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

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[ABSTRACT]

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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.

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

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

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

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

where λ_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 $k_i \in \{1,2,\ldots\}$, $l_i \in \{0,1,\ldots\}$ and $m_i \in \{-\ell_i,\ldots,\ell_i\}$, for each $i \in \{1,2,\ldots\}$.

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 $l \in \{0, \ldots, l_{\max}\}$, limiting the maximum angular momentum we consider in our basis. Hence, for a given value of m, we have a basis size of

$$N = \sum_{l=0}^{l_{\max}} N_l. \tag{3}$$

In the limit as $N \to \infty$, 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

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

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 $\mathcal{D}^n$,

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

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

$$|\psi_1, \ldots, \psi_n\rangle = |\psi_1\rangle \otimes \cdots \otimes |\psi_n\rangle \tag{6}$$

and the following notation for anti-symmetric tensor products

$$|[\psi_1, \ldots, \psi_n]\rangle = \left|\psi_{[1,\ldots,n]}\right\rangle = \sqrt{n!}\hat{A}\,|\psi_1, \ldots, \psi_n\rangle \tag{7}$$

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

$$\hat{A}\,|\psi_1, \ldots, \psi_n\rangle = \frac{1}{n!} \sum_{\sigma \in S_n} \operatorname{sgn}(\sigma) \left|\psi_{\sigma(1)}, \ldots, \psi_{\sigma(n)}\right\rangle, \tag{8}$$

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

$$\left|\psi_{[a_1,\ldots,a_n]}\right\rangle = 0 \quad \text{if any} \quad a_i = a_j, \tag{9}$$

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

$$\hat{P}_{i,j} \left|\psi_{[1,\dots,n]}\right\rangle = - \left|\psi_{[1,\dots,n]}\right\rangle, \tag{10}$$

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 $\mathcal{H}_T = \Lambda^{n_\mathrm{e}}(\mathcal{H})$. 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 $m = 0, 1, \dots, n_\mathrm{e}$.

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

$$\hat{H}_T = \sum_{m=1}^{n_\mathrm{e}} \hat{K}_m + \sum_{m=1}^{n_\mathrm{e}} \hat{V}_m + \sum_{m=1}^{n_\mathrm{e}} \sum_{n=m+1}^{n_\mathrm{e}} \hat{V}_{m,n}, \tag{11}$$

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

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

$$\hat{H}_{T,\mathrm{e}} = \hat{K}_1 + \hat{V}_1, \tag{12}$$

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

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

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 $|\chi_{a_1}^{(N)}\rangle, \dots, |\chi_{a_{n_\mathrm{e}}}^{(N)}\rangle \in \{\,|\chi_i^{(N)}\rangle\}_{i=1}^{2N}$, the Slater determinant of these spin orbitals is of the form

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

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 $\mathcal{H}_T = \Lambda^{n_\mathrm{e}}(\mathcal{H})$.

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,

$$\left\{\,|\chi_{[a_1,\dots,a_{n_\mathrm{e}}]}^{(N)}\rangle : a_1, \dots, a_{n_\mathrm{e}} \in \{1, \dots, 2N\}\right\}, \tag{15}$$

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

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

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, as the number of Slater determinants scales as $\binom{2N}{n_e}$. A common method of mitigating this computationaly complexity, is to partition the target orbitals into a core 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 electron states, while allowing the valence electrons to interact fully with the projectile.

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 Laguerrre basis, and that these pseudostates and their pseudoenergies are dependent on the size of the Laguerre basis utilised.

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, $\epsilon_1^{(N)} < \ldots < \epsilon_{N_T}^{(N)}$, which allows us to express the separability of the spectrum in the form

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

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

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

and so in the limit as $N \to \infty$, 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 $N \to \infty$; that is,

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

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,

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

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

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

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.

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

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

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 un-symmetrised 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 un-symmetrised 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 un-symmetrised total wavefunction $|\psi^{(+)}\rangle$ we perform a multichannel expansion, projecting it onto the target psuedostates,

$$|\psi^{(N,+)}\rangle = \hat{I}_T^{(N)}\,|\psi^{(+)}\rangle = \sum_{i=1}^{N_T} |\Phi_i^{(N,+)}\rangle\,\langle\Phi_i^{(N,+)}|\psi^{(+)}\rangle = \sum_{i=1}^{N_T} |\Phi_i^{(N,+)}, F_i^{(N,+)}\rangle\,, \tag{23}$$

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

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

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

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

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

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

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 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 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

$$\langle\phi_j^{(N)}, \Phi_i^{(N)}|\,\hat{P}_{0,m} = -\,\langle\phi_j^{(N)}, \Phi_i^{(N)}|\,. \tag{27}$$

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 $|\Psi^{(N,+)}\rangle$.

