Laguerre functions are represented as
\[ \varphi_{a}(r) = \sqrt{\frac{\lambda_{a}!}{(2l_{a} + 2 + i_{a})}} (\lambda r)^{l_{a}+1} e^{-\lambda r/2} L_{i_{a}}^{l_{a}+1}(\lambda r) \]

(3.11)

where \( i_{a} = 0, 1, 2, \ldots \ldots \)
In order to calculate target states from expansions of this type we insert the expansions into the Schrödinger equation (2.15) and folded on the left with each of the configurations. This yields the generalized eigenvalue problem, which in terms of the antisymmetrized configurations \( \tilde{\Phi}^{ab} \) is

\[
\tilde{A}_{nls} \tilde{c}_{\pi nls} = \epsilon_{\pi nls} \tilde{b}_{nls} \tilde{c}_{\pi nls}. \tag{3.12}
\]

\( A_{nls} \) is the partial wave Hamiltonian matrix defined by

\[
A^{abcd}_{nls} = \left< \Phi^{ab}_{nls} \right| H_1 + H_2 + V_{12} \left| \Phi^{cd}_{nls} \right> = \left< \Phi^{ab}_{nls} \right| \left( -\frac{1}{2r_1^2} \frac{\partial}{\partial r_1} \left( r_1^2 \frac{\partial}{\partial r_1} \right) + \frac{l_1(l_1+1)}{2r_1^2} - \frac{1}{2r_2^2} \frac{\partial}{\partial r_2} \left( r_2^2 \frac{\partial}{\partial r_2} \right) + \frac{l_2(l_2+1)}{2r_2^2} - \frac{2}{r_1} \frac{2}{r_2} + \sum_i \frac{4\pi}{2l+1} \frac{r_i^l}{r_i^{l+1}} Y_l Y_i \left| \Phi^{cd}_{nls} \right> \right). \tag{3.13}
\]

The overlap of two atomic state functions in terms of explicit radial orbitals expansion is written as

\[
\left< \psi^{\,\pi' \ell' m' s'}_{\ell m s} \right| \psi_{\pi \ell m s} \right> = \delta_{\pi' \pi} \delta_{\ell' \ell} \delta_{m' m} \delta_{s' s} = \sum_{\text{cd}} \tilde{c}_{\pi' \ell' \pi \ell}^{cd} \tilde{c}_{\pi \ell m s}^{ab} \left< \Phi^{cd}_{nls} \right| \left( \tilde{\Phi}^{ab}_{nls} \right> = \sum_{\text{cd}} \tilde{c}_{\pi' \ell' \pi \ell}^{cd} \left< \Phi^{cd}_{nls} \right| \left( \tilde{\Phi}^{ab}_{nls} \right> = \sum_{\text{cd}} \tilde{c}_{\pi' \ell' \pi \ell}^{cd} \tilde{b}_{nls}^{(cd)(ab)} \tilde{c}_{\pi \ell m s}^{ab} \delta_{\ell' \ell} \delta_{m' m} \delta_{s' s} \delta_{m \ell}, \tag{3.14}
\]

where

\[
\sum_{\text{cd}} \tilde{c}_{\pi' \ell' \pi \ell}^{cd} \tilde{b}_{nls}^{(cd)(ab)} \tilde{c}_{\pi \ell m s}^{cd} = \delta_{\pi' \pi} \tag{3.15}
\]

The dimensionality of the system of equations is just the number of symmeterized configurations in the expansion for given \( \pi l s \) of the target.

The eigenvalue equation (3.12) is solved by using explicit equations (3.13) - (3.15).
3.1.2 Fischer’s Numerical HF and MCHF Wave Functions

Charlotte Froese Fischer (1973) has provided extensive numerical procedures for solving Hartree-Fock (HF) equations and Multiconfiguration Hartree-Fock (MCHF) equations. The numerical procedures adopted by Fischer perform radial integrations of numerical wave functions for Hydrogen by assuming exact hydrogenic wave functions.

Before we incorporate Fischer’s numerical orbitals for Helium, into our numerical orbital CC code, we will show the successful modification of analytical orbital CC code to a new CC code (numerical).

Fischer writes an expansion of the exact total wave function for the ground state of Helium in terms of complete basis of configuration state functions as

$$\Psi(1s^2\,1S) = \sum_i \sum_m \sum_n a_{nm\ell} \left| nlm'\ell\,1S \right>$$ (3.16)

which is exactly the same as CI expansion given in equation (3.04), with

$$a_{nm\ell} = \widetilde{\mathcal{C}}_{\gamma l\pi s}^{ab} \text{ and } \left| nlm'\ell\,1S \right> = \widetilde{\mathcal{D}}_{lsm\ell m'}^{ab}.$$ (12)

We choose as basis functions, Slaters given by equation (3.10) and compute an accurate approximation to $\Psi(1s^2\,1S)$ by selecting the exponent $\mu$ values following a systematic procedure defined as follows. Starting with $l = 0$, increase the number of configurations in the sum until the change in ground state energy $\Delta E_{nl}$ is sufficiently small. These energy values are compared with Fischer’s (1973) values in Table 3.1.
Table 3.1: Convergence of Helium energies (a.u.) for the ground state $1s^2 \tilde{S}$, with present CI results using Slaters, compared with CFF results.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>$l$</th>
<th>$n$</th>
<th>$\mu$</th>
<th>CI</th>
<th>CFF</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1s^2$</td>
<td>0</td>
<td>1</td>
<td>1.7</td>
<td>-2.850000</td>
<td>-2.861680</td>
</tr>
<tr>
<td>$1s2s$</td>
<td>0</td>
<td>1</td>
<td>2.5</td>
<td>-2.860888</td>
<td>-2.877997</td>
</tr>
<tr>
<td>$1s3s$</td>
<td>0</td>
<td>1</td>
<td>1.5</td>
<td>-2.878108</td>
<td>-2.878871</td>
</tr>
<tr>
<td>$1s4s$</td>
<td>0</td>
<td>1</td>
<td>4.0</td>
<td>-2.878789</td>
<td>-2.878990</td>
</tr>
<tr>
<td>$1s2p$</td>
<td>1</td>
<td>2</td>
<td>2.5</td>
<td>-2.898203</td>
<td>-2.898554</td>
</tr>
<tr>
<td>$1s3p$</td>
<td>1</td>
<td>2</td>
<td>3.5</td>
<td>-2.899860</td>
<td>-2.900150</td>
</tr>
<tr>
<td>$1s4p$</td>
<td>1</td>
<td>2</td>
<td>5.0</td>
<td>-2.900169</td>
<td>-2.900399</td>
</tr>
<tr>
<td>$1s3d$</td>
<td>2</td>
<td>3</td>
<td>3.5</td>
<td>-2.901936</td>
<td>-2.902179</td>
</tr>
<tr>
<td>$1s4d$</td>
<td>2</td>
<td>3</td>
<td>5.0</td>
<td>-2.902283</td>
<td>-2.902523</td>
</tr>
<tr>
<td>$1s4f$</td>
<td>3</td>
<td>4</td>
<td>4.5</td>
<td>-2.902666</td>
<td>-2.902909</td>
</tr>
<tr>
<td>$1s5g$</td>
<td>4</td>
<td>5</td>
<td>6.0</td>
<td>-2.902790</td>
<td>-2.903033</td>
</tr>
</tbody>
</table>

Fischer's ground state energy result involving one configuration is better as compared to our value as each orbital in Fischer's expansion can be written as a sum of quite a number of Slaters whereas each Slater in equation (3.10) for our CI expansion represents one of the orbitals as $1s$, $2s$, $2p$, $3s$, $3p$, $3d$ and so on. As our overall basis set increases, the quality of the wave functions should approach each other as is evident from Table 3.1.

A set of seven analytical Slaters was converted to seven numerical orbitals and used to test the phase shift results at 10eV incident energy involving nine target states. Further detailed comparisons of phase shifts with other results available in literature will be given in the next chapters. Table 3.2 shows an encouraging comparison of the phase shifts of both analytical and numerical CC calculations.
Table 3.2: A comparison of phase shifts for numerical and analytical LBAS close-coupling calculations at 10eV incident energy for the first five partial waves. A set of seven orbitals and nine target states forms the basis of this comparison.

<table>
<thead>
<tr>
<th>$l$</th>
<th>CC analytical</th>
<th>CC numerical</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.057605</td>
<td>2.057710</td>
</tr>
<tr>
<td>1</td>
<td>0.211743</td>
<td>0.211740</td>
</tr>
<tr>
<td>2</td>
<td>0.036313</td>
<td>0.036310</td>
</tr>
<tr>
<td>3</td>
<td>0.008246</td>
<td>0.008246</td>
</tr>
<tr>
<td>4</td>
<td>0.003686</td>
<td>0.003686</td>
</tr>
</tbody>
</table>

The numerical scattering results are as accurate as obtained from analytic calculations. The above results prove that LBAS analytic computations can be replaced by equivalent numerical ones. This leads us to believe that our modified close-coupling program with numerical orbitals is as good for low-energy Helium scattering, as is the present analytic orbital code.

Our first test with Fischer’s numerical orbitals was to perform a one-state (ground-state) CC numerical orbital calculation. This was compared with another calculation using the ground state calculated from our program. As expected both calculations gave identical results for phase-shifts. The calculations could not be extended to include more target states because Fischer’s code would generate a different set of orbitals for different states. There was no way to readily overcome this limitation of her code.
The reason why Fischer's numerical orbitals could not be used as a basis in our present numerical CC package is as follows;

The total wave function for the Helium target is,

\[ \Psi_r = \sum_{ab} \tilde{C}^{ab}_{r} \Phi^{ab} = \sum_{ab} C^{ab}_{r} \Phi^{ab} \]  \hspace{1cm} (3.17)

where \( \Phi^{ab} \) comprises of the same set of input orbitals for all the target states involved in the scattering calculations. Since

\[ \Phi^{ab} = \phi_a(1) \phi_b(2) \]  \hspace{1cm} (3.18)

The potential matrix element, as detailed in chapter two is given by

\[ \langle \Psi_r | V | \Psi_{r'} \rangle = \sum_{abcd} C^{ab}_{r} C^{cd}_{r'} \langle \phi_a \phi_b | V | \phi_c \phi_d \rangle. \]  \hspace{1cm} (3.19)

For the present scattering calculations the potential scattering matrix elements \( \langle \phi_a \phi_b | V | \phi_c \phi_d \rangle \) will be the same for all the target states; only the CI coefficients \( C^{ab}_{r} C^{cd}_{r'} \) will vary. However in Fischer's wave functions the radial orbitals being different for different states will change both the potential matrix element and CI coefficients. The condition \( \langle \Psi_r | \Psi_{r'} \rangle = \delta_{rr'} \) is essential for the present CC calculations involving two or more states, where as for Fischer wave functions we checked that it is not because in her code a separate optimization of orbitals is performed for each state. There is no option to fix the same set of orbitals for different states.
Some algebraic equations were derived in an attempt to develop a direct relation of the present CI coefficients using Slater functions, with Fischer’s CI coefficients using Hydrogenic wave functions, but it did not lead to a simple direct comparison of the two.

3.1.3 Comparison of LBAS Numerical CI Coefficients with Roothaan’s Mixing Coefficients

We made an attempt to use Roothaan-Hartree-Fock atomic wave functions for Helium available in “Atomic Data and Nuclear Tables” given by Clementi & Roetti (1974). Clementi & Roetti employ orbitals, which are a linear combination of Slaters, and moreover the orbitals are orthogonal. We used the exponents of the basis functions to be used in analytic wave functions expanded in the Roothaan-Hartree-Fock method and compared the CI coefficients. Roothaan’s wave function for the Helium target state (ground state) $1s^21S$ is written in the notation of Clementi and Roetti as

$$
\Psi(r_1, r_2) = \Phi_{1s}(r_1) \Phi_{1s}(r_2) = \sum_i C_i \chi_i(r_1) \sum_j C_j \chi_j(r_2) = \sum_{ij} C_i C_j \chi_i(r_1) \chi_j(r_2)
$$

(3.20)

where $\chi(r_j)$ are Slaters. The Slaters used by Roothaan are of different type for 1s, 2s and 2p orbitals. The present CC code uses the expansion as

$$
\Psi'(r_1, r_2) = \sum_{ab} C_{\gamma}^{ab} \Phi^{ab}(r_1, r_2) = \sum_{ab} C_{\gamma}^{ab} \varphi_a(r_1) \varphi_b(r_2)
$$

(3.21)

where $\varphi_{a,b}(r)$ are Slater functions.
Testing for He $^1S$ state using 1s orbital only, and comparing with the values from Clementi and Roetti, data tables (1974) there was no close relation between the coefficients $C_j C_j$ and the $C^{ab}$ even when we employed the same basis functions as Clementi and Roetti. There seemed to be no direct simple comparison of the CI coefficients of these two methods even for the simplest ground-state case. Hence Roothaan’s mixing coefficient technique was also unsuitable for our numerical close-coupling calculations.

Because of the difficulties outlined with the use of Roothaan-Hartree-Fock method and Fischer’s MCHF code, it was decided that for inert gases apart from Helium, Fischer’s code would never provide useful method for generating a large set of target states for use in our CC program. Therefore we turned to another atomic structure package.

3.1.4 Configuration-Interaction method of Alan Hibbert

The atomic structure package, CIV3 of Alan Hibbert (1975), in contrast to that of Fischer has the option of using the same set of orbitals to generate the ground and excited states, which is the basic requirement for generating a suitable target state expansion for the CC code.

The wave functions used by Hibbert have the same general CI form as in equation (3.04) used by our CC code. For example the ground state of Helium denoted by $1s^2$ $^1S$ can be written as a representation of symmeterized configurations as
\[ \Psi'(1S) = C_1 \bar{\Phi}_1 (1s^2 \, ^1S) + C_2 \bar{\Phi}_2 (1s2s \, ^1S) + C_3 \bar{\Phi}_3 (2s^2 \, ^1S) + C_4 \bar{\Phi}_4 (2p^2 \, ^1S) \\
+ C_5 \bar{\Phi}_5 (2p3p \, ^1S) + C_6 \bar{\Phi}_6 (3d^2 \, ^1S) + \ldots \ldots \ldots \]
\[ = \sum_{ab} \bar{C}^{ab} \bar{\Phi}^{ab} \] (3.22)

with \( l_a = l_b \). Thus his expansion in terms of CI coefficients is equivalent to the summation over \( a, b \) of the \( \bar{C}^{ab} \). The ordering of his configuration expansion is in general different from the one employed in our close-coupling LBAS package and his CI coefficients have to be reordered before applying his wave functions to our code.

Similarly for the 1s2p \(^1P^0\) state

\[ \Psi'(P^0) = C_1 \bar{\Phi}_1 (1s2p \, ^1P^0) + C_2 \bar{\Phi}_2 (1s3p \, ^1P^0) + C_3 \bar{\Phi}_3 (2s2p \, ^1P^0) \\
+ C_4 \bar{\Phi}_4 (2s3p \, ^1P^0) + C_5 \bar{\Phi}_5 (2p3d \, ^1P^0) + \ldots \ldots \ldots \] (3.23)

where \( |l_a - l_b| = 1 \)

The radial functions used by Hibbert are expressed in the analytic form as a general Slater sum

\[ \phi_{nl}^H(r) = \sum_j p_{jnl} r^{l+1} e^{-\mu_{nl} r} \] (3.24)

in contrast to our configurations that are made up of single Slaters or single Laguerre functions. This package has more complex orbitals. Incorporating this more general orbital structure meant, we had to rewrite extensively the subroutines involving the potential matrix elements in the LBAS code.

The orbitals are assumed to form an orthonormal set. The orthogonality of orbitals with different \( l \) is guaranteed by the orthogonality of the spherical harmonics.
However, for orbitals with the same \( l \), the radial functions must themselves form an orthonormal set;

\[
\int_0^\infty \varphi_{n_i}^H(r) \varphi_{n_i'}^H(r) \, dr = \delta_{nn'}.
\] (3.25)

It should be noted that as the size of the CI expansions are increased, our target states and those generated by Hibbert’s program should be of a similar quality and this was confirmed by testing as detailed in chapter four section 4.4.

