

---

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

---

Tom Ross supervised by Professor Igor Bray

---

[ABSTRACT]

# Contents

<b>1</b>	<b>Introduction</b>	<b>3</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	Projectile States . . . . .	6
2.1.4	Total Wavefunction . . . . .	7
2.1.5	Convergent Close-Coupling Equations . . . . .	8
2.1.6	Transition Amplitudes . . . . .	11
2.1.7	Cross Sections . . . . .	11
2.1.8	S-Wave Model . . . . .	11
2.2	Electron-Impact Hydrogen Scattering . . . . .	11
2.2.1	Elastic Scattering . . . . .	11
2.2.2	Excitation . . . . .	11
2.2.3	Ionisation . . . . .	11
2.3	Electron-Impact Helium Scattering . . . . .	11
2.3.1	Additional Considerations for a Helium Target . . . . .	11
2.3.2	Elastic Scattering . . . . .	11
2.3.3	Excitation . . . . .	11
2.3.4	Ionisation . . . . .	12
<b>3</b>	<b>Survey of Experimental Literature</b>	<b>12</b>
<b>4</b>	<b>Survey of Theoretical Literature</b>	<b>12</b>
4.1	Electron-Impact Hydrogen Ionisation Calculations . . . . .	12
4.1.1	Convergent Close-Coupling Calculations . . . . .	12
4.1.2	Exterior-Complex-Scaling Calculations . . . . .	12
4.1.3	Ansatz of Zatsarinny and Bartschat . . . . .	12
4.2	Electron-Impact Helium Ionisation Calculations . . . . .	12
4.2.1	Convergent Close-Coupling Calculations . . . . .	12
4.2.2	Exterior-Complex-Scaling Calculations . . . . .	12
4.2.3	Ansatz of Zatsarinny and Bartschat . . . . .	12
<b>5</b>	<b>Conclusion</b>	<b>12</b>
<b>A</b>	<b>Properties of Utilised Bases</b>	<b>14</b>
A.1	Spherical Harmonics . . . . .	14
A.1.1	Completeness . . . . .	14
A.2	Laguerre Radial Basis . . . . .	14
A.2.1	Completeness . . . . .	14
A.3	Laguerre Basis . . . . .	14
A.3.1	Completeness . . . . .	14
A.4	Plane Waves . . . . .	14

<b>B Numerical Techniques</b>	<b>14</b>
B.1 Basis Expansion . . . . .	14
B.2 Diagonalisation . . . . .	14

## List of Figures

## List of Tables

# 1 Introduction

## Applications of Electron-Impact Hydrogen Scattering

## Specific Applications of Electron-Impact Hydrogen Ionisation

## Development of Quantum Scattering Theory

# 2 Theory

We shall describe the development of the Convergent Close-Coupling (CCC) method for generalised projectile-target scattering, before describing its application to the cases of: electron-impact hydrogen (e-H) scattering, and electron-impact helium (e-He) scattering. In particular, we shall explore the treatment of target ionisation within the CCC method. Note that in the general treatment, we restrict our attention to electron projectiles and atomic/ionic targets consisting of  $n_e$  electrons.

To do (1)

To do (2)

## 2.1 Convergent Close-Coupling Method

In brief, the CCC method utilises the method of basis expansion, discussed in further detail in [subsection B.1](#), to numerically solve the Lippmann-Schwinger equation, for a projectile-target system, to yield the transition amplitudes, which are convergent as the size of the basis is increased. The rate of convergence depends on many factors, such as the complexity and geometry of the projectile-target system for example, as well as the choice of basis used in the expansion. Furthermore, by selecting a complete basis, ionisation transition amplitudes can be treated in a similar manner to discrete excitation transition amplitudes.

### 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  $L^2(\mathbb{R}^3)$  - shown in [subsubsection A.3.1](#), 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 elements of certain 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.

Further properties of the Laguerre basis are discussed in [subsection A.3](#).

