INFLUENCE OF ELECTRON CORRELATION

ON SCATTERING CROSS-SECTIONS

FOR He

by

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ABSTRACT

Part I

Total cross sections for high-energy inelastic collisions
between helium atoms originally in their ground state have been
obtained within the framework of the first Born approximation.
The ground state of the helium atoms was described by the 35-
configuration CI wavefunction of Weiss expressed in the form of
a natural expansion, thereby facilitating an examination of the
influence of ground state correlation effects on the scattering
cross sections.

Part II

The natural expansion of the Weiss 35-configuration
CI wavefunction for helium was used to assess the behaviour
of high-energy electron-capture cross sections for the reaction
$H^+ + He(1s^2) \longrightarrow H(n\ell) + He^+(1s)$ when the target is described
by wavefunctions of varying sophistication. The impulse approxi-
mation and the continuum distorted wave approximation were used to
evaluate the above cross sections for proton impact energies
ranging from 25 keV to 3.5 MeV. It was found that, in contrast
with the impulse approximation, the continuum distorted wave
(CDW) method is easily applied to electron capture reactions
and overall gave the better agreement with experiment. The CDW
method was also used to obtain capture cross sections for alpha
particles impinging on a helium target.

CONTENTS

CHAPTER 0.1

General Introduction

The Correlation Problem

In the quantum mechanical treatment of an atomic or molecular system we would like, in general, to possess a knowledge of the exact wavefunction which contains all the 'information' for that system. However, in order to obtain this wavefunction it is necessary to find an exact solution to the many-electron Schrodinger equation which, in practice, is unobtainable. As a consequence, varying degrees of approximation to the exact wavefunction are made. The first and simplest of such approximations is due to Hartree[1], where we assume that the total wavefunction $\Psi(1,2,3,\ldots.n)$ for an n-electron system may be written as the product of one-electron wavefunctions:

$$\Psi(1,2,3,\ldots.n) = \psi_1(1)\,\psi_2(2)\,\psi_3(3)\ldots\,\psi_n(n) \; ,$$

$$(0.1.1)$$

where $\psi_i(i)$ depends on the space and spin coordinates of electron i. One of the assumptions in equation (0.1.1) is that the electrons behave 'independently' of one another; that is, each electron moves in the average electrostatic potential due to the presence of all the other electrons. Furthermore, we are not taking into account the indistinguishability of the electrons, nor the Pauli exclusion principle which states that the total wavefunction of a system must be antisymmetric with respect to the interchange of coordinates of any two electrons:

$$\Psi(1,2,3\ldots.i,j\ldots.n) = -\,\Psi(1,2,3\ldots.j,i\ldots.n) \; .$$

Therefore it is more accurate to write

$$\Psi (1,2,3....n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_1(1) & \psi_2(1) & \psi_3(1)..... & \psi_n(1) \\ \psi_1(2) & \psi_2(2) & \psi_3(2)..... & \psi_n(2) \\ \psi_1(3) & \psi_2(3) & \psi_3(3)..... & \psi_n(3) \\ & & & \\ \psi_1(n) & \psi_2(n) & \psi_3(n)..... & \psi_n(n) \end{vmatrix} .$$

(0.1.2)

This form of writing the many electron wavefunction is known as a Slater determinant[2] and the component one-particle functions are referred to as spin orbitals. There are only two possible spin states which an electron can possess. Any spin orbital may be written as the product of a spatial orbital ϕ and a spin function α or β :

$$\psi_{2i-1} = \phi_i \alpha \qquad (0.1.3a)$$

$$\psi_{2i} = \phi_i \beta . \qquad (0.1.3b)$$

When Ψ in equation (0.1.2) is determined numerically by an iterative self-consistent-field procedure it is termed the Hartree-Fock (HF) wavefunction[3]. It corresponds to the best possible energy, within the variational principle, compatible with a single Slater determinant - termed the Hartree-Fock energy E_{HF}. The HF orbitals are constrained to form an orthonormal set and. the factor $1/\sqrt{n!}$ ensures Ψ is normalized to unity.

In reality, each electron lies in a 'coulomb hole', a region which is largely devoid of other electrons owing to coulombic repulsions. Within the HF approximation, the probability of finding two electrons with parallel spins at the same point in

space is zero. Such a point may be termed the centre of a 'Fermi hole'[4], and is a consequence of the antisymmetry of the wave-function. However, for electrons with anti-parallel spins a non-zero probability is predicted. Therefore the Fermi hole accounts for part, but not all, of the coulomb hole. The correlation problem is concerned with introducing flexibility into the wave-function over and above that given by the HF approximation, thereby describing the remaining part of the coulomb hole - that part which arises from interactions with anti-parallel spin electrons. In passing we note that recently it has been shown that the size of the Fermi hole is much smaller than previously believed[5], thereby accentuating the importance of electron correlation.

In general, the correlation energy ΔE of a system is defined[6] as that part of the exact non-relativistic energy E_{exact} that cannot be accounted for when using the best single Slater determinant wavefunction. Thus,

$$\Delta E = E_{exact} - E_{HF} \qquad (0.1.4)$$

The correlation energy of an atom or molecule is usually of the order of magnitude of 1% of the total energy. Although this is a relatively small contribution to the total energy it is comparable to spectral transition energies, binding energies and rotational barriers in molecules. Many physical quantities such as absorption frequencies and force constants are directly related to total energies and can therefore be correlation dependent. Other quantities are related to expectation values other than that of the Hamiltonian, for example: dipole and higher multipole moments, spin densities and field gradients. Most of the operators

involved for such properties are one-electron operators so that, according to the Møller-Plesset theorem[7], their expectation values are affected by correlation corrections to the wavefunction only to the second order in perturbation theory based on the HF wavefunction as the zeroth order approximation. Thus, correlation effects generally have only a minimal influence on such expectation values unless of course the HF value is unusually small: a notable example being the dipole moment of CO for which it is necessary to allow for correlation in order to determine the correct sign of the dipole[8]. Expectation values of two-particle operators, which depend on the two-particle distribution are, not surprisingly, very dependent on correlation effects, an example of this being the calculation of incoherent X-ray scattering factors.

Many methods of analysing and studying correlation effects have been proposed. The work of Nesbet[9], Brueckner[10] and Sinanoglu[10] has been particularly note-worthy. However, much of the early work on the problem was due to Hylleraas[11] who proposed three methods of constructing correlated wavefunctions, all of which are still in use today. We give here a brief description of one of these methods. For a more detailed treatment we refer the reader to the literature[12].

Configuration Interaction Wavefunctions and Natural Expansions.

The method of Hylleraas referred to above is known as the superposition of configurations or configuration interaction (CI) method. In this approach the wavefunction is expanded as a linear combination of Slater determinants, each of which is composed from a basis set of orbitals; the problem being to determine the coefficients. Application of the variation theorem to such a

trial wavefunction leads to the following matrix equation determining
the expansion coefficients:

$$\underline{H}\,\underline{c}^m = E^m\,\underline{S}\,\underline{c}^m .$$

(0.1.5)

The H matrix has elements

$$H_{ij} = \langle \Phi_i | H | \Phi_j \rangle ,$$

where Φ_i is the ith configuration (determinant or linear
combination of determinants) and the $\underline{S}$, or overlap, matrix has
elements

$$S_{ij} = \langle \Phi_i | \Phi_j \rangle .$$

The vector $\underline{c}^m$ has components $C_i{}^m$ corresponding to the coefficient
of the ith configuration and associated with the mth eigenvalue
E^m . Frequently the basis orbitals are chosen to be orthonormal,
which leads to the overlap matrix taking the form of the unit
matrix. In this instance the solution to equation (0.1.5)
reduces to the problem of solving the secular equation:

$$\begin{vmatrix} H_{11} - E & H_{12} & H_{13} \cdots & H_{1n} \\ H_{21} & H_{22} - E & H_{23} \cdots & H_{2n} \\ & & & \\ H_{n1} & H_{n2} & H_{n3} \cdots & H_{nn} - E \end{vmatrix} = 0 .$$

(0.1.6)

A CI calculation therefore generally takes the following form:

(1) Choose a set of orbitals - usually, though not necessarily,
chosen to be orthogonal.

(2)   Construct a set of configurations from these orbitals

appropriate to the particular atomic or molecular state.

(3)   Calculate the matrix elements H_{ij} between configurations.

(4)   Solve the secular equation.

Clearly, provided that the set of basis orbitals can

be made complete and provided that all possible configurations

are included the method can, in principle, yield the exact non-

relativistic energy limit.   In practice, of course, there is

a restriction on the number of configurations that can be

conveniently handled.   The main drawback of the method is that,

at the outset, it is not certain which configurations will be

most effective in lowering the energy.   In addition, it is found

that the energy convergence is notoriously slow.