3.1.5 Interfacing CIV3 code into the LBAS CC Package

A number of optimization procedures were used to achieve the best target wave functions for Helium, using CIV3 package. Each orbital in Hibbert’s package can be optimized over more than one state/symmetry. For example the 2s orbital can be optimized over \( ^1S \) and \( ^3S \), 2p can be optimized over \( (1s) \, ^1S \), \( (1s2p) \, ^1P \), \( (1s2p) \, ^3P \) symmetries and so on. A set of seven orbitals 1s 2s 2p 3s 3p 4s 3d has been obtained by adopting a systematic optimization procedure. The optimization has been performed over 14 configurations leading to \( ^1S \) symmetry, 7 for \( ^3S \), 10 each for \( ^1P \) and \( ^3P \), 8 for \( ^1D \) and 5 for \( ^3D \) symmetry. The 54 configurations represent different energy eigenvalues and the corresponding CI coefficients for Helium obtained are used for scattering calculations.

The flexibility with this package is, that various optimization procedures can be adopted to achieve a set of good orbitals and CI coefficients, required for a particular type of scattering calculation. Further details on different methods of optimization
along with the comparison of scattering results with those of Saha (1989) are detailed in chapter four.

For electron-Helium scattering, Hibbert’s wave function in CI form would be

\[
\Psi_{\gamma \pi l,m}^a (1,2) = \sum_{ab} C_{\gamma \pi l,m}^{ab} \Phi_{\gamma \pi l,m}^{ab} (1,2)
\]

(3.26)

where

\[
\Phi_{\gamma \pi l,m}^{ab} (1,2) = \chi_{\pi l,m} \Phi_{\gamma \pi l,m}^{ab} (1,2)
\]

(3.27)

\[
\Phi_{\gamma \pi l,m}^{ab} (1,2) = \Phi_{\gamma \pi l,m}^{ab} (\vec{r}_1, \vec{r}_2) = \frac{\phi^H_a (r_1)}{r_1} \frac{\phi^H_b (r_2)}{r_2} \mathcal{U}_{(\lambda, \kappa, \kappa') l,m} (\vec{r}_1, \vec{r}_2).
\]

(3.28)

and \(\phi^H_a\) is an Hibbert’s orbital.

Hibbert’s orbitals are considerably more complex than ours in that they are a sum of Slater’s (equation 3.24). We follow here the notation used by Hibbert for the coefficients \(p_a^a, p_b^b\) where \(a, b\) are indices \((a \equiv n_a l_a, b \equiv n_b l_b)\) not powers. Formally, if we expand the CI wave function using our orbitals (equations 2.03 – 2.08) and Hibbert’s (equations 3.26 – 3.28), comparing the two expansions gives the relation

\[
\sqrt{C_{\gamma \pi l,m}^{aa}} \phi_a = \sqrt{C_{\gamma \pi l,m}^{aa}} \phi_a^H.
\]

(3.29)

In writing this relation we have assumed that the number of orbitals specified for each target state is the same and that the ordering of the orbitals is the same for both expansions. However this relationship is not correct mathematically in general since each \(\phi_a\) comprises a single Slater compared to the sum of Slaters in Hibbert’s expansion. It is correct only when a single Slater is chosen for the expansion.
However the reason we give the connection becomes evident when we use the numerical orbital option developed in our code. When we replace the analytic Slaters by numerical orbitals, we can use the numerical orbitals generated by the Hibbert code directly in our code. This means we can interface the Hibbert CI package directly with our coupled-channels program.

The Hibbert numerical orbitals are used as a sophisticated basis in the modified numerical CC code to perform scattering calculations. Details of calculations illustrating the implementation are shown in chapter four. Phase shifts have been calculated at low incident energies and results are compared with Saha (1989) and Nesbet (1979).

In chapter five, our best basis expansion of numerical orbitals is used for inelastic electron-Helium low-energy scattering where excellent results for elastic and inelastic excitation cross sections and positions of low-lying resonances along with others’ results are detailed.

3.2 Neon Target States using CIV3 Package of Hibbert

While it is the case that the scattering calculations in this thesis are restricted to Helium, we did examine the use of Hibbert’s packages as to their practicality for other inert gas structure calculations. Here we briefly summarise its use for Neon target states.
The numerical code is being extended to electron-Neon scattering for future work, which uses radial wave functions from CIV3. The wave functions for the N-electron target states $\Psi_r$ and their corresponding energies $\varepsilon_r$ are calculated by solving the equation

$$\langle \Psi_r | H_{ff} | \Psi_{r'} \rangle = \varepsilon_r \delta_{rr'}$$

(3.30)

in the same way as already explained for Helium.

The target wave functions are constructed in the same CI expansion as already described for Helium in equation (2.03). The radial components of these orbitals, $\phi_{n,l}(r)$ are expanded in Slater form as in equation (3.24). The orbitals in all cases will be stored in a numerical form only. In the present work the $\phi_{n,l}(r)$ radial wave functions are obtained using the CIV3 package. The Neon target states correspond to 17 states LS coupling scheme. These states are constructed from seven Hartree-Fock basis orbitals 1s, 2s, 2p, 3s, 3p, 3d and 4s. The coefficients $p_j$ and exponent parameters $\mu_j$ for each orbital are obtained in the same manner as outlined by Zeman & Bartschat (1997).

The Clementi & Roetti (1974) tables are used for the first guess 1s, 2s and 2p orbitals describing the Neon ground state. To describe the electron-Neon scattering requires a description of the excited states as well as the ground state. To calculate the excited states, the ground state orbitals are used as an initial guess for the ion core ($1s^2 \, 2s^2 \, 2p^5$) and CIV3 is used to determine the excited state orbitals. Firstly the 3s orbital is obtained by optimizing over the energy eigenvalues for $(2p^53s) \, ^3P$ and $(2p^53s) \, ^1P$ states. The 2p orbital is again optimized over these two states as well as the ground
state. All three states are given equal weights as recommended by Hibbert. The 3s orbital is then re-optimized over these three states followed by a re-optimization of the 2p orbital. The re-optimization of the 2p orbital was performed over these three states with relative weights of 6.5, 1.0 and 1.0 for $^1S$, $^1P$ and $^3P$ states, in order to best approximate the level splitting between the ground state and the two $P$ states. The 3p, 3d and 4s orbitals are optimized on the six $(2p^53p)^1S$, $^3S$, $^1P$, $^3P$, $^1D$, $^3D$, six $(2p^53d)^1P$, $^3P$, $^1D$, $^3D$, $^1F$, $^4F$ and two $(2p^54s)^1P$, $^3P$ states respectively. The coefficients and exponent parameters are given in Table 3.3 and compared with the Zeman and Bartschat (1997) values.

Table 3.3: The coefficient and exponent parameters for the atomic orbitals compared with Zeman & Bartschat (1997).

<table>
<thead>
<tr>
<th>Orbital</th>
<th>$J$</th>
<th>$I$</th>
<th>$p_j$ (Present)</th>
<th>$\mu_j$ (Present)</th>
<th>$p_j$</th>
<th>$\mu_j$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3s</td>
<td>1</td>
<td>1</td>
<td>0.05129</td>
<td>8.03716</td>
<td>0.0606</td>
<td>7.8288</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2</td>
<td>-0.17404</td>
<td>3.32228</td>
<td>-0.1951</td>
<td>3.435</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3</td>
<td>1.00670</td>
<td>0.81367</td>
<td>1.0067</td>
<td>0.8524</td>
</tr>
<tr>
<td>4s</td>
<td>1</td>
<td>1</td>
<td>0.02494</td>
<td>8.19146</td>
<td>0.0223</td>
<td>8.2413</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2</td>
<td>-0.08821</td>
<td>3.25784</td>
<td>-0.0805</td>
<td>3.2245</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3</td>
<td>0.47999</td>
<td>0.87589</td>
<td>0.4358</td>
<td>0.8824</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>4</td>
<td>-1.08063</td>
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<td>0.4171</td>
</tr>
<tr>
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<td>2.5370</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2</td>
<td>0.28107</td>
<td>4.75245</td>
<td>0.2810</td>
<td>4.7542</td>
</tr>
<tr>
<td></td>
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<td>0.23309</td>
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<td>1.4935</td>
</tr>
<tr>
<td></td>
<td>4</td>
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<td>0.01369</td>
<td>9.59416</td>
<td>0.0136</td>
<td>9.5941</td>
</tr>
<tr>
<td>3p</td>
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<td>0.11928</td>
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<td>0.1186</td>
<td>3.2147</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3</td>
<td>-0.99847</td>
<td>0.55083</td>
<td>-0.9985</td>
<td>0.5494</td>
</tr>
<tr>
<td>3d</td>
<td>1</td>
<td>3</td>
<td>1.00000</td>
<td>0.33643</td>
<td>1.0000</td>
<td>0.3363</td>
</tr>
</tbody>
</table>
Our values for the coefficients and exponents differ slightly from the Zeman & Bartschat (1997) values. These orbitals produce 17 LS-coupled target state energies as detailed in Table 3.4. We cannot show the comparison of our target energies here with Zeman & Bartschat (1997) as their results detail the jLS 31 levels of Neon rather than LS-coupled states and at present the calculation of 31 energy levels of Neon in the jLS coupling scheme is beyond the scope of this work.

Table 3.4: A list of 17 LS-coupled target energies for Neon.

<table>
<thead>
<tr>
<th>State</th>
<th>Present (atomic units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2p⁶) ¹S₀</td>
<td>-128.5326028</td>
</tr>
<tr>
<td>(2p⁵3s) ³P</td>
<td>-127.9267576</td>
</tr>
<tr>
<td>(2p⁵3s) ³P</td>
<td>-127.9188067</td>
</tr>
<tr>
<td>(2p⁵3p) ³S</td>
<td>-127.8626516</td>
</tr>
<tr>
<td>(2p⁵3p) ³D</td>
<td>-127.8568833</td>
</tr>
<tr>
<td>(2p⁵3p) ¹D</td>
<td>-127.8542206</td>
</tr>
<tr>
<td>(2p⁵3p) ³P</td>
<td>-127.8530377</td>
</tr>
<tr>
<td>(2p⁵3p) ¹P</td>
<td>-127.8530377</td>
</tr>
<tr>
<td>(2p⁵3p) ¹S</td>
<td>-127.8248043</td>
</tr>
<tr>
<td>(2p⁵3d) ³P</td>
<td>-127.8028894</td>
</tr>
<tr>
<td>(2p⁵3d) ¹P</td>
<td>-127.8025159</td>
</tr>
<tr>
<td>(2p⁵3d) ³F</td>
<td>-127.8024703</td>
</tr>
<tr>
<td>(2p⁵3d) ¹F</td>
<td>-127.8024129</td>
</tr>
<tr>
<td>(2p⁵3d) ³D</td>
<td>-127.8017160</td>
</tr>
<tr>
<td>(2p⁵3d) ¹D</td>
<td>-127.8017160</td>
</tr>
<tr>
<td>(2p⁵4s) ³P</td>
<td>-127.8163384</td>
</tr>
<tr>
<td>(2p⁵4s) ¹P</td>
<td>-127.8146085</td>
</tr>
</tbody>
</table>
The calculations of above-mentioned set of orbitals for Neon involved numerous complications. The CIV3 package of Hibbert (1975) is not a very straightforward code for inert gases other than Helium. Even for Helium wave-function calculations, we made several consultations with Hibbert electronically and his prompt response helped us enormously. Certain similar input files for Neon wave function calculations to be used in CIV3 codes were received from Bartschat on request through electronic mail. All these efforts have led us to the stage that in our numerical close-coupling code, we can extend our calculations to electron-Neon scattering employing the above numerical set of orbitals extracted from Hibbert's package when the final form of the momentum-space Clebsch-Gordan Algebra is completed. This work is beyond the scope of this thesis.
Chapter 4

Calculations of the Low-Energy Elastic Scattering of Electrons from Helium

This chapter addresses the practical problem of finding good basis expansions for Helium target states in both configuration-interaction and frozen-core modes using Slaters as well as Laguerres as basis orbitals. The close-coupling calculations of phase shifts of electrons from Helium atoms using both analytical and numerical orbital options are also included. The calculations have been divided into two parts. The first part describes the selection of an optimized basis within the limits of our computer resources for the phase shift calculations of electron-Helium scattering. A basis is determined using both Slaters and Laguerres. The basis is optimized by seeking the best energies for the first five target states. We use our own Helium structure code for this purpose, which has the option of calculating the target states using Slaters/Laguerres in both CI and FC expansions. The limitation of the CI expansion procedure using a large number of Slaters as basis functions is also discussed. The Laguerre CI expansions on the other hand can be used with safety even for a largish number of expansion functions. FC expansions using both Slaters and Laguerres are included as well. They do not give as accurate thresholds as the CI states but have been used extensively for intermediate energy scattering. We have preferred employing a larger set of basis orbitals with a lesser number of target states. This type of compromise was necessary because we did not have the computational facilities to include all the target states generated by a large basis set and for low energy scattering this is a reasonable strategy. Further in the first part, as well as using our own structure code with Slaters, target states obtained from the CIV3 package of Hibbert
using a Slater expansion are also included. Two different optimization procedures of obtaining the target wave expansion in Hibbert’s package are presented. The reason for interfacing Hibbert’s package with our numerical orbital CC code is to demonstrate that the Hibbert package is a viable alternative for target structure beyond the Helium system.

The second part of the chapter focuses on the phase shift calculations for elastic scattering at various low energies < 20 eV, using frozen-core (FC) methods with Slaters as well as Laguerres for the basis. The comparison of phase shifts is mainly displayed with Saha (1989) and Nesbet (1979). Only in Nesbet’s (1979) and Saha’s (1989) work, are detailed phase shifts presented for a number of individual partial waves. Nesbet’s (1979) calculations were performed using CI expansions of fifteen optimized Hartree-Fock radial orbitals (1s-5s, 2p-6p, 3d-5d and 4f-5f) in the matrix-variational method. In his phase shift calculations, each target state configuration is included that can be coupled to form a scattering state of specified symmetry, e.g., \(^2S\) for s-wave scattering by \(^1S\) (ground state) of He.

Saha’s results are based on the calculation of the target Helium by a MCHF wave function expansion. The method of construction of basis functions in Saha’s (1989) calculations is detailed as; First, the 1s wave function of the target helium atom is obtained by the Hartree-Fock calculation of the 1s\(^2\) \(^1S\) ground state. Then the correlated ground-state wave function of the target is calculated by the MCHF wave function expansion over the 32 configuration states coupled to form a \(^1S\) term. These configurations are generated by the single and double replacements of the 1s orbital of the helium atom by the excited orbitals 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f, 5s, 5p, and
5d. These orbitals were then used by Saha (1989) as an input with a large number of configurations, which represent electron correlation and polarization effects, for his phase shifts calculations.

A comparison of results from our CC code using target states generated by a numerical form of Slaters, with analytical results is also included in this section. Finally, a further comparison with Saha (1989) was carried out using wave functions constructed from CIV3 package of Hibbert and employing two different optimization procedures.

4.1 Basis Expansions in CI and FC Modes

4.1.1 CI Expansions using Slaters

As explained in chapter three, we preferred using Slaters as basis functions, since it was then easier to interface our LBAS code with wave functions from other packages available in the literature. The CI states calculated were constructed from nineteen radial orbital basis functions (Slaters) including the 1s-11s, 2p-5p, 3d-5d and 4f orbitals. This was the largest CI Slater basis that could be trialled, given our computing resources.

The Slater exponents (equation 3.10) and orbital labels were chosen so as to achieve the best first five target state (1^1S, 2^1^3S and 2^1^3^P) energies. A number of trials for this selection were performed. The exponent parameters and the orbital labels for the Slaters in equation (3.10) are given in the following Table 4.1.
Table 4.1: Orbital labels and the exponent parameters for the Slaters (see Eq. 3.10) in CI expansion mode for our Helium structure program.