### 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

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

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

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

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  $\sigma$ . Note that we have neglected the commonly included  $\frac{1}{n!}$  factor in the anti-symmetriser operator. 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  $\mathcal{H}_T = \Lambda^{n_e}(\mathcal{H})$ . Note that 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,  $\{|\Phi_i\rangle\}_{i=1}^\infty \in \mathcal{H}_T$ , are then approximated by expanding the many-electron 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,  $\{|\Phi_i^{(N)}\rangle\}_{i=1}^{N_T}$ , 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  $\epsilon_i^{(N)}$  are the pseudoenergies of the pseudostates. Note that the number of target pseudostates,  $N_T$ , depends on the number of Slater determinants utilised in the expansion of  $\hat{H}_T$ . The process of selecting which Slater determinants to use in the expansion is not trivial, and will be discussed in further detail in [section 2.3.1](#).

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 diagonalisation procedure is discussed in further detail in [subsection B.2](#).

**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. 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

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

where  $\epsilon_i^{(N)} < 0$  for  $i = 1, \dots, N_B$ , and where  $\epsilon_i^{(N)} \geq 0$  for  $i = N_B + 1, \dots, N_T$ . 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.

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

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

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,

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

### 2.1.3 Projectile States

The projectile states,  $|\mathbf{k}\rangle \in \mathcal{H}$ , are defined to be eigenstates of the free Hamiltonian; that is,

$$\hat{K}_0 |\mathbf{k}\rangle = \frac{k^2}{2} |\mathbf{k}\rangle. \quad (20)$$

It follows that the coordinate-space representation of projectile states are plane waves; that is,

$$\langle \mathbf{r} | \mathbf{k} \rangle = (2\pi)^{-\frac{3}{2}} \exp(i\mathbf{k} \cdot \mathbf{r}). \quad (21)$$

Further properties of the plane waves are discussed in [subsection A.4](#).

### 2.1.4 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,

$$\hat{H}|\Psi^{(+)}\rangle = E|\Psi^{(+)}\rangle, \quad (22)$$

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

$$\hat{H} = \hat{H}_T + \hat{K}_0 + \hat{V}_0 + \sum_{m=1}^{n_e} \hat{V}_{0,m}, \quad (23)$$

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.

To ensure that the total wavefunction is anti-symmetric we utilise the anti-symmetriser, defined in Equation 8, to construct a multichannel expansion of the form

$$|\Psi^{(+)}\rangle = \hat{A}|\psi^{(+)}\rangle = \left[1 - \sum_{m=1}^{n_e} \hat{P}_{0,m}\right] |\psi^{(+)}\rangle, \quad (24)$$

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 un-symmetrised total wavefunction. 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. As the target states are already anti-symmetric by construction, the anti-symmetriser has assumed a simpler form - requiring only permutations of the un-symmetrised projectile state with the spin-orbital states of the target electrons.

To construct the un-symmetrised total wavefunction,  $|\psi^{(+)}\rangle$ , we project it onto the target pseudostates,

$$|\psi^{(N,+)}\rangle = \hat{I}_T^{(N)} |\psi^{(+)}\rangle = \sum_{i=1}^{N_T} |\Phi_i^{(N,+)}\rangle \langle \Phi_i^{(N,+)} | \psi^{(+)} \rangle = \sum_{i=1}^{N_T} |\Phi_i^{(N,+)}\rangle \otimes |F_i^{(N,+)}\rangle, \quad (25)$$

where  $|F_i^{(N,+)}\rangle = \langle \Phi_i^{(N,+)} | \psi^{(+)} \rangle \in \mathcal{H}$ , and note that as a result of Equation 19, that

$$|\psi^{(+)}\rangle = \lim_{N \rightarrow \infty} \hat{I}_T^{(N)} |\psi^{(+)}\rangle = \lim_{N \rightarrow \infty} |\psi^{(N,+)}\rangle. \quad (26)$$

Similarly, we define

$$|\Psi^{(N,+)}\rangle = \hat{A}|\psi^{(N,+)}\rangle = \left[1 - \sum_{m=1}^{n_e} \hat{P}_{0,m}\right] |\psi^{(N,+)}\rangle, \quad (27)$$

and observe that

$$|\Psi^{(+)}\rangle = \lim_{N \rightarrow \infty} |\Psi^{(N,+)}\rangle. \quad (28)$$