Lowdin[14] has defined natural spin orbitals $\chi_i(\underline{x}_i)$

as being those orbitals which produce a diagonal representation

of the first order density matrix $\rho(\underline{x}_1', \underline{x}_1)$, that is:

$$\rho(\underline{x}_1', \underline{x}_1) = n \int \Psi(\underline{x}_1', \underline{x}_2, \dots \underline{x}_n) \Psi^*(\underline{x}_1, \underline{x}_2, \dots \underline{x}_n) d\underline{x}_2 \dots d\underline{x}_n$$

$$= \sum_i c_i \chi_i(\underline{x}_1') \chi_i^*(\underline{x}_1) , \qquad\qquad (0.1.7)$$

where $\underline{x}_j$ refers to the space and spin coordinates of electron j.

The constant c_i is known as the occupation number of the

i^{th} natural orbital (NO).   Using a theorem due to Schmidt[15] it

may be shown that the use of the highest N occupied natural

orbitals in a CI wavefunction leads to the most rapidly convergent

expansion possible for any basis set of N orbitals.   Formally this

result is of little value since in order to determine the natural

orbitals it is first necessary to know the density matrix, which

in turn demands a knowledge of the exact wavefunction. However, this result may be utilised by performing an approximate CI calculation, determining approximate natural orbitals, and then repeating the procedure but now using only those natural orbitals of highest occupation number and augmenting the basis set with a number of new functions. Among such procedures we may mention the 'pseudo-natural orbital' techniques of Edmiston and Krauss[16] and the 'iterative NO-CI' procedure of Bender and Davidson[17]. Alternatively, natural orbitals may be used for a different purpose — namely, as an instrument to further our understanding of electron correlation, and its influence in many physical problems; for example, atomic and molecular scattering reactions. This end may be achieved by expanding an existing CI wavefunction in terms of natural orbitals which are then grouped into natural configurations. This is generally known as the natural expansion of the wavefunction. Such an expansion is well ordered by virtue of the energetically decreasing importance of each additional natural configuration, thereby conveniently 'partitioning' the wavefunction for use in further calculations[18].

The Scattering Matrix

In the present work, we are concerned with total scattering cross sections which include transition probabilities for direct and rearrangement collisions respectively. As shown in Appendix A, the total cross section for a transition between states m and n is given by

$$Q = \frac{\mu^2}{4\pi^2} \frac{k_n}{k_m} \int |T_{mn}|^2 \, d\Omega \, , \qquad (0.1.8)$$

where μ is the reduced mass of the colliding systems, and k_m, k_n

are the associated relative momenta. T_{mn} is given by

$$T_{mn} = \langle \psi_n \mid V \mid \Psi_m^+ \rangle . \qquad (0.1.9)$$

Here V is the perturbation corresponding to the unperturbed Hamiltonian H_0, such that $H = H_0 + V$. ψ_m, ψ_n are eigenfunctions of H_0 corresponding to total energies E_m, E_n respectively. Ψ_m^+ is an eigenfunction of the total Hamiltonian H, and it may be shown that

$$\Omega^+ \psi_m = \Psi_m^+ , \qquad (0.1.10)$$

where Ω^+ is the Møller operator[a]. This establishes the important fact that Ω^+ acting on a continuum eigenfunction of H_0 generates the continuum eigenfunction of H which has the same energy E_m, and which satisfies outgoing-wave boundary conditions. Ψ_m^+, being an eigenfunction of the total Hamiltonian H, represents a complete solution of the scattering problem. Therefore, Ψ_m^+ contains the description of all possible reactions and the only problem remaining is the extraction from Ψ_m^+ of the information which refers specifically to the reaction of interest. If equation (0.1.9) could be solved exactly, then all the information about any particular reaction would be available; that is, we would have solved the complete scattering problem. In practice, however, such a solution is not readily obtainable, and many theories to evaluate T_{mn}, or its equivalent, have been proposed. The simplest of these is to replace Ψ_m^+ by ψ_m, to give

$$T_{mn} = \langle \psi_n \mid V \mid \psi_m \rangle , \qquad (0.1.11)$$

which is just the first Born Approximation.

It is not intended here to consider all the different theories proposed to date. For an excellent treatment of this,

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[a] See Appendix A.

which includes references to several experiments which support, or contradict, the many theories, the reader is referred to McDowell and Coleman[19].

Aims of the Present Work

In attempting to describe any reaction which includes a system more complicated than hydrogen, any theory, no matter how good, will suffer from a limitation; namely, that the many electron wavefunction is not known exactly. This necessitates the use of approximate wavefunctions and, as a consequence, some authors, in testing their theories, have not included electron correlation in their calculation, thereby introducing a source of error over and above that due to the approximations made in the theory. Hence, a degree of uncertainty must be associated with any conclusions drawn. The aims of this work are to remove this degree of uncertainty by the systematic introduction of electron correlation, via the natural expansion, into some first and second order approximations of atomic scattering, thereby enabling us to make a number of comments on the theories examined. It must be pointed out at this stage that only high energy collisions (and therefore approximations) are considered; i.e., at impact velocities which are greater than the velocity of the orbital electrons of the target atom.

In Part I, a brief outline is given of the first Born Approximation which is applied here to the inelastic collisions between helium atoms. In Part II, we examine the effects of electron correlation on the Impulse approximation, and on the Continuum Distorted Wave approximation; in the present study both are applied to electron capture by protons in helium. For the sake of completeness we include, in Appendix A, the formal time-dependent theory of scattering.

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P A R T   I

GROUND-STATE CORRELATION EFFECTS

IN He-He INELASTIC SCATTERING

CHAPTER 1.1

Introduction

The study of transition probabilities and collision
cross sections for helium atoms is of importance in such diverse
fields as astrophysics[1], electron microscopy, radiation damage,
atmospheric physics, and research into controlled thermonuclear
fusion[2]. It is of no surprise therefore, that there is such a large
interest in the quest for theories which will lead to the easy
and accurate evaluation of scattering cross sections. However,
up to the present time, no exact theories exist, even for a
hydrogenic target system. As mentioned previously, when evaluating
the various cross sections for many electron targets, there are
uncertainties due to approximations made in the theory, and due to
the approximate nature of the wavefunctions used in the application
of the theory. Therefore, any study of the effects of electron
correlation is bound within the framework of the particular theory
under examination.

The first Born Approximation (FBA) has been widely applied
by many workers to the evaluation of excitation, ionization, and
electron capture cross sections, because it is relatively easily
applied to large atoms and, for sufficiently high projectile energy,
it is often in reasonable agreement with experiment[3-8]. In order
to estimate the possible error due to the use of approximate
wavefunctions in the Born Approximation, the differential cross
section for a given inelastic scattering reaction may be evaluated
using several different formulae which are formally equivalent but
which give different results for approximate wavefunctions, since

they weight the regions of coordinate space differently. Of

these formulae, the two most commonly used are often referred to

as the 'length' and 'velocity' formulae[8], by analogy with similar

expressions introduced by Chandrasekhar[9] in his work on photoionization.

Accurate cross sections for the $1\ ^1S \longrightarrow n^1P$ (n = 2 to 6) and

$1^1S \longrightarrow n^1D$ (n = 3 to 6) excitations of helium, for both electron

and proton impact, have been calculated by Bell, Kennedy and

Kingston[10]. To a very good approximation the results of these

calculations may be regarded as 'exact', within the FBA, since the

discrepancy between 'length' and 'velocity' forms is seen to be

very small[10]. Calculations have also been performed using

analytical Hartree-Fock (HF) functions[11], unrestricted HF functions[12]

and a 6-term explicitly correlated wavefunction[13]. A comparison

of these calculations with 'accurate' FBA results confirms the

suggestion of Altshuler[14] that scattering cross sections are

sensitive to the description of electron correlation – particularly

in the ground state of the target atom. Although the magnitude

of the total 'correlation effect' is, on the whole, fairly well

established, the nature of this sensitivity is not well known. With

this in mind, Banyard and Seddon[15,16] have examined cross sections

for the $1^1S \longrightarrow 2^1P$ and $1^1S \longrightarrow 3^1P$ excitations of He and Li^+,

arising from the scattering of e^-, H^+ and H. Electron correlation

was introduced into the description of the ground states in a

systematic and well-ordered manner by using configuration interaction

wavefunctions of Weiss[17] expressed in the form of natural expansions[18].