<table>
<thead>
<tr>
<th>Orbital</th>
<th>$n_a$</th>
<th>$\mu_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s-11s</td>
<td>1-11</td>
<td>2.00</td>
</tr>
<tr>
<td>2p-5p</td>
<td>2-5</td>
<td>1.00</td>
</tr>
<tr>
<td>3d-5d</td>
<td>3-5</td>
<td>0.75</td>
</tr>
<tr>
<td>4f</td>
<td>4</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Further a number of trials were performed using subsets of the above basis including three, thirteen and nineteen Slater functions. A comparison of first five state energies in a.u. with three, thirteen and nineteen orbitals with the experimental values, which are available from NIST (http://physics.nist.gov/), Atomic Spectra Database Levels Data for Helium are shown in Table 4.2. The three-orbital basis comprised the 1s, 2s and 2p orbitals and the thirteen orbital basis included 1s-5s, 2p-5p, 3d-5d and 4f orbitals. The inclusion of more $s$, $p$ and $d$ orbitals is needed to improve the $2^{1,3}S$ and $2^{1,3}P$ state energies. Inclusion of more $s$ orbitals, 6s-11s improves further the $1^{1}S$ and $2^{1,3}S$ energies, as is indicated in the above table. Note that correct ordering of the first four excited levels compared to experiment is achieved only for the nineteen-orbital basis.
Table 4.2: Helium Target-State Energies (a.u.) with Slater Orbitals in CI expansion mode. The experimental energies for these states are also included.

<table>
<thead>
<tr>
<th>States</th>
<th>3 Orbitals</th>
<th>13 Orbitals</th>
<th>19 Orbitals</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Binding Energy</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$1^1S$</td>
<td>-2.844320</td>
<td>-2.872505</td>
<td>-2.897197</td>
<td>-2.904779</td>
</tr>
<tr>
<td>$2^3S$</td>
<td>-0.583333</td>
<td>-2.113905</td>
<td>-2.174740</td>
<td>-2.176116</td>
</tr>
<tr>
<td>$2^1S$</td>
<td>0.010987</td>
<td>-2.033821</td>
<td>-2.144059</td>
<td>-2.146845</td>
</tr>
<tr>
<td>$2^3P$</td>
<td>-2.048544</td>
<td>-2.130200</td>
<td>-2.131995</td>
<td>-2.134040</td>
</tr>
<tr>
<td>$2^1P$</td>
<td>-1.980262</td>
<td>-2.120686</td>
<td>-2.120686</td>
<td>-2.124704</td>
</tr>
</tbody>
</table>

4.1.2 FC Expansions using Slatners

In this section, we introduce the approximation of treating the Helium target by the frozen-Core expansions, where we restrict one of the electrons to be the 1s He$^+$ orbital. The FC approximation simplifies convergence studies to a great degree because only those configurations involving one-electron excitation are present. The same Slater functions made up of radial orbitals as used for CI calculations, are used in the FC approximation. The procedure adopted for the selection of the Slater parameters (equation 3.10) is to achieve the best first five target state energies for a given orbital set. The exponent parameters and the orbital labels for the Slatners in FC mode are given in Table 4.3 and a list of the target state energies are given in Table 4.4.
Table 4.3: Orbital labels and the exponent parameters for the Slaters in the nineteen-orbital FC expansion mode for our Helium structure program.

<table>
<thead>
<tr>
<th>Orbital</th>
<th>$n_a$</th>
<th>$\mu_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s-7s</td>
<td>1-7</td>
<td>2.00</td>
</tr>
<tr>
<td>2p-5p</td>
<td>2-7</td>
<td>1.00</td>
</tr>
<tr>
<td>3d-5d</td>
<td>3-6</td>
<td>0.75</td>
</tr>
<tr>
<td>4f</td>
<td>4-5</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Table 4.4: Helium Target-State Energies (a.u.) with Slater Orbitals in nineteen-orbital FC expansion mode.

<table>
<thead>
<tr>
<th>States</th>
<th>19 Orbitals</th>
<th>Binding Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1^1S$</td>
<td>-2.872506</td>
<td></td>
</tr>
<tr>
<td>$2^3S$</td>
<td>-2.162092</td>
<td></td>
</tr>
<tr>
<td>$2^1S$</td>
<td>-2.131277</td>
<td></td>
</tr>
<tr>
<td>$2^3P$</td>
<td>-2.122354</td>
<td></td>
</tr>
<tr>
<td>$2^1P$</td>
<td>-2.117343</td>
<td></td>
</tr>
</tbody>
</table>

A comparison of target state energies for CI and FC expansions for Slaters from Table 4.2 and Table 4.4 shows that CI state energies are certainly better for all the five states than those of FC. But unfortunately we could not continue our full CI scattering calculations using this large number of Slaters due to numerical instabilities generated
by Slaters of s-type leading to the large magnitude and alternation of sign in the CI coefficients. This problem is discussed further in section 4.2.1 after we have discussed basis expansions using Laguerres for both CI and FC modes.

4.1.3 CI Expansions using Laguerres

We constructed a similar type of basis to that of the Slaters, using CI expansions of nineteen Laguerres (equation 3.11) following the same procedure of varying the orbital powers and the exponent parameters to minimise the first five target state ($1^1S$, $2^1S$, $2^1P$) energies. By choosing the exponents, $\lambda_a = 2 \mu_a$ ($\mu_a$ values from Table 4.1 for Slaters) such as $\lambda_a = 4.0$ for 1s-11s orbitals and $\lambda_a = 2.0$ for 2p-3p orbitals etc., we get the same CI target state energies as given in Table 4.3 for Slaters. However we are primarily interested in low-energy scattering below the inelastic threshold, we decided to proceed by optimising the energy of the ground state, ensuring that the energies of the next few excited states were still good compared to the experimentally measured threshold. Thus a better ground state energy was determined by varying the exponents for the Laguerres basis. The optimised exponents and the orbital powers chosen for CI expansions using Laguerres from equation (3.11) are shown in Table 4.5, which give us a better ground state energy than produced by Slater basis in CI mode. The $2^3S$ excited state energy levels are still close to the values given in Table 4.3 for Slaters whereas $2^3P$ state energies are a little higher than before. This “best” set of the first five target energies is given in Table 4.6.
Table 4.5: Orbital powers and exponent parameters for the Laguerre functions (see Eq. 3.11) in CI expansion mode.

<table>
<thead>
<tr>
<th>Orbital</th>
<th>$l_a$</th>
<th>$\lambda_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s-11s</td>
<td>0-10</td>
<td>3.0</td>
</tr>
<tr>
<td>2p-5p</td>
<td>0-3</td>
<td>2.8</td>
</tr>
<tr>
<td>3d-5d</td>
<td>0-2</td>
<td>2.8</td>
</tr>
<tr>
<td>4f</td>
<td>0</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Table 4.6: Helium Target-State Energies (a.u.) with nineteen Laguerre Orbitals in CI expansion mode.

<table>
<thead>
<tr>
<th>States</th>
<th>19 Orbitals</th>
<th>Binding Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1^1S$</td>
<td>-2.899994</td>
<td></td>
</tr>
<tr>
<td>$2^3S$</td>
<td>-2.173982</td>
<td></td>
</tr>
<tr>
<td>$2^1S$</td>
<td>-2.142126</td>
<td></td>
</tr>
<tr>
<td>$2^3P$</td>
<td>-2.128664</td>
<td></td>
</tr>
<tr>
<td>$2^1P$</td>
<td>-2.117164</td>
<td></td>
</tr>
</tbody>
</table>
4.1.4 FC Expansions using Laguerres

In this expansion we chose the same number of orbitals and the same orbital exponents as for the Laguerre CI expansion in order to minimise the first five target energies. The first five target energy levels are shown in Table 4.7.

Table 4.7: Helium Target-State Energies (a.u.) with Laguerre Orbitals in FC expansion mode.

<table>
<thead>
<tr>
<th>States</th>
<th>19 Orbitals Binding Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(^1)S</td>
<td>-2.875303</td>
</tr>
<tr>
<td>2(^3)S</td>
<td>-2.161334</td>
</tr>
<tr>
<td>2(^1)S</td>
<td>-2.139344</td>
</tr>
<tr>
<td>2(^3)P</td>
<td>-2.120023</td>
</tr>
<tr>
<td>2(^1)P</td>
<td>-2.113821</td>
</tr>
</tbody>
</table>

We display the first five-target state energies achieved from the CI and FC expansions with Slaters as well as with Laguerres together with the experimental values in Table 4.8. The calculations for low-energy scattering will make use of these sets of target states.
Table 4.8: Comparison of Helium Target-State Energies using nineteen Slaters/Laguerres in both CI and FC modes. Our Helium structure program was used for each determination. The experimental energies are also included.

<table>
<thead>
<tr>
<th>States</th>
<th>Slaters CI</th>
<th>Laguerres CI</th>
<th>Slaters FC</th>
<th>Laguerres FC</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1^1S$</td>
<td>-2.897197</td>
<td>-2.899994</td>
<td>-2.872506</td>
<td>-2.875303</td>
<td>-2.904779</td>
</tr>
<tr>
<td>$2^3S$</td>
<td>-2.174740</td>
<td>-2.173982</td>
<td>-2.162092</td>
<td>-2.161334</td>
<td>-2.176116</td>
</tr>
<tr>
<td>$2^1S$</td>
<td>-2.144059</td>
<td>-2.142126</td>
<td>-2.131277</td>
<td>-2.139344</td>
<td>-2.146845</td>
</tr>
<tr>
<td>$2^3P$</td>
<td>-2.131995</td>
<td>-2.128664</td>
<td>-2.122354</td>
<td>-2.120023</td>
<td>-2.134040</td>
</tr>
<tr>
<td>$2^1P$</td>
<td>-2.120686</td>
<td>-2.117164</td>
<td>-2.117343</td>
<td>-2.113821</td>
<td>-2.124707</td>
</tr>
</tbody>
</table>

4.1.5 Helium Target States using the CIV3 Package of Hibbert

As mentioned in previous chapters, the main aim of the present work was to modify the existing close-coupling code in order to interface with other atomic structure packages. While not essential for Helium where we have our own purpose built program, for general targets a mainstream package is required. Some atomic structure packages give the target wave functions only numerically, for complex atoms in particular while others represent the target states as a sum of analytic Slater functions for the orbitals. To enable us to use these packages in the close-coupling approach, our numerical close-coupling code should produce similar scattering results whether using Slaters in the numerical orbital form or in their analytical form.
As explained in chapter three each Hibbert's orbital is represented as a sum of a number of analytic Slaters. This sum of analytic Slaters once converted to a numerical orbital spread over various radial integration points can be interfaced into the corresponding orbital in our close-coupling code. In the following subsections we describe two different optimisation procedures to the best basis, one for the CI expansion mode and the other for the FC mode. Phase shifts calculated using this basis are shown in section 4.2

4.1.5.1 First Optimisation Procedure using Hibbert's Orbitals

In the initial input to CIV3, Clementi and Roetti (1974) tables are used for 1s wave functions of the target Helium atom. The excited orbitals 2s 2p 3s 3p 3d 4s 4p 4d 5f 5s 5p and 5d are optimised to 1s² ¹S ground state using the CIV3 package of Alan Hibbert (1975). The correlated ground-state wave function of the target Helium atom is calculated by the CI expansion over the 32 configuration states that coupled to form a ¹S term. The coefficients, powers of r and exponent parameters for the analytical Slaters given in equation (3.24) are given in Table 4.9. The eigenenergy of the ¹S state of Helium was found to be -2.9030167a.u., which is quite close to -2.9032971a.u., as used by Saha (1989) for his electron-Helium scattering calculations.
Table 4.9: The coefficients and exponent parameters for the analytical Hibbert's Slaters (see Eqn. 3.24) using CI expansion for the optimisation of orbitals (First optimisation Procedure) for the ground state. The ground state energy with this orbital basis is -2.9030167 a.u.

<table>
<thead>
<tr>
<th>Orbital</th>
<th>j</th>
<th>I__</th>
<th>P_j</th>
<th>\mu_j</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s</td>
<td>1</td>
<td>1</td>
<td>0.76837</td>
<td>1.41714</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1</td>
<td>0.22346</td>
<td>2.37682</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1</td>
<td>0.04082</td>
<td>4.39628</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1</td>
<td>-0.00994</td>
<td>6.52699</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1</td>
<td>0.00230</td>
<td>7.94252</td>
</tr>
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<td>2s</td>
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<td>1</td>
<td>2.18799</td>
<td>1.59618</td>
</tr>
<tr>
<td></td>
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<td>2</td>
<td>-2.42243</td>
<td>1.78873</td>
</tr>
<tr>
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<td>1</td>
<td>3.22260</td>
<td>2.12508</td>
</tr>
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<td>2</td>
<td>-7.34765</td>
<td>2.16596</td>
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</tr>
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</tr>
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</tr>
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</tr>
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</tr>
<tr>
<td></td>
<td>3</td>
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<td>2.72013</td>
</tr>
<tr>
<td>5p</td>
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<td>2</td>
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<td>3.56841</td>
</tr>
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<td>0.68989</td>
<td>4.47919</td>
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<tr>
<td></td>
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<td>7.61488</td>
</tr>
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<td>4</td>
<td>5</td>
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<td>3.95163</td>
</tr>
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<td>3</td>
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<td>3.60351</td>
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<td>3</td>
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<td>3.57578</td>
</tr>
<tr>
<td></td>
<td>2</td>
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</tr>
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<td>3</td>
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</tr>
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<td>5.41289</td>
<td>4.87911</td>
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<td>4.80229</td>
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</table>
4.1.5.2 Second Optimisation Procedure using Hibbert’s Orbitals

An alternative optimisation procedure using Hibbert’s code was adopted to achieve a set of frozen-core target states using a set of thirteen orbitals as, 1s-5s, 2p-5p, 3d-4d and 4f. In this procedure, we start again with Clementi and Roetti’s (1974) values for 1s wave function of the Helium atom. The 2s orbital is optimised over 1s\(^2\) \(^1\)S and 2s\(^1\)S\(^3\)S states using the CIV3 package of Hibbert. In a similar way 2p is optimised over 1s\(^2\) \(^1\)S and 2p\(^3\)P states and so on. A complete set of thirteen optimised orbitals is then run in the non-optimisation mode of CIV3 code to obtain energy eigenvalues and eigenvectors for the 25 configurations in the FC mode.

A set of eigenvectors (CI coefficients) is chosen for a particular eigenstate with a specific symmetry and used to perform scattering calculations with our frozen-core close-coupling model, as detailed in section 4.2. The coefficients, powers of \(r\) and exponent parameters for the analytical Slaters represented by equation (3.24) and optimised in this type of mode are given in Table 4.10. The construction of this table is similar to Table 4.9, the powers of \(r\) remain same where as the coefficients and exponents will vary due to a different mode of optimisation apart from the common 1s orbital.

In the FC mode of this package yields a set of 5 configurations leading to \(^1\)S symmetry, 4 configurations giving \(^3\)S symmetry, 4 configurations forming \(^1\)\(^3\)P symmetry each, 3 configurations forming \(^1\)\(^3\)D each and one configuration leading to \(^1\)\(^3\)F each.
Table 4.10: The coefficients and exponent parameters for the analytical Hibbert's Slaters optimised (Second Optimisation Procedure) to different symmetries in FC mode.