2.1.4 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.

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

$$\hat{H}\,|\Psi\rangle = \hat{H}_{\mathrm{A}}\,|\Psi\rangle + \hat{V}\,|\Psi\rangle = E\,|\Psi\rangle\,, \tag{28}$$

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

$$[E - \hat{H}_{\mathrm{A}}]\,|\Psi\rangle = \hat{V}\,|\Psi\rangle\,. \tag{29}$$

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

$$\hat{H}_{\mathrm{A}}\,|\Omega_\alpha\rangle = \varepsilon_\alpha\,|\Omega_\alpha\rangle\,, \tag{30}$$

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

$$\hat{G}_{(E)}[E - \hat{H}_{\mathrm{A}}] = \hat{I} = [E - \hat{H}_{\mathrm{A}}]\hat{G}_{(E)}, \tag{31}$$

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

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

where C_α 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 ε_α is equal to E. The inclusion of the selected asymptotic eigenstates is required as they are in the kernel of $[E - \hat{H}_{\mathrm{A}}]$ - thus forming the homogenous solutions to the Lippmann-Schwinger equation. This can be seen by applying the operator $[E - \hat{H}_{\mathrm{A}}]$ on the left of Equation 32,

$$[E - \hat{H}_{\mathrm{A}}]\,|\Psi\rangle = \sum_{\alpha:\varepsilon_\alpha = E} \int C_\alpha[E - \hat{H}_{\mathrm{A}}]\,|\Omega_\alpha\rangle + [E - \hat{H}_{\mathrm{A}}]\hat{G}_{(E)}\hat{V}\,|\Psi\rangle = \hat{V}\,|\Psi\rangle\,. \tag{33}$$

At this point, we note that selecting the values of the coefficients C_α 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

$$|\Psi_\alpha\rangle = |\Omega_\alpha\rangle + \hat{G}_{(E)}\hat{V}\,|\Psi_\alpha\rangle\,, \tag{34}$$

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

$$|\Psi_\alpha\rangle = [\hat{I} + \hat{G}_{(E)}\hat{T}]\,|\Omega_\alpha\rangle\,, \tag{35}$$

which is equivalently defined by writing

$$\hat{T}\,|\Omega_\alpha\rangle = \hat{V}\,|\Psi_\alpha\rangle\,. \tag{36}$$

Furthermore, we have that

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

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

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

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

$$\langle\Omega_\alpha|\Omega_\beta\rangle = \delta_{\alpha,\beta}, \tag{38}$$

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

$$\langle\Omega_\alpha|E - \hat{H}_{\mathrm{A}}|\Omega_\beta\rangle = (E - \varepsilon_\beta)\,\langle\Omega_\alpha|\Omega_\beta\rangle = (E - \varepsilon_\alpha)\delta_{\alpha,\beta}. \tag{39}$$

From the definition Equation 31, we must have that

$$\langle\Omega_\alpha|\hat{G}_{(E)}[E - \hat{H}_{\mathrm{A}}]|\Omega_\beta\rangle = \langle\Omega_\alpha|\hat{I}|\Omega_\beta\rangle = \delta_{\alpha,\beta} \tag{40}$$

whence it follows that

$$\langle\Omega_\alpha|\hat{G}_{(E)}|\Omega_\beta\rangle = \frac{\delta_{\alpha,\beta}}{E - \varepsilon_\alpha} \tag{41}$$

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

$$\hat{G}_{(E,\pm)} = \lim_{\eta\to 0}\sum_\gamma \int \frac{|\Omega_\gamma\rangle\langle\Omega_\gamma|}{E - \varepsilon_\gamma \pm \mathrm{i}\eta} = \sum_\gamma \int \frac{|\Omega_\gamma\rangle\langle\Omega_\gamma|}{E - \varepsilon_\gamma \pm \mathrm{i}0}, \tag{42}$$

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

$$\langle\Omega_\alpha|\hat{T}|\Omega_\beta\rangle = \langle\Omega_\alpha|\hat{V}|\Omega_\beta\rangle + \sum_\gamma \int \frac{\langle\Omega_\alpha|\hat{V}|\Omega_\gamma\rangle\ \langle\Omega_\gamma|\hat{T}|\Omega_\beta\rangle}{E - \varepsilon_\gamma \pm \mathrm{i}0}, \tag{43}$$