In the present work we extend their analysis of ground state

correlation effects to a consideration of helium-helium scattering,

where both the projectile and target atoms are initially in their

ground state. Altogether, five possible inelastic reactions are considered:

two single excitation reactions,
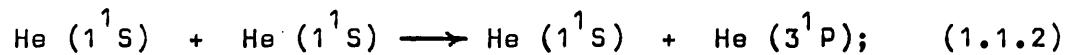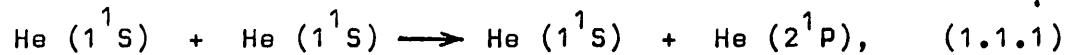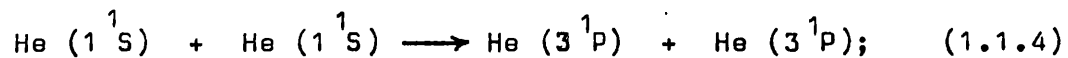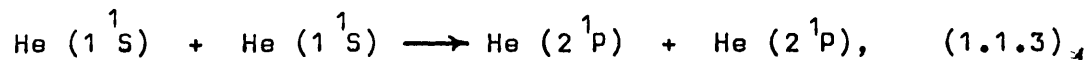
$$He\ (1^1S)\ +\ He\ (1^1S)\ \longrightarrow\ He\ (1^1S)\ +\ He\ (2^1P), \qquad (1.1.1)$$

$$He\ (1^1S)\ +\ He\ (1^1S)\ \longrightarrow\ He\ (1^1S)\ +\ He\ (3^1P); \qquad (1.1.2)$$

two double excitations,

$$He\ (1^1S)\ +\ He\ (1^1S)\ \longrightarrow\ He\ (2^1P)\ +\ He\ (2^1P), \qquad (1.1.3)$$

$$He\ (1^1S)\ +\ He\ (1^1S)\ \longrightarrow\ He\ (3^1P)\ +\ He\ (3^1P); \qquad (1.1.4)$$

and the mixed double excitation,

$$He\ (1^1S)\ +\ He\ (1^1S)\ \longrightarrow\ He\ (2^1P)\ +\ He\ (3^1P). \qquad (1.1.5)$$
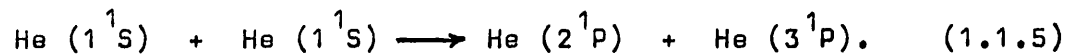
A brief comment is also made regarding the elastic scattering cross section.

CHAPTER 1.2

First Born Approximation in Atom-Atom Scattering

The theory of the first Born Approximation is well known, and therefore it is only necessary to give a brief outline of the FBA in the case of atom-atom collisions, essentially to establish definitions for the purpose of discussion.

Consider an atom A with N_A electrons, nuclear charge Z_A, reduced mass M and LAB velocity v_o incident upon an atom B with N_B electrons and nuclear charge Z_B. We require to solve the non-relativistic Schrodinger equation for the system[a]

$$\left[-\frac{1}{2M}\nabla_R^2 + H_A + H_B + V(\underline{r}_A,\underline{r}_B,\underline{R}) - E_T \right] \Psi(\underline{r}_A,\underline{r}_B,\underline{R}) = 0 , \quad (1.2.1)$$

where $\underline{r}_A$ and $\underline{r}_B$ represent collectively the internal electronic coordinates of the atoms and $\underline{R}$ is the internuclear distance. The first term of equation (1.2.1) represents the kinetic energy of atom A, H_A and H_B give the internal energies of the atoms and $V(\underline{r}_A,\underline{r}_B,\underline{R})$ is the interaction potential:

$$V(\underline{r}_A,\underline{r}_B,\underline{R}) = \frac{Z_A Z_B}{R} - Z_B \sum_{s=1}^{N_A} \left| \underline{R} + \underline{r}_{A_s} \right|^{-1} - Z_A \sum_{t=1}^{N_B} \left| \underline{R} - \underline{r}_{B_t} \right|^{-1}$$

$$+ \sum_{s=1}^{N_A} \sum_{t=1}^{N_B} \left| \underline{R} + \underline{r}_{A_s} - \underline{r}_{B_t} \right|^{-1} . \quad (1.2.2)$$

E_T is equal to the projectile kinetic energy ($\frac{1}{2}Mv_o^2$) plus the sum of the energies of the two atoms in their initial states m and p ($E_o = E_A^m + E_B^p$). We expand $\Psi(\underline{r}_A,\underline{r}_B,\underline{R})$ as follows:

$$\Psi(\underline{r}_A, \underline{r}_B, \underline{R}) = \sum_i F_i(\underline{R}) \Psi_i(\underline{r}_A, \underline{r}_B) , \quad (1.2.3)$$

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[a] Atomic units are used throughout this thesis, unless stated otherwise

where $\left\{ \psi_i \right\}$ is the complete set of orthonormal eigenfunctions of the pseudo-molecule AB satisfying

$$\left[H_A(\underline{r}_A) + H_B(\underline{r}_B) \right] \psi_i(\underline{r}_A, \underline{r}_B) = (\varepsilon_A^a + \varepsilon_B^b) \psi_i(\underline{r}_A, \underline{r}_B)$$

$$= E_i \, \psi_i(\underline{r}_A, \underline{r}_B) \, . \qquad (1.2.4)$$

When AB is in a state i, atom A is in state a and atom B is in state b. For $\psi_i(\underline{r}_A, \underline{r}_B)$ we choose

$$\psi_i(\underline{r}_A, \underline{r}_B) = U_a(\underline{r}_A) V_b(\underline{r}_B) \, , \qquad (1.2.5)$$

where $U(\underline{r}_A)$ and $V(\underline{r}_B)$ are the eigenfunctions for the individual atoms, satisfying

$$H_A \, U_a(\underline{r}_A) = \varepsilon_A^a \, U_a(\underline{r}_A) \, , \qquad (1.2.6a)$$

$$H_B V_b(\underline{r}_B) = \varepsilon_B^b V_b(\underline{r}_B) \, . \qquad (1.1.6b)$$

Clearly, equation (1.2.5) neglects electron correlation between electrons in different atoms. However, this 'independent particle' approximation will be very good in the asymptotic region where $\underline{R} \longrightarrow \infty$.

Substituting equations (1.2.3) and (1.2.5) into equation (1.2.1), then simplifying by making use of equation (1.2.4), multiplying throughout by $\psi_j^*(\underline{r}_A, \underline{r}_B)$ and finally integrating over $\underline{r}_A$, $\underline{r}_B$ we obtain

$$(\nabla_{\underline{R}}^2 + k_j^2) F_j(\underline{R}) = -2M \int V(\underline{r}_A, \underline{r}_B, \underline{R}) \psi(\underline{r}_A, \underline{r}_B, \underline{R}) \psi_j^*(\underline{r}_A, \underline{r}_B) d\underline{r}_A \, d\underline{r}_B ,$$

$$(1.2.7)$$

where $k_j^2 = 2M(E_T - E_j)$. Substituting again for $\psi(\underline{r}_A, \underline{r}_B, \underline{R})$, equation (1.2.7) becomes

$$(\nabla_{\underline{R}}^2 + k_j^2) F_j(\underline{R}) = -2M \sum_i V_{ij}(\underline{R}) \, F_i(\underline{R}) \, , \qquad (1.2.8)$$

where $V_{ij}(\underline{R}) = \int V(\underline{r}_A, \underline{r}_B, \underline{R}) \Psi_i(\underline{r}_A, \underline{r}_B) \Psi_j^*(\underline{r}_A, \underline{r}_B) \, d\underline{r}_A \, d\underline{r}_B$. (1.2.9)

In Born's method two approximations are made:

(i) Neglect V_{ii} for all i : we assume there is no electrostatic interaction between projectile and target atoms.

(ii) Neglect $F_i(\underline{R})$, except for $i = 0$. This means that all the coupling terms V_{ij} on the right hand side of equation (1.2.8) are assumed zero except V_{oj} which couples the states involved in the excitation.

