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# Ionisation Amplitudes in Electron-Impact Helium Collisions within the S-Wave Model

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[ABSTRACT]

## Contents

<b>1</b>	<b>Introduction</b>	<b>2</b>
<b>2</b>	<b>Theory</b>	<b>3</b>
2.1	Convergent Close-Coupling Method . . . . .	3
2.1.1	Laguerre Basis . . . . .	3
2.1.2	Target States . . . . .	4
2.1.3	Total Wavefunction . . . . .	6
2.1.4	Convergent Close-Coupling Equations . . . . .	8
2.2	Scattering Statistics . . . . .	13
2.2.1	Scattering Amplitudes . . . . .	13
2.2.2	Cross Sections . . . . .	15
<b>3</b>	<b>Survey of Literature</b>	<b>16</b>
3.1	Electron-Impact Hydrogen Ionisation . . . . .	16
3.1.1	Considerations for a Hydrogen Target . . . . .	16
3.1.2	Convergent Close-Coupling Calculations . . . . .	16
3.1.3	Ansatz of Zatsarinny and Bartschat . . . . .	18
3.2	Electron-Impact Helium Ionisation . . . . .	19
3.2.1	Additional Considerations for a Helium Target . . . . .	19
3.2.2	Convergent Close-Coupling Calculations . . . . .	20
3.2.3	Exterior-Complex-Scaling Calculations . . . . .	20
<b>4</b>	<b>Conclusion</b>	<b>20</b>

## List of Figures

1	e-H Singlet and Triplet SDCS . . . . .	17
2	e-H Singlet and Triplet SDCS with Ansatz . . . . .	18

## List of Tables

# 1 Introduction

The field of computational atomic collision theory has been subject to rapid progress during the past few decades, with the increasing capability of computational hardware and software, and the development of new and extant techniques and methods. Notably, the Convergent Close-Coupling (CCC) method, which was initially developed to model the scattering processes of an electron projectile on a hydrogen target [1], has been established as both numerically tractable and accurate while retaining the property of being a unitary formulation. Proven capable of modelling elastic scattering and discrete excitations [1] as well as ionisation processes [2, 3, 4] for the two-body system of hydrogen, the CCC method was extended to hydrogenic targets [5], and further to three-body systems [6, 7, 8], such as for helium targets [9, 10, 11]. The CCC method was also extended to include double-photon ionisation of helium-like targets [12, 13, 14].

While the CCC method yielded accurate total ionisation cross sections (TICS) for electron-impact ionisation on targets such as hydrogen and helium, the calculation of differential cross sections - namely the single-, double-, and triple-differential cross sections (SDCS, DDCS, TDCS) - were seen to fail to demonstrate convergence, discussed in detail by Bray [3]. That the scattering amplitudes calculated using the CCC method would lead to a good level of agreement with experimental values for the total ionisation cross sections, despite the non-convergence of the differential cross sections, proved quite puzzling. It was demonstrated by Bray [3], in the context of the Temkin-Poet model (also known as the S-wave model) [15, 16] of electron-impact hydrogen ionisation, that the SDCS is expected to be zero past the point of equal-energy-sharing between the projectile and ionised electrons. However, issues arise for the singlet case as the SDCS assumes a non-zero value at the point of equal-energy-sharing, leading to a discontinuity. These issues are compounded by the CCC method being restricted to evaluating ionisation amplitudes only for a countable number of outgoing projectile energies.

It was later shown by Stelbovics [4], that the behaviour of the singlet SDCS about the equal-energy-sharing point was indeed analogous to that of a Fourier series of a step function about the point of discontinuity. Specifically: that the singlet SDCS would not necessarily be zero past the point of equal-energy-sharing but would tend to zero, that the ionisation amplitudes would converge to half the step height at the equal-energy-sharing point, and thus that the SDCS would converge to one quarter the step height at this point. Accounting for this behaviour, Bray [8], was then able to demonstrate the validity of the CCC method by reproducing differential cross sections for electron-impact hydrogen ionisation which were in agreement with experimental results, as well as with the results of another computational approach: exterior complex scaling (ECS) [17].

However, the issue of the calculation of ionisation amplitudes for outgoing projectile energies, outside the countable number which the CCC method is restricted to, remains. The current approach is to interpolate the ionisation amplitudes, between these restricted points, across the continuum of on-shell projectile energies, as discussed in [8]. An ansatz has been suggested by Zatsarinny and Bartschat [18] which, alternatively, removes this restriction and allows for the evaluation of the ionisation amplitudes across all on-shell projectile energies. The application of this ansatz to electron-impact hydrogen ionisation by Bray *et al.* [19] suggested that the ansatz was unphysical, but that it did provide an effective scheme for evaluating ionisation amplitudes.

The topic of this project will be the application of the ansatz of Zatsarinny and Bartschat to the electron-impact ionisation of helium, with and without excitation, within the CCC method and in the context of the S-wave model. We shall explore the suitability of this ansatz in evaluating the ionisation amplitudes, and determine if and where any limitations in its use may exist.

## 2 Theory

We shall describe a brief derivation of the Convergent Close-Coupling (CCC) method for generalised electron-projectile atomic/ionic-target scattering, similar in form to the derivations presented in [7, 20]. The specific considerations for the application of the CCC method to the cases of electron-impact hydrogen (e-H) scattering, and electron-impact helium (e-He) scattering, are discussed in [subsubsection 3.1.1](#) and [subsubsection 3.2.1](#) respectively. We shall focus on the treatment of target ionisation, both with and without excitation, by consideration of the ionisation amplitudes within the CCC method.

### 2.1 Convergent Close-Coupling Method

In brief, the CCC method utilises the method of basis expansion to numerically solve the Lippmann-Schwinger equation in a momentum-space representation, for a projectile-target system, to yield the transition amplitudes, which are checked for convergence as the size of the basis is increased. The scattering statistics can then be extracted from the transition amplitudes.

The rate of convergence, depends on many factors, such as the complexity of the target structure, the coupling between transition channels, and the choice of basis used in the expansion. With the selection of an appropriate basis, unbounded continuum waves can be accurately represented by a finite amount of basis states, which allows ionisation amplitudes to be treated in a similar manner to discrete excitation amplitudes within the CCC method. A Laguerre basis is well-suited to this task; the benefits of this basis are discussed in further detail in [7, 5-9].

#### 2.1.1 Laguerre Basis

To describe the target structure, the CCC method utilises a Laguerre basis  $\{|\varphi_i\rangle\}_{i=1}^{\infty}$  for the Hilbert space  $L^2(\mathbb{R}^3)$ , for which the coordinate-space representation is of the form

$$\langle \mathbf{r} | \varphi_i \rangle = \varphi_i(r, \Omega) = \frac{1}{r} \xi_{k_i, l_i}(r) Y_{l_i}^{m_i}(\Omega), \quad (1)$$

where  $Y_{l_i}^{m_i}(\Omega)$  are the spherical harmonics, and where  $\xi_{k_i, l_i}(r)$  are the Laguerre radial basis functions, which are of the form

$$\xi_{k, l}(r) = \sqrt{\frac{\lambda_l (k-1)!}{(2l+1+k)!}} (\lambda_l r)^{l+1} \exp\left(-\frac{1}{2} \lambda_l r\right) L_{k-1}^{2l+2}(\lambda_l r), \quad (2)$$

where  $\lambda_l$  is the exponential fall-off, for each  $l$ , and where  $L_{k-1}^{2l+2}(\lambda_l r)$  are the associated Laguerre polynomials. Note that we must have that  $k_i \in \{1, 2, \dots\}$ ,  $l_i \in \{0, 1, \dots\}$  and  $m_i \in \{-l_i, \dots, l_i\}$ , for each  $i \in \{1, 2, \dots\}$ .

This Laguerre basis is utilised due to: the Laguerre basis functions  $\{\varphi_i(r, \Omega)\}_{i=1}^{\infty}$  forming a complete basis for the Hilbert space  $L^2(\mathbb{R}^3)$ , the short-range and long-range behaviour of the radial basis functions being well suited to describing bound target states and providing a basis for expanding continuum states in, and because it allows the matrix representation of numerous operators to be calculated analytically.

Practically, we cannot utilise a basis of infinite size. Hence, we truncate the Laguerre radial basis  $\{\xi_{k, l}(r)\}_{k=1}^{N_l}$  to a certain number of radial basis functions  $N_l$ , for each  $l$ , and we also truncate  $l \in \{0, \dots, l_{\max}\}$ , limiting the maximum angular momentum we consider in our basis. Hence, for a

given value of  $m$ , we have a basis size of

$$N = \sum_{l=0}^{l_{\max}} N_l. \quad (3)$$

In the limit as  $N \rightarrow \infty$ , the truncated basis will tend towards completeness, and it is in this limit that we discuss the convergence of the Convergent Close-Coupling method. We have presented the Laguerre basis with full generality, however we note that in the S-wave model we have  $l_{\max} = 0$ , which allows for the simplification of numerous expressions and computations.