<table>
<thead>
<tr>
<th>Orbital</th>
<th>j</th>
<th>$I_j$</th>
<th>$p_j$</th>
<th>$\mu_j$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s</td>
<td>1</td>
<td>1</td>
<td>0.76837</td>
<td>1.41714</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1</td>
<td>0.22346</td>
<td>2.37682</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1</td>
<td>0.04082</td>
<td>4.39628</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1</td>
<td>-0.00994</td>
<td>6.52699</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1</td>
<td>0.00230</td>
<td>7.94252</td>
</tr>
<tr>
<td>2s</td>
<td>1</td>
<td>1</td>
<td>0.52093</td>
<td>1.70510</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2</td>
<td>-1.10428</td>
<td>0.76844</td>
</tr>
<tr>
<td>3s</td>
<td>1</td>
<td>1</td>
<td>0.78935</td>
<td>0.94203</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2</td>
<td>-7.34765</td>
<td>0.94767</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3</td>
<td>4.69212</td>
<td>0.49379</td>
</tr>
<tr>
<td>4s</td>
<td>1</td>
<td>1</td>
<td>0.16848</td>
<td>2.10213</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2</td>
<td>-1.62989</td>
<td>0.23322</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3</td>
<td>-1.19680</td>
<td>0.80241</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>4</td>
<td>2.45455</td>
<td>0.75660</td>
</tr>
<tr>
<td>5s</td>
<td>1</td>
<td>1</td>
<td>0.11363</td>
<td>2.30792</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2</td>
<td>2.33075</td>
<td>0.30542</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3</td>
<td>-0.88053</td>
<td>1.09233</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>4</td>
<td>1.53234</td>
<td>0.23449</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>5</td>
<td>-3.09480</td>
<td>0.47782</td>
</tr>
<tr>
<td>2p</td>
<td>1</td>
<td>2</td>
<td>1.00000</td>
<td>0.77394</td>
</tr>
<tr>
<td>3p</td>
<td>1</td>
<td>2</td>
<td>0.56714</td>
<td>1.04829</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3</td>
<td>-1.02742</td>
<td>0.42651</td>
</tr>
<tr>
<td>4p</td>
<td>1</td>
<td>2</td>
<td>1.58699</td>
<td>0.64858</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3</td>
<td>-1.94649</td>
<td>0.69408</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>4</td>
<td>0.99980</td>
<td>0.28032</td>
</tr>
<tr>
<td>5p</td>
<td>1</td>
<td>2</td>
<td>6.04119</td>
<td>0.26159</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3</td>
<td>-0.30462</td>
<td>2.54476</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>4</td>
<td>-1.27303</td>
<td>1.35142</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>5</td>
<td>-5.71075</td>
<td>0.53776</td>
</tr>
<tr>
<td>3d</td>
<td>1</td>
<td>3</td>
<td>1.00000</td>
<td>0.52846</td>
</tr>
<tr>
<td>4d</td>
<td>1</td>
<td>3</td>
<td>0.95489</td>
<td>0.18653</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>4</td>
<td>-0.46953</td>
<td>1.06665</td>
</tr>
<tr>
<td>5d</td>
<td>1</td>
<td>3</td>
<td>0.36337</td>
<td>0.75020</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>4</td>
<td>-0.59640</td>
<td>0.33637</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>5</td>
<td>0.98086</td>
<td>0.14567</td>
</tr>
<tr>
<td>4f</td>
<td>1</td>
<td>4</td>
<td>1.00000</td>
<td>0.26527</td>
</tr>
</tbody>
</table>
A comparison of the energies of the first five target states with two sets of orbital bases (three and thirteen orbitals) is shown in Table 4.11. The three orbital set is comprised of 1s, 2s and 2p orbitals. A small increase in $2^{1,3}S$ energies is caused by the inclusion of more orbitals, whereas p-state energies change only in the fifth place by including 3p 4p and 5p orbitals. This comparison of the Hibbert's energy eigenvalues leads us to conclude that 1s, 2s and 2p orbitals of CIV3 package are a good starting basis for CC scattering calculations in the frozen-core approximations.

The optimisation procedure of thirteen orbitals was further extended to nineteen orbitals by including 6s-11s orbitals (as already used for our own analytical orbitals). The energies of all np states with nineteen orbital basis change only marginally. So our largest orbital basis was set at thirteen orbitals.

**Table 4.11: Hibbert's State Energies in a.u. for three and thirteen orbitals in FC mode (Second Optimisation Procedure).**

<table>
<thead>
<tr>
<th>States</th>
<th>3 Orbitals</th>
<th>13 Orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Binding Energy</td>
<td></td>
</tr>
<tr>
<td>$1^1S$</td>
<td>-2.8616799</td>
<td>-2.8616799</td>
</tr>
<tr>
<td>$2^3S$</td>
<td>-2.1246292</td>
<td>-2.1269934</td>
</tr>
<tr>
<td>$2^1S$</td>
<td>-2.0785682</td>
<td>-2.0804501</td>
</tr>
<tr>
<td>$2^3P$</td>
<td>-2.0786253</td>
<td>-2.0787557</td>
</tr>
<tr>
<td>$2^1P$</td>
<td>-2.0633733</td>
<td>-2.0638152</td>
</tr>
</tbody>
</table>
4.2 Elastic Scattering Results at Low Incident Energies

This section presents the electron-Helium elastic scattering phase shifts at a range of low incident energies of electron including 0.58eV, 5eV, 10eV and 18eV. We used both Slaters and Laguerres as basis functions in the CI and FC modes and performed phase shifts calculations for the first three partial waves.

Our aim has not been to attempt to produce better low-energy phase shifts than those of definitive calculations of Nesbet or Saha (and earlier investigations cited by these authors) but rather to explore the issues arising in generating CI and FC target wave functions by a variety of methods and seeking to interface them into a single momentum space CC code.

We begin by using nineteen Slater orbitals both in the analytical as well as numerical form constructed from our own Helium structure program in the FC mode, and at various incident energies. Several sets of target states including, one (1^1S), three (1^1S+2^1S), five (1^1S+2^1S+2^1P) and nine (1^1S+2^1S+2^1P+3^1P+4^1P) are trialled.

We also present in this section, the phase shift results calculated by using a range of target states generated by Hibbert's code. All results are compared with Saha (1989) and at certain places with Nesbet (1979).
4.2.1 Instabilities in CI Expansions using Slatlers

A significant problem occurs when large numbers of Slatlers are used to construct orbitals and CI expansions. It is due to the lack of orthogonality of Slatlers. As the number of Slatlers increases this leads to the unfortunate consequence that the CI coefficients grow dramatically and alternate in sign. An example of this effect is shown in Table 4.12 for the CI expansion of the helium ground state using the Slater basis (1s-8s, 2p-5p, 3d-5d and 4f). This increase in coefficient size and alternation in sign places a practical limit on the size of Slater-type expansions since the CC potentials are always calculated numerically, and round off errors build to such an extent that large errors can occur even when individual contributions to the potential are calculated to six-figure accuracy.

In Table 4.12, we also show the advantage that an expansion in Laguerre functions has. The orthogonality of this set ensures the expansion has CI coefficients that do not grow significantly as the number of basis functions increases. The Laguerre basis parameters were chosen to span the same function space as the Slatlers in Table 4.12. Due to this reason we could not perform reliably accurate CI calculations with states generated by more than a few orbitals of each symmetry.

Table 4.13 displays the comparison of s-wave phase shifts at 0.58eV and 10.0eV incident energies with nineteen Slatlers as basis in both CI and FC expansion modes. Several increasing target states bases are included.
Table 4.12: A comparison of CI expansion coefficients using Laguerres and Slaters forming the ground state. For this expansion twenty-four CI coefficients are present.

<table>
<thead>
<tr>
<th></th>
<th>Laguerres</th>
<th>0.9606</th>
<th>-0.2498</th>
<th>-0.0309</th>
<th>0.0966</th>
<th>-0.0040</th>
<th>-0.0046</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slaters</td>
<td></td>
<td>0.5099</td>
<td>0.5062</td>
<td>-2.3436</td>
<td>-0.3826</td>
<td>10.6506</td>
<td>-30.9402</td>
</tr>
<tr>
<td>Laguerres</td>
<td></td>
<td>-0.0117</td>
<td>0.0023</td>
<td>-0.0022</td>
<td>-0.0015</td>
<td>0.0062</td>
<td>0.0022</td>
</tr>
<tr>
<td>Slaters</td>
<td></td>
<td>0.9533</td>
<td>-20.9404</td>
<td>96.4473</td>
<td>-161.014</td>
<td>-1.0065</td>
<td>26.6280</td>
</tr>
<tr>
<td>Laguerres</td>
<td></td>
<td>0.0001</td>
<td>-0.0010</td>
<td>-0.0006</td>
<td>-0.0005</td>
<td>0.0012</td>
<td>0.0008</td>
</tr>
<tr>
<td>Slaters</td>
<td></td>
<td>-131.642</td>
<td>324.966</td>
<td>-337.878</td>
<td>0.7457</td>
<td>-21.5704</td>
<td>112.161</td>
</tr>
<tr>
<td>Laguerres</td>
<td></td>
<td>-0.0001</td>
<td>-0.0005</td>
<td>-0.0003</td>
<td>0.0003</td>
<td>0.0005</td>
<td>0.0007</td>
</tr>
<tr>
<td>Slaters</td>
<td></td>
<td>-285.68</td>
<td>429.057</td>
<td>-276.55</td>
<td>-0.3113</td>
<td>10.1896</td>
<td>-55.0896</td>
</tr>
</tbody>
</table>

Table 4.13: S-wave phase shifts for CI and FC results at 0.58eV and 10eV incident energies with various numbers of Helium target states using nineteen Slaters.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>CI/FC</th>
<th>1 State</th>
<th>2 States</th>
<th>5 States</th>
<th>9 States</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.58</td>
<td>CI</td>
<td>2.8309</td>
<td>1.9657</td>
<td>1.3657</td>
<td>1.2138</td>
</tr>
<tr>
<td></td>
<td>FC</td>
<td>2.8315</td>
<td>2.8381</td>
<td>2.8453</td>
<td>2.8585</td>
</tr>
<tr>
<td>10.0</td>
<td>CI</td>
<td>2.0074</td>
<td>1.8856</td>
<td>1.6668</td>
<td>1.5435</td>
</tr>
<tr>
<td></td>
<td>FC</td>
<td>2.0116</td>
<td>2.0014</td>
<td>2.0457</td>
<td>2.0640</td>
</tr>
</tbody>
</table>

75
The above comparison of CI and FC scattering results at two different incident energies using Slaters as basis functions demonstrates how quickly roundoff errors affect the CC equations when only a few CI target states are used if large numbers of Slaters are used to generate the configurations. The phase shifts do not converge for a CI calculation purely due to roundoff. With potential matrix elements computed to an accuracy of five to six significant figures it appears that CI calculations with large bases are not practical in our CC code. The frozen-core calculations however do give convergent results for the phase shifts using Slaters, over the range of target states involved. As a result further close-coupling calculations in this chapter are restricted to the frozen-core model only, as for FC calculations; the s-wave phase-shifts are exactly same with both Slater and Laguerre basis. However, in chapter five we demonstrate that we are able to perform full CI calculations using Laguerres but restricted to thirteen orbital basis functions.

4.2.2 Numerical considerations for solving the CC equations

The momentum-space CC equations have discretised momentum integration. Typical convergence of the numerical solutions with increasing number of quadrature points for the integration is illustrated in Table 4.14. Calculations were performed at energies including 0.58eV, 10.0eV and 18eV, using nineteen Slaters/Laguerres in the FC approximation. Reasonable convergence was obtained with a 48-point integration mesh. Most calculations that follow use the 48-point meshes due to time considerations for the runs. Spot checks with 64-point meshes were carried out from time to time.
Table 4.14: Comparison of s-wave phase shifts with varying number of mesh points using FC states and nineteen Slater's.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Mesh points</th>
<th>1 State $1^1S$</th>
<th>3 States $2^1S$</th>
<th>5 States $2^13^1P$</th>
<th>9 States $3^13^1P+4^13^1P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.58</td>
<td>32</td>
<td>2.8315</td>
<td>2.7751</td>
<td>2.8238</td>
<td>2.8245</td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>2.8315</td>
<td>2.7813</td>
<td>2.8453</td>
<td>2.8585</td>
</tr>
<tr>
<td></td>
<td>64</td>
<td>2.8315</td>
<td>2.7631</td>
<td>2.7228</td>
<td>2.7989</td>
</tr>
<tr>
<td>10.0</td>
<td>32</td>
<td>2.0115</td>
<td>2.0232</td>
<td>2.0440</td>
<td>2.0654</td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>2.0116</td>
<td>2.0252</td>
<td>2.0457</td>
<td>2.0640</td>
</tr>
<tr>
<td></td>
<td>64</td>
<td>2.0116</td>
<td>2.0225</td>
<td>2.0528</td>
<td>2.0543</td>
</tr>
<tr>
<td>18.0</td>
<td>32</td>
<td>1.7512</td>
<td>1.7691</td>
<td>1.7927</td>
<td>1.8209</td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>1.7513</td>
<td>1.7711</td>
<td>1.8032</td>
<td>1.8263</td>
</tr>
<tr>
<td></td>
<td>64</td>
<td>1.7513</td>
<td>1.7732</td>
<td>1.8059</td>
<td>1.8285</td>
</tr>
</tbody>
</table>

Other numerical considerations involved computing the partial wave momentum-space potentials $V(k, k')$. For large values of $|k - k'|$ the potentials are very small. Since the Gaussian quadratures for the momentum-space integrals invariably involved $k$ and $k'$ that ranged from zero to infinity, the coupled channel package contains an option to set the potentials to zero when the momenta are large because the numerical answer for $V(k, k')$ was inaccurate due to the oscillatory nature of the radial integrals involving the continuum waves. The program controlled the setting of the potentials to zero by a variable (called kcut) in the input to the program. The radial integrals themselves were computed with quadratures containing 8000 radial integration points. The number of 8000 was determined to be satisfactory for the 48- and 64-point momentum space grids by convergence testing.
4.2.3 Phase Shifts using Analytical and Numerical Orbitals

Table 4.15 shows the comparison of s, p and d wave phase shifts with Saha's (1989) results at low incident energies in the range 0.58eV-18eV. These results are obtained by performing FC calculations using nineteen Slaters or the equivalent Laguerres in our CC program. The program gave the same results whether we used Slaters or Laguerres to construct the target states. Nine excited target states \((1^1S+2^1S+2^13P+3^13P+4^13P)\) were included for the above calculations with 8000 radial integration points and 48 mesh points. Tests for convergence ensured that this choice of radial integration and quadrature mesh was sufficient for high accuracy in all potentials.

An analysis of Table 4.15 shows that the results are in excellent agreement with Saha (1989) as well as Nesbet (1979) at these low energies. This set of nineteen basis functions was the largest set used for the FC expansion. For CI expansions use of Slaters was highly inaccurate and we had to restrict ourselves to Laguerre basis functions.

The present CC code for electron-Helium scattering was modified to include an option for calculating the radial integrals for different operators numerically using numerical orbitals. The nineteen radial orbitals taken in the Slater form produce nineteen numerical orbitals by running the original analytic CC code and these numerical orbitals are used for scattering calculations in FC mode.
Table 4.15: A comparison of s, p and d wave phase shifts using FC nine target States and nineteen Slater orbitals, with Saha (1989) and Nesbet's (1979) results.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>j-value</th>
<th>Present</th>
<th>Saha</th>
<th>Nesbet</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.58</td>
<td>0</td>
<td>2.8585</td>
<td>2.8676</td>
<td>2.8672</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.0139</td>
<td>0.0133</td>
<td>0.0134</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.0016</td>
<td>0.0018</td>
<td>0.0018</td>
</tr>
<tr>
<td>5.02</td>
<td>0</td>
<td>2.3053</td>
<td>2.3392</td>
<td>2.3398</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.1242</td>
<td>0.1238</td>
<td>0.1236</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.0148</td>
<td>0.0148</td>
<td>0.0153</td>
</tr>
<tr>
<td>10.0</td>
<td>0</td>
<td>2.0640</td>
<td>2.0629</td>
<td>2.0670</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.2146</td>
<td>0.2185</td>
<td>0.2161</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.0299</td>
<td>0.0296</td>
<td>0.0304</td>
</tr>
<tr>
<td>18.0</td>
<td>0</td>
<td>1.8263</td>
<td>1.7993</td>
<td>1.8228</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.2992</td>
<td>0.3089</td>
<td>0.3074</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.0541</td>
<td>0.0534</td>
<td>0.0547</td>
</tr>
</tbody>
</table>

The CI mode of calculations does not produce converging results for Slaters as an input, as detailed in the last section. The scattering results, such as s-, p- and d-wave phase shifts at first few incident energies are as accurate as obtained from analytic FC calculations. The computational time efficiency of the numerical CC code is increased with 5000 radial integration points needed for the potentials, as the results are exactly same as with 8000 points. Table 4.16 compares results for FC calculations using nineteen Slater orbitals. The “analytical” Slaters indicates the usual mode of calculation for the potentials, whereas the “numerical” Slaters refers to that option of running the code with numerically generated input orbitals.
Table 4.16: Comparison of analytical and numerical results at various incident energies, using nineteen Slaters basis functions in the nine-state target expansion.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>j-value</th>
<th>Analytical Slaters</th>
<th>Numerical Slaters</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.58</td>
<td>0</td>
<td>2.8585</td>
<td>2.8458</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.0138</td>
<td>0.0134</td>
</tr>
<tr>
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<td>2</td>
<td>0.0016</td>
<td>0.0017</td>
</tr>
<tr>
<td>5.02</td>
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<td>2.3053</td>
<td>2.2973</td>
</tr>
<tr>
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<td>0.1242</td>
<td>0.1214</td>
</tr>
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<td>0.0148</td>
<td>0.0152</td>
</tr>
<tr>
<td>10.0</td>
<td>0</td>
<td>2.0639</td>
<td>2.0137</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.2146</td>
<td>0.2112</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.0300</td>
<td>0.0303</td>
</tr>
<tr>
<td>18.0</td>
<td>0</td>
<td>1.8263</td>
<td>1.7848</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.2992</td>
<td>0.2969</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.0541</td>
<td>0.0541</td>
</tr>
</tbody>
</table>

A second comparison of the analytic and numerical options, with Saha's (1989) results is shown in Table 4.17.