Hence, from equation (1.2.3),

$$\Psi(\underline{r}_A, \underline{r}_B, \underline{R}) = F_o(\underline{R}) \Psi_o(\underline{r}_A, \underline{r}_B)$$

$$= F_o(\underline{R}) U_m(\underline{r}_A) \mathcal{V}_p(\underline{r}_B) \quad .$$

From (i) above, $F_o(\underline{R})$ must have the form of an undistorted plane wave and so we may write

$$\Psi(\underline{r}_A, \underline{r}_B, \underline{R}) = e^{i\underline{k}_o \cdot \underline{R}} U_m(\underline{r}_A) \mathcal{V}_p(\underline{r}_B) \quad , \qquad (1.2.10)$$

consequently, equation (1.2.8) becomes

$$(\nabla_{\underline{R}}^2 + k_j^2) F_j(\underline{R}) = -2m V_{oj} e^{i\underline{k}_o \cdot \underline{R}} \quad . \qquad (1.2.11)$$

In the limit of $\underline{R} \longrightarrow \infty$, the right hand side of equation (1.2.11) vanishes and $F_j(\underline{R})$ then satisfies the equation for a free particle of energy $(E_T - E_j)$. Clearly $F_j(\underline{R})$ has the asymptotic form of a scattered wave:

$$F_j(\underline{R}) = \frac{e^{i\underline{k}_j \cdot \underline{R}}}{R} f_{oj}(\underline{K}) \quad , \qquad (1.2.12)$$

where $\underline{K} = \underline{k}_o - \underline{k}_j$, the change in momentum on collision, and $f_{oj}(\underline{K})$ is the scattering amplitude. Equation (1.2.11) can be solved[a] for $F_j(\underline{R})$ in terms of $f_{oj}(\underline{K})$. A direct comparison of this solution with equation (1.2.12) yields the expression for the scattering amplitude:

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[a] See, for example, Chapter IV, reference 5.

$$f_{mn \atop pq}(\underline{K}) = -\frac{m}{2\pi} \int e^{i\underline{K}\cdot\underline{R}} V(\underline{r}_A,\underline{r}_B,\underline{R}) U_m(\underline{r}_A) U_n^*(\underline{r}_A) \mathcal{V}_p(\underline{r}_B) \mathcal{V}_q^*(\underline{r}_B) \cdot$$

$$\cdot \, d\underline{r}_A \, d\underline{r}_B \, d\underline{R} \quad , \tag{1.2.13}$$

where n and q denote the final states of atoms A and B respectively.
Integrating over $\underline{R}$ by using Bethe's[19] integral, we obtain:

$$f_{mn \atop pq}(\underline{K}) = \frac{-2m}{K^2}\left[\delta_{mn}\delta_{pq}Z_A Z_B - Z_B\delta_{pq}\eta_{mn}^A(-K) - Z_A\delta_{mn}\mathcal{E}_{pq}^B(\underline{K})\right.$$

$$\left. + \eta_{mn}^A(-K)\,\mathcal{E}_{pq}^B(\underline{K})\right] \quad , \tag{1.2.14}$$

where $\quad \delta_{ij} = 1 \, , \, i = j$

$\qquad\quad \delta_{ij} = 0 \, , \, i \neq j \, .$

Therefore we have, finally

$$f_{mn \atop pq}(\underline{K}) = \frac{-2m}{K^2}\left[\delta_{mn}Z_A - \eta_{mn}^A(-\underline{K})\right]\left[\delta_{pq}Z_B - \mathcal{E}_{pq}^B(\underline{K})\right] \quad , \tag{1.2.15}$$

where the scattering form factors η_{mn}^A and $\mathcal{E}_{pq}^B$ are given by:

$$\eta_{mn}^A(-\underline{K}) = \sum_{s=1}^{N_A} \int e^{-i\underline{K}\cdot\underline{r}_{As}} U_m(\underline{r}_A) U_n^*(\underline{r}_A) \, d\underline{r}_A \quad , \tag{1.2.16a}$$

$$\mathcal{E}_{pq}^B(\underline{K}) = \sum_{t=1}^{N_B} \int e^{i\underline{K}\cdot\underline{r}_{Bt}} \mathcal{V}_p(\underline{r}_B)\mathcal{V}_q^*(\underline{r}_B) \, d\underline{r}_B \quad . \tag{1.2.16b}$$

In terms of momentum variables, the differential cross section is given by

$$I_{mn \atop pq}(\underline{K}) = \frac{2\pi K}{k_o^2} \left| f_{mn \atop pq}(\underline{K}) \right|^2 \quad . \tag{1.2.17}$$

The total cross section is

$$Q(T) = \int_{K_{min}}^{K_{max}} I_{mn \atop pq}(\underline{K}) \, dK \quad , \tag{1.2.18}$$

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where T is the kinetic energy of the incoming projectile in the LAB frame. Thus,

$$Q(T) = \frac{4\pi m}{T} \int_{K_{min}}^{K_{max}} \left[\delta_{mn} Z_A - \eta_{mn}^A(-\underline{K}) \right]^2 \left[\delta_{pq} Z_B - \varepsilon_{pq}^B(\underline{K}) \right]^2 K^{-3} dK.$$

(1.2.19)

The limits K_{max} and K_{min} are determined from the kinematics of the reaction, and are given by

$$K_{\substack{max \\ min}} = m \left(\frac{2T}{m_p} \right)^{\frac{1}{2}} \pm \left[2m \left(\frac{TM}{m_p} - \Delta E_{\substack{mn \\ pq}} \right) \right]^{\frac{1}{2}}$$

(1.2.20)

where m_p is the mass of the projectile, and $\Delta E_{\substack{mn \\ pq}}$ is the sum of the excitation energies of the projectile and target systems $(\Delta E_{mn} + \Delta E_{pq})$.

Equation (1.2.19) describes elastic scattering under the condition that the kroenecker deltas are unity; K_{min} then becomes zero. At sufficiently high projectile energy, the value for K_{max} is effectively infinite, and it can be shown[19] that the elastic cross section $Q(T)$ then behaves as BT^{-1}, where the constant B can be referred to as the cross section coefficient.

Calculating the limit as $K \longrightarrow 0$ of the quantity $\left| \varepsilon_{pq}^B(\underline{K}) \right|^2 \bigg/ K^2$ we find that the operator in this expression reduces to $\sum_t \underline{r}_{B_t}$ and, as a result equation (1.2.16a) is often referred to as the length formula. However, it may be shown[20] that an equivalent form of equation (1.2.16a) is

$$\varepsilon_{pq}^B(\underline{K}) = \frac{8i\pi^2 K}{2\Delta E_{pq} + K^2} \sum_{t=1}^{N_B} \int e^{i\underline{K} \cdot \underline{r}_{B_t}} \mathcal{V}_p(\underline{r}_B) \nabla_{\underline{r}_{B_t}} \mathcal{V}_q^*(\underline{r}_B) d\underline{r}_B ,$$

(1.2.21)

and now the operator arising from the limiting process above has

been reduced to $\sum_t \dot{\underline{r}}_{B_t}$; hence equation (1.2.21) is referred

to as the velocity formula. For approximate wavefunctions,

equations (1.2.16a) and (1.2.21) do not yield the same results,

since the two formulae weight the regions of configuration space

differently. The velocity formula draws its major contribution

from regions of space closer to the nucleus than does the length

formula and, consequently, for approximate wavefunctions the

velocity formulation often gives better agreement with results

calculated from 'exact' wavefunctions. In his study of electron

correlation effects in atomic scattering reactions, Seddon[20]

concludes that, for the CI wavefunctions used, the velocity

formula generally gives more accurate results than the length

formula. Consequently, in the present work, we have used the

velocity formulation in evaluating the form factors η^A_{mn} and

ε^B_{pq}.

CHAPTER 1.3

Wavefunctions and Results

In the evaluation of equation (1.2.21), applied to helium-helium scattering, we have taken for the ground state wavefunction the natural expansion of the 35-configuration CI wavefunction of Weiss[21], truncated to include only the first X terms. Thus, as X is increased from unity (approximating the HF equivalent wavefunction[22]) to fifteen (equal to Weiss' total wavefunction), electron correlation is introduced into the ground state through configurations which are well ordered by virtue of their energetically decreasing importance. This helium wavefunction, denoted by $\Psi_X(1,2)$, may be written as

$$\Psi_X(\underline{r}_1,\underline{r}_2) = N_X \sum_{i=1}^{X} a_i \, \Phi_i(\underline{r}_1,\underline{r}_2) \qquad (X = 1,2,3, \ldots 15).$$

$$(1.3.1)$$

The natural configurations Φ_i are of the form

$$\Phi_i(1,2) = (2\lambda_i + 1)^{-\frac{1}{2}} \, S \sum_{\mu=-\lambda_i}^{\lambda_i} \chi_\mu^i(1) \; \chi_{-\mu}^i(2) , \qquad (1.3.2)$$

where $S = \left[\alpha(1)\beta(2) - \beta(1)\alpha(2) \right]$ and the natural orbitals χ_μ^i are linear combinations of the 15 basis Slater-type orbitals (STO's)

$$\chi_\mu^i = \sum_{j=1}^{15} b_j^i \, \phi_{n_j \lambda_j \mu} , \qquad (1.3.3)$$

where

$$\phi_{n_j \lambda_j \mu}(r,\theta,\phi) = r^{n_j - 1} e^{-J_j r} Y_{\lambda_j \mu}(\theta,\phi) \qquad (1.3.4)$$

and

$$b_j^i = \frac{a_i(2J_j)^{n_j+\frac{1}{2}}}{(2n_j)!^{\frac{1}{2}}} . \qquad (1.3.5)$$

Note that $b_j^i = 0$ for $\ell_i \neq \ell_j$ for S states of helium (this does not apply for S states of larger atoms[23]). Each wavefunction Ψ_X was renormalized to unity by a multiplying factor N_X:

$$ N_X = \left[\sum_{i=1}^{X} a_i^2 \right]^{-\frac{1}{2}} . \qquad (1.3.6) $$

The total energy expectation value E_X for each ground state wavefunction $\Psi_X(1,2)$ was used to obtain the $1\,^1S \longrightarrow n\,^1P$ excitation energy ΔE_X. The energies E_X are shown in Table 1.1 along with the natural expansion coefficients a_i. The quantum numbers ℓ of the STO's used to construct each natural configuration are also indicated.

