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

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[ABSTRACT]

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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 shall restrict our attention to electron projectiles and atomic/ionic targets.

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

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

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 α_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, $\{\varphi_i(\mathbf{r}, \Omega)\}_{i=1}^{\infty}$, 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 both 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 Projectile-Target System

Possessing now a suitable basis to work with, we proceed to represent the projectile-target system in this basis by the method of basis expansion. We first construct the projectile states, and the target states, before considering how to combine the two into a set of total states.

Recall that we restrict our attention to the case of an electron projectile, and an atomic/ionic target consisting of n_e electrons. We shall adopt the convention that the projectile electron space is denoted by \mathcal{H}_0 , the m -th target electron space by \mathcal{H}_m , for $m = 1, \dots, n_e$, and a one-electron space by \mathcal{H}_e . Furthermore, operators which act on the m -th electron space (including the projectile electron), will be indexed by m , for $m = 0, 1, \dots, n_e$.

Projectile States The projectile states, $|\mathbf{k}\rangle \in \mathcal{H}_P$, where $\mathcal{H}_P = \mathcal{H}_0 = \mathcal{H}_e$ is the projectile electron space, are defined to be eigenstates of the free Hamiltonian; that is,

$$\hat{K}_0 |\mathbf{k}\rangle = \frac{k^2}{2} |\mathbf{k}\rangle. \quad (4)$$

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

$$\langle \mathbf{r} | \mathbf{k} \rangle = (2\pi)^{-\frac{3}{2}} \exp(i\mathbf{k} \cdot \mathbf{r}). \quad (5)$$

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

Target States

Target Space For a one-electron atomic/ionic target (such as H, He^+ , \dots), the space of target states, \mathcal{H}_T , is simply constructed from the one-electron space of the target electron, $\mathcal{H}_1 = \mathcal{H}_e$. However, for a many-electron atomic/ionic target (such as He), the construction of the space of target states requires a more nuanced approach.

Firstly, we note that as electrons are indistinguishable, the one-electron space of each target electron must be identical; that is, $\mathcal{H}_m = \mathcal{H}_e$ for $m = 1, \dots, n_e$ where n_e is the number of target electrons. Furthermore, the space of target states, \mathcal{H}_T , must be constructed from the spaces of target electron in a way which preserves the indistinguishableness of each electron, and which adheres to Pauli's exclusion principle - that no more than one electron can occupy a given state (including

spin). This is achieved by constructing the space of target states from the anti-symmetrised tensor product of the spaces of the target electrons,

$$\mathcal{H}_T = \left\{ \hat{A}_{n_e} |\psi\rangle : |\psi\rangle \in \bigotimes_{m=1}^{n_e} \mathcal{H}_e \right\} \quad (6)$$

where the operator, \hat{A}_{n_e} , anti-symmetrises the tensor product of n_e indistinguishable electron states.

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

$$\hat{H}_T = \sum_{m=1}^{n_e} \hat{K}_m + \sum_{m=1}^{n_e} \hat{V}_m + \sum_{m=1}^{n_e} \sum_{n=m+1}^{n_e} \hat{V}_{m,n} \quad (7)$$

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,

$$\hat{H}_{T,e} = \hat{K}_1 + \hat{V}_1 \quad (8)$$

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

$$\langle \phi_i^{(N)} | \hat{H}_{T,e} | \phi_j^{(N)} \rangle = \varepsilon_i^{(N)} \delta_{i,j}. \quad (9)$$

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

$$|\chi_{a_1}^{(N)}, \dots, \chi_{a_{n_e}}^{(N)}\rangle = \frac{1}{\sqrt{n_e!}} \sum_{\sigma \in S_{n_e}} \text{sgn}(\sigma) |\chi_{a_{\sigma(1)}}^{(N)}\rangle \otimes \dots \otimes |\chi_{a_{\sigma(n_e)}}^{(N)}\rangle \in \mathcal{H}_T \quad (10)$$

where S_{n_e} is the symmetric group on n_e elements, the sum is taken over all permutations, $\sigma \in S_{n_e}$, and where $\text{sgn}(\sigma)$ is the sign of the permutation σ . We note that Slater determinants are anti-symmetric under pairwise exchange of any two orbitals, and hence adhere to Pauli's exclusion principle.