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 43, is solved in momentum space. We split the Hamiltonian, from Equation 21, into an asymptotic Hamiltonian and a decaying potential in the form

$$\hat{H} = \hat{H}_T + \hat{K}_0 + \hat{V}_0 + \sum_{m=1}^{n_e} \hat{V}_{0,m} = \hat{H}_A + \hat{W}, \tag{44}$$

where the asymptotic Hamiltonian is of the form

$$\hat{H}_A = \hat{H}_T + \hat{K}_0 + \hat{U}_0, \tag{45}$$

and where the decaying potential is of the form

$$\hat{W} = \hat{V}_0 + \sum_{m=1}^{n_e} \hat{V}_{0,m} - \hat{U}_0, \tag{46}$$

where $\hat{U}_0$ is the asymptotic potential acting on the projectile. The asymptotic eigenstates are therefore taken to be of the form

$$|\Omega_\alpha\rangle = |\Phi_{i_\alpha}\mathbf{k}_\alpha\rangle \approx |\Phi^{(N)}_{i_\alpha}\mathbf{k}_\alpha\rangle\,, \tag{47}$$

with corresponding asymptotic eigenenergies

$$\varepsilon_\alpha = \epsilon_{i_\alpha} + \tfrac{1}{2}k^2_\alpha \approx \epsilon^{(N)}_{i_\alpha} + \tfrac{1}{2}k^2_\alpha, \tag{48}$$

where $\{\,|\Phi^{(N)}_i\rangle\}^{N_T}_{i=1}$ are the target pseudostates, defined in Equation 16, and where $|\mathbf{k}\rangle$ are the plane/coulomb/distorted waves, defined to be eigenstates of the projectile component of the asymptotic Hamiltonian,

$$[\hat{K}_0 + \hat{U}_0]\,|\mathbf{k}\rangle = \tfrac{1}{2}k^2\,|\mathbf{k}\rangle\,. \tag{49}$$

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

$$|\Psi^{(+)}_\alpha\rangle = \hat{A}\,|\psi^{(+)}_\alpha\rangle \approx \hat{A}\hat{I}^{(N)}_T\,|\psi^{(+)}_\alpha\rangle = \hat{A}\,|\psi^{(N,+)}_\alpha\rangle = |\Psi^{(N,+)}_\alpha\rangle\,, \tag{50}$$

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 decaying potential $\hat{W}$ by the expression

$$\hat{T}\,|\Phi^{(N)}_{i_\alpha}\mathbf{k}_\alpha\rangle = \hat{W}\,|\Psi^{(N,+)}_\alpha\rangle = \hat{W}\hat{A}\hat{I}^{(N)}_T\,|\psi^{(+)}_\alpha\rangle = \hat{W}\hat{A}\,|\psi^{(N,+)}_\alpha\rangle\,. \tag{51}$$

However, we can recast this potential in a way which accounts for the explicit anti-symmetrisation of the total wavefunction. To do this, we first note that

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

with this operator expanding to the form

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

whence we define the explicitly anti-symmetrised potential $\hat{V}$ to be of the form

$$\hat{V} = \hat{W} + [E - \hat{H}] \sum_{m=1}^{n_e} \hat{P}_{0,m} = \hat{V}_0 + \sum_{m=1}^{n_e} \hat{V}_{0,m} - \hat{U}_0 + [E - \hat{H}] \sum_{m=1}^{n_e} \hat{P}_{0,m} \tag{52}$$

for which we can see that the explicit anti-symmetrisation of $|\psi_\alpha^{(+)}\rangle$ is handled by $\hat{V}$,

$$\hat{H}\,|\psi_\alpha^{(+)}\rangle = \hat{H}_{\mathrm{A}}\,|\psi_\alpha^{(+)}\rangle + \hat{V}\,|\psi_\alpha^{(+)}\rangle = E\,|\psi_\alpha^{(+)}\rangle\,. \tag{53}$$

This allows us to write the $\hat{T}$ operator in the form

$$\hat{T}\,|\Phi_{i_\alpha}^{(N)}\mathbf{k}_\alpha\rangle = \hat{V}\hat{I}_T^{(N)}\,|\psi_\alpha^{(+)}\rangle = \hat{V}\,|\psi_\alpha^{(N,+)}\rangle\,. \tag{54}$$