The normalized excited state wavefunctions, which are orthogonal to the ground state wavefunction, are of the form

$$ \Psi_n(1,2) = \frac{1}{\sqrt{2}} \left[\mathcal{U}_{1s}(1)\, \mathcal{U}_{np_0}(2) + \mathcal{U}_{np_0}(1)\, \mathcal{U}_{1s}(2) \right] , \qquad (1.3.7) $$

where $\mathcal{U}_{1s}(r,\theta,\phi) = 2\,\alpha^{3/2} \exp(-\alpha r)\, Y_{0,0}(\theta,\phi)$ $\qquad (1.3.8)$

and $\mathcal{U}_{np_0}(r,\theta,\phi) = N_{np}\,(c + dr)r \exp(-\beta r) Y_{1,0}(\theta,\phi).$ $\qquad (1.3.9)$

For a $2p_0$ orbital,

$$ c = 1 \; ; \; d = 0 \; ; \; N_{2p} = \frac{2\beta^{5/2}}{\sqrt{3}} \qquad (1.3.10) $$

and for a $3p_0$ orbital,

$$ c = \frac{2}{\beta} \; ; \; d = -1 \; ; \; N_{3p} = \frac{4\beta^{7/2}}{3\sqrt{2}} . \qquad (1.3.11) $$

The optimized exponents (α, β) and energies for the $2\,^1P$ and $3\,^1P$ states of helium are shown in Table 1.2. For comparison, the Hartree-Fock and exact energies are also given. We see that the optimum value for α is almost identical to Z - the nuclear charge;

this is expected since the screening of the nucleus by the p

electron is very small. The optimized values for β are close

to $(Z - 1)/n$ indicating that the 1s electron screens the nucleus

to the extent of a large fraction of an electronic charge.

The use of wavefunctions (1.3.7) and (1.3.1) in equation

(1.2.21) enables us to evaluate the form factors η and ε

analytically, leaving only the final integration in (1.2.19)

to be performed numerically. Great care was taken to ensure

numerical accuracy of at least four significant figures.

We have defined the terms 'single excitation', 'double

excitation', and 'mixed double excitation' in equations (1.1.1)

to (1.1.5). Results for the single and double excitations to the

$3\,{}^1P$ state are given in Tables 1.3 and 1.4, respectively. Results

for the single and double excitations to the $2^1 P$ state are

presented in Tables 1.5 and 1.6, respectively, and finally, the

mixed double excitation results are given in Table 1.7. The

symmetry of the basis orbitals used to construct each additional

natural configuration, as X is increased, is given by Banyard

and Baker[22]; however, for convenience, they are also quoted in the

tables after each X value. Values of the total cross section

Q(T) for the five reactions (when X = 15) are compared graphically

in Figure 1.1.

CHAPTER 1.4

Discussion

Since our analysis is concerned with ground state correlation effects, our discussion will concentrate on results for transitions to the excited state which should, intuitively, be least influenced by correlation, namely, the 3 ^{1}P state.

Correlation effects influence $Q(T)$ through improvements in (i) the transition energy, and (ii) the wavefunction used in the evaluation of the form factors. The nature of this dual dependence as X is increased has already been discussed by Seddon and Banyard[16]. Essentially, at low energies, the changes which occur in the cross sections are dependent on the monotonic increase which occurs in the transition energy ΔE_X as X varies from 1 to 15. When T is large, however, the initial introduction of correlation causes changes in $Q(T)$ through variations which occur in the integrand of equation (1.2.21). As X increases beyond 6, the variations in the cross sections become once again dominated by the behaviour of ΔE_X. Table 1.3 shows that for low impact energies the non-correlated result (X = 1) is reduced by about a quarter when using the total CI wavefunction (X = 15). However, as T increases, the results for X = 1 and 15 are seen to converge. The initial introduction of correlation, based on p-orbitals and therefore of an essentially angular nature, causes a drop in the value of $Q(T)$ at low T and an increase at large T which results in an improvement and worsening, respectively, of the agreement with the X = 15 values. The addition of purely radial correlation through the inclusion of a configuration based on s-orbitals as X = 2 $\longrightarrow$ 3 causes a reduction in $Q(T)$ for all T.

However, at high energy, the results are still inferior to the

non-correlated values, when compared with X = 15, even though we

have accounted for 85% of the correlation energy at X = 3: at low

energies, on the other hand, a significant improvement has occurred.

Table 1.3 also reveals that, relative to X = 1, the point of

cross-over of the X = 3 values occurs at a higher energy than

that observed for X = 2. This latter trend continues as X increases

and when X = 6 the cross-over point is in excess of 35000 keV.

In the energy range considered here, the results for 6 $\leqslant$ X $\leqslant$ 15

exhibited a general convergence towards X = 15 as a consequence of

being dependent essentially on the transition energy. Overall,

p-based configurations were found to be of greater relative

significance than other angular-based configurations in their

influence on Q(T) - irrespective of their ordering in X. Such a

feature, reflecting the symmetry of the excited states, may well

be modified if the 2 ^{1}P and 3 ^{1}P wavefunctions were of correlated

form.

Inspection of Table 1.4 shows that, as expected, the Q(T)

values for the single atom excitation to the 3 ^{1}P state are larger

than those for the double excitation. However, from a percentage

point of view, correlation effects are seen to be of less importance.

As X increases, the trends in relative magnitudes shown in Table

1.4 follow those for the double excitation but the cross-over

points, with respect to X = 1, were found to occur at lower energies.

As before, p-based configurations gave rise to the greatest change

when introducing angular correlation. In passing, we note that

the influence of correlation in the present case is less than

that determined[16] for the 3 ^{1}P excitation of He by He$^+$ ions

although, in that instance, the Q(T) values are larger due to the

long range nature of the interaction forces - c.f. Table 4 of Seddon and Banyard[16]. A further comparison with Table 4 of the earlier work indicates that, at comparable velocities, the present results are in close agreement with those for $H - He(1\ ^1S \longrightarrow 3\ ^1P)$ scattering.

Turning now to the $1\ ^1S \longrightarrow 2\ ^1P$ excitation, Tables 1.5 and 1.6 show that the cross sections for the double and single $2\ ^1P$ excitation reactions are, of course, considerably larger than their $3\ ^1P$ counterparts. For the $2\ ^1P$ excitation the trends in $Q(T)$ as X is increased were found to parallel those for the $3\ ^1P$. This also holds for comparisons between double excitations except that, in contrast with $(3\ ^1P, 3\ ^1P)$, the cross sections for the $(2\ ^1P, 2\ ^1P)$ excitation for X = 3 were found to be superior to those for X = 1 over the whole energy range when compared with X = 15 as a reference. As shown in Tables 1.5 and 1.6, the influence of angular correlation on $Q(T)$ was once again dominated by the p-based configurations. For the mixed $(2\ ^1P, 3\ ^1P)$ excitation, presented in Table 1.7, $Q(T)$ corresponds most closely in magnitude with $(3\ ^1P, 3\ ^1P)$. This feature arises not only because of the nature of the integrand in equation (1.2.19) but also from the size of the lower limit K_{min}. Consequently, as X increases, the trends in $Q(T)$ at high T follow those for the double $3\ ^1P$ excitation.

The energy dependence of the single, double and mixed excitation cross sections for X = 15 can be compared by inspection of Figure 1.1. We note that double and mixed excitations peak at a common T value; a similar observation holds for the single excitation. This behaviour has been rationalized in an earlier work[15]. We note also that the double, mixed double, and single

excitation cross sections all exhibit a high energy 'tail' which
is very flat. This rather unphysical feature is a consequence of
the Born approximation, which predicts a comparatively large
tail in the differential scattering cross section $I_{mn}(\underline{K})$ for
large K values – the region which is of particular ^{pq} importance
in evaluating very high impact energy cross sections. Although
not obviously apparent from Figure 1.1 (due to the different scales
used) the single, double, and mixed double excitation high energy
tails are all of approximately the same magnitude.