### 2.1.2 Target States

Possessing now a suitable basis to work with, we proceed to represent the target in this basis by the method of basis expansion. Firstly, we note that electrons are indistinguishable fermionic particles; that is, no two electrons can be distinguished from each other, and they must satisfy Pauli's exclusion principle - that an electron state cannot be occupied by more than one electron. Since electrons are indistinguishable, we might naively suppose that the space of states consisting of  $n$  electrons is simply the  $n$ -th tensor power of the one-electron space,  $T^n(\mathcal{H})$ , defined by

$$T^n(\mathcal{H}) = \{|\psi_1\rangle \otimes \cdots \otimes |\psi_n\rangle : |\psi_1\rangle, \dots, |\psi_n\rangle \in \mathcal{H}\}, \quad (4)$$

where  $\mathcal{H}$  is the space of one-electron states. However this fails to account for Pauli's exclusion principle, since any one-electron state may be occupied up to  $n$  times. Hence, the space of states consisting of  $n$  electrons is instead defined to be the quotient space  $\Lambda^n(\mathcal{H})$  of  $T^n(\mathcal{H})$  by  $\mathcal{D}^n$ ,

$$\Lambda^n(\mathcal{H}) = T^n(\mathcal{H}) / \mathcal{D}^n, \quad (5)$$

where  $\mathcal{D}^n \subset T^n(\mathcal{H})$  is the subspace of tensor products which contain any one-electron state more than once. The space  $\Lambda^n(\mathcal{H})$  is known as the  $n$ -th exterior power of  $\mathcal{H}$ , and is identifiable as the subspace of  $T^n(\mathcal{H})$  consisting of anti-symmetric tensors. Note that we shall adopt the following notation for tensor products

$$|\psi_1, \dots, \psi_n\rangle = |\psi_1\rangle \otimes \cdots \otimes |\psi_n\rangle \quad (6)$$

and the following notation for anti-symmetric tensor products

$$|[\psi_1, \dots, \psi_n]\rangle = |\psi_{[1, \dots, n]}\rangle = \sqrt{n!} \hat{A} |\psi_1, \dots, \psi_n\rangle \quad (7)$$

where  $\hat{A} : T^n(\mathcal{H}) \rightarrow \Lambda^n(\mathcal{H})$  is the anti-symmetriser operator which we define to be of the form

$$\hat{A} |\psi_1, \dots, \psi_n\rangle = \frac{1}{n!} \sum_{\sigma \in S_n} \text{sgn}(\sigma) |\psi_{\sigma(1)}, \dots, \psi_{\sigma(n)}\rangle, \quad (8)$$

where  $S_n$  is the symmetric group on  $n$  elements, the sum is taken over all permutations  $\sigma \in S_n$ , and where  $\text{sgn}(\sigma)$  is the signature of the permutation  $\sigma$ . It follows from this construction that

$$|\psi_{[a_1, \dots, a_n]}\rangle = 0 \quad \text{if any } a_i = a_j, \quad (9)$$

hence satisfying Pauli's exclusion principle. Furthermore, we have that

$$\hat{P}_{i,j} |\psi_{[1, \dots, n]}\rangle = -|\psi_{[1, \dots, n]}\rangle, \quad (10)$$

where  $\hat{P}_{i,j}$  is the pairwise exchange operator, permuting the states  $|\psi_i\rangle$  and  $|\psi_j\rangle$ . We note that in this context, the states  $|\psi_i\rangle$  include both coordinate and spin states.

It follows that for an atomic/ionic target, consisting of  $n_e$  electrons, the space of target states is of the form  $\mathcal{H}_T = \Lambda^{n_e}(\mathcal{H})$ . We shall adopt the convention that operators which act on the  $m$ -th electron space (including the projectile electron), will be indexed by  $m$ , for  $m = 0, 1, \dots, n_e$ .

**Target Hamiltonian** The target Hamiltonian, for an atomic/ionic target with  $n_e$  electrons, is of the form

$$\hat{H}_T = \sum_{m=1}^{n_e} \hat{K}_m + \sum_{m=1}^{n_e} \hat{V}_m + \sum_{m=1}^{n_e} \sum_{n=m+1}^{n_e} \hat{V}_{m,n}, \quad (11)$$

where  $\hat{K}_m$  and  $\hat{V}_m$  are the target electron kinetic and electron-nuclei potential operators, for  $m = 1, \dots, n_e$ , and where  $\hat{V}_{m,n}$  are the electron-electron potential operators, for  $m, n = 1, \dots, n_e$ .

**Target Diagonalisation** The target Hamiltonian, restricted to just one target electron,

$$\hat{H}_{T,e} = \hat{K}_1 + \hat{V}_1, \quad (12)$$

is expanded in a Laguerre basis  $\{|\varphi_i\rangle\}_{i=1}^N$  and diagonalised to yield a set of one-electron atomic orbitals  $\{|\phi_i^{(N)}\rangle\}_{i=1}^N$  which are orthonormal and satisfy

$$\langle \phi_i^{(N)} | \hat{H}_{T,e} | \phi_j^{(N)} \rangle = \varepsilon_i^{(N)} \delta_{i,j}. \quad (13)$$

From these one-electron atomic orbitals, we generate a set of one-electron spin orbitals  $\{|\chi_i^{(N)}\rangle\}_{i=1}^{2N}$  for which  $|\chi_{2i-1}^{(N)}\rangle$  and  $|\chi_{2i}^{(N)}\rangle$  both correspond to  $|\phi_i^{(N)}\rangle$  but have spin projection  $\frac{1}{2}$  and  $-\frac{1}{2}$  respectively. These one-electron spin orbitals are then combined to construct Slater determinants; for any selection of  $n_e$  one-electron spin orbitals  $|\chi_{a_1}^{(N)}\rangle, \dots, |\chi_{a_{n_e}}^{(N)}\rangle \in \{|\chi_i^{(N)}\rangle\}_{i=1}^{2N}$ , the Slater determinant of these spin orbitals is of the form

$$|\chi_{[a_1, \dots, a_{n_e}]}^{(N)}\rangle = \sqrt{n_e!} \hat{A} |\chi_{a_1}^{(N)}, \dots, \chi_{a_{n_e}}^{(N)}\rangle = \frac{1}{\sqrt{n_e!}} \sum_{\sigma \in S_{n_e}} \text{sgn}(\sigma) |\chi_{a_{\sigma(1)}}^{(N)}, \dots, \chi_{a_{\sigma(n_e)}}^{(N)}\rangle, \quad (14)$$

as per [Equation 7](#) and [Equation 8](#). We note that Slater determinants are anti-symmetric under pairwise exchange of any two orbitals, and are zero if constructed with two spin orbitals in the same state. Hence they adhere to Pauli's exclusion principle and are indeed elements of  $\mathcal{H}_T = \Lambda^{n_e}(\mathcal{H})$ .

The true target states  $\{|\Phi_\alpha\rangle\} \in \mathcal{H}_T$  are then approximated by expanding the full target Hamiltonian  $\hat{H}_T$  in a basis of Slater determinants,

$$\{|\chi_{[a_1, \dots, a_{n_e}]}^{(N)}\rangle : a_1, \dots, a_{n_e} \in \{1, \dots, 2N\}\}, \quad (15)$$

and diagonalising to yield a set of target pseudostates  $\{|\Phi_n^{(N)}\rangle\}_{n=1}^{N_T}$  which are orthonormal and satisfy

$$\langle \Phi_i^{(N)} | \hat{H}_T | \Phi_j^{(N)} \rangle = \epsilon_i^{(N)} \delta_{i,j}, \quad (16)$$

where  $\epsilon_n^{(N)}$  is the pseudoenergy corresponding to the pseudostate  $|\Phi_n^{(N)}\rangle$ . Note that the number of target pseudostates  $N_T$  depends on the number of Slater determinants utilised in the expansion

of  $\hat{H}_T$ . Note also that the  $(N)$  superscript has been introduced to indicate that these are not true eigenstates of the target Hamiltonian, only of its representation in the truncated Laguerre basis, and that these pseudostates and their pseudoenergies are dependent on the size of the Laguerre basis utilised.

The process of selecting which Slater determinants to use in the expansion is not trivial, as the number of Slater determinants scales as  $\binom{2N}{n_e}$ . A common method of mitigating this computational complexity, is to partition the target orbitals into a core set and valence set of orbitals, with the core orbitals being limited to a much smaller set of states, while the valence orbitals are not so constrained. This provides an effective model for targets with a mostly fixed set of core electron states, while allowing the valence electrons to interact fully with the projectile.

**Completeness of Target Pseudostates** As a result of the completeness of the Laguerre basis, the set of target pseudostates will be separable into a set of bounded pseudostates which will form an approximation of the true target discrete spectrum, and a set of unbounded pseudostates which will provide a discretisation of the true continuum of unbounded states. Without loss of generality, we order the target pseudostates by increasing pseudoenergy,  $\epsilon_1^{(N)} < \dots < \epsilon_{N_T}^{(N)}$ , which allows us to express the separability of the spectrum in the form

$$\{|\Phi_n^{(N)}\rangle\}_{n=1}^{N_T} = \{|\Phi_n^{(N)}\rangle\}_{n=1}^{N_B} \cup \{|\Phi_n^{(N)}\rangle\}_{n=N_B+1}^{N_T}, \quad (17)$$

where  $\epsilon_n^{(N)} < 0$  for  $n = 1, \dots, N_B$ , and where  $\epsilon_n^{(N)} \geq 0$  for  $n = N_B + 1, \dots, N_T$ . Note that  $N_B$  is the number of bounded pseudostates, and we write  $N_U = N_T - N_B$  to represent the number of unbounded pseudostates, both of which are dependent on  $N$  by consequence of the construction of the target pseudostates.