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

$$\begin{aligned}\langle \mathbf{k}_f \Phi_{n_f}^{(N)}|\hat{T}|\Phi_{n_i}^{(N)}\mathbf{k}_i\rangle = {} & \langle \mathbf{k}_f \Phi_{n_f}^{(N)}|\hat{V}|\Phi_{n_i}^{(N)}\mathbf{k}_i\rangle \\ & + \sum_{n=1}^{N_T} \int \mathrm{d}\mathbf{k}\, \frac{\langle \mathbf{k}_f \Phi_{n_f}^{(N)}|\hat{V}|\Phi_n^{(N)}\mathbf{k}\rangle\ \langle \mathbf{k}\Phi_n^{(N)}|\hat{T}|\Phi_{n_i}^{(N)}\mathbf{k}_i\rangle}{E - \epsilon_n^{(N)} - \frac{1}{2}k^2 \pm \mathrm{i}0},\end{aligned} \tag{55}$$

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 $\hat{K}$,

$$\begin{aligned}\langle \mathbf{k}_f \Phi_{n_f}^{(N)}|\hat{K}|\Phi_{n_i}^{(N)}\mathbf{k}_i\rangle = {} & \langle \mathbf{k}_f \Phi_{n_f}^{(N)}|\hat{V}|\Phi_{n_i}^{(N)}\mathbf{k}_i\rangle \\ & + \sum_{n=1}^{N_T} \mathcal{P} \int \mathrm{d}\mathbf{k}\, \frac{\langle \mathbf{k}_f \Phi_{n_f}^{(N)}|\hat{V}|\Phi_n^{(N)}\mathbf{k}\rangle\ \langle \mathbf{k}\Phi_n^{(N)}|\hat{K}|\Phi_{n_i}^{(N)}\mathbf{k}_i\rangle}{E - \epsilon_n^{(N)} - \frac{1}{2}k^2},\end{aligned} \tag{56}$$

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

$$\langle \mathbf{k}_f \Phi_{n_f}^{(N)}|\hat{K}|\Phi_{n_i}^{(N)}\mathbf{k}_i\rangle = \sum_{n=1}^{N_T} \langle \mathbf{k}_f \Phi_{n_f}^{(N)}|\hat{T}|\Phi_n^{(N)}\mathbf{k}_n\rangle \left(\delta_{n,i} + \mathrm{i}\pi k_n \langle \mathbf{k}_n \Phi_n^{(N)}|\hat{K}|\Phi_{n_i}^{(N)}\mathbf{k}_i\rangle\right), \tag{57}$$

where k_n are the on-shell projectile momenta which satisfy

$$E = \epsilon_n^{(N)} + \tfrac{1}{2}k_n^2 \quad \text{for} \quad n = 1, \ldots, N_T. \tag{58}$$

2.2 Scattering Statistics

At this point, we shall utilise the S-wave model, wherein we restrict our attention to the target states $\{\,|\Phi_i^{(N)}\rangle\}_{i=1}^{N_T}$ for which $l = 0$. This allows for a simpler presentation of theoretical results, and calculations performed in the S-wave model are often sufficient to explore the behaviour of scattering phenomena with the benefit of a significant reduction in computational complexity. Much of the following treatment is readily generalisable to a full treatment of angular momentum.

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, and neglecting constant factors, the scattering amplitudes can be written in the form

$$F_{\alpha,\beta} = -\langle \mathbf{k}_\alpha \Phi_\alpha | \hat{V} | \Psi_\beta \rangle = -\langle \mathbf{k}_\alpha \Phi_\alpha | \hat{T} | \Phi_\beta \mathbf{k}_\beta \rangle \,, \tag{59}$$

where the target state $|\Phi_\alpha\rangle$ can be a bounded discrete state or an unbounded continuum state, corresponding to either a discrete excition or an ionisation transition. Note that despite the duplicated notation, we are referring to the scattering amplitudes $F_{\alpha,\beta}$, not the one-electron states in the multichannel expansion Equation 23.