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,

$$\{|\chi_{a_1}^{(N)}, \dots, \chi_{a_{n_e}}^{(N)}\rangle : a_1, \dots, a_{n_e} \in \{1, \dots, 2N\}\} \quad (11)$$

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

$$\langle \Phi_i^{(N)} | \hat{H}_T | \Phi_j^{(N)} \rangle = \epsilon_i^{(N)} \delta_{i,j}. \quad (12)$$

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. In general, bounded states have negative energy and unbounded states have positive energy, however this is not necessarily the case - a note which will be relevant in the treatment of the meta-stable positive-energy discrete states of helium. The treatment of these meta-stable states of helium will be discussed in further detail in [section 2.3.1](#), while for now we shall simply distinguish bounded and unbounded states by the sign of their energy. 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

$$\{|\Phi_i^{(N)}\rangle\}_{i=1}^{N_T} = \{|\Phi_i^{(N)}\rangle\}_{i=1}^{N_B} \cup \{|\Phi_i^{(N)}\rangle\}_{i=N_B+1}^{N_T} \quad (13)$$

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 identity operator for the space of target states, \mathcal{H}_T , can be represented in the form

$$\hat{I}_T = \sum_{i=1}^{\infty} |\Phi_i\rangle \langle \Phi_i| + \int_{\mathbf{q}: q^2 \geq 0} d\mathbf{q} |\mathbf{q}\rangle \langle \mathbf{q}| \quad (14)$$

where $\{|\Phi_i\rangle\}_{i=1}^{\infty}$ is the true target discrete spectrum and where $\{|\mathbf{q}\rangle : q^2 \geq 0\}$ is the true continuum spectrum, of singly ionised target states. Furthermore, we note that the projection operator for the target pseudostates, $\hat{I}_T^{(N)}$, is of the form

$$\hat{I}_T^{(N)} = \sum_{i=1}^{N_T} |\Phi_i^{(N)}\rangle \langle \Phi_i^{(N)}| = \sum_{i=1}^{N_B} |\Phi_i^{(N)}\rangle \langle \Phi_i^{(N)}| + \sum_{i=N_B+1}^{N_T} |\Phi_i^{(N)}\rangle \langle \Phi_i^{(N)}| \quad (15)$$

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

$$\lim_{N \rightarrow \infty} \sum_{i=1}^{N_B} |\Phi_i^{(N)}\rangle \langle \Phi_i^{(N)}| = \sum_{i=1}^{\infty} |\Phi_i\rangle \langle \Phi_i| \quad (16)$$

and the sum over the unbounded pseudostates will converge to a discretisation of the integral over the true continuum spectrum

$$\lim_{N \rightarrow \infty} \sum_{i=N_B+1}^{N_T} |\Phi_i^{(N)}\rangle \langle \Phi_i^{(N)}| = \int_{\mathbf{q}: q^2 \geq 0} d\mathbf{q} |\mathbf{q}\rangle \langle \mathbf{q}|. \quad (17)$$

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,

$$\lim_{N \rightarrow \infty} \hat{I}_T^{(N)} = \hat{I}_T \quad (18)$$

which can be equivalently stated as

$$\lim_{N \rightarrow \infty} \text{span}\{|\Phi_i^{(N)}\rangle\}_{i=1}^{N_T} = \mathcal{H}_T. \quad (19)$$

Total State

Total Space The construction of the total space for an electron projectile and an atomic/ionic target, with n_e electrons, echoes the considerations and process of constructing the target space for the many-electron target, presented in [section 2.1.2](#). In brief, the projectile electron and target electron(s) are indistinguishable, and thus have the same one-electron space, \mathcal{H}_e . Hence, the space of projectile-target states, \mathcal{H} , is constructed from the anti-symmetrised tensor product of the projectile electron space, and the spaces of the target electrons,

$$\mathcal{H} = \left\{ \hat{A}_{1+n_e} |\psi\rangle : |\psi\rangle \in \bigotimes_{m=1}^{1+n_e} \mathcal{H}_e \right\} \quad (20)$$

where the operator, \hat{A}_{1+n_e} , anti-symmetrises the tensor product of $1 + n_e$ indistinguishable electron states.