The projection operator for the target pseudostates,  $\hat{I}_T^{(N)}$ , is of the form

$$\hat{I}_T^{(N)} = \sum_{n=1}^{N_T} |\Phi_n^{(N)}\rangle\langle\Phi_n^{(N)}| = \sum_{n=1}^{N_B} |\Phi_n^{(N)}\rangle\langle\Phi_n^{(N)}| + \sum_{n=N_B+1}^{N_T} |\Phi_n^{(N)}\rangle\langle\Phi_n^{(N)}|, \quad (18)$$

and so in the limit as  $N \rightarrow \infty$ , the sum over the bounded pseudostates will converge to the sum over the true target discrete states and the sum over the unbounded pseudostates will converge to a discretisation of the integral over the true continuum spectrum. Whence, it follows that projection operator for the target pseudostates converges to the identity operator, for  $\mathcal{H}_T$ , in the limit as  $N \rightarrow \infty$ ; that is,

$$\lim_{N \rightarrow \infty} \hat{I}_T^{(N)} = \hat{I}_T. \quad (19)$$

A more rigorous discussion on the suitability of representing unbounded states in the Laguerre basis is provided in [7, 5-9].

### 2.1.3 Total Wavefunction

The total wavefunction  $|\Psi^{(+)}\rangle \in \Lambda^{1+n_e}(\mathcal{H})$  is defined to be an eigenstate of the total Hamiltonian  $\hat{H}$  with total energy  $E$  and specified to have outgoing spherical-wave boundary conditions,

$$\hat{H} |\Psi^{(+)}\rangle = E |\Psi^{(+)}\rangle, \quad (20)$$

where  $\hat{H}$  is of the form

$$\hat{H} = \hat{H}_T + \hat{K}_0 + \hat{V}_0 + \sum_{m=1}^{n_e} \hat{V}_{0,m}, \quad (21)$$

where  $\hat{H}_T$  is the target Hamiltonian, defined in Equation 11,  $\hat{K}_0$  is the projectile electron kinetic operator,  $\hat{V}_0$  is the projectile electron-nuclei potential operator, and  $\hat{V}_{0,m}$  are the projectile electron-target electron potential operators. The following treatment of the total wavefunction is of a similar form to [20, 202-204].

To ensure that the total wavefunction is anti-symmetric we utilise the anti-symmetriser, defined in Equation 8, to construct it explicitly

$$|\Psi^{(+)}\rangle = \hat{A} |\psi^{(+)}\rangle = \left[ 1 - \sum_{m=1}^{n_e} \hat{P}_{0,m} \right] |\psi^{(+)}\rangle, \quad (22)$$

where  $\hat{P}_{0,m}$  are the pairwise electron exchange operators defined in Equation 10, and where  $|\psi^{(+)}\rangle \in \mathcal{H}_T \otimes \mathcal{H}$  is the unsymmetrised total wavefunction. As the target states are already anti-symmetric by construction, the anti-symmetriser has assumed a simpler form - requiring only permutations of the unsymmetrised projectile state with the spin-orbital states of the target electrons. Note that we have omitted the  $(1 + n_e)!$  term in  $\hat{A}$ , since it is a scalar term which can be normalised away when required.

To construct the unsymmetrised total wavefunction  $|\psi^{(+)}\rangle$  we perform a multichannel expansion, projecting it onto the target pseudostates,

$$|\psi^{(N,+)}\rangle = \hat{I}_T^{(N)} |\psi^{(+)}\rangle = \sum_{n=1}^{N_T} |\Phi_n^{(N)}\rangle \langle \Phi_n^{(N)} | \psi^{(+)} \rangle = \sum_{n=1}^{N_T} |\Phi_n^{(N)}\rangle F_n^{(N)}, \quad (23)$$

where  $|F_n^{(N)}\rangle = \langle \Phi_n^{(N)} | \psi^{(+)} \rangle$  are the multichannel weight functions, and note that as a result of Equation 19, that

$$|\psi^{(+)}\rangle = \lim_{N \rightarrow \infty} \hat{I}_T^{(N)} |\psi^{(+)}\rangle = \lim_{N \rightarrow \infty} |\psi^{(N,+)}\rangle. \quad (24)$$

Similarly, the total wavefunction constructed from the projection of the unsymmetrised total wavefunction onto the target pseudostates is written in the form

$$|\Psi^{(N,+)}\rangle = \hat{A} |\psi^{(N,+)}\rangle = \left[ 1 - \sum_{m=1}^{n_e} \hat{P}_{0,m} \right] |\psi^{(N,+)}\rangle, \quad (25)$$

and we note that as a result of Equation 19, that

$$|\Psi^{(+)}\rangle = \lim_{N \rightarrow \infty} |\Psi^{(N,+)}\rangle. \quad (26)$$

However, after projecting the unsymmetrised total wavefunction with the projection operator for the target pseudostates, the multichannel expansion is not uniquely defined, since for any state  $|\omega^{(N)}\rangle \in \ker(\hat{A}\hat{I}_T^{(N)})$  and scalar  $\alpha \in \mathbb{C}$ , the multichannel expansion of  $|\psi^{(N,+)}\rangle + \alpha |\omega^{(N)}\rangle$  will be identical to that of  $|\psi^{(N,+)}\rangle$ . To resolve this dilemma, we first note that the multichannel weight functions  $|F_n^{(N)}\rangle$  are within the span of the one-electron spin orbitals  $\{|\chi_i^{(N)}\rangle\}_{i=1}^{2N}$ , used to construct



the Slater determinants, Equation 14, with which the target states are expanded. Hence, we impose the constraint that for any of the one-electron spin orbitals  $|\chi_i^{(N)}\rangle$ , that

$$\hat{P}_{0,m} |\Phi_n^{(N)} \chi_i^{(N)}\rangle = - |\Phi_n^{(N)} \chi_i^{(N)}\rangle. \quad (27)$$

which can be seen as an explicit imposition of Equation 10. With this constraint in place, it can then be shown that  $\dim \ker(\hat{A}\hat{I}_T^{(N)}) = 0$ , whence it follows that the multichannel expansion of  $|\psi^{(N,+)}\rangle$  is now unique in determining  $|\Psi^{(N,+)}\rangle$ .

### 2.1.4 Convergent Close-Coupling Equations

We present a derivation for the Convergent Close-Coupling (CCC) equations, beginning with the Schrödinger equation for the total wavefunction  $|\Psi^{(+)}\rangle$  presented in Equation 20. This shall be re-arranged to yield the Lippmann-Schwinger equation, which will then be solved using the CCC formalism to obtain the matrix elements of the  $\hat{T}$  operator - with which scattering statistics can be calculated.

**Lippmann-Schwinger Equation** We consider an eigenstate  $|\Psi\rangle$  of a Hamiltonian  $\hat{H}$ , with eigenenergy  $E$ , for which the Schrödinger equation is of the form

$$\hat{H} |\Psi\rangle = \hat{H}_A |\Psi\rangle + \hat{V} |\Psi\rangle = E |\Psi\rangle, \quad (28)$$

where  $\hat{H}_A$  is the unbounded asymptotic Hamiltonian and  $\hat{V}$  is a potential. This expression can be rearranged to the form

$$[E - \hat{H}_A] |\Psi\rangle = \hat{V} |\Psi\rangle. \quad (29)$$

Suppose that  $\{|\Omega_\alpha\rangle\}$  are the (countably and uncountably infinite) eigenstates of the asymptotic Hamiltonian, with corresponding eigenvalues  $\varepsilon_\alpha$ ,

$$\hat{H}_A |\Omega_\alpha\rangle = \varepsilon_\alpha |\Omega_\alpha\rangle. \quad (30)$$

We note that where  $\varepsilon_\alpha = E$ , it follows that  $|\Omega_\alpha\rangle \in \ker(E - \hat{H}_A)$ ; for a given energy  $E$ , we denote these particular asymptotic states by  $|\Omega_\alpha^{(E)}\rangle$  and say that they are on-shell states, and that the energies of these states are on-shell. We now define the Green's operator  $\hat{G}_{(E)}$ , to be such that

$$\hat{G}_{(E)}[E - \hat{H}_A] = \hat{I} = [E - \hat{H}_A]\hat{G}_{(E)}, \quad (31)$$

whence we obtain a general form of the Lippmann-Schwinger equation,

$$|\Psi\rangle = \sum_{\alpha: \varepsilon_\alpha = E} \int C_\alpha |\Omega_\alpha^{(E)}\rangle + \hat{G}_{(E)} \hat{V} |\Psi\rangle, \quad (32)$$

where  $C_\alpha$  are arbitrary scalar coefficients. We note that in this context, the sum taken over the indexes of the asymptotic eigenstates represents a sum over the countably infinite states, and an integration over the uncountably infinite states, for which the eigenenergy  $\varepsilon_\alpha$  is equal to  $E$ . The inclusion of the selected asymptotic eigenstates is required as they are in the kernel of  $[E - \hat{H}_A]$ , thus

forming the homogenous solutions to the Lippmann-Schwinger equation. This can be demonstrated by applying the operator  $[E - \hat{H}_A]$  on the left of Equation 32,

$$\begin{aligned} [E - \hat{H}_A] |\Psi\rangle &= \sum_{\alpha: \varepsilon_\alpha = E} \int C_\alpha [E - \hat{H}_A] |\Omega_\alpha^{(E)}\rangle + [E - \hat{H}_A] \hat{G}_{(E)} \hat{V} |\Psi\rangle \\ &= \sum_{\alpha: \varepsilon_\alpha = E} \int C_\alpha |0\rangle + \hat{I} \hat{V} |\Psi\rangle \\ &= \hat{V} |\Psi\rangle. \end{aligned}$$