For discrete excitations, the numerically calculated scattering amplitude is simply of the form

$$F^{(N)}_{f,i} = -\langle \mathbf{k}_f \Phi^{(N)}_{n_f} | \hat{T} | \Phi^{(N)}_{n_i} \mathbf{k}_i \rangle \,. \tag{60}$$

However, for ionisations the numerically calculated scattering amplitudes require a more carefully considered treatment. We shall restrict our attention to the case of single ionisation. 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 $|\Phi^+_\alpha\rangle$ and a continuum wave $|\mathbf{q}_\alpha\rangle$; that is,

$$|\Phi_\alpha \mathbf{k}_\alpha\rangle = |\Phi^+_\alpha \mathbf{q}_\alpha \mathbf{k}_\alpha\rangle \,, \tag{61}$$

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

$$E = \epsilon_\alpha + \tfrac{1}{2}k^2_\alpha = \epsilon^+_\alpha + \tfrac{1}{2}q^2_\alpha + \tfrac{1}{2}k^2_\alpha. \tag{62}$$

It follows from the completeness of the target pseudostates Equation 19 that the ionised asymptotic state can be expanded in terms of the unbounded target pseudostates, with the expansion becoming increasingly accurate as N increases. Hence, for ionisations, the numerically calculated scattering amplitude can be written in the form

$$\begin{aligned} F^{(N)}_{\alpha,i} &= -\langle \mathbf{k}_\alpha \mathbf{q}_\alpha \Phi^+_\alpha | \hat{I}^{(N)}_T \hat{T} | \Phi^{(N)}_{n_i} \mathbf{k}_i \rangle \\ &= -\sum_{n=1}^{N_T} \langle \mathbf{k}_\alpha \mathbf{q}_\alpha \Phi^+_\alpha | \Phi^{(N)}_n \rangle \, \langle \Phi^{(N)}_n | \hat{T} | \Phi^{(N)}_{n_i} \mathbf{k}_i \rangle \\ &= -\sum_{n=1}^{N_T} \langle \mathbf{q}_\alpha \Phi^+_\alpha | \Phi^{(N)}_n \rangle \, \langle \mathbf{k}_\alpha \Phi^{(N)}_n | \hat{T} | \Phi^{(N)}_{n_i} \mathbf{k}_i \rangle \,. \end{aligned} \tag{63}$$

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 $F^{(N)}_{\alpha,i}$ for ionised asymptotic states $|\Phi^+_\alpha \mathbf{q}_\alpha \mathbf{k}_\alpha\rangle$ which satisfy

$$\epsilon_\alpha = \epsilon^+_\alpha + \tfrac{1}{2}q^2_\alpha = \epsilon^{(N)}_{n_\alpha}, \tag{64}$$

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

$$\langle \mathbf{q}_\alpha \Phi^+_\alpha | \Phi^{(N)}_n \rangle = \delta_{n_\alpha, n} \langle \mathbf{q}_\alpha \Phi^+_\alpha | \Phi^{(N)}_n \rangle \,, \tag{65}$$

whence the ionisation scattering amplitudes can be evaluated as

$$F^{(N)}_{\alpha,i} = -\langle \mathbf{q}_\alpha \Phi^+_\alpha | \Phi^{(N)}_{n_\alpha} \rangle \, \langle \mathbf{k}_\alpha \Phi^{(N)}_{n_\alpha} | \hat{T} | \Phi^{(N)}_{n_i} \mathbf{k}_i \rangle \,, \tag{66}$$

at these q_α which satisfy Equation 64. This is the approach taken in the CCC method to calculate the ionisation scattering amplitudes, and we note that it is constrained to evaluating these amplitudes only at certain energies permitted by the target pseudoenergies. Evaluating the ionisation scattering amplitudes at any other energies requires an interpolation between the energies at which it can be evaluated at.

2.2.2 Cross Sections

2.3 Electron-Impact Hydrogen Scattering

2.3.1 Elastic Scattering

2.3.2 Excitation

2.3.3 Ionisation

Singlet Case

Triplet Case

2.4 Electron-Impact Helium Scattering

2.4.1 Additional Considerations for a Helium Target

Frozen-Core Model

Meta-stable States

2.4.2 Elastic Scattering

2.4.3 Excitation

Auto-Ionisation

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, $\{Y_l^{-l}(\Omega),\ldots,Y_l^l(\Omega)\}_{l=0}^{\infty}$, 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 harmonic completeness (1)

laguerre radial completeness (2)

basis expansion (3)

target diagonalisation (4)

To do...

- ☐ 1 (p. 16): spherical harmonic completeness Prove that the set of spherical harmonics forms, $\{Y_l^{-l}(\Omega), \ldots, Y_l^l(\Omega)\}_{l=0}^{\infty}$, forms an orthonormal, complete basis for the Hilbert space $L^2(S^2)$.
- ☐ 2 (p. 16): 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 $L^2([0,\infty))$.
- ☐ 3 (p. 16): basis expansion Elaborate on the method of basis expansion for Hilbert spaces.
- ☐ 4 (p. 16): target diagonalisation Elaborate on the diagonalisation procedure for the target states.