However, after projecting the un-symmetrised total wavefunction with the projection operator for the target pseudostates, the multichannel expansion is not uniquely defined, since for any state,  $|\omega^{(N)}\rangle = \hat{I}_T^{(N)} |\omega\rangle \in \ker(\hat{A})$ , and constant  $\alpha \in \mathbb{C}$ , 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 impose the constraint that for any



of the one-electron atomic orbitals,  $|\phi_j^{(N)}\rangle \in \mathcal{H}$ , used in the construction of the target pseudostates in [Equation 12](#), that

$$\langle \phi_j^{(N)} | \otimes \langle \Phi_i^{(N)} | \hat{P}_{0,m} = - \langle \phi_j^{(N)} | \otimes \langle \Phi_i^{(N)} |. \quad (29)$$

Whence it follows that the multichannel expansion of  $|\psi^{(N,+)}\rangle + \alpha |\omega^{(N)}\rangle$  will be identical to that of  $|\psi^{(N,+)}\rangle$  only in the case where  $\alpha = 0$ , or  $|\omega^{(N)}\rangle = |0\rangle$ ; that is to say,  $|\psi^{(N,+)}\rangle$  will now uniquely determine  $|\Psi^{(N,+)}\rangle$ .

### 2.1.5 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 22](#). This shall be re-arranged to yield the Lippmann-Schwinger equation, which will then be solved using the CCC formalism.

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

$$\hat{H} |\Psi\rangle = \hat{H}_A |\Psi\rangle + \hat{V} |\Psi\rangle = E |\Psi\rangle, \quad (30)$$

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

$$[E - \hat{H}_A] |\Psi\rangle = \hat{V} |\Psi\rangle. \quad (31)$$

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

$$\hat{H}_A |\Omega_\alpha\rangle = \varepsilon_\alpha |\Omega_\alpha\rangle, \quad (32)$$

and note that where  $\varepsilon_\alpha = E$ , it follows that  $|\Omega_\alpha\rangle \in \ker(E - \hat{H}_A)$ . We now define the Green's operator  $\hat{G}_{(E)}$ , to be such that

$$\hat{G}_{(E)}[E - \hat{H}_A] = \hat{I} = [E - \hat{H}_A]\hat{G}_{(E)}, \quad (33)$$

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

$$|\Psi\rangle = \sum_{\alpha: \varepsilon_\alpha = E} \int C_\alpha |\Omega_\alpha\rangle + \hat{G}_{(E)} \hat{V} |\Psi\rangle, \quad (34)$$

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 eigen-energy  $\varepsilon_\alpha$  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 seen by applying the operator  $[E - \hat{H}_A]$  on the left of [Equation 34](#),

$$[E - \hat{H}_A] |\Psi\rangle = \sum_{\alpha: \varepsilon_\alpha = E} \int C_\alpha [E - \hat{H}_A] |\Omega_\alpha\rangle + [E - \hat{H}_A] \hat{G}_{(E)} \hat{V} |\Psi\rangle = \hat{V} |\Psi\rangle. \quad (35)$$

At this point, we note that selecting the values of the coefficients  $C_\alpha$  amounts to specifying a boundary condition for the eigenstate  $|\Psi\rangle$ . Hence we may simplify the generalised sum/integral to a simpler form, without loss of generality, by writing

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

where  $|\Omega_\alpha\rangle \in \ker(E - \hat{H}_A)$ . We now define the  $\hat{T}$  operator, which is such that

$$|\Psi_\alpha\rangle = [\hat{I} + \hat{G}_{(E)} \hat{T}] |\Omega_\alpha\rangle, \quad (37)$$

which is equivalently defined by writing

$$\hat{T} |\Omega_\alpha\rangle = \hat{V} |\Psi_\alpha\rangle. \quad (38)$$

Furthermore, we have that

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

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

$$\hat{T} |\Omega_\alpha\rangle = [\hat{V} + \hat{V} \hat{G}_{(E)} \hat{T}] |\Omega_\alpha\rangle, \quad (39)$$

yielding the formulation of the Lippmann-Schwinger equation in terms of  $\hat{T}$ . 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

$$\langle \Omega_\alpha | \Omega_\beta \rangle = \delta_{\alpha,\beta}, \quad (40)$$

where  $\delta_{\alpha,\beta}$  appropriately represents the Kronecker delta and Dirac delta for the asymptotic states, and that these states satisfy

$$\langle \Omega_\alpha | E - \hat{H}_A | \Omega_\beta \rangle = (E - \varepsilon_\beta) \langle \Omega_\alpha | \Omega_\beta \rangle = (E - \varepsilon_\alpha) \delta_{\alpha,\beta}. \quad (41)$$