At this point, we note that selecting the values of the coefficients  $C_\alpha$  amounts to specifying a boundary condition for the eigenstate  $|\Psi\rangle$ . By consequence of the linearity of Equation 32, we may therefore simplify the generalised sum/integral, without loss of generality, by considering eigenstates of the form

$$|\Psi_\alpha\rangle = |\Omega_\alpha^{(E)}\rangle + \hat{G}_{(E)} \hat{V} |\Psi_\alpha\rangle, \quad (33)$$

for a particular  $|\Omega_\alpha^{(E)}\rangle \in \ker(E - \hat{H}_A)$ , and we say that  $|\Psi_\alpha\rangle$  is the eigenstate of  $\hat{H}$  corresponding to the boundary condition specified by the asymptotic eigenstate  $|\Omega_\alpha^{(E)}\rangle$ . We now define the  $\hat{T}$  operator to be such that

$$|\Psi_\alpha\rangle = [\hat{I} + \hat{G}_{(E)} \hat{T}] |\Omega_\alpha^{(E)}\rangle, \quad (34)$$

which is equivalently defined by writing

$$\hat{T} |\Omega_\alpha^{(E)}\rangle = \hat{V} |\Psi_\alpha\rangle. \quad (35)$$

Furthermore, we have that

$$\begin{aligned} |\Psi_\alpha\rangle &= |\Omega_\alpha^{(E)}\rangle + \hat{G}_{(E)} \hat{V} |\Psi_\alpha\rangle \\ &= |\Omega_\alpha^{(E)}\rangle + \hat{G}_{(E)} \hat{V} [\hat{I} + \hat{G}_{(E)} \hat{T}] |\Omega_\alpha^{(E)}\rangle \\ &= [\hat{I} + \hat{G}_{(E)} \hat{V} + \hat{G}_{(E)} \hat{V} \hat{G}_{(E)} \hat{T}] |\Omega_\alpha^{(E)}\rangle \\ &= [\hat{I} + \hat{G}_{(E)} (\hat{V} + \hat{V} \hat{G}_{(E)} \hat{T})] |\Omega_\alpha^{(E)}\rangle, \end{aligned}$$

whence it follows that  $\hat{T}$  can be written in the form

$$\hat{T} |\Omega_\alpha^{(E)}\rangle = [\hat{V} + \hat{V} \hat{G}_{(E)} \hat{T}] |\Omega_\alpha^{(E)}\rangle, \quad (36)$$

yielding the formulation of the Lippmann-Schwinger equation in terms of the  $\hat{T}$  operator. At this point we consider the explicit form of the Green's operator  $\hat{G}_{(E)}$ . First, we note that the asymptotic eigenstates are complete in the sense that they provide a resolution of the identity

$$\hat{I} = \sum_\gamma \int |\Omega_\gamma\rangle \langle \Omega_\gamma|, \quad (37)$$

and a spectral decomposition of the asymptotic Hamiltonian

$$\hat{H}_A = \sum_\gamma \int \varepsilon_\gamma |\Omega_\gamma\rangle \langle \Omega_\gamma|.$$

It therefore follows from the definition of the Green's operator, [Equation 31](#), that we must have

$$\begin{aligned} \hat{G}_{(E)}[E - \hat{H}_A] &= \hat{I} \\ \sum_{\gamma} \int (E - \varepsilon_{\gamma}) \hat{G}_{(E)} |\Omega_{\gamma}\rangle \langle \Omega_{\gamma}| &= \sum_{\gamma} \int |\Omega_{\gamma}\rangle \langle \Omega_{\gamma}|, \end{aligned}$$

whence it follows that the spectral decomposition of the Green's operator is of the form

$$\hat{G}_{(E)} = \sum_{\gamma} \int \frac{|\Omega_{\gamma}\rangle \langle \Omega_{\gamma}|}{E - \varepsilon_{\gamma}}. \quad (38)$$

However, this expression is not well-defined, as it is singular for the asymptotic states  $|\Omega_{\gamma}^{(E)}\rangle$  for which  $\varepsilon_{\gamma} = E$ . This problem can be overcome by regularising the Green's operator to either the incoming  $\hat{G}_{(E,-)}$  or outgoing  $\hat{G}_{(E,+)}$  forms,

$$\hat{G}_{(E,\pm)} = \lim_{\eta \rightarrow 0} \sum_{\gamma} \int \frac{|\Omega_{\gamma}\rangle \langle \Omega_{\gamma}|}{E - \varepsilon_{\gamma} \pm i\eta} = \sum_{\gamma} \int \frac{|\Omega_{\gamma}\rangle \langle \Omega_{\gamma}|}{E - \varepsilon_{\gamma} \pm i0}, \quad (39)$$

where the presence of the imaginary limit ensures that the integral is well-defined for all  $\varepsilon_{\gamma}$ . We elect to use the outgoing Green's operator  $\hat{G}_{(E,+)}$  as we are concerned with the outgoing behaviour of the eigenstate  $|\Psi_{\alpha}^{(+)}\rangle$ . We can now re-write the Lippmann-Schwinger equation in the following form

$$\langle \Omega_{\alpha} | \hat{T} | \Omega_{\beta}^{(E)} \rangle = \langle \Omega_{\alpha} | \hat{V} | \Omega_{\beta}^{(E)} \rangle + \sum_{\gamma} \int \frac{\langle \Omega_{\alpha} | \hat{V} | \Omega_{\gamma} \rangle \langle \Omega_{\gamma} | \hat{T} | \Omega_{\beta}^{(E)} \rangle}{E - \varepsilon_{\gamma} + i0}, \quad (40)$$

which expresses the representation of the operator  $\hat{T}$ , for a given energy  $E$ , in terms of the asymptotic eigenstates  $\{|\Omega_{\alpha}\rangle\}$  and the on-shell asymptotic eigenstates  $\{|\Omega_{\beta}^{(E)}\rangle\}$ .

**Convergent Close-Coupling Formalism** In the Convergent Close-Coupling formalism, the Lippmann-Schwinger equation in terms of the  $\hat{T}$  operator, [Equation 40](#), is solved in momentum space. We preface this discussion with a minor note, that the notation for the asymptotic Hamiltonian  $\hat{H}_A$  is to be distinguished from the notation for the anti-symmetriser  $\hat{A}$ .

We split the Hamiltonian, from [Equation 21](#), into an asymptotic Hamiltonian and a potential in the form

$$\hat{H} = \hat{H}_T + \hat{K}_0 + \hat{V}_0 + \sum_{m=1}^{n_e} \hat{V}_{0,m} = \hat{H}_A + \hat{W}, \quad (41)$$

where the asymptotic Hamiltonian is of the form

$$\hat{H}_A = \hat{H}_T + \hat{K}_0 + \hat{U}_0, \quad (42)$$

and where the potential, modelling the interaction between the projectile and target states, is of the form

$$\hat{W} = \hat{V}_0 + \sum_{m=1}^{n_e} \hat{V}_{0,m} - \hat{U}_0, \quad (43)$$

where  $\hat{U}_0$  is an asymptotic potential acting on the projectile, which can be chosen arbitrarily. A suitable choice for this potential is that of a Coulomb potential with a charge corresponding to the asymptotic charge of the target system, whence  $\langle \mathbf{r} | \hat{W} \rangle = W(r, \Omega) \rightarrow 0$  as  $r \rightarrow \infty$ . Such a selection for  $\hat{U}_0$  adapts the projectile states to the target system, without loss of generality, and can lead to improvement in computational performance, as discussed in [20, 204].