Table 4.17: Comparison of analytical and numerical thirteen-Slater results with Saha's (1989) results at 10.0eV incident energy.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>j-value</th>
<th>Analytical</th>
<th>Numerical</th>
<th>Saha</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0</td>
<td>0</td>
<td>2.0643</td>
<td>2.0624</td>
<td>2.0629</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.2162</td>
<td>0.2184</td>
<td>0.2185</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.0304</td>
<td>0.0306</td>
<td>0.0296</td>
</tr>
</tbody>
</table>
As shown in Table 4.17, the convergence of first three phase shifts using numerical Slaters gave us the confidence to use numerical CC code for further calculations, and moreover there is a perfect agreement of the results with Saha. The p-wave phase shift result for analytic Slaters slightly deviates a little from the corresponding numerical Slaters result. Differences of 1% were regarded as tolerable, given the nature of the coding to interface both options.

4.2.4 Phase Shifts using Hibbert’s Orbitals in Numerical Orbital CC Code

In this section elastic scattering calculations using Hibbert’s orbitals are discussed. In order to use Hibbert’s orbitals our CC code had, as we already explained to be used in the numerical orbital version. Phase shift calculations using the Slaters from Hibbert’s code, constructed by the first optimisation procedure as discussed in section 4.1.5.1 are considered first. Then calculations with the Slaters extracted by the second optimisation procedure described in section 4.1.5.2 are given.

In the first calculation, a set of thirteen analytical wave functions (Table 4.9) optimised to the best ground state in the CI expansion mode was converted to numerical orbitals for input in the CC code and only one target state i.e., the $1s^2 \, ^1S$ ground-state of Helium, was used for phase shift calculations. The s-, p- and d-wave phase-shifts at a range of incident energies (0.58eV-18.0eV) are compared with those of Saha (1989) as shown in Table 4.18.
Table 4.18: A comparison of Phase Shifts for the first three partial waves using Hibbert's thirteen orbitals in the CI mode and one target state (ground state), with Saha's (1989) results at various incident energies.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>j-value</th>
<th>Numerical Orbitals (Hibbert)</th>
<th>Saha 1S</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.58</td>
<td>0</td>
<td>2.8569</td>
<td>2.8676</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.0039</td>
<td>0.0133</td>
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<td></td>
<td>2</td>
<td>0.0001</td>
<td>0.0018</td>
</tr>
<tr>
<td>5.02</td>
<td>0</td>
<td>2.3417</td>
<td>2.3392</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.0752</td>
<td>0.1238</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.0021</td>
<td>0.0148</td>
</tr>
<tr>
<td>10.0</td>
<td>0</td>
<td>2.0631</td>
<td>2.0629</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.1552</td>
<td>0.2185</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.0081</td>
<td>0.0296</td>
</tr>
<tr>
<td>18.0</td>
<td>0</td>
<td>1.7868</td>
<td>1.7993</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.2401</td>
<td>0.3089</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.0211</td>
<td>0.0534</td>
</tr>
</tbody>
</table>

The results are reasonably accurate for the first partial wave but for higher partial waves the scattering calculations certainly require the inclusion of more states. Including only the 1s$^2$1S state cannot account for the dipole polarisation of the Helium target. It is necessary to include the manifold of $^13P$ states for accurate phase shifts beyond the $l = 0$ partial wave.
But as we have demonstrated, CI expansions using orbitals generated by large number of Slater functions are an impractical option for the coupled channels code we have, therefore we turn immediately to the numerical CC code using the set of thirteen Hibbert's Slaters (Table 4.10) obtained by the second optimisation procedure, which generated target states in the FC mode. The target energy levels (Table 4.11) and CI coefficients needed for the scattering calculations are obtained from the CIV3 code when these optimised orbitals (Table 4.10) are run in the non-optimisation mode. The first three partial wave shifts are calculated using our numerical CC code at an incident energy of 5.02eV and are compared with Saha's (1989) results in Table 4.19, for various numbers of target states. This table includes the results for varying number of orbitals as well, varying target state numbers. A similar set of phase shift results are calculated at 10.0eV incident energy again using Hibbert's wave functions are tabulated in Table 4.20 and compared with those of Saha.

The set of thirteen orbitals comprise 1s-5s, 2p-5p, 3d-5d and 4f, the nine orbital basis include 1s-5s, 2p-5p and the set of seven is made up from 1s-4s, 2p-4p orbitals. Five orbital set comprises 1s-2s, 2p-3p and the three orbital set comprises 1s, 2s and 2p.
Table 4.19: A comparison of phase shifts with Saha's (1989) Results at 5.02eV incident energy using Hibbert's Wave Functions in the FC mode converted to numerical form. Thirteen orbitals include (1s-5s, 2p-5p, 3d-5d and 4f), nine (1s-5s, 2p-5p), seven (1s-4s, 2p-4p), five (1s-3s, 2p-3p) and three (1s, 2s, 2p).

<table>
<thead>
<tr>
<th>No. of Orbitals</th>
<th>j-value</th>
<th>1 State 1^1S</th>
<th>5 States +2^1,3S +2^1,3P</th>
<th>9 States +3^1,3S +4^1,3P</th>
<th>15 States +3^1,3S +4^1,3S +3^1,3D</th>
<th>Saha</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>0</td>
<td>2.3097</td>
<td>2.3157</td>
<td>2.3182</td>
<td>2.3393</td>
<td>2.3392</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.0687</td>
<td>0.0925</td>
<td>0.0950</td>
<td>0.1230</td>
<td>0.1238</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.0121</td>
<td>0.0123</td>
<td>0.0122</td>
<td>0.0141</td>
<td>0.0148</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>2.3087</td>
<td>2.3236</td>
<td>2.3327</td>
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<tr>
<td></td>
<td>1</td>
<td>0.0781</td>
<td>0.0938</td>
<td>0.0940</td>
<td>0.0989</td>
<td>0.1238</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.0098</td>
<td>0.0100</td>
<td>0.0100</td>
<td>0.0131</td>
<td>0.0148</td>
</tr>
<tr>
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<td>2.3065</td>
<td>2.3345</td>
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<td>2.3186</td>
<td>2.3392</td>
</tr>
<tr>
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<td>0.0893</td>
<td>0.0953</td>
<td>0.1056</td>
<td>0.1238</td>
</tr>
<tr>
<td></td>
<td>2</td>
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<td>0.0121</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5 States 1^1S+2^1,3P +3^1,3P</td>
<td>5 States 1^1S+2^1,3S +2^1,3P</td>
<td>7 States 1^1S+2^1,3S +2^1,3P +3^1,3D</td>
<td>15 States (as above)</td>
<td></td>
</tr>
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<td>2.3393</td>
<td>2.3393</td>
<td>2.3392</td>
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<td>0.1123</td>
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</tr>
<tr>
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<td>0.0097</td>
<td>0.0094</td>
<td>0.0100</td>
<td>0.0112</td>
<td>0.0148</td>
</tr>
<tr>
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<td>2.3078</td>
<td>2.3149</td>
<td>2.3368</td>
<td>2.3389</td>
<td>2.3392</td>
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<tr>
<td></td>
<td>2</td>
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<td>0.0031</td>
<td>0.0089</td>
<td>0.0110</td>
<td>0.0148</td>
</tr>
</tbody>
</table>
Table 4.20: Comparison of phase shifts with Saha’s results at 10.0eV incident energy using Hibbert’s Slaters in the FC mode converted to numerical form. The orbitals and states are as given in the previous table.

<table>
<thead>
<tr>
<th>Number of Orbitals</th>
<th>j-value</th>
<th>1 State</th>
<th>9 States</th>
<th>15 States</th>
<th>Saha</th>
</tr>
</thead>
<tbody>
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<td>13</td>
<td>0</td>
<td>2.0264</td>
<td>2.0286</td>
<td>2.0610</td>
<td>2.0629</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.1419</td>
<td>0.1725</td>
<td>0.1762</td>
<td>0.2185</td>
</tr>
<tr>
<td></td>
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<td>0.0209</td>
<td>0.0219</td>
<td>0.0296</td>
</tr>
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</tr>
<tr>
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<td>0.2185</td>
</tr>
<tr>
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<td>0.0210</td>
<td>0.0296</td>
</tr>
<tr>
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<td>2.0598</td>
<td>2.0629</td>
</tr>
<tr>
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<td>0.1896</td>
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<tr>
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<td>0.0296</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7 States</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1^1S_2^1^3S_+</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2^1^3P_+ 3^1^3P_</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0</td>
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</tr>
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<td>0.0201</td>
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<td>0.0296</td>
</tr>
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<td></td>
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<td>5 States</td>
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<td></td>
</tr>
<tr>
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<td></td>
<td></td>
<td>1^1S_2^1^3S_+</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2^1^3P_</td>
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<td></td>
</tr>
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<td>2.0567</td>
<td>2.0629</td>
</tr>
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<td>0.1701</td>
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<td>0.2185</td>
</tr>
<tr>
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<td>0.0091</td>
<td>0.0189</td>
<td>0.0296</td>
</tr>
</tbody>
</table>

An analysis of the Tables 4.19 and 4.20 reveals a systematic improvement with increasing number of orbitals for a fixed set of target states and for fixed orbitals but increasing target-state size. The s-wave phase-shifts converge to Saha’s (1989) results by the inclusion of more number of orbitals, but the p and d-wave phase shifts are poor. The cause for this is that in seeking to get good threshold energies for the low-
lying target states the manifolds of $^{1,3}P$ states lack pseudostates with positive energies that are necessary to get the dipole polarizability accurately.

4.2.5 Phase Shifts Results using Analytical Slaters in FC expansion mode

As already explained in section 4.2.1, due to the instability of the numerical potential construction in the CC code with higher s-type analytical Slaters we could not perform any meaningful scattering calculations using Slaters in a full CI expansion. We performed some scattering calculations using a range of analytical Slaters bases in the analytic orbital CC code in the FC mode. The results are displayed in Table 4.21. The nineteen and thirteen orbitals have the same $nl$ quantum numbers as already used in the phase shift calculations of Tables 4.19 - 4.20.

A comparison of thirteen- and nine-orbitals results does not show any significant change in the phase shifts. The systematic decrease in the p- and d- phase shifts can be seen in going down to two orbitals, except for some instabilities for three-orbital results. It can also be noted that the results of Table 4.21 with the analytic Slater orbitals used to generate the FC wave functions agree well for the $l = 0$ partial wave with those formed from the numerical orbitals and the FC wave functions of Hibbert in Table 4.19. For the p and d wave phase shifts our orbital set produces pseudostates in $^{1,3}P$ than does the basis formed by CIV3. Thus the dipole polarization is included better with the basis of Table 4.21.
Table 4.21: Comparison of s, p and d wave phase shifts using FC target states and analytic Slater orbitals with Saha (1989) at 5.02eV.

<table>
<thead>
<tr>
<th>Number of Orbitals</th>
<th>j-value</th>
<th>1 State</th>
<th>5 States</th>
<th>9 States</th>
<th>Saha</th>
</tr>
</thead>
<tbody>
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<td>2.2983</td>
<td>2.3216</td>
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</tr>
<tr>
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<td>0.1238</td>
</tr>
<tr>
<td></td>
<td>2</td>
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</tr>
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<td>0.1238</td>
</tr>
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<td>0.0148</td>
</tr>
<tr>
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<td>2.3392</td>
</tr>
<tr>
<td></td>
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<td>0.1238</td>
</tr>
<tr>
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<td>0.0065</td>
<td>0.0101</td>
<td>0.0153</td>
<td>0.0148</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>5 States 1s+2l\textsuperscript{3}p \ +3l\textsuperscript{3}p</th>
<th>5 States 1s+2l\textsuperscript{3}S \ +2l\textsuperscript{3}P</th>
<th>7 States 1s+2l\textsuperscript{3}S \ +2l\textsuperscript{3}P \ +3l\textsuperscript{3}P</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1</td>
<td>3</td>
</tr>
<tr>
<td>5 States</td>
<td>5 States</td>
<td>7 States</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>1</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>5</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
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<tr>
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<td>0</td>
<td>1</td>
</tr>
<tr>
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<td>---------------------------------------------------------------</td>
<td>---------------------------------------------------------------</td>
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</tr>
<tr>
<td>2</td>
<td>0.0100</td>
<td>0.0099</td>
</tr>
</tbody>
</table>
4.3 Conclusions

This completes our calculations on low energy electron-Helium elastic scattering in both CI and FC modes. Either type of basis function Laguerres or Slaters can be used for “analytic” FC calculations. CI calculations could be performed successfully using Laguerres as the basis functions. A Slater basis fails for CI as it generates states with CI coefficients that lead to inaccurate target state representations when largish basis are employed.

We have learnt that the most practical approach of constructing a target-state set is by the FC approximation if Slater functions are to be used. Since Hibbert’s package can be used to generate such a FC target set, it would appear that this approach would have to be adopted to construct target states for the other inert gases such as Neon or Argon, at least in the near future.

We also noted that if we used Laguerre functions for the orbital basis, then the target states could be written in terms of CI expansions with nice properties. Thus in principle a structure code could be built using Laguerre functions for more general targets. Owing to the considerable complexity of such a task it could not be attempted here. In the next chapter we employ a Laguerre orbital set to generate full CI target states in order to study low-energy inelastic scattering.
Chapter 5

Inelastic Scattering of Electrons by Helium Atoms

In this chapter, the results for inelastic scattering are calculated using the close-coupling code. The code has been used in both, numerical as well as analytical orbital options to search for resonances. The quality of the CI basis target states is assessed by calculating the position of the resonance below $2^3S$ threshold (the only resonance possible), as explained further in section 5.1 and analytical code has been used to perform the actual inelastic cross section calculations. Inelastic scattering for electron-Helium, has been studied experimentally several times by various methods including Johnston & Burrow (1983), Phillips & Wong (1981), Brunt et al (1977), Cvejanovic et al (1974), Golden et al (1974), Gibson & Dodler (1969) and Andrick & Ehrhardt (1966). The experimental results of Cvejanovic et al (1974), Cvejanovic & Read (1973) and many others show the existence of a resonance below $2^3S$ threshold at 19.367eV. Some other old theoretical calculations reported resonance energies as, 19.386eV (Temkin et al 1972), 19.400eV (Sinfailam & Nesbet 1972), 19.690eV (Perkins 1971), 19.340eV (Weiss & Krauss 1970) and 19.330eV (Burke et al 1969). Much theoretical effort has also been put into establishing the behaviour of the electron excitation cross sections with energy, particularly from the $1^1S$ ground state of Helium and the two relatively long-lived metastable states $2^3S$ and $2^1S$. A detailed comparison of the resonance below $2^3S$ threshold has been carried out with Berrington et al (1975, 1985) and Oberoi & Nesbet (1973) and detailed in section 5.2.2.
The work described in this chapter is an extension of the study of electron–Helium scattering at low energies between 18-23eV as in this energy range we get a low-lying resonances below $2^3S$ threshold. This work is unique in its form, as close-coupling equations including the first five target states ($1s^2 \, 1S$, $2^3S$ and $2^3P$) using the CI wave function, have not been solved in literature for inelastic scattering.