For elastic scattering the non-correlated (X = 1) and
correlated (X = 15) values for B, the cross section coefficient,
are 4.734 and 4.747, respectively (measured in units of 10^{-18} m^2
per keV). Such small changes for the elastic cross section arise
from the fact that, within the first Born approximation, we are
evaluating a one-particle expectation property over a pure state
and therefore it is easily shown that correlation effects are of
second order. However, for inelastic scattering, where we are
dealing with transitions between different states, correlation can
make a first-order contribution which, as seen, is clearly significant.
This, then, also rationalises the fact that, as observed earlier,
the double excitation cross sections are more sensitive to electron
correlation than are the single excitation cross sections.

Summary

The influence of an ordered introduction of ground state
correlation has been examined for He – He scattering within the
first Born approximation when one or both atoms are excited to
low-lying n ^{1}P states. Electron correlation proved to be most
significant at low projectile energies. For the double excitations,

where correlation effects were of greatest importance, the cross
sections were reduced by about a quarter at low T values. As
observed earlier, correlation gave rise to similar trends irrespective
of whether the excited state was $2\,^1P$ or $3\,^1P$ - the cross sections
possessing a maximum at approximately the same impact energy.
The initial introduction of correlation for He was of an angular
character and accounted for nearly half the total correlation energy;
this resulted in a sizeable improvement over the non-correlated
cross sections only for low energy double excitations - in all
other cases the agreement with the total correlated result became
worse. A general improvement over the non-correlated results was
not achieved until approximately 93% of the ground state correlation
energy had been recovered. The observation regarding the relative
importance of p-based angular correlation effects in the ground
state when determining $Q(T)$ suggests an extension of our analysis
to include correlation effects in the excited states.

It may be of further interest to study reactions in
which the initial state of the target and projectile atoms is not
necessarily the ground state. This would then facilitate an
examination of excited-state correlation effects in atom-atom
scattering reactions.

TABLE 1.1   Natural Expansion of Weiss' 35-Configuration

CI Wavefunction for Helium

(See equation (1.3.1) of text)

X	Coefficient[a] of the X'th configuration a_i	ℓ	Total Energy E_x	$\%E_{corr}$[b]
1	-0.995982	0 (s)	-2.86169	0
2	0.061906	1 (p)	-2.88201	48.4
3	0.061628	0 (s)	-2.89747	85.1
4	0.012644	2 (d)	-2.89927	89.4
5	0.011139	1 (p)	-2.90094	93.4
6	0.007902	0 (s)	-2.90173	95.3
15	0.000652	0 (s)	-2.90320	98.8

(a)   See Reference (22)

(b) $\% \, E_{corr} = 100 \left[E_x - E_{HF} \right] \Big/ \left[E_{exact} - E_{HF} \right]$

TABLE 1.2   Excited State Wavefunctions for Helium

(See equation (1.3.7) of text)

Excited State	α	β	E	Hartree -Fock Energy	Exact Energy
2 ^{1}P	2.003	0.4825	−2.12239	−2.12246[a]	−2.12384[b]
3 ^{1}P	2.00	0.323	−2.05471	−2.05474[a]	−2.05515[b]

(a)   See Reference (24)

(b)   Theoretical value taken from Reference (25)

TABLE 1.3   Cross sections Q(T) (in units of 10^{-24} m^2) for the reaction

He(1 ^{1}S)+He(1 ^{1}S) $\longrightarrow$ He(3 ^{1}P)+He(3 ^{1}P) for various orders of truncation

X in the natural expansion of the ground state wavefunction

T(keV)	X=1(s)	X=2(p)	X=3(s)	X=4(d)	X=5(p)	X=6(s)	X=15(s)
100	0.1386	0.1171	0.0959	0.0938	0.0889	0.0880	0.0867
200	0.7202	0.6720	0.5881	0.5786	0.5570	0.5530	0.5466
400	1.432	1.418	1.294	1.278	1.242	1.235	1.225
600	1.568	1.587	1.469	1.454	1.417	1.411	1.400
1000	1.417	1.461	1.369	1.356	1.326	1.320	1.312
2000	0.9707	1.015	0.9597	0.9517	0.9318	0.9286	0.9236
4000	0.5693	0.5999	0.5694	0.5650	0.5536	0.5518	0.5491
8000	0.3084	0.3262	0.3103	0.3079	0.3019	0.3010	0.2995
12000	0.2112	0.2237	0.2129	0.2113	0.2072	0.2066	0.2056

TABLE 1.4   As in Table 1.3 for the reaction He(1 ^{1}S)+He(1 ^{1}S) $\longrightarrow$ He(1 ^{1}S)+He(3 ^{1}P)

T(keV)	X=1(s)	X=2(p)	X=3(s)	X=4(d)	X=5(p)	X=6(s)	X=15(s)
100	96.24	97.04	94.44	94.07	92.61	92.45	92.29
200	56.60	57.82	56.81	56.64	55.87	55.80	55.76
400	29.86	30.65	30.22	30.14	29.75	29.72	29.70
600	20.13	20.69	20.42	20.37	20.10	20.08	20.07
1000	12.16	12.50	12.34	12.31	12.15	12.14	12.14
2000	6.095	6.270	6.191	6.175	6.096	6.090	6.088
4000	3.050	3.137	3.098	3.090	3.051	3.048	3.047
8000	1.525	1.569	1.549	1.546	1.526	1.524	1.524
12000	1.017	1.046	1.033	1.030	1.017	1.016	1.016

TABLE 1.5   As in Table 1.3, for the reaction He(1 ^{1}S)+He(1 ^{1}S) $\longrightarrow$ He(2 ^{1}P)+He(2 ^{1}P)

T(keV)	X=1(s)	X=2(p)	X=3(s)	X=4(d)	X=5(p)	X=6(s)	X=15(s)
100	2.360	2.016	1.646	1.608	1.521	1.506	1.482
200	10.53	9.849	8.574	8.429	8.103	8.043	7.945
400	19.53	19.29	17.49	17.26	16.75	16.66	16.51
600	21.05	21.22	19.53	19.30	18.79	18.70	18.55
1000	18.89	19.37	18.05	17.87	17.44	17.37	17.25
2000	12.93	13.44	12.65	12.53	12.26	12.21	12.14
4000	7.596	7.948	7.519	7.454	7.297	7.272	7.232
8000	4.121	4.328	4.104	4.070	3.986	3.973	3.952
12000	2.824	2.969	2.818	2.795	2.738	2.728	2.714

TABLE 1.6   As in Table 1.3, for the reaction $He(1\ ^1S)+He(1\ ^1S) \longrightarrow He(1\ ^1S)+He(2\ ^1P)$

T(keV)	X=1(s)	X=2(p)	X=3(s)	X=4(d)	X=5(p)	X=6(s)	X=15(s)
100	314.2	317.9	309.2	307.9	302.9	302.3	301.8
200	181.3	185.6	182.2	181.6	178.9	178.7	178.5
400	95.05	97.72	96.25	95.98	94.63	94.52	94.47
600	64.02	65.88	64.94	64.76	63.86	63.79	63.76
1000	38.62	39.77	39.22	39.11	38.57	38.53	38.52
2000	19.36	19.94	19.67	19.61	19.34	19.32	19.32
4000	9.686	9.977	9.841	9.815	9.679	9.669	9.666
8000	4.843	4.989	4.921	4.908	4.840	4.835	4.834
12000	3.229	3.326	3.281	3.272	3.227	3.224	3.223

TABLE 1.7   As in Table 1.3, for the reaction $He(1^1S)+He(1^1S) \longrightarrow He(2^1P)+He(3^1P)$

T(keV)	X=1(s)	X=2(p)	X=3(s)	X=4(d)	X=5(p)	X=6(s)	X=15(s)
100	0.5692	0.4837	0.3957	0.3868	0.3661	0.3624	0.3569
200	2.737	2.559	2.234	2.197	2.113	2.098	2.073
400	5.257	5.201	4.730	4.671	4.535	4.510	4.471
600	5.712	5.771	5.328	5.269	5.132	5.108	5.070
1000	5.149	5.295	4.948	4.900	4.786	4.766	4.735
2000	3.528	3.679	3.470	3.440	3.366	3.354	3.335
4000	2.072	2.176	2.062	2.045	2.003	1.996	1.986
8000	1.124	1.185	1.125	1.116	1.094	1.090	1.085
12000	0.7699	0.8125	0.7723	0.7662	0.7509	0.7485	0.7448