Total Hamiltonian The total Hamiltonian of the projectile-target system, \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 7](#), \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.

Total State Construction The total state of the projectile-target system, $|\Psi^{(+)}\rangle \in \mathcal{H}$, specified to have outgoing spherical-wave boundary conditions, is defined to be an eigenstate of the total Hamiltonian, \hat{H} ,

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

with total energy E . To ensure that the total state is anti-symmetric, we construct it using a multichannel expansion of the form

$$|\Psi^{(+)}\rangle = \left[1 - \sum_{m=1}^{n_e} \hat{P}_{0,m} \right] |\psi^{(+)}\rangle \quad (23)$$

where $\hat{P}_{0,m}$ are the pairwise electron exchange operators, for $m = 1, \dots, n_e$, exchanging the projectile electron state and m -th target electron state, and where $|\psi^{(+)}\rangle \in \bigotimes_{m=1}^{1+n_e} \mathcal{H}_e$ is the un-symmetrised total state. We neglect to anti-symmetrise the target electrons with each other, since both the true target states, and the target pseudostates, are already anti-symmetric.

To construct the un-symmetrised total state, $|\psi^{(+)}\rangle$, we observe that,

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

as a result of Equation 18, where we have defined

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

where $|F_i^{(N,+)}\rangle = \langle \Phi_i^{(N,+)} | \psi^{(+)} \rangle \in \mathcal{H}_e$. Similarly, we observe that

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

where we have defined

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

However, after projecting the un-symmetrised total state with the projection operator for the target pseudostates, the multichannel expansion is not uniquely defined, since for any state, $|\omega^{(N,+)}\rangle$, such that

$$|\omega^{(N,+)}\rangle \in \ker \left(\left[1 - \sum_{m=1}^{n_e} \hat{P}_{0,m} \right] \hat{I}_T^{(N)} \right) \quad (28)$$

and constant θ , the multichannel expansion of $|\psi^{(N,+)}\rangle + \theta \hat{I}_T^{(N)} |\omega^{(N,+)}\rangle$ 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, $|\phi_j^{(N)}\rangle \in \mathcal{H}_e$, used in the construction of the target pseudostates in Equation 8, that

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

for all $|\gamma^{(N,+)}\rangle \in \bigotimes_{m=1}^{1+n_e} \mathcal{H}_e$. Whence it follows that the multichannel expansion of $|\psi^{(N,+)}\rangle + \theta \hat{I}_T^{(N)} |\omega^{(N,+)}\rangle$ will be identical to that of $|\psi^{(N,+)}\rangle$ only in the case where $\theta = 0$, or $|\omega^{(N,+)}\rangle = |0\rangle$; that is to say, $|\psi^{(N,+)}\rangle$ will now uniquely determine $|\Psi^{(N,+)}\rangle$.

2.1.3 Close-Coupling Equations

2.1.4 Transition Amplitudes

2.1.5 Cross Sections

Total Cross Sections

Differential Cross Sections

2.1.6 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 $L^2(\mathbb{R}^3)$.

A.4 Plane Waves

B Numerical Techniques

B.1 Basis Expansion

B.2 Diagonalisation

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

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

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

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

To do...

- ☐ 1 (p. 3): Remove unnecessary commas.
- ☐ 2 (p. 3): Replace 'expansion' with 'representation'.
- ☐ 3 (p. 9): 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. 11): 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. 11): 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. 11): basis expansion Elaborate on the method of basis expansion for Hilbert spaces.
- ☐ 7 (p. 11): target diagonalisation Elaborate on the diagonalisation procedure for the target states.