From the definition [Equation 33](#), we must have that

$$\langle \Omega_\alpha | \hat{G}_{(E)} [E - \hat{H}_A] | \Omega_\beta \rangle = \langle \Omega_\alpha | \hat{I} | \Omega_\beta \rangle = \delta_{\alpha,\beta} \quad (42)$$

whence it follows that

$$\langle \Omega_\alpha | \hat{G}_{(E)} | \Omega_\beta \rangle = \frac{\delta_{\alpha,\beta}}{E - \varepsilon_\alpha} \quad (43)$$

and so the Green's operator can be expanded in the set of asymptotic states to be written in the form

$$\hat{G}_{(E,\pm)} = \lim_{\eta \rightarrow 0} \sum_\gamma \int \frac{|\Omega_\gamma\rangle \langle \Omega_\gamma|}{E - \varepsilon_\gamma \pm i\eta} = \sum_\gamma \int \frac{|\Omega_\gamma\rangle \langle \Omega_\gamma|}{E - \varepsilon_\gamma \pm i0}, \quad (44)$$

where the imaginary limit exists to ensure the integral is well-defined for all  $\varepsilon_\gamma$ . With an expression for the Green's operator in hand, we can now re-write the Lippmann-Schwinger equation in the following form

$$\langle \Omega_\alpha | \hat{T} | \Omega_\beta \rangle = \langle \Omega_\alpha | \hat{V} | \Omega_\beta \rangle + \sum_\gamma \int \frac{\langle \Omega_\alpha | \hat{V} | \Omega_\gamma \rangle \langle \Omega_\gamma | \hat{T} | \Omega_\beta \rangle}{E - \varepsilon_\gamma \pm i0}, \quad (45)$$

which conveniently expresses all matrix elements in terms of the asymptotic eigenstates.

**Convergent Close-Coupling Formalism** In the Convergent Close-Coupling formalism, the Lippmann-Schwinger equation in terms of the  $\hat{T}$  operator, Equation 45, is solved in momentum space. The asymptotic eigenstates taken to be of the form

$$|\Omega_\alpha\rangle = |\Phi_{i_\alpha} \mathbf{k}_\alpha\rangle \approx |\Phi_{i_\alpha}^{(N)} \mathbf{k}_\alpha\rangle, \quad (46)$$

with corresponding asymptotic eigenenergies

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

where  $\{|\Phi_i^{(N)}\rangle\}_{i=1}^{N_T}$  are the target pseudostates, defined in Equation 16, and where  $|\mathbf{k}\rangle$  are plane waves, defined in Equation 21. 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 24, where  $\hat{A}$  is the anti-symmetriser operator, defined in Equation 8, and is subject to the constraints imposed in Equation 29 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  $\hat{V}$  by the expression

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

However, in the case where the potential  $\hat{V}$  can be re-written in a way which accounts for the anti-symmetrisation of the un-symmetrised wavefunction  $|\psi_\alpha^{(S)}\rangle$  with total spin  $S$  (as is the case for hydrogen and helium targets), we may instead write

$$\hat{V}^{(S)}\hat{I}_T^{(N)}|\psi_\alpha^{(S)}\rangle = \hat{V}\hat{A}\hat{I}_T^{(N)}|\psi_\alpha^{(S)}\rangle, \quad (50)$$

in which case the  $\hat{T}$  operator is instead written as

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

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

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

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  $|\Psi_i^{(N,S)}\rangle$  can be derived. However, it is possible to re-write the Convergent Close-Coupling equations in terms of an operator  $\hat{K}$ ,