FIGURE 1.1   Comparisons of the single and double excitation cross
sections Q(T) (in units of $10^{-24} m^2$) vs T. The left-
hand scale refers to the solid curve and the right-
hand scale is for the double excitations shown by
the broken curve.
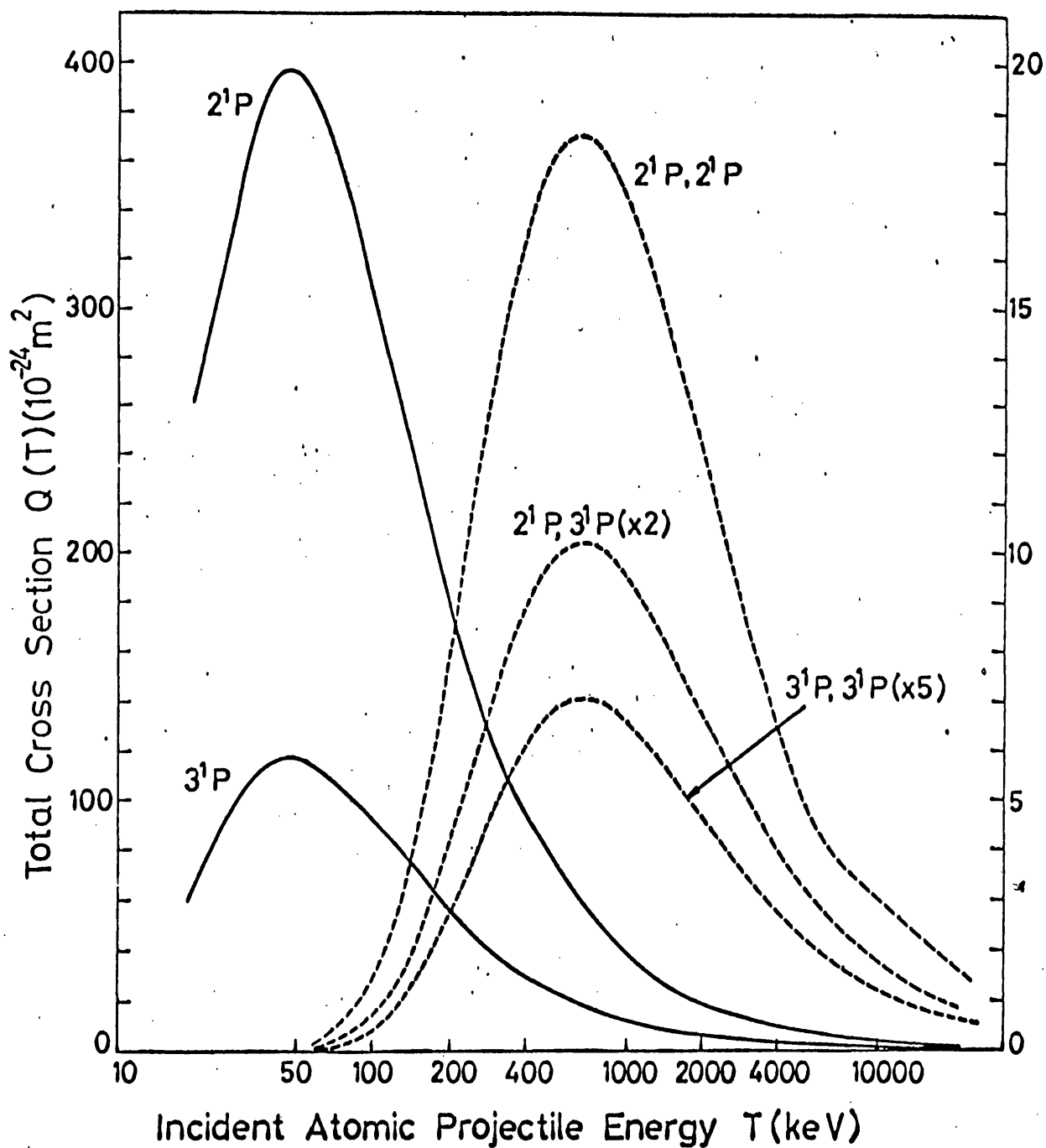
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P A R T   I I

CORRELATION   EFFECTS   IN   ELECTRON   CAPTURE

CROSS   SECTIONS   FOR   A   HELIUM   TARGET

CHAPTER 2.1

Introduction

If, during a collision between two systems of particles, one or more particles are exchanged between the systems, the process is termed a rearrangement collision. In the field of atomic physics, examples of these processes include electron capture by ions (or atoms) from atoms; the exchange contribution to the scattering amplitude for electron scattering by atoms, in which the incident electron may be captured into a bound state of the atom, and an atomic electron ejected; the formation of positronium by positron impact on atoms. Similar reactions involving muons rather than electrons can also be studied. The application of the theory of rearrangement collisions extends beyond the confines of atomic or ionic physics into nuclear and elementary particle physics. In this and the following chapters of this thesis we will be concerned primarily with electron capture processes of the type

$$X^+ + A \longrightarrow X + A^+ , \qquad (2.1.1)$$
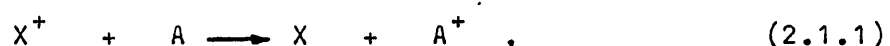
where X^+ is a structureless projectile and A is an atom in its ground state. This type of process has been the subject of several theoretical investigations which have been discussed in reviews by Gerjuoy[1], Bates and McCarroll[2], and Bransden[3], where full references to earlier work may be found. A common conclusion of these reviews is that second-order methods are needed to describe rearrangement processes adequately. It is of considerable interest to examine why this should be so.

For many years it had been thought that there were no fundamental theoretical problems concerning high energy collisions, because the Born approximation was expected to be valid whenever the incoming particle velocities were high compared with the velocities of the atomic electrons. However, this validity became to be questioned for rearrangement processes, although for a long time the situation was far from clear.

Consider a fast structureless particle (1) incident on a system composed of a core (2) and a bound electron (3). During the course of the collision, particle (3) is transferred to give a bound state of (1,3). Let V_{ij} be the interaction potential between particle (i) and particle (j). Taking H_o as the kinetic energy operator, the total Hamiltonian is

$$H = H_o + V_{12} + V_{13} + V_{23} \quad . \tag{2.1.2}$$

We may suppose the initial and final unperturbed systems to have Hamiltonians

$$H_i = H_o + V_{23} \quad , \quad H_f = H_o + V_{13} \quad , \tag{2.1.3}$$

so that the corresponding perturbations are

$$V_i = V_{12} + V_{13} \quad , \quad V_f = V_{12} + V_{23} \quad . \tag{2.1.4}$$

The 'post' form of the first Born approximation T matrix element is[a]

$$T^B_{if} = \left\langle \mathcal{Y}_f \middle| V_f \middle| \mathcal{Y}_i \right\rangle \quad = \quad \left\langle \mathcal{Y}_f \middle| V_{12} + V_{23} \middle| \mathcal{Y}_i \right\rangle , \tag{2.1.5}$$

where $\mathcal{Y}_i$ and $\mathcal{Y}_f$ are the initial and final wavefunctions involved. The earliest quantal calculations of electron capture cross sections were based on a simplified version of the first

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[a] See appendix A

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Born approximation. Oppenheimer[4] and Brinkman and Kramers[5],
who studied protons interacting with hydrogen atoms, argued that
the internuclear potential V_{12} should not have an appreciable
effect on the electron capture probability, and consequently
they omitted this potential in their calculations (referred to
as the OBK approximation). This neglect seemed justified since
at sufficiently high velocities of impact Ψ_i and Ψ_f are
almost orthogonal and independent of the coordinates involved
in V_{12}. Further support was lent to this approach when Mott[6]
pointed out that, on physical grounds, one would expect that the
only effect of the V_{12} interaction would be to change slightly
the direction of propagation of the incoming plane wave. It is
certainly true that in an exact treatment of the problem the
contribution from the internuclear potential is negligible[a],
but it does not necessarily follow that an approximate treatment
will display the same features. Indeed, when compared with the
experimental cross section for the process

$$H^+ + H(1s) \longrightarrow H + H^+ \qquad\qquad (2.1.6)$$

it is found that the OBK cross section[4,5] is clearly much larger
than the measured value[7] over the energy range 25 keV - 250 keV.