Burke et al (1969) solved close-coupling equations including five target states but because of the complexity of the equations, were forced to make a simplification in the exchange term in order to make them numerically tractable. Even though their work was in reasonable accord with experiment and with the calculations of Oberoi & Nesbet (1973), there was clearly a need to look at the effect of the approximations in the exchange potential. Subsequently, Burke et al (1971) described a new approach to the electron-atom collision problem based on R-matrix method. Later Berrington et al (1974, 1985), Fon et al (1989) and Fon & Lim (1990) have published results but all are based on the R-matrix method.

To test our code for the search of resonances we have chosen Berrington et al’s (1975) calculation, an early reference, for comparison, as this paper details cross-sections for $n = 1$ to 2 and $n = 2$ to 2 in the energy range of 18eV to 23eV with reliability. The later publication of Berrington et al (1985) is an eleven target-state calculation and that of Fon et al (1989) is a 19-state calculation but these papers primarily focus on resonance structure between the $n = 3$ and $n = 4$ excitation thresholds. Our aim was to first study the lowest resonance in detail and then calculate the inelastic and elastic cross sections for all transitions between the ground and $n = 2$ states.
To investigate the lowest resonance we have utilised the input target structure exactly as employed by Berrington et al (1975) and then converted it into the numerical form of the wave functions for use in our numerical code. Later in section 5.2 an analytic approach of solving close-coupling equations using our own target Helium structure has been detailed and these analytical results have shown us a breakthrough. But before going into the details of the discussion of analytic results for resonances, a comparison of the energy of the lowest resonance has been done with Berrington et al's (1975) results.

5.1 Numerical Calculations of Lowest Resonance using Hibbert's Basis

As already discussed in chapter three, an interface has been developed to permit use of Hibbert's target-states generated in the analytic Slater form into our numerical orbital close-coupling code. In order to test the adaptation of the CC code, a set of scattering calculations using Helium configuration-interaction target states produced by the programs of Hibbert (1975), were performed above the inelastic scattering threshold. In that region there is a low-lying resonance feature that has been observed.

The atomic eigenstates used in our calculations are constructed from six radial orbitals, 1s 2s 2p 3s 3p and 3d. We used the same set of orbitals as Berrington et al (1975) whose parameters are displayed in Table 5.1. Berrington et al (1975) used Hibbert's orbitals given by equation (3.24) for their calculations. The orbitals are orthogonal and normalised. The 1s orbital is the He$^+$ ground state orbital and represents the inner electron in the excited states. The 2s and 3s orbitals are simultaneously optimised on the energies of the $2^3S$ and $2^1S$ excited states. In the
latter case this means optimising on the second eigenvalue of the $^1S$ Hamiltonian matrix, since the first eigenvalue represents the ground state. The 2p orbital is optimised simultaneously on the energies of the $2^3P$ and $2^1P$ excited states. The exponent of the 3p orbital is adjusted to represent the dipole polarizability of the ground state. Finally the 3d orbital represents part of the quadrupole polarizability of the ground state.

Table 5.1: The atomic orbital coefficients, exponents and powers of $r$ for the Hibbert's Slaters used as basis by Berrington et al (1975).

<table>
<thead>
<tr>
<th>Orbital</th>
<th>$I_j$</th>
<th>$p_j$</th>
<th>$\mu_j$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s</td>
<td>1</td>
<td>5.65685</td>
<td>2.00000</td>
</tr>
<tr>
<td>2s</td>
<td>1</td>
<td>5.18595</td>
<td>1.94041</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-3.56793</td>
<td>1.14606</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.62621</td>
<td>1.14302</td>
</tr>
<tr>
<td>3s</td>
<td>1</td>
<td>1.95927</td>
<td>0.68756</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-4.29173</td>
<td>1.31441</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.06025</td>
<td>0.62856</td>
</tr>
<tr>
<td>2p</td>
<td>2</td>
<td>1.37228</td>
<td>1.42412</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>-0.10240</td>
<td>0.65178</td>
</tr>
<tr>
<td>3p</td>
<td>2</td>
<td>2.26802</td>
<td>1.31000</td>
</tr>
<tr>
<td>3d</td>
<td>3</td>
<td>0.19309</td>
<td>0.80000</td>
</tr>
</tbody>
</table>

The atomic eigenstates generated from Hibbert's package, which are represented as a linear sum of configurations formed from these orbitals (equations (3.22) and (3.23)), have a different ordering for the configurations for the $2^3,1^1P$ symmetries compared to
our close-coupling code. For $1^1S$, $2^1S$ and $2^3S$ symmetries the order of the configurations is the same as required for our code. For each set of Hibbert’s states a preprocessing routine is used to make sure the configurations are recorded together with the corresponding CI coefficients in a form suitable for our coupled channels programs. Thus for example

$$
\Psi(1^1S, 2^1S) = C_1 \Phi_1 (1s^2) + C_2 \Phi_2 (1s2s) + C_3 \Phi_3 (2s^2) + C_4 \Phi_4 (1s3s) + C_5 \Phi_5 (2s3s)
$$

$$
+ C_6 \Phi_6 (3s^2) + C_7 \Phi_7 (2p^2) + C_8 \Phi_8 (2p3p) + C_9 \Phi_9 (3p^2) + C_{10} \Phi_{10} (3d^2)
$$

$$
\Psi(2^3S) = C_1 \Phi_1 (1s2s) + C_2 \Phi_2 (1s3s) + C_3 \Phi_3 (2s3s) + C_4 \Phi_4 (2p3p)
$$

(5.01)

For $2^3P$ symmetries the order is,

$$
\Psi(2^3P) = C_1 \Phi_1 (1s2p) + C_2 \Phi_2 (1s3p) + C_3 \Phi_3 (2s2p) + C_4 \Phi_4 (2s3p)
$$

$$
+ C_5 \Phi_5 (3s2p) + C_6 \Phi_6 (3s3p) + C_7 \Phi_7 (2p3d) + C_8 \Phi_8 (3p3d)
$$

(5.02)

[Barrenton]

$$
\Psi(2^3P) = C_1 \Phi_1 (1s2p) + C_2 \Phi_2 (2s2p) + C_3 \Phi_3 (3s2p) + C_4 \Phi_4 (1s3p)
$$

$$
+ C_5 \Phi_5 (2s3p) + C_6 \Phi_6 (3s3p) + C_7 \Phi_7 (2p3d) + C_8 \Phi_8 (3p3d)
$$

(5.03)

[The input for the CC code]

The CI coefficients in the given bases, are illustrated in Table 5.2, with the corresponding energies of the configurations along with their experimental values. This set of Slater orbitals used to make the CI states are converted to numerical orbitals and the resulting wave functions and energies are input to the close-coupling code for the scattering calculations. The s-wave phase shift is calculated over the energy range of 18.600eV to 19.300eV as the first inelastic threshold (for $2^3S$) occurs at 19.335eV.
Table 5.2: The CI coefficients and energies of the first five states of Helium. The ordering of the CI coefficients (read from left to right) is as given by the Hibbert CI expansions of equations (5.01-5.02). The experimental values are also included.

<table>
<thead>
<tr>
<th>State</th>
<th>CI Coefficients</th>
<th>Energy (a.u.)</th>
<th>Energy (Experiment)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1^1S$</td>
<td>0.958697 -0.276955 -0.029577 0.008378</td>
<td>-2.883427</td>
<td>-2.904779</td>
</tr>
<tr>
<td></td>
<td>-0.009378 -0.001733 -0.005937 -0.023775</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.050560 -0.000862</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2^2S$</td>
<td>-0.527845 0.849224 0.000850 0.014065</td>
<td>-2.172895</td>
<td>-2.176116</td>
</tr>
<tr>
<td>$2^1S$</td>
<td>0.123258 0.400481 -0.015593 -0.907679</td>
<td>-2.143697</td>
<td>-2.146845</td>
</tr>
<tr>
<td></td>
<td>-0.002922 -0.000855 -0.004323 -0.013270</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.009386 0.002488</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2^2P$</td>
<td>0.778869 -0.626625 0.005093 0.020698</td>
<td>-2.132331</td>
<td>-2.134040</td>
</tr>
<tr>
<td></td>
<td>-0.000625 -0.005960 0.003930 0.014118</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2^1P$</td>
<td>0.827964 -0.560439 -0.001608 -0.006375</td>
<td>-2.122886</td>
<td>-2.124704</td>
</tr>
<tr>
<td></td>
<td>0.001000 0.005200 0.003009 0.017417</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

To demonstrate our code is interfacing correctly, we have chosen to perform a comparison of the low-energy calculations below the first inelastic threshold, the $2^1S$. Just below the threshold (experimentally observed at 19.818eV, above the elastic threshold) there is an experimentally observed $^2S$ resonance with energy at 19.367eV. Our results for the s-wave phase shift can be compared directly with those of Berrington et al (1975). The comparison is shown in Figure 5.1. The first thing to
Figure 5.1: A comparison of s-wave phase shifts with Berrington et al (1975) using the same analytical Slater basis as Berrington but converted to numerical input in our CC calculations.
notice is that the position of their resonance is shifted from ours. The position of our resonance is found to be at 18.878eV whereas theirs is at 19.380eV. But they explain that they have adopted a renormalization procedure (which is explained in detail in following sections in this chapter) to obtain this value. Subtracting out their renormalization gives their true resonance energy at 18.900eV in excellent agreement with ours. This test demonstrates that our numerical orbital close-coupling model is ideally suited for low-lying resonances using Helium target structures from others’ packages.

5.2 Low-Energy Elastic and Inelastic Scattering using CI States generated by a Laguerre Basis

In the remaining sections we report the best calculations that we were able to perform for elastic and inelastic scattering up to $2^1P$ threshold. As discussed in chapter four the optimum orbitals for numerical applications when large calculations have to be carried out are those generated by Laguerre orbitals. So after having demonstrated in the previous section that we can interface with Hibbert’s package, which uses Slaters, we return to the Laguerre basis target states. The first step in this process was to get the best CI target states from our own existing Helium structure code (section 4.1). The exponents for Laguerre basis (See Table 4.5) were optimised to achieve the best set of eigenenergies for the first five states, close to the experimental values. A set of 13 orbitals including 1s-7s, 2p-6p and 3d were chosen with exponent $= 3.0$ for the s-orbitals and 2.8 for p and d orbitals for a full CI calculation (as detailed in section 4.1.3). The energies of the configurations along with their experimental values are displayed in Table 5.3.
Table 5.3: A comparison of Helium target state energies calculated using Laguerres as basis in CI expansion mode, with experimental values from NIST. Excited state energies are with respect to the ground state.

<table>
<thead>
<tr>
<th>State</th>
<th>Energy (au)</th>
<th>State energies (eV) (present work)</th>
<th>State energies (eV) (experimental values)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1\textsuperscript{S}</td>
<td>-2.899994</td>
<td>19.74</td>
<td>19.82</td>
</tr>
<tr>
<td>2\textsuperscript{3}S</td>
<td>-2.173978</td>
<td>20.60</td>
<td>20.61</td>
</tr>
<tr>
<td>2\textsuperscript{1}S</td>
<td>-2.142126</td>
<td>20.98</td>
<td>20.96</td>
</tr>
<tr>
<td>2\textsuperscript{3}P</td>
<td>-2.128664</td>
<td>21.29</td>
<td>21.22</td>
</tr>
<tr>
<td>2\textsuperscript{1}P</td>
<td>-2.117164</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A number of attempts were made to improve the state energies by including more orbitals into our calculations. With more s-orbitals, the ground state energy improves but the 2\textsuperscript{3}S energies become higher than before, which leads to 2\textsuperscript{3}S having 19.726eV or 19.732eV and 2\textsuperscript{1}S with 20.553eV or 20.557eV, which are further away from the experimental values. Adding one more p-orbital to the present set just improves the 2\textsuperscript{3}S threshold from 19.740eV to 19.750eV, whereas 2\textsuperscript{3}P goes down from 20.980eV to 20.900eV and 2\textsuperscript{1}P also goes down from 21.290eV to 21.193eV. All these tests performed for the choice of an accurate set of orbitals lead us to believe that the 13 set of orbitals basis chosen gives first five best eigenstates, very close to the experimental energies.

It should also be pointed out that a frozen-core description of the low-lying target states is deficient in the extreme. Using the same basis but restricting the most tightly bound electron to the He\textsuperscript{+} 1s orbital gives a very poor set of thresholds for the first four excited states (Table 5.4). Thus a FC set of states cannot produce realistic resonance scattering in this low-energy region. Ideally we could increase the number
of orbitals in our basis to achieve more accurate thresholds but convergence is slow and the present excited states are accurate enough given the experimental accuracy. We have also performed most of the calculations by including excited states for the low-lying states.

Table 5.4: A comparison of FC and CI energies using thirteen Laguerres as basis functions in our analytical CC code, with experimental values from NIST.

<table>
<thead>
<tr>
<th>State</th>
<th>Energy (FC) (eV)</th>
<th>Energy (CI) (eV)</th>
<th>Experimental (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2^3S$</td>
<td>21.58</td>
<td>19.74</td>
<td>19.82</td>
</tr>
<tr>
<td>$2^1S$</td>
<td>23.17</td>
<td>20.60</td>
<td>20.61</td>
</tr>
<tr>
<td>$2^3P$</td>
<td>23.22</td>
<td>20.98</td>
<td>20.96</td>
</tr>
<tr>
<td>$2^1P$</td>
<td>23.86</td>
<td>21.29</td>
<td>21.22</td>
</tr>
</tbody>
</table>

5.2.1 The $2^3S$ Resonance below $2^3S$ Threshold

The experiment of Cvejanovic & Read (1973) shows the $2^3S$ resonance at 19.367eV. Sanche & Schulz (1972) obtained 19.350eV for the position of the $2^3S$ resonance in a transition experiment. Cvejanovic et al (1974) used a new threshold excitation technique to establish the resonance energy at 19.367eV.

Searching for the lowest resonance around 19.300eV, a large number of runs were performed using the full CI Helium target states with thirteen Laguerres as basis functions. Initially, the first five Helium eigenstates were included for the scattering calculations. The incident energies chosen are from the range 19.200eV to 19.700eV, as threshold for $2^3S$ occurs at 19.757eV. We demonstrate in Figure 5.2 the $2^3S$
contribution to the ground state elastic scattering cross section in the five-state calculations. The well-known $^2S$ resonance below the $^2\bar{S}$ threshold gives a window in the cross section and an analysis of the s-wave phase shift gives the resonance energy of 19.304eV. A cut in the cross section of Berrington et al's results appears, as we do not have their cross section data below a value of $2.6\pi a_0^2$. The shift in the position of window from our results is again due to the renormalization of their incident energies as discussed in the last section. A small feature in the cross section at 20.6eV is observed, the details of which are explained in further section 5.2.3 while discussing the eigenphase sum analysis. We are getting an approximate 8-10% background scattering in comparison to their results, the reason for which is not clear here.

The $^2S$ phase shift in the region of the resonance is shown in Figure 5.3. To check the convergence of this resonance with a larger target-state basis, the above calculations were repeated with the same set of orbitals but including nine target states ($1s^2\,^1S$, $2^3\,^1S$, $2^3\,^1P$, $3^3\,^1S$, $3^3\,^1P$). Certainly, the energies of the states except for the first five are not as good as experimental values but the position of the resonance is essentially unaltered i.e., 19.293eV, which is quite close to the 19.304eV achieved by the calculation using five targets states.