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

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 be reconstructed from the  $K$  matrix by the identity

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

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

$$E = \epsilon_n^{(N)} + \frac{1}{2}k_n^2. \quad (55)$$

### 2.1.6 Transition Amplitudes

### 2.1.7 Cross Sections

#### Total Cross Sections

#### Differential Cross Sections

### 2.1.8 S-Wave Model

## 2.2 Electron-Impact Hydrogen Scattering

### 2.2.1 Elastic Scattering

### 2.2.2 Excitation

### 2.2.3 Ionisation

#### Singlet Case

#### Triplet Case

## 2.3 Electron-Impact Helium Scattering

### 2.3.1 Additional Considerations for a Helium Target

#### Frozen-Core Model

#### Meta-stable States

meta-stable  
states (3)

### 2.3.2 Elastic Scattering

### 2.3.3 Excitation

#### Auto-Ionisation

#### 2.3.4 Ionisation

### 3 Survey of Experimental Literature

### 4 Survey of Theoretical Literature

#### 4.1 Electron-Impact Hydrogen Ionisation Calculations

##### 4.1.1 Convergent Close-Coupling Calculations

##### 4.1.2 Exterior-Complex-Scaling Calculations

##### 4.1.3 Ansatz of Zatsarinny and Bartschat

#### 4.2 Electron-Impact Helium Ionisation Calculations

##### 4.2.1 Convergent Close-Coupling Calculations

##### 4.2.2 Exterior-Complex-Scaling Calculations

##### 4.2.3 Ansatz of Zatsarinny and Bartschat

### 5 Conclusion

## References

## A Properties of Utilised Bases

### A.1 Spherical Harmonics

#### A.1.1 Completeness

### A.2 Laguerre Radial Basis

#### A.2.1 Completeness

### A.3 Laguerre Basis

#### A.3.1 Completeness

It is shown in [subsubsection A.2.1](#), that the Laguerre radial basis functions,  $\{\xi_{k,l}(r)\}_{k=1}^{\infty}$ , for each  $l$ , forms a complete basis for the Hilbert space  $L^2([0, \infty))$ . Similarly, it is also shown in [subsubsection A.1.1](#), that the set of spherical harmonics,  $\{Y_l^{-l}(\Omega), \dots, Y_l^l(\Omega)\}_{l=0}^{\infty}$ , forms an orthonormal, complete basis for the Hilbert space  $L^2(S^2)$ . Hence, the Laguerre basis functions  $\{\varphi_i(r, \Omega)\}_{i=1}^{\infty}$ , form a complete basis for the Hilbert space  $L^2(\mathbb{R}^3)$ .

spherical har-  
monic complete-  
ness [\(4\)](#)

laguerre radial  
completeness  
[\(5\)](#)

### A.4 Plane Waves

## B Numerical Techniques

### B.1 Basis Expansion

### B.2 Diagonalisation

basis expansion  
[\(6\)](#)

target diagonali-  
sation [\(7\)](#)

**To do...**

- ☐ 1 (p. 3): Remove unnecessary commas.
- ☐ 2 (p. 3): Replace 'expansion' with 'representation'.
- ☐ 3 (p. 11): meta-stable states How are positive energy discrete states handled? Do positive energy discrete states overlap with the continuum? Do we simply include the positive energy discrete states in the continuum with a Dirac mass function?
- ☐ 4 (p. 14): spherical harmonic completeness Prove that the set of spherical harmonics forms,  $\{Y_l^{-l}(\Omega), \dots, Y_l^l(\Omega)\}_{l=0}^{\infty}$ , forms an orthonormal, complete basis for the Hilbert space  $L^2(S^2)$ .
- ☐ 5 (p. 14): laguerre radial completeness Prove that the Laguerre radial basis functions,  $\{\xi_{k,l}(r)\}_{k=1}^{\infty}$ , for each  $l$ , forms a complete basis for the Hilbert space  $L^2([0, \infty))$ .
- ☐ 6 (p. 14): basis expansion Elaborate on the method of basis expansion for Hilbert spaces.
- ☐ 7 (p. 14): target diagonalisation Elaborate on the diagonalisation procedure for the target states.