The asymptotic eigenstates are therefore taken to be of the form

$$|\Omega_\alpha\rangle = |\Phi_\alpha \mathbf{k}_\alpha\rangle \approx |\Phi_{n_\alpha}^{(N)} \mathbf{k}_\alpha\rangle, \quad (44)$$

where  $\{|\Phi_n^{(N)}\rangle\}_{i=1}^{N_T}$  are the target pseudostates, defined in Equation 16, which satisfy

$$\langle \Phi_i^{(N)} | \hat{H}_T | \Phi_j^{(N)} \rangle = \epsilon_i^{(N)} \delta_{i,j}, \quad (45)$$

and where  $|\mathbf{k}_\alpha\rangle$  are the continuum waves (which could be plane, distorted, or Coulomb waves depending on the choice of  $\hat{U}_0$ ), defined to be eigenstates of the projectile component of the asymptotic Hamiltonian,

$$[\hat{K}_0 + \hat{U}_0] |\mathbf{k}_\alpha\rangle = \frac{1}{2} k_\alpha^2 |\mathbf{k}_\alpha\rangle, \quad (46)$$

whence it can be seen that the asymptotic eigenenergies are of the form

$$\varepsilon_\alpha = \epsilon_{n_\alpha} + \frac{1}{2} k_\alpha^2 \approx \epsilon_{n_\alpha}^{(N)} + \frac{1}{2} k_\alpha^2. \quad (47)$$

Furthermore, the total wavefunction is taken to be of the form

$$|\Psi_\alpha^{(+)}\rangle = \hat{A} |\psi_\alpha^{(+)}\rangle \approx \hat{A} \hat{I}_T^{(N)} |\psi_\alpha^{(+)}\rangle = \hat{A} |\psi_\alpha^{(N,+)}\rangle = |\Psi_\alpha^{(N,+)}\rangle, \quad (48)$$

as in Equation 22, where  $\hat{A}$  is the anti-symmetriser operator, defined in Equation 8, and is subject to the constraints imposed in Equation 27 to ensure uniqueness. We note that with these expressions for the asymptotic eigenstates and the total wavefunction, that the  $\hat{T}$  operator is related to the potential  $\hat{W}$  by the expression

$$\hat{T} |\Phi_{n_\alpha}^{(N)} \mathbf{k}_\alpha\rangle = \hat{W} |\Psi_\alpha^{(N,+)}\rangle = \hat{W} \hat{A} \hat{I}_T^{(N)} |\psi_\alpha^{(+)}\rangle = \hat{W} \hat{A} |\psi_\alpha^{(N,+)}\rangle. \quad (49)$$

However, it is possible to recast the potential  $\hat{W}$  in a form  $\hat{V}$  which accounts for the explicit anti-symmetrisation of the total wavefunction; that is, which allows us to write the CCC equations without direct reference to the anti-symmetriser  $\hat{A}$ . To do this, we first note that

$$0 = [E - \hat{H}] |\Psi_\alpha^{(+)}\rangle = [E - \hat{H}] \hat{A} |\psi_\alpha^{(+)}\rangle,$$

with the operator on the right hand side expanding to the form

$$[E - \hat{H}] \hat{A} = \left[ E - \hat{H} - [E - \hat{H}] \sum_{m=1}^{n_e} \hat{P}_{0,m} \right] = \left[ E - \hat{H}_A - \hat{W} - [E - \hat{H}] \sum_{m=1}^{n_e} \hat{P}_{0,m} \right],$$

where again we make sure to distinguish the notation for the asymptotic Hamiltonian  $\hat{H}_A$  and the anti-symmetriser  $\hat{A}$ . We therefore define the explicitly anti-symmetrised potential  $\hat{V}$  to be of the form

$$\hat{V} = \hat{W} + [E - \hat{H}] \sum_{m=1}^{n_e} \hat{P}_{0,m} = \hat{V}_0 + \sum_{m=1}^{n_e} \hat{V}_{0,m} - \hat{U}_0 + [E - \hat{H}] \sum_{m=1}^{n_e} \hat{P}_{0,m}, \quad (50)$$

for which we can see that

$$0 = [E - \hat{H}] \hat{A} |\psi_\alpha^{(+)}\rangle = [E - [\hat{H}_A + \hat{V}]] |\psi_\alpha^{(+)}\rangle,$$

which is to say that the Lippmann-Schwinger equation [Equation 40](#) can be written in terms of the unsymmetrised total wavefunction  $|\psi_\alpha^{(+)}\rangle$ , rather than the anti-symmetric total wavefunction  $|\Psi_\alpha^{(+)}\rangle$ . Specifically, this allows us to write the  $\hat{T}$  operator in the form

$$\hat{T} |\Phi_{n_\alpha}^{(N)} \mathbf{k}_\alpha\rangle = \hat{V} \hat{I}_T^{(N)} |\psi_\alpha^{(+)}\rangle = \hat{V} |\psi_\alpha^{(N,+)}\rangle. \quad (51)$$

We then have the Convergent Close-Coupling equations in terms of the  $\hat{T}$  operator

$$\begin{aligned} \langle \mathbf{k}_f \Phi_{n_f}^{(N)} | \hat{T} | \Phi_{n_i}^{(N)} \mathbf{k}_i \rangle &= \langle \mathbf{k}_f \Phi_{n_f}^{(N)} | \hat{V} | \Phi_{n_i}^{(N)} \mathbf{k}_i \rangle \\ &+ \sum_{n=1}^{N_T} \int d\mathbf{k} \frac{\langle \mathbf{k}_f \Phi_{n_f}^{(N)} | \hat{V} | \Phi_n^{(N)} \mathbf{k} \rangle \langle \mathbf{k} \Phi_n^{(N)} | \hat{T} | \Phi_{n_i}^{(N)} \mathbf{k}_i \rangle}{E - \epsilon_n^{(N)} - \frac{1}{2}k^2 \pm i0}, \end{aligned} \quad (52)$$

forming a set of  $\mathbb{C}$ -valued matrix equations which are numerically solved to yield the  $T$  matrix, from which information about the total wavefunction  $|\Psi_i^{(N,+)}\rangle$  can be derived. However, it is possible to re-write the Convergent Close-Coupling equations in terms of an operator  $\hat{K}$ ,

$$\begin{aligned} \langle \mathbf{k}_f \Phi_{n_f}^{(N)} | \hat{K} | \Phi_{n_i}^{(N)} \mathbf{k}_i \rangle &= \langle \mathbf{k}_f \Phi_{n_f}^{(N)} | \hat{V} | \Phi_{n_i}^{(N)} \mathbf{k}_i \rangle \\ &+ \sum_{n=1}^{N_T} \mathcal{P} \int d\mathbf{k} \frac{\langle \mathbf{k}_f \Phi_{n_f}^{(N)} | \hat{V} | \Phi_n^{(N)} \mathbf{k} \rangle \langle \mathbf{k} \Phi_n^{(N)} | \hat{K} | \Phi_{n_i}^{(N)} \mathbf{k}_i \rangle}{E - \epsilon_n^{(N)} - \frac{1}{2}k^2}, \end{aligned} \quad (53)$$

where  $\mathcal{P}$  indicates that the principal value of the integral is taken, which forms a set of  $\mathbb{R}$ -valued matrix equations which can be solved more efficiently, to yield the  $K$  matrix. The  $T$  matrix can then be reconstructed from the  $K$  matrix by the identity [\[7, 9\]](#)

$$\langle \mathbf{k}_f \Phi_{n_f}^{(N)} | \hat{K} | \Phi_{n_i}^{(N)} \mathbf{k}_i \rangle = \sum_{n=1}^{N_T} \langle \mathbf{k}_f \Phi_{n_f}^{(N)} | \hat{T} | \Phi_n^{(N)} \mathbf{k}_n \rangle (\delta_{n,i} + i\pi k_n \langle \mathbf{k}_n \Phi_n^{(N)} | \hat{K} | \Phi_{n_i}^{(N)} \mathbf{k}_i \rangle), \quad (54)$$

where  $k_n$  are the on-shell projectile momenta which satisfy

$$E = \epsilon_n^{(N)} + \frac{1}{2}k_n^2 \quad \text{for } n = 1, \dots, N_T. \quad (55)$$

We note that the matrix equations [Equation 52](#), as well as [Equation 53](#) and [Equation 54](#), are computationally parameterised by the set of target pseudostates  $\{|\Phi_n^{(N)}\rangle\}_{n=1}^{N_T}$  and the discretisation of the projectile spectrum. In turn, the target pseudostates are parameterised by the number of Slater determinants  $N_T$  used in their construction, and the number of basis functions  $N$  used to construct the one-electron orbitals from which the Slater determinants are built. Furthermore, we note that matrix equations in this form do not explicitly include the constraints, detailed in [Equation 27](#), which guarantee the uniqueness of the explicitly anti-symmetrised multichannel expansion. The manifestation of these constraints for the case of a hydrogen target is discussed in [subsubsection 3.1.2](#).

## 2.2 Scattering Statistics

At this point, we shall make use of the S-wave model, wherein all partial wave expansions are limited to the  $l = 0$  terms; this has the effect of restricting our attention to asymptotic eigenstates  $|\Phi_n^{(N)}\mathbf{k}\rangle$  for which the target pseudostate has  $l = 0$ . This allows for a simpler presentation of the theory, and a significant reduction in computational complexity. Furthermore, calculations performed in the S-wave model are sufficient for the emergence of scattering phenomena which is of interest in this project. Much of the following treatment is generalisable to the inclusion of arbitrary angular momentum.

Lastly, we note that many of the following statistics can be constructed for a particular symmetry of the system which is conserved by the scattering process; examples include total spin and angular momentum. We shall refrain from specifying the forms of these statistics for specific symmetries, in lieu of providing a clearer, more general treatment.