The largest calculation attempted was with fifteen target states ($1s^2\,^1S$, $2^3\,^1S$, $2^3\,^1P$, $3^3\,^1S$, $3^3\,^1P$, $3^3\,^1D$, $4^3\,^1S$ and $4^3\,^1P$). The position of $2^3S$ resonance is at 19.292eV, which is almost the same value as the result achieved using nine states. The inclusion of the extra states, which bear little relation to physical excited states (so they are
Figure 5.2: $^2S$ elastic cross sections contrasting with results obtained by Berrington et al (1975) are displayed in the above diagram. The full curve represents CC results with five target states and broken curve is the Berrington et al's (1975) data.
Figure 5.3: A comparison of s-wave phase shifts with Berrington et al (1975). Present results include five, nine and fifteen-target state analytical orbital CC calculations.
effectively pseudostates) increases the background elastic scattering phase shifts slightly but makes little difference to elastic or inelastic cross sections.

The above resonance analysis shows that even five state CI calculations are sufficient to describe the $2^3S$ lowest-lying resonance. It is apparent that these results differ significantly from those of Berrington et al so we return to a discussion of the reason for this.

### 5.2.2 Discussion of Results of the Lowest $2^3S$ Resonance

A comparison of the s-wave phase shift with Berrington et al's (1975) results shows that our position of resonance is 0.080eV below their value 19.380eV for resonance. A detailed analysis of their results indicates that they have re-normalised the incident electron energy to get the $2^3S$ excitation threshold at the observed energy of 19.818eV. Their actual resonance energy without re-normalisation occurs at 18.900eV. In a later publication on eleven-state calculation using a different basis, Berrington et al (1985), made a similar adjustment to the state energies by subtracting 1.208eV from the $1^3S$ ground state to give the $2^3S$ threshold at the experimentally observed energy of 19.820eV. With this ground-state energy rescaling their lowest-lying excited states have thresholds close to the experimental ones. In a nineteen-state calculation, Fon et al (1989) have just extended their work by including more states, which actually does not change the position of the lowest resonance, but the width of the resonance has reduced, whereas rescaling to the energies has the similar pattern.
For completeness, we will discuss some further calculations. Oberoi & Nesbet (1973) calculated the scattering of electrons by Helium in the low-energy region as well. For s-wave scattering, they have used only s and p orbitals and carried out a configuration-interaction calculation including all configurations of the type 1sns and 1smp. Their computed energies for the various n = 2 states are in agreement with experimental values whereas the ground state energy is poor: -2.870588a.u. as compared to the experimental value, -2.9047794a.u. of Moore (Atomic Energy Levels, 1949). Because of this poor ground state energy the \( 2^3S \) threshold lies at 18.920eV instead of the experimental value of 19.820eV. The energies of other thresholds differ similarly from the experimental values. Inspite of these differences the relative spacing of the n = 2 thresholds computed by them are in reasonable good agreement with the experimental values. Therefore, they also adopted a re-normalisation procedure for the first threshold and a scaling procedure for the other thresholds. They fixed the computed \( 2^3S \) threshold at its experimental value of 19.820eV and scaled the energies of other thresholds with respect to this value to get a good agreement between the computed thresholds so scaled and the experimental thresholds. They added 0.900eV to the total energy when presenting their results, which is the difference between the computed and the experimental one of the \( 2^3S \) threshold energy. In actual scattering calculations however, they have not parameterised the target state energies and have used the unscaled computed energies.

Thus an analysis of the literature shows that in all previous cases rescaling of state energies or renormalisation of incident electron energies has been adopted to reproduce the experimental \( 2^3S \) resonance at 19.380eV, below the first inelastic cross section. By using a reasonable Laguerre orbital basis and including CI target states
with good threshold energies compared to experiment we have been able to avoid the
need to rescale. It can be seen that our $2^3S$ threshold itself at 19.750eV is only
0.006eV lower than 19.818eV observed value. Our calculated position of resonance
(19.30eV) is also below the observed resonance (19.38eV) by approximately an
amount of 0.08eV.

### 5.2.3 Eigenphase-sum analysis

In order to study information analogous to elastic phase shifts above the inelastic
threshold we use the technique of eigenphases. In Figure 5.4, we show the sum of
eigenphases for $L = 0, 1, 2$ and 3 calculated with the five-state CC calculation. The
eigenphases are obtained by diagonalizing the partial-wave $S$-matrix by an orthogonal
transformation. The $S$-matrix elements are related to the $T$-matrix elements by,

$$ S_{ji} = \delta_{ji} - 2\pi i k \langle T_{ji} \rangle $$

(5.04)

and then diagonalized in the usual manner by the transformation,

$$ U^T S U = e^{2\pi P} $$

(5.05)

where the diagonal elements of $P$ are the eigenphases. The s-wave eigenphase shows
a rise and a drop just below and above the $^2S$ resonance below the $2^3S$ threshold.
There is a further systematic drop in eigenphase till the next threshold occurs. The
situation becomes more complicated at the $2^1S$ threshold. The $^2S$ eigenphase sum
indicates a resonant state of $\text{He}^-$ lying close to the $2^1S$ threshold. The eigenphase
increases by $\pi/4$ radians as this threshold is approached from above and then drops
back which indicates that the state is a virtual state of the $e^- + \text{He} (2^1S)$ system. A
similar effect has been noted by Berrington et al (1975) in Figure 5.4.
Figure 5.4: The eigenphase sums for the s, p, d and f waves. The full curve represents CC results and the broken curves are the results of Berrington et al (1975). The positions of various thresholds are indicated on the figure.
The effect of this virtual state on the elastic cross-section is also visible in Figure 5.3. The presence of an almost superimposed virtual state and cusp gives the cross section a different shape. This effect was first seen by Cvejanovic et al. (1973, 1974) and was confirmed by Berrington et al. (1975).

Two other resonances are indicated by the eigenphase sums in Figure 5.4. There is a \(^2\)P resonance just above the \(^2\)S threshold and the \(^2\)D resonance near the \(^2\)P threshold. These resonances are broader than \(^2\)S resonance since they lie above the channels to which they are strongly coupled. These resonances play a dominant role in the \(^2\)S - \(^2\)S excitation cross sections detailed in section 5.4.2.

### 5.2.4 Other Resonances and Cusps

The rapid rise in the \(^2\)S contribution to the \(^1\)S – \(^2\)S cross section from threshold causes a small cusp near \(^2\)S threshold in the elastic cross section. This effect has been seen by Cvejanovic et al. (1974), Golden et al. (1974) and Berrington et al. (1975). The present CC results shown in Figure 5.5 are in essential agreement with Berrington et al’s \(^2\)S measurements. The \(^2\)P and \(^3\)D contributions by Berrington et al are not available. The detailed features of \(^2\)S, \(^2\)P and \(^3\)D contributions to this cross section are given in the next section, 5.2.5. The experimental results for the individual contributions to this cross section are not available. The elastic cross section shown in Figure 5.2 decreases both above and below the threshold in agreement with the theoretical results of Berrington et al. (1975) and experimental results of Brongersma et al. (1972). The excited-state thresholds are summarised in Table 5.5.
Figure 5.5: The contributions due to $^2S$, $^2P$ and $^2D$ to the $1^1S - 2^3S$ cross section. Full curves show the CC results and broken curve demonstrates the $^2S$ results obtained by Berrington et al (1975). Four threshold energies are displayed as well.
Table 5.5: Comparison of threshold energies for the first four excited states of Helium obtained from our analytic CC calculations with Berrington et al’s thresholds

<table>
<thead>
<tr>
<th>Helium State Symmetry</th>
<th>Excited state thresholds for CI states used in present work (eV)</th>
<th>5-state, 11-state and 19-state thresholds of Berrington et al (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2^2S</td>
<td>19.757</td>
<td>19.820</td>
</tr>
<tr>
<td>2^1S</td>
<td>20.623</td>
<td>20.617</td>
</tr>
<tr>
<td>2^3P</td>
<td>20.990</td>
<td>20.967</td>
</tr>
<tr>
<td>2^1P</td>
<td>21.303</td>
<td>21.219</td>
</tr>
</tbody>
</table>

In order to match their excited-state threshold energies with the experimentally observed thresholds as described in Table 5.5, Berrington et al (1975, 1985) and Fon et al (1989) have made a small adjustment of approximately 1% to their theoretical excited-state energies so that they could reproduce their experimental energies relative to the 2^3S state energy.

Further, for consistency in their calculations within their inner and outer regions, a corresponding adjustment has also been made in the diagonal elements of the inner-region Hamiltonian matrix before diagonalization. They used these adjusted channel energies in the external region to solve the R-matrix equations. No such empirical adjustment of excited-state energies or re-normalisation of incident energies was necessary in solving our close-coupling equations with full CI target states.
5.2.5 The $^2S$, $^2P$ and $^2D$ Contributions to $1^1S - 2^3S$ and $1^1S - 2^1S$ Cross Sections

The effect of the resonant state near the $2^1S$ threshold can also be seen in the $^2S$ contribution to the $1^1S - 2^3S$ and $1^1S - 2^1S$ cross sections shown in Figures 5.5 and Figure 5.6 respectively. A drop in $^2S$ partial cross section contribution to $1^1S - 2^3S$ (Figure 5.5) and a peak in the same contribution to $1^1S - 2^1S$ (Figure 5.6) cross section near $2^1S$ threshold are important features of these plots and were seen by Berrington et al (1975) as well. The magnitude of the $1^1S - 2^3S$ excitation cross section close to $2^3S$ threshold is also of interest since this is related to the width of 19.300eV resonance. Burke (1965) and Golden et al (1974) have used an argument based on analytical methods to relate the resonance parameters to the behaviour of the cross sections close to $2^3S$ thresholds. A peak in $^2S$ contribution to $1^1S - 2^3S$ cross section near $2^1P$ threshold is observed where such a feature is not seen in Berrington et al's results.

We observe in Figure 5.5 a predominant peak in the $^2P$ contribution to the $1^1S - 2^3S$ cross section near first threshold that correspond to a $^2P$ resonance and two small peaks near the $2^3P$ and $2^1P$ thresholds. Two broad peaks in the $^2P$ partial wave for $1^1S - 2^1S$ cross section are quite noticeable at the $2^3P$ and $2^1P$ thresholds in Figure 5.6, which are rather not visible in Berrington et al's (1975) work.

The $^2D$ partial wave contribution to the $1^1S - 2^3S$ scattering shows an enhancement between the $2^1S$ and $2^1P$ thresholds. No data is available by Berrington et al (1975) for $^2P$ and $^2D$ partial waves for this cross section. The $^2S$ cusp at the $2^1S$ threshold
Figure 5.6: The contributions due to $^2S$, $^2P$ and $^2D$ to the $1^1S - 2^1S$ cross sections. Full curves show CC results and broken curves display corresponding results obtained by Berrington et al (1975). Our three threshold energies are displayed as well.
occurs in the middle of $^2\text{P}$ and $^2\text{D}$ resonances, which clearly does not play an important role in this cross section.

In Figure 5.6, a peak in $^2\text{D}$ partial wave near $2^1\text{P}$ resonance for $1^1\text{S} - 2^1\text{S}$ cross section contribution is noted in contrast to the smooth variation predicted by Berrington et al (1975). In general the trends of the partial cross sections from the CI close-coupling calculations are similar to those of Berrington et al but seem to show some more structure.

5.3 Excitation Cross sections from $n = 1$ to $n = 2$ states

5.3.1 $1^1\text{S} - 2^3\text{S}$ Excitation Cross Sections

The excitation cross sections are obtained by summing the partial wave cross sections for s, p, d and f partial waves. In Figure 5.7 we compare our results for the electron-impact excitation from the ground state of Helium to the metastable $2^3\text{S}$ state with theoretical results of Berrington et al (1975) and experimental results of Brongersma et al (1972). Later work by Berrington et al (1985) has been presented but it mainly concentrates on $n = 3$ and above thresholds and energies up to 30eV.

A major peak close to threshold corresponding to the $^2\text{P}$ resonance dominates the cross section in Figure 5.7. Two small peaks are observed at $2^3\text{P}$ and $2^1\text{P}$ thresholds. The peak around $2^3\text{P}$ threshold is quite dominant in the theory of Berrington et al and in the experiment as well. The predominant peak between $2^3\text{S}$ and $2^1\text{S}$ thresholds in our cross section is due to the major contribution by the $^2\text{P}$ partial wave as previously
Figure 5.7: $1^1S - 2^3S$ excitation cross section. Full curve represents our analytical CC results; broken curve is the calculations of Berrington et al (1975) and chain curve are the experimental results of Brongersma et al (1972). The position of all the four thresholds in the given energy range are indicated.
described in Figure 5.5. Two enhancements at $2^3P$ and $2^1P$ thresholds are due to $^2D$ partial wave contribution. In contrast to others our calculations give a slightly higher energy than $2^1S$ threshold and an enhancement is due to the major contributions of the s and d-partial waves. Overall our CI calculations show more enhancements near the inelastic thresholds than was indicated by Berrington and co-workers.

5.3.2 $1^1S - 2^1S$ Excitation Cross Sections

We present this cross section in Figure 5.8, again compared with Berrington et al (1975) but also with Oberoi & Nesbet's (1973) calculations. This cross section is also obtained by summing individual s, p, d and f-wave cross section contributions, results of which are already displayed in Figure 5.6. In this cross section we find similar enhancements of structure compared to which is similar to the structure indicated by Oberoi & Nesbet.

Firstly, near threshold our cross section does not exhibit the narrow peak arising from the $^2S$ resonant state in the calculations of Berrington. Instead we get a broad feature near the $2^1S$ threshold. Oberoi & Nesbet do not express any peak in this range; rather they show a steady rise near threshold.

Secondly, we get one sharp and another broad peak occurring near $2^3P$ and $2^1P$ thresholds respectively, in agreement with Oberoi & Nesbet. The cusp effects are quite noticeable features near the $2^3P$ and $2^1P$ thresholds, which are rather small in Berrington's work. Similar to Oberoi & Nesbet, we obtain a third peak around $~21.700eV$ and a cusp around $~22.000eV$. 

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Figure 5.8: A comparison of our analytical CC five-states calculations for the $1^1S$ – $2^1S$ excitation cross sections. The present calculations are represented by the full curve. The broken curve corresponds to Berrington et al (1975) and the chain curve displays Oberoi & Nesbet’s (1973) calculations. This graph includes location of three resonances in the given energy range.
Thirdly, above the n = 2 thresholds our cross section rises more rapidly than that of Berrington et al’s due to the contribution from higher partial waves. Our calculation does not include the effect of resonances associated with n = 3 thresholds in this case.

To a certain extent the overall agreement in the magnitude of the cross section is satisfactory and our results lie midway between those of Berrington et al and Oberoi & Nesbet. However our results indicate structure, which is also suggested by Oberoi & Nesbet (1973) although the details are different. In contrast no structure is indicated in Berrington et al’s results.

5.3.3 1^1S - 2^3P and 1^1S - 2^1P Excitation Cross Sections

The excitation cross sections for these transitions are shown in Figure 5.9 and again are compared with the results of Berrington et al (1975) and Oberoi & Nesbet (1973). In 1^1S - 2^3P cross section plot, the cross section rises from 2^3P threshold and a broad peak is noted near 2^1P threshold similar to Oberoi & Nesbet’s results. A few more broad enhancements are noticeable for energies < 22eV. There is a dip observed in the energy range > 22eV that is due to the drop in p-wave cross section. We agree reasonably well with Oberoi & Nesbet. The Berrington et al’s results show a steady rise and are lower than ours over the whole energy range.

The 1^1S - 2^1P cross section rises slowly from 2^1P threshold with a small feature around ~21.6eV whereas Berrington et al’s cross section rises smoothly. Our cross-sections follow more closely Oberoi & Nesbet’s cross sections but remain below Berrington et al’s results. This cross section is not much influenced by resonances
**Figure 5.9:** The excitations cross sections due to $1^1S - 2^3P$ and $1^1S - 2^1P$ excitations are demonstrated above. Present analytical CC results are represented by the full curve, whereas the broken and chain curves correspond to the calculation undertaken by Berrington *et al* (1975) and Oberoi & Nesbet (1973) respectively. Three thresholds are also displayed on the energy axis.
related to $n = 2$ thresholds. A few cusps and broad peaks are seen in Oberoi &
Nesbet’s results but overall these three theoretical calculations are in reasonable
agreement.