### 2.2.1 Scattering Amplitudes

Once calculated, the matrix elements of the  $\hat{T}$  operator yield the transition amplitudes between asymptotic states, which can then be used to calculate the scattering amplitudes. In general terms, the scattering amplitudes can be written in the form

$$f_{\alpha,\beta} = f_{\alpha,\beta}(\mathbf{k}_\alpha, \mathbf{k}_\beta) = \langle \mathbf{k}_\alpha \Phi_\alpha | \hat{V} | \Psi_\beta \rangle = \langle \mathbf{k}_\alpha \Phi_\alpha | \hat{T} | \Phi_\beta \mathbf{k}_\beta \rangle, \quad (56)$$

where the target state  $|\Phi_\alpha\rangle$  can be a bounded discrete state or an unbounded continuum state, corresponding to either an elastic scattering / a discrete excitation transition, or an ionisation transition. For discrete excitations, the numerically calculated scattering amplitude is simply of the form

$$f_{f,i}^{(N)} = f_{n_f,n_i}^{(N)}(\mathbf{k}_f, \mathbf{k}_i) = \langle \mathbf{k}_f \Phi_{n_f}^{(N)} | \hat{T} | \Phi_{n_i}^{(N)} \mathbf{k}_i \rangle, \quad (57)$$

for on-shell transitions,

$$\epsilon_{n_f}^{(N)} + \frac{1}{2}k_f^2 = E = \epsilon_{n_i}^{(N)} + \frac{1}{2}k_i^2, \quad (58)$$

with elastic scattering occurring in the case where  $n_f = n_i$ ,

$$f_i^{(N)}(\mathbf{k}_f, \mathbf{k}_i) = f_{n_i,n_i}^{(N)}(\mathbf{k}_f, \mathbf{k}_i) = \langle \mathbf{k}_f \Phi_{n_i}^{(N)} | \hat{T} | \Phi_{n_i}^{(N)} \mathbf{k}_i \rangle. \quad (59)$$

However, the numerically calculated scattering amplitudes for ionisations require a more carefully considered treatment - which we present in a form similar to that described in [8, 19]. We shall restrict our attention to the case of single ionisation, but leave open the consideration of ionisation with excitation. The ionised asymptotic state  $|\Phi_\alpha \mathbf{k}_\alpha\rangle$  corresponds to the breakup of the target state  $|\Phi_\alpha\rangle$  into a singly-ionised target state  $|\Phi_{n_\alpha}^+\rangle$  (which may be excited) and an ionised electron in the form of a Coulomb wave  $|\mathbf{q}_\alpha\rangle$ ; that is,

$$|\Phi_\alpha \mathbf{k}_\alpha\rangle = |\Phi_{n_\alpha}^+ \mathbf{q}_\alpha \mathbf{k}_\alpha\rangle, \quad (60)$$

where the energy of the ionised asymptotic state is of the form

$$E = \epsilon_\alpha + \frac{1}{2}k_\alpha^2 = \epsilon_{n_\alpha}^+ + \frac{1}{2}q_\alpha^2 + \frac{1}{2}k_\alpha^2 \quad (61)$$

where  $\epsilon_{n_\alpha}^+$  is the energy of the singly-ionised target state, and where  $\frac{1}{2}q_\alpha^2$  is the energy of the Coulomb wave. It is important to note that in this formulation, the asymptotic state  $|\Phi_\alpha \mathbf{k}_\alpha\rangle$  separates into

the asymptotic projectile state  $|\mathbf{k}_\alpha\rangle$  and the asymptotic target state  $|\Phi_\alpha\rangle = |\Phi_{n_\alpha}^+ \mathbf{q}_\alpha\rangle$ , within which the Coulomb wave  $|\mathbf{q}_\alpha\rangle$  is modelled - thus excluding from consideration a three-body boundary condition. This presents an issue however as Coulomb waves are not bounded states, and thus their coordinate-space representations are not elements of  $L^2(\mathbb{R}^3)$ . This is the space wherein the coordinate-space representations of the one-electron states, comprising the target pseudostates, are spanned in terms of the Laguerre basis, Equation 1. However it can be shown, as discussed in [7], that while the projection of a continuum wave onto a  $N$ -dimensional Laguerre basis is only conditionally convergent as  $N$  increases, it is numerically stable. Hence, for ionisations, the numerically calculated scattering amplitude can be written in the form

$$\begin{aligned} f_{\alpha,i}^{(N)} &= f_{n_\alpha,n_i}^{(N)}(\mathbf{k}_\alpha, \mathbf{q}_\alpha, \mathbf{k}_i) = \langle \mathbf{k}_\alpha \mathbf{q}_\alpha \Phi_{n_\alpha}^+ | \hat{I}_T^{(N)} \hat{T} | \Phi_{n_i}^{(N)} \mathbf{k}_i \rangle \\ &= \sum_{n=1}^{N_T} \langle \mathbf{k}_\alpha \mathbf{q}_\alpha \Phi_{n_\alpha}^+ | \Phi_n^{(N)} \rangle \langle \Phi_n^{(N)} | \hat{T} | \Phi_{n_i}^{(N)} \mathbf{k}_i \rangle \\ &= \sum_{n=1}^{N_T} \langle \mathbf{q}_\alpha \Phi_{n_\alpha}^+ | \Phi_n^{(N)} \rangle \langle \mathbf{k}_\alpha \Phi_n^{(N)} | \hat{T} | \Phi_{n_i}^{(N)} \mathbf{k}_i \rangle. \end{aligned} \quad (62)$$

However, this expression is problematic as it involves a summation over not necessarily on-shell terms  $\langle \mathbf{k}_\alpha \Phi_n^{(N)} |$ . If we restrict our attention to only evaluating the ionisation scattering amplitudes  $f_{\alpha,i}^{(N)}$  for ionised asymptotic states  $|\Phi_{n_\alpha}^+ \mathbf{q}_\alpha \mathbf{k}_\alpha\rangle$  for which the ionised target energy satisfies

$$\epsilon_\alpha = \epsilon_{n_\alpha}^+ + \frac{1}{2} q_\alpha^2 = \epsilon_{n_\alpha}^{(N)}, \quad (63)$$

for one of the target pseudoenergies  $\epsilon_{n_\alpha}^{(N)}$ , corresponding to the target pseudostate  $|\Phi_{n_\alpha}^{(N)}\rangle$ , then we must have that

$$\langle \mathbf{q}_\alpha \Phi_{n_\alpha}^+ | \Phi_n^{(N)} \rangle = \delta_{n_\alpha,n} \langle \mathbf{q}_\alpha \Phi_{n_\alpha}^+ | \Phi_n^{(N)} \rangle, \quad (64)$$

whence the ionisation scattering amplitudes can be evaluated as

$$f_{n_\alpha,n_i}^{(N)}(\mathbf{k}_\alpha, \mathbf{q}_\alpha, \mathbf{k}_i) = \langle \mathbf{q}_\alpha \Phi_{n_\alpha}^+ | \Phi_{n_\alpha}^{(N)} \rangle \langle \mathbf{k}_\alpha \Phi_{n_\alpha}^{(N)} | \hat{T} | \Phi_{n_i}^{(N)} \mathbf{k}_i \rangle, \quad (65)$$

at these  $q_\alpha$  which satisfy Equation 63.

However, we note that a consequence of the assumed separability of the asymptotic state in Equation 44 is that the anti-symmetrisation of the asymptotic state is neglected. Clearly this cannot be entirely neglected in the case of ionisation resulting in two unbounded electron states, even if one is screened by the other. Inclusion of the anti-symmetrisation of the ionised asymptotic state, with respect to the two unbounded electron states, results in the transformation

$$|\Phi_{n_\alpha}^+ \mathbf{q}_\alpha \mathbf{k}_\alpha\rangle \mapsto [1 - \hat{P}_{0,n_e}] |\Phi_{n_\alpha}^+ \mathbf{q}_\alpha \mathbf{k}_\alpha\rangle = |\Phi_{n_\alpha}^+ \mathbf{q}_\alpha \mathbf{k}_\alpha\rangle - e^{i\theta_\alpha} |\Phi_{n_\alpha}^+ \mathbf{k}_\alpha \mathbf{q}_\alpha\rangle, \quad (66)$$

where  $\theta_\alpha \in \{0, \pi\}$  is the exchange phase, corresponding to the exchange of the projectile and ionised electron states. Whence, as described in [3, 4, 8], we perform an ad-hoc anti-symmetrisation of the scattering amplitude to account for this, resulting in a corrected ionisation amplitude  $F_{n_\alpha,n_i}^{(N)}$  of the form

$$F_{n_\alpha,n_i}^{(N)}(\mathbf{k}_\alpha, \mathbf{q}_\alpha, \mathbf{k}_i) = f_{n_\alpha,n_i}^{(N)}(\mathbf{k}_\alpha, \mathbf{q}_\alpha, \mathbf{k}_i) - e^{-i\theta_\alpha} f_{n_\alpha,n_i}^{(N)}(\mathbf{q}_\alpha, \mathbf{k}_\alpha, \mathbf{k}_i), \quad (67)$$

and which satisfies

$$F_{n_\alpha,n_i}^{(N)}(\mathbf{k}_\alpha, \mathbf{q}_\alpha, \mathbf{k}_i) = -e^{-i\theta_\alpha} F_{n_\alpha,n_i}^{(N)}(\mathbf{q}_\alpha, \mathbf{k}_\alpha, \mathbf{k}_i). \quad (68)$$

We note that in the CCC method, we refer to  $f_{\alpha,i}^{(N)}$  as the ionisation amplitudes (or as the unsymmetrised ionisation amplitudes when specificity is required), and we refer to  $F_{\alpha,i}^{(N)}$  as the anti-symmetrised ionisation amplitudes. We note that while the anti-symmetrised ionisation amplitudes are used for comparison with experimental results, we make reference to the unsymmetrised ionisation amplitudes in the discussion of ionisation in the CCC method in [section 3](#). Lastly, we note that we are constrained to evaluating these amplitudes only for a countable number of outgoing projectile energies, bound by the constraint defined in [Equation 63](#). Evaluating the ionisation scattering amplitudes at any other energy requires an interpolation between these energies.

### 2.2.2 Cross Sections

We present expressions for the partial and total cross sections, in a manner similar to [\[7, 10\]](#). In general terms, the partial cross sections are of the form

$$\sigma_{\alpha,\beta} = \sigma_{\alpha,\beta}(\mathbf{k}_\alpha, \mathbf{k}_\beta) = \frac{k_\alpha}{k_\beta} |f_{\alpha,\beta}|^2 = \frac{k_\alpha}{k_\beta} |\langle \mathbf{k}_\alpha \Phi_\alpha | \hat{T} | \Phi_\beta \mathbf{k}_\beta \rangle|^2, \quad (69)$$

with the specific notation for elastic, discrete excitation, and ionisation cross sections paralleling the notation used in [Equation 57](#), [Equation 59](#), and [Equation 62](#) respectively.

The total cross section (TCS), for a given initial asymptotic state, is obtained as a sum of all partial cross sections for which the outgoing asymptotic projectile energy is positive,

$$\sigma_{T;i}^{(N)} = \sum_{f:k_f>0} \sigma_{f,i}^{(N)}, \quad (70)$$

while the total ionisation cross section (TICS), for a given initial asymptotic state, is obtained as a sum of all partial cross sections for which the outgoing asymptotic target state is positive (and thus unbounded),

$$\sigma_{I;i}^{(N)} = \sum_{f:k_f>0, \epsilon_\alpha^{(N)}>0} \sigma_{\alpha,i}^{(N)}. \quad (71)$$

We also consider the various differential cross sections in the context of ionisation transitions, following in the form of [\[21\]](#). Evaluating the partial cross sections, for an ionisation transition, yields the triple-differential cross section (TDCS),

$$\frac{d\sigma_{\alpha,i}^{(N)}}{d\Omega_{k_\alpha} d\Omega_{q_\alpha} de_{q_\alpha}}(\mathbf{k}_\alpha, \mathbf{q}_\alpha, \mathbf{k}_i) = \frac{k_\alpha q_\alpha}{k_i} |F_{n_\alpha, n_i}^{(N)}(\mathbf{k}_\alpha, \mathbf{q}_\alpha, \mathbf{k}_i)|^2, \quad (72)$$

where  $e_{q_\alpha} = \frac{1}{2}q_\alpha^2 \in [0, E - \epsilon_{n_\alpha}^+]$  is the energy of the outgoing projectile electron, and where  $\Omega = (\theta, \phi)$  refers to the spherical coordinates of momentum-space. Integrating the TDCS over the spherical coordinates of either the outgoing asymptotic projectile electron, or the outgoing ionised target electron, yields the double-differential cross section (DDCS). Furthermore, integrating the DDCS over the spherical coordinates of the remaining electron, whichever one that may be, yields the single-differential cross section (SDCS), which is of the form

$$\frac{d\sigma_{\alpha,i}^{(N)}}{de_{q_\alpha}}(e_{q_\alpha}) = \frac{k_\alpha q_\alpha}{k_i} \int_{S^2} d\Omega_{k_\alpha} \int_{S^2} d\Omega_{q_\alpha} |F_{n_\alpha, n_i}^{(N)}(\mathbf{k}_\alpha, \mathbf{q}_\alpha, \mathbf{k}_i)|^2, \quad (73)$$

where we recall that the energies of the incoming and outgoing projectile states, as well as the ionised electron state, are constrained to be on-shell as specified in [Equation 61](#). Integration of the SDCS over the projectile (or target) electron energy yields the total ionisation cross section.



### 3 Survey of Literature

Having now established the framework of the CCC method for electron-impact scattering on atomic/ionic targets, as well as the accompanying terminology and notation, we will proceed to examine the literature on extant calculations for hydrogen and helium targets. Specifically, we will discuss the history of the issues, both resolved and unresolved, faced in the calculation of ionisation amplitudes and differential cross sections, within the CCC method.

#### 3.1 Electron-Impact Hydrogen Ionisation

Historically, the CCC method was first developed for and applied to electron scattering on a hydrogen target [1]. It is a well studied problem, being the natural test case for any model or computational method investigating electron scattering on atoms, and as a result many of the scattering phenomena that emerge, or are expected to emerge, are well known and understood. As a consequence, there exists a mature body of experimental and computational data with which to compare. Hence, we will first examine the ionisation amplitudes and differential cross sections in the context of a hydrogen target, before extending to helium targets - noting that many aspects of electron-impact ionisation of helium can be observed in this simpler context.

##### 3.1.1 Considerations for a Hydrogen Target

For a hydrogen target, we note that the total spin  $S \in \{0, 1\}$  of the projectile-target system is conserved by the scattering process. It follows that the (coordinate-and-spin) exchange operator  $\hat{P}_{0,1}$  can thus be written in the form

$$\hat{P}_{0,1}^{(S)} = \hat{R}_{0,1} \hat{X}_{0,1}^{(S)} = (-1)^{S+1} \hat{R}_{0,1}, \quad (74)$$

where  $\hat{R}_{0,1}$  is the coordinate exchange operator, and  $\hat{X}_{0,1}$  is the spin exchange operator. Furthermore, the explicitly anti-symmetrised potential Equation 50 is of the form

$$\hat{V}^{(S)} = \hat{V}_0 + \hat{V}_{0,1} - \hat{U}_0 + [E - \hat{H}] \hat{P}_{0,1}^{(S)} = \hat{V}_0 + \hat{V}_{0,1} - \hat{U}_0 + (-1)^{S+1} [E - \hat{H}] \hat{R}_{0,1}, \quad (75)$$

and, as noted in [7, 5], can be rewritten to manifest the constraint on the multichannel expansion Equation 27, guaranteeing a unique unsymmetrised total wavefunction  $|\psi^{(N,S,+)}\rangle$ , by re-writing  $\hat{V}$  in the form

$$\hat{V}^{(S)}(\theta) = \hat{V}_0 + \hat{V}_{0,1} - \hat{U}_0 - E\theta\hat{I}_0 + (-1)^{S+1} [E(1 - \theta) - \hat{H}] \hat{R}_{0,1}, \quad (76)$$

for arbitrary  $\theta \in \mathbb{R}$  such that  $\theta \neq 0$ . It can be shown that while  $\hat{V}^{(S)}(\theta)$  is dependent on  $\theta$ ,  $\hat{T}^{(S)}$  is not. Furthermore, the anti-symmetrised ionisation amplitudes are of the form

$$F_{n_\alpha, n_i}^{(N)}(\mathbf{k}_\alpha, \mathbf{q}_\alpha, \mathbf{k}_i) = f_{n_\alpha, n_i}^{(N)}(\mathbf{k}_\alpha, \mathbf{q}_\alpha, \mathbf{k}_i) - (-1)^{S+1} f_{n_\alpha, n_i}^{(N)}(\mathbf{q}_\alpha, \mathbf{k}_\alpha, \mathbf{k}_i). \quad (77)$$

##### 3.1.2 Convergent Close-Coupling Calculations

That the CCC method yielded accurate calculations for the TICS, in addition to elastic and discrete excitation cross sections [1], was readily established by Bray and Stelbovics [2]. It was observed however, as discussed by Bray [3], that the differential cross sections (SDCS, DDSCS, TDCS) were not so well behaved, and it was even contemplated if convergence could be achieved for a finite

*Figure 1: Triplet and singlet single-differential cross sections (SDCS) for 2 Ry electron-impact ionisation of hydrogen in S-wave model. The data points, for each CCC calculation, have been connected for visual clarity. Original figure from [3, FIG 2].*

basis size. The behaviour of the SDCS, Equation 73, was representative of the problems faced by all differential cross sections at the time, and is shown in Figure 1.

For the triplet case,  $S = 1$ , the SDCS was seen to tend to zero at the equal-energy-sharing point  $e_{q\alpha} = \frac{1}{2}E$ , and remain zero past this point. This was to be expected as the Pauli's exclusion principle would require that the SDCS be zero at the  $e_{q\alpha} = \frac{1}{2}E$  to avoid the outgoing projectile and ionised electron doubly occupying the same electron state. Furthermore, it can be seen that the restriction of the SDCS being non-zero only for  $e_{q\alpha} \in [0, \frac{1}{2}E)$  avoids double counting the indistinguishable electrons, while the SDCS past this region can be reconstructed from the SDCS within this region due to the symmetry of the system. In a sense, the SDCS across the region  $[0, E]$  is folded up into  $[0, \frac{1}{2}E]$  within the CCC method.