5.4 Excited-State Cross Sections from $n = 2$ initial to $n = 2$
final states

Because the total spin of electron-Helium system is conserved in the scattering,
scattering from the ground state leads only to doublet scattering. In contrast, for
scattering from excited states we have the possibility of $s = 1/2$ (doublet) and $s = 3/2$
(quartet) scattering. Spin polarised experiments are necessary to separate out the
doublet and quartet contributions to the cross sections.

5.4.1 $2^3S - 2^3S$ Total Elastic Cross Sections

The doublet contribution to the $2^3S - 2^3S$ total elastic cross section is shown in Figure
5.10. A prominent peak near the $2^3S$ threshold and two small peaks near the $2^1S$ and
$2^3P$ thresholds are evident. Our cross sections are slightly lower than Berrington et
al’s results, but the overall features look similar.

The individual $2^S$, $2^P$ and $2^D$ contributions to this $2^3S$ total elastic cross section are
shown in Figure 5.11. $2^S$ cross-section has a sharp peak near the $2^3S$ threshold,
showing the effect of the $2^S$ virtual state. The first peaks due to $2^P$ and $2^D$ resonances
near the $2^3S$ and $2^1S$ thresholds respectively contribute to the corresponding peaks in
the total cross section. The $2^S$ cross-section contributions by Berrington et al are not
available at energies $>20.4$eV.
Figure 5.10: The doublet contribution to the $2^3S - 2^3S$ total elastic cross sections is shown in the above figure. The comparisons of the present analytical CC results with those of Berrington et al (1975) have been displayed by the solid and broken curve respectively. The figure includes the position of all the four thresholds on the energy axis.
Figure 5.11: This figure exhibits the individual $^2S$, $^2P$ and $^2D$ contributions to the doublet cross sections of $^2S - ^3S$ calculated by our CC model via the solid curves, whereas their contrasts with the results obtained by Berrington et al (1975) are displayed through the broken curves. The figure includes the threshold positions as well.
We also see a second broad $^3P$ peak above $^3P$ threshold similar to Berrington et al, indicating the rise in eigenphase in this energy region as demonstrated in Figure 5.5. This can be associated with another resonant state of He$^-$. The second peak in $^3D$ contribution is near the $^3P$ threshold. The two $^3D$ peaks seem to be enhancements of cross sections rather than resonances. We note some differences with Berrington et al’s results as they show a single peak in this region.

The quartet contribution to this cross section is exhibited in Figure 5.12. A sharp rise in total cross section between $^3S$ and $^1S$ thresholds and then a gradual drop in cross section agrees fairly well with Berrington et al’s results. There appears to be some more structure near the $^3P$ and $^1P$ thresholds in this cross section, a dip in this $^3S$ – $^3S$ quartet cross section is due to fall in f-partial wave contribution.

### 5.4.2 $^3S$ - $^1S$ Excitation Cross Sections

This excitation cross section along with Berrington et al’s (1975) calculations is shown in Figure 5.13. The trends in cross sections for both the results are similar, although our calculations reveal a more pronounced peak at $^1S$ threshold, by a factor of two. The other small peak is due to $^3D$ contribution near the $^1P$ threshold. A small feature is observed around $\sim$21.5eV, which is due to the second peak in $^3D$ contribution. Above 22eV the overall agreement between two models is reasonable.

The individual contribution from $^3S$, $^3P$ and $^3D$ resonances to this excitation cross section are presented in Figure 5.14, with results compared with those of Berrington et al. We get an enhanced peak at threshold arising from the $^2S$ resonance in contrast
Figure 5.12: The quartet contributions to the $2^3S - 2^3S$ and $2^3S - 2^3P$ cross sections by our analytic CC calculations are presented above. Full curve represents the current results, while the broken curve portrays Berrington et al.'s (1975) calculations. All threshold positions are also displayed.
Figure 5.13: The excited state cross sections due to $2^2S - 2^1S$ are shown above. Our present analytical CC results are represented by the full curve and Berrington et al.'s (1975) results are displayed by the broken curve.
Figure 5.14: This figure shows the individual contributions of $^2S$, $^2P$ and $^2D$ to the $^2S$ – $^2S$ excitation cross sections. Comparisons between our analytical CC contributions (full curve) and Berrington et al.'s (1975) calculations (broken curve) are incorporated above. The thresholds lying in the considered energy range are also indicated.
to Berrington et al, where no peak can be seen in their calculations. The $^2S$ contribution to this cross section is higher than their results over the entire energy range.

Again we find a longer peak (by a factor of two), due to the $^2P$ resonance contribution near the $2^1S$ threshold. The $^2D$ cross section rises smoothly from threshold and we find a prominent peak in this contribution near the $2^3P$ threshold where as Berrington et al have shown a broad feature.

No comparison can be made for individual contributions for energies >21.7eV as no data for Berrington et al’s (1975) results is available over this energy range, for these contributions.

5.4.3 $2^3S - 2^3P$ and $2^3S - 2^1P$ Excitation Cross Sections

Figure 5.15 illustrates the doublet contributions to $2^2S - 2^3P$ excitation cross section and the result comparison with Berrington et al (1975) and Oberoi & Nesbet (1973). The cross section displays a sharp peak due to a large p-wave contribution near the $2^3P$ threshold. Another small peak is observed near the $2^3P$ threshold from the d-wave contribution. The shape of our cross section corresponds to that of Oberoi & Nesbet, though we are 20% to 30% lower than their results. We differ from Berrington et al’s results at higher energies as we are getting a small contribution to this cross sections from higher partial waves.
Figure 5.15: The excitation cross sections resulting from $2^3S - 2^3P$ (doublet) and $2^3S - 2^1P$ transitions are shown above. Comparisons of present CC results (solid curve) with Berrington et al. (1975) (broken curve) and Oberoi & Nesbet’s (1973) (chain curve) results are displayed by the above diagram.
The quartet contribution to this cross section was already given in Figure 5.12. There is good agreement with Berrington et al.'s results.

The excitation $2^3P - 2^1P$ cross section is displayed in Figure 5.15. In contrast to the $2^3S - 2^3P$ cross section results, it shows a good agreement with Berrington et al. and Oberoi & Nesbet's calculations. This cross section is not affected by $n = 2$ resonances, which lie lower in energy.

### 5.4.4 $2^1S - 2^1S$ Elastic Cross Sections

This elastic cross section along with the calculations of Berrington et al. (1975) and Oberoi & Nesbet (1973) is presented in Figure 5.16. Our total cross section shows a drop above the $2^1S$ threshold energy and then a sharp peak near the $2^3P$ threshold and another broad peak at $2^1P$ threshold.

Individual contributions by $^2S$, $^2P$ and $^2D$ partial wave cross sections displayed in Figure 5.17 show the origin of the structure in the cross sections. The presence of the $^2S$ virtual state near the $2^1S$ threshold gives rise to a very large elastic cross section close to the threshold. The sharp peak near $2^3P$ threshold is due to peaks in $^2P$ and $^2D$ partial waves. The broad peak at $2^1P$ threshold is due to the $^2D$ resonance. Beyond $2^1P$ threshold, a dip and another enhancement is observed which plays no important role. The shapes of the three curves are similar whereas at higher energies our total cross-section lies in between the other two results. No data is available for comparison by Berrington et al. and Oberoi & Nesbet for individual contributions to this elastic cross section.
Figure 5.16: This figure exhibits the comparisons of our analytical CC results (solid curve) for $2^1S - 2^1S$ elastic cross sections with Berrington et al’s (1975) (broken curve) and Oberoi & Nesbet’s (1973) (chain curve) calculations. Threshold energies are also indicated.
Figure 5.17: This figure shows the individual contributions of $^2\text{S}$, $^2\text{P}$ and $^2\text{D}$ to the $2^1\text{S}$ – $2^1\text{S}$ elastic cross sections calculated by our CC code. No results are available for comparisons.
5.4.5 $2^1S - 2^3P$, $2^1S - 2^1P$ and $2^3P - 2^1P$ Excitation Cross Sections

These inelastic cross section results are presented in Figure 5.18. We obtain a large $2^1S - 2^3P$ cross section at $2^3P$ threshold and then a cusp near the $2^1P$ threshold. Our peak in this cross section is higher by a factor of four, compared with that of Berrington et al. At higher energies the shapes of the two curves are similar and we agree well.

Our results of $2^1S - 2^1P$ cross section agree well with Berrington et al and the trends of the two curves (present and Berrington’s) are similar over the whole energy range. The $2^3P - 2^1P$ inelastic cross sections are also exhibited in Figure 5.18. This curve grows slowly with energy and is unaffected with the low-lying resonances. This cross section required a large amount of calculation because this transition involves both the parities, natural and unnatural. The final cross section is the sum of the individual excitation cross sections due to each parity.

5.4.6 $2^3P - 2^3P$ and $2^1P - 2^1P$ Elastic Cross Sections

These elastic cross sections from $2^3P$ and $2^1P$ states are exhibited in Figure 5.19 along with the curves of Berrington et al (1975) and Oberoi & Nesbet (1973). The calculations of these cross sections for doublet and quartet scattering involved contributions from both the parities. These calculations again required a heavy computation for result comparisons.
Figure 5.18: A comparison of our analytical CC (full curves) results of $2^1S - 2^3P$, $2^1S - 2^1P$ and $2^3P - 2^1P$ excitation cross sections with those of Berrington et al (1975) (broken curves) is displayed in the above figure.
Figure 5.19: Our close-coupling elastic cross sections due to $2^3P - 2^3P$ (doublet and quartet) and $2^1P - 2^1P$ transitions are represented by the full curves, whereas their comparison with the results of Berrington et al (1975) and Oberoi & Nesbet (1973) are portrayed by the broken curves and chain curves respectively.
A large value of cross section in all the above curves can be seen at $2^3P$ and $2^1P$ thresholds. The cross sections are quite large at these thresholds and thereafter they have a smooth decrease with increasing incident energy. Our curves lie in between those of Berrington et al and Oberoi & Nesbet for all other energies except at $2^1P$ threshold where we get large $2^1P - 2^1P$ cross-section.

This completes our calculations on the search of resonances and the elastic & inelastic cross sections from the first five states of Helium using the analytical orbital close-coupling code with Laguerre basis used in the CI expansion mode.

5.5 Conclusions

We have found a more accurate lowest resonance position differing from others, using a better set of wave function in our close-coupling analytical and numerical codes. Our calculations using CI target states did not use any rescaling of target state energies or any re-normalisation technique of incident energies, to match the experimental thresholds. We were able to still get the reasonable positions of thresholds without adopting any of the above processes.

The comparison of our elastic and inelastic cross sections with other theoretical results of Berrington et al (1975), Oberoi & Nesbet (1973) and experimental results of Brongersma et al (1972) show generally similar trends. The main differences of our calculations are that for several transitions ($1^1S - 2^3S$, $2^3S - 2^1S$, $2^1S - 2^1S$, $2^3P - 2^3P$ (doublet) and $2^1S - 2^3P$), the threshold features show an enhancement compared to those of Berrington et al.
In general our calculations showed more structure than was evident in the work of Berrington and co-workers. However it was interesting to note that in this regard we were very similar to the calculations of Oberoi & Nesbet. It therefore seems to us that the type of wave functions employed to describe the target do have an influence in some subsets of the inelastic cross sections.

We demonstrate that our close-coupling code becomes a successful general program for both types, analytical and numerical calculations of low-energy electron-Helium elastic and inelastic scattering. The basis developed is therefore well suited to further applications, in particular to extending the work to search for resonances in electron-Helium scattering with positions lying between \( n > 2 \) to \( n \leq 3 \) states of Helium.
Chapter 6

Summary and Possibilities for Future Work

The thesis was concerned with extending the momentum-space close coupling method, which uses analytic orbitals and its implementation for electron-Helium scattering in the LBAS package of programs to incorporate the use of purely numerically generated orbitals. This was necessary in order to interface the LBAS suite of programs with the most popular existing scattering packages. A great deal of work was involved to learn and analyse these packages to give the best wave functions.

The most important aspect in chapter one was to express in detail, the need for modifying the existing analytic close-coupling code in order to accept more general numerical orbitals. A brief outline of two atomic structure packages used in our work, one which calculates the target wave functions only numerically (Fischer’s package) and the other (Hibbert’s package) which expresses the orbitals as sum of analytic Slaters, was also presented there.

Chapter two presented the elements of coupled-channels theory for electron-Helium scattering in terms of momentum-space coupled equations for the T-matrix. This theory included all of the physics that dominates elastic and inelastic transitions between ground and excited Helium states. To extend the present work to Neon or Argon targets would require extensive modification of the programs and was not attempted here.
A description of the calculation of target states for both Helium and Neon targets using Hibbert's package was presented in chapter three. Moreover, the way our existing analytic orbital CC Helium code has been modified to incorporate numerical orbitals and CI target states was also detailed in this chapter. Two atomic structure packages to provide target wave functions for the numerical electron-Helium CC package presented were investigated here. The strengths and weaknesses of incorporating these packages into our numerical CC code were discussed. Fischer's numerical wave functions could not be used as a successful basis in our CC numerical code due to the orthogonality problems of the target states as a result of different optimized orbitals being generated for different state wave functions. On the other hand, Hibbert's package contained options for forcing use of the same set of orbitals to generate the ground and excited states and hence orthogonality of the target states that was a basic requirement of CC code and was therefore preferable to Fischer's package. The need for modification of potential matrix elements for the extension of the numerical electron-Helium work to numerical electron-Neon scattering calculations was also expressed.

The calculation procedures and the resulting scattering observables relevant to electron-Helium low-energy elastic scattering were presented in chapter four. This chapter contained mainly the results related to elastic scattering. Two options of wave functions (in both CI and FC modes) to be used for scattering calculations were discussed. A large set of basis orbitals (Slaters/Laguerres) but with a lesser number of target states to reduce the computational time was used in both CI and FC modes. Good agreement with other calculations was demonstrated.
Some numerical instability in CI calculations using Slaters was observed. The reason for this was that the CI expansions with Slaters lead to CI coefficients of large magnitude and alternating in sign, thus increasing rounding errors significantly. On the other hand Laguerre based expansions produced CI coefficients, which did not grow in magnitude and which as a consequence reduced rounding errors to a significant level. This chapter included the comparisons of numerical calculations of scattering observables with others’ work as well.

An important aim of this work was not only developing the numerical close-coupling equations in order to use others’ packages for complex atoms, but also to apply this numerical CC code with CI target states constructed from a basis of Laguerre functions, to study low-energy electron-Helium inelastic scattering. This study was carried out in chapter five. In particular we showed that with the use of accurate CI wave functions the position of the lowest-lying Helium resonance was accurately produced in contrast to previous calculations.

The application of full CI target wave functions to low-energy inelastic scattering in this thesis was new; previous investigations had used frozen-core wave functions. Our results for resonances and positions of inelastic thresholds did not require any scaling of target-state energies or any renormalization of incident electron energies to match the experimental thresholds. This was in contrast to the R-matrix formulations. Overall our elastic and inelastic transition cross sections were in good agreement with the R-matrix formulations and the experiments. Extensions to scattering at higher energies above the $n > 2$ states of Helium were not attempted in this work. Our low-energy studies indicate the close-coupling model is adequate but inclusion of the
complete manifold of target states including pseudostates for each orbital basis set would be desirable but could not be attempted as this required computing resources that were not available to us.

The present numerical CC computer code may now be readily extended to treat other inert gas atoms such as Neon or Argon by generating target states using Hibbert's code. The present calculations also indicate that for target states generated by large numbers of expansion functions of Slater type, numerical problems and loss of accuracy are inevitable when applied in momentum-space coupled channels codes. For this reason it would appear that for the longer term, the development of a general structure code using Laguerre functions rather than Slater functions will be of considerable importance.
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