However, for the singlet case,  $S = 0$ , the SDCS exhibited much less regular behaviour and did not display the positive characteristics as seen for the triplet case. The SDCS oscillated dramatically in the region  $e_{q\alpha} \in [0, \frac{1}{2}E)$ , before tending towards zero, but remaining non-zero, past  $e_{q\alpha} = \frac{1}{2}E$ . Expanding the basis size did little to dampen the oscillatory behaviour nor to flatten the SDCS to be non-zero past the equal-energy-sharing point. The issues present in the singlet SDCS were recognised at the time to likely be the result of step-function like behaviour in the SDCS: approaching a non-zero value at the equal-energy-sharing point  $e_{q\alpha} = \frac{1}{2}E$ , followed by a discontinuous step to being uniformly zero in the region  $[\frac{1}{2}E, E]$ . The irregularity in the SDCS can then be seen as a consequence of using a finite-dimensional basis to ultimately represent discontinuous behaviour, which is rarely adequately convergent until a large number of terms are used.

Indeed, this was later shown to be the case by Stelbovics [4], through comparison of the asymptotic form of the ionised total wavefunction obtained by the CCC method, with the form obtained using an analytically-based technique, in the S-wave model. The value of the SDCS at the equal-energy-sharing point, calculated using the CCC method, was also compared with the values obtained by the ECS method [22]. In his analysis, it was demonstrated for the triplet case, that if the ionisation amplitudes converge then they converge correctly. Furthermore, it was demonstrated for the singlet case that the SDCS, calculated at the equal-energy-sharing point using the CCC method, does achieve a good level of agreement with the results obtained with the ECS methods. Most significantly, it was observed that the singlet SDCS did indeed exhibit behaviour similar to a Fourier series of a step function: a slow convergence in the representation of a discontinuous function, non-zero values in a region which should be uniformly zero, and the convergence of the ionisation amplitudes to half the step height at the equal-energy-sharing points, and thus the convergence of the SDCS to one quarter of the step height at this point.

With the underlying cause of the irregular behaviour of the singlet SDCS now understood, the step-like behaviour across all the differential cross sections could be accounted and corrected for, with confidence in the validity of the treatment. This was accomplished by Bray [8], who demonstrated that by adjusting the differential cross sections to account for the behaviour of the Fourier-like expansions of step-like terms, that the CCC method yields ionisation amplitudes and differential cross sections which achieve a great level of agreement with experimental values, as well with calculations obtained using ECS methods. It was also demonstrated that with this adjustment, accurate calculations could be performed using a relatively small basis size. This was demonstrated

not only for electron-impact ionisation of hydrogen, but also for helium (within the frozen core model), as well as for double photoionisation of helium.

### 3.1.3 Ansatz of Zatsarinny and Bartschat

The question of correctness in the treatment of ionisation processes in the CCC method was arguably resolved, having been demonstrated numerically and justified on theoretical grounds. Despite this, there remains the limitation of the ionisation amplitudes only being calculable, in the manner of Equation 65, for the countable number of outgoing projectile electron energies that satisfy Equation 63. This is undesirable, as the calculation of the differential cross sections requires integrating the ionisation amplitudes over continuous sets of values.

To overcome this dilemma, the standard technique used in the CCC method is to calculate the ionisation amplitudes at those points which satisfy Equation 63, and then interpolate between these points, thus allowing the differential cross sections to be calculated. However, this procedure is sensitive to the distribution of target pseudoenergies and may result in interpolating over sparse regions of the outgoing projectile energy.

In light of this, an ansatz has been suggested by Zatsarinny and Bartschat [18] which allows for an alternatively simpler calculation of the ionisation amplitudes. Starting with Equation 62, recall that the numerically calculated (unsymmetrised) ionisation amplitudes are given by the expression

$$f_{n_\alpha, n_i}^{(N)}(\mathbf{k}_\alpha, \mathbf{q}_\alpha, \mathbf{k}_i) = \sum_{n=1}^{N_T} \langle \mathbf{q}_\alpha \Phi_{n_\alpha}^+ | \Phi_n^{(N)} \rangle \langle \mathbf{k}_\alpha \Phi_n^{(N)} | \hat{T} | \Phi_{n_i}^{(N)} \mathbf{k}_i \rangle,$$

with the presence of the off-shell term  $\langle \mathbf{k}_\alpha \Phi_n^{(N)} |$  prohibiting the evaluation of this sum except where  $q_\alpha$  satisfies Equation 63. The suggested ansatz of Zatsarinny and Bartschat, is to instead replace this off-shell term with  $\langle \mathbf{k}_n \Phi_n^{(N)} |$  where  $k_n$  are the on-shell projectile momenta satisfying Equation 55, whence the ionisation amplitudes is instead of the form

$$f_{n_\alpha, n_i}^{(N)}(\mathbf{k}_\alpha, \mathbf{q}_\alpha, \mathbf{k}_i) = \sum_{n=1}^{N_T} \langle \mathbf{q}_\alpha \Phi_{n_\alpha}^+ | \Phi_n^{(N)} \rangle \langle \mathbf{k}_n \Phi_n^{(N)} | \hat{T} | \Phi_{n_i}^{(N)} \mathbf{k}_i \rangle, \quad (78)$$

where the sum can now be evaluated without further restriction. The benefit of this ansatz is that it is not constrained to evaluating the ionisation amplitudes for only certain values of  $q_\alpha$  and can be easily calculated using the on-shell matrix elements of the  $\hat{T}$  operator, already determined in the CCC calculation.

The correctness and the utility of this ansatz was investigated by Bray *et al.* [19] in the context of electron-impact ionisation of hydrogen, within the S-wave model and also with a more general treatment of angular momentum. By comparing the SDCS (and their  $l$  components) resulting from the extant interpolation scheme, with the SDCS resulting from the ansatz, it was shown that while not in perfect agreement, the ansatz did demonstrate an effective level of agreement. In the context of the S-wave model, the SDCS resulting from the ansatz is presented for both the singlet and triplet cases in Figure 2.

Figure 2: Triplet and singlet single-differential cross sections (SDCS) for 54.4 eV electron-impact ionisation of hydrogen in S-wave model. Original figure from [19, FIG 1].

The behaviour of the ansatz in the vicinity of the equal-energy-sharing point for the singlet case raised suspicions on the correctness of the ansatz. As Stelbovics demonstrated [4] for the singlet case in the S-wave model, the ionisation amplitudes exhibit a step-like behaviour about the equal-energy-sharing point, which results in tumultuous behaviour in the CCC calculation as a consequence of the discontinuity. Despite this, the ionisation amplitudes are still expected to converge to half the step height, and thus the SDCS to a quarter of the step height, at the point of equal-energy-sharing. It is therefore notable that the SDCS resulting from the ansatz did not demonstrate any convergence to the expected quarter-step-height value. This characteristic (or lack thereof) of the ansatz was seen to suggest that it does not have a justifiable physical origin, despite of its otherwise acceptable level of agreement.

Overall, the ansatz was suggested to constitute a useful interpolation scheme which could be used with an expectation of accuracy, provided that the target pseudoenergies formed a sufficiently dense discretisation of the outgoing energy continuum. That the ansatz can be readily extended to more complex targets, eliminating the need for the interpolation over ionisation amplitudes while retaining an acceptable level of validity, is what motivates this project.

## 3.2 Electron-Impact Helium Ionisation

Having examined the CCC approach to electron-impact ionisation of hydrogen, the simplest atomic target, we now consider its application to a helium target; this forms the motivation for this project, as we consider the electron-impact ionisation of helium, with and without excitation.

### 3.2.1 Additional Considerations for a Helium Target

Much of the CCC method, derived in subsection 2.1, is naturally extended from a hydrogen target to a helium target. However, the presence of an additional electron does introduce additional complexity in the modelling of target structure, as target states are no longer described in terms of a single wavefunction, but rather a Slater determinant of one-electron wavefunctions - significantly increasing the dimensionality of the calculation. Furthermore, the helium target states can have a total spin  $s_T \in \{0, 1\}$ , which couples with the spin of the projectile electron  $s_0 = \frac{1}{2}$ , increasing the complexity of the spin algebra beyond that encountered for hydrogen.

We have described the construction of Slater determinants and provided a brief overview of how their dimensionality may be handled in subsubsection 2.1.2, however we shall not describe in explicit detail here how they are constructed in the CCC method. For a more detailed treatment of the target structure, and the handling of spin in electron-impact helium collisions, we refer to the work of Fursa, Bray and Stelbovics [9, 10, 11, 23]. Lastly, we note that the explicitly anti-symmetrised potential Equation 50, for a helium target, is of the form

$$\hat{V} = \hat{V}_0 + \hat{V}_{0,1} + \hat{V}_{0,2} - \hat{U}_0 + [E - \hat{H}][\hat{P}_{0,1} + \hat{P}_{0,2}], \quad (79)$$

where it should be reiterated that this potential is modified form of the asymptotic potential, and does not include the potential terms of the helium target Hamiltonian.

**3.2.2 Convergent Close-Coupling Calculations****3.2.3 Exterior-Complex-Scaling Calculations****4 Conclusion**

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