Bates and Dalgarno[8] argued that while the previously
mentioned orthogonality condition held if Ψ_i and Ψ_f were
exact, it did not do so for the first Born wavefunctions actually
employed and consequently it may be necessary to reintroduce the
term $\langle \Psi_f | V_{12} | \Psi_i \rangle$. The errors which the approximate
wavefunctions introduced into $\langle \Psi_f | V_{23} | \Psi_i \rangle$ might well
be compensated for by those in $\langle \Psi_f | V_{12} | \Psi_i \rangle$, and it
seemed clear that the matrix element (2.1.5) would be reduced

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[a] See Chapter 2.2, p.59

by interference waves from the two centres. The improvement in
the calculated cross sections was marked. In an independent
calculation, Jackson and Schiff[9], who also argued that the neglect
of V_{12} in equation (2.1.5) was unjustified, obtained similar
results. In an extensive analysis, Mapleton[10] obtained Born
cross sections for reaction (2.1.6) for capture into the
1s, 2s, 2p, 3s, 3p, 4s, and 5s states. His estimate of the total
capture cross section arising from this calculation agreed well
with that of Bates and Dalgarno[8] and, in particular was found to
be in good agreement with the experiment of Wittkower et al.[7]
Mapleton[11] has also considered the reaction

$$H^+ + He(1s^2) \longrightarrow H(n_1 \ell_1 m_1) + He^+(n_2 \ell_2 m_2) \qquad (2.1.7)$$
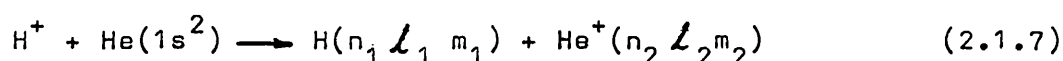
with the following $(n_1 \ell_1 , n_2 \ell_2)$ combinations; (1s, 2s), (1s, 2p),
(2s, 1s), (2s, 2s), (2s, 2p), (2p, 1s), (2p, 2s), (3s, 1s),
(3p, 1s) and (3d, 1s). The resultant first Born total capture
cross section is in very good agreement with the measurements of
Welsh et al[12] at energies above 40 keV. The close agreement
between the Born cross sections and the experimental values is
remarkable, especially since there appears to be little theoretical
justification for this approximation. It would seem that this
agreement is fortuitous since the first Born approximation
differential cross section has a zero and a large angle tail which
are unphysical and arise from the difference between the OBK and
core terms which, for the first Born approximation, are both
large and of opposite sign. Therefore, it would appear that the
use of the first Born approximation for larger target atomic
systems is not advisable, since the cancellation of errors may
no longer be so favourable. A more profound objection to the

use of the Born approximation in rearrangement collisions arises

from the work of Aaron, Amando and Lee[13], who claim to prove

that in any rearrangement collision the Born Series necessarily

diverges. However, Bransden[3] has commented that calculations in

which just the first one or two terms in the Born Series are

retained are not necessarily meaningless; see also the discussion

of Gerjuoy[1].

In the light of the preceding paragraphs, it is evident

that second-order approximations may be necessary to describe

high-energy electron capture processes adequately. In this

connection we mention, in passing, the second Born approximation,

for which detailed analysis of electron capture cross sections

has not been carried out. However, some interesting results

which refer to the high energy limit behaviour of the capture

cross section have been obtained by Drisko[14], who considered

the reaction

$$H^+ + H(1s) \longrightarrow H(1s) + H^+ . \qquad (2.1.8)$$

In his analysis, he used a 'peaking' approximation to evaluate

some integrals, and showed that the contribution to T_{if} from

the proton-proton potential, which plays an important role in the

first Born approximation, is exactly cancelled (to order $1/M_{projectile}$)

in the high energy limit by two of the second Born approximation

terms.

A very interesting approximation is that of the expansion

in atomic and molecular eigenfunctions - in which one expands the

total three-body wavefunction in terms of eigenfunctions of the

subsystems (2 + 3) or (1 + 2) - in that ultimately it may prove

to be a good bridge between low and high energy calculations. In

the charge exchange problem, Bates[15] has shown that advantage may

be taken of the small ratio of the mass of the exchanged electron
to that of the heavy particles to reduce the coupled partial
integro-differential equations of the expansion method to coupled
partial differential equations, for which reliable approximations
are available. An equivalent formalism using the impact parameter
method has also been given by Bates[15] and later rederived by
Mittleman[16], and also by Sil[17] who explicitly employed a variational
method. The application of the expansion method to many-electron
systems has received considerable attention. Two-state calculations
on

$$H^+ \; + \; He(1s^2) \; \longrightarrow \; H(1s) \; + \; He^+(1s) \qquad\qquad (2.1.9)$$
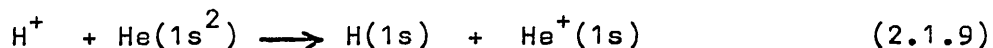
have been reported by Green et al[18] and by Bransden and Sin Fai
Lam[19], and Sin Fai Lam[20] has carried out a five-state calculation.
The procedure is similar to that adopted by Fulton and Mittleman[21]
and will not be described in detail. For the ground state wavefunction
of helium, the first authors[18] take $\Psi(\underline{r}_1 \, , \, \underline{r}_2)$ to be written as

$$\Psi(\underline{r}_1 \, , \, \underline{r}_2) = N \left(e^{-\alpha r_1 - \beta r_2} + e^{-\alpha r_2 - \beta r_1} \right) \; , \qquad (2.1.10)$$

where α and β are variationally determined constants, chosen
to minimise the approximate eigenenergy. Bransden and Sin Fai
Lam used, in turn, the following representations for the helium
wavefunction:

$$\Psi^{(1)}(\underline{r}_1, \underline{r}_2) = N_1 e^{-\alpha(r_1 + r_2)} \; , \qquad\qquad (2.1.11)$$

$$\Psi^{(2)}(\underline{r}_1, \underline{r}_2) = \left[e^{-\alpha r_1} + c e^{-\beta r_1} \right] \left[e^{-\alpha r_2} + c e^{-\beta r_2} \right] \, , \quad (2.1.12)$$

and $$\Psi^{(3)}(\underline{r}_1, \underline{r}_2) = e^{-\alpha r_1 - \beta r_2} + e^{-\beta r_1 - \alpha r_2} \; , \qquad (2.1.13)$$

but otherwise followed Green et al. The two-state cross sections
obtained are in apparently good agreement with the experimental

results of Barnett and Reynolds[22], in the energy range 15 to 40 keV.

However, theoretical arguments suggest that at moderate energies,

as much as 30% of the observed total capture cross section may

arise from capture into excited states (Mapleton[24]), therefore

the calculated values probably overestimate the cross section for

the process (2.1.9) by as much as 30%. More recent measurements

of total cross sections by Berkner et al[23] and Welsh et al[12],

which agree within experimental error with the earlier measurements

of Barnett and Reynolds in the energy range where they overlap,

are substantially lower than the calculations of Bransden and

Sin Fai Lam at energies above 2 MeV, the computed cross sections

being in error by as much as a factor of four at 10 MeV. It

was also found that the considerable disagreement with experiment

was not improved by employing the refined wavefunctions $\psi^{(2)}$

and $\psi^{(3)}$ rather than the simple function $\psi^{(1)}$. It is

evident, therefore, that additional theoretical work will be

required before a significant improvement is achieved, and it may

be anticipated that, to reduce the computed cross sections

substantially, it will not be sufficient merely to add discrete

terms to the expansion, but it will be necessary to consider

representing the continuum in some way. In this respect, the

impulse approximation, which takes some account of the continuum

states, does have an advantage over the atomic expansions method.

The quantum mechanical impulse approximation represents

an attempt to describe many-body scattering in terms of known

two-body scattering amplitudes. This approximation, which

originated from the work of Fermi[25] was applied by Chew[26] to the

problem of high energy neutron-deutron scattering. The assumptions

involved in Chew's work were examined by Chew and Wick[27] and by

Ashkin and Wick[28], and the approximation was further generalized

by Chew and Goldberger[29] within the framework of the formal theory

of scattering. The impulse approximation to the T matrix element

corresponding to equation (2.1.5) is given by[a]

$$T_{if}^{IMP} = \langle \gamma_f | V_{12} + V_{23} | (\omega_{13}^+ + \omega_{12}^+ - 1) \gamma_i \rangle \qquad (2.1.14)$$

where ω_{ij}^+ is a two-body operator defined in chapter 2.2. If

V_{12} is neglected, and consequently ω_{12}^+ replaced by unity, equation

(2.1.14) reduces to

$$T_{if}^{IMP} = \langle \gamma_f | V_{23} | \omega_{13}^+ \gamma_i \rangle \qquad . \qquad (2.1.15)$$

From a theoretical point of view, the impulse approximation is

more satisfactory than the first Born approximation for high

energy electron capture as it replaces the Born matrix element

(2.1.5) by the exact two-body matrix element and only retains

the assumption that the binding forces may be neglected. Account

should also be taken of the fact that, at high energies, observed

capture cross sections are known to be very small compared with

cross sections for target ionization and excitation reactions.

Therefore, coupling to the excitation and ionization channels must

play an important role in electron capture processes. All such

couplings are ignored in the first Born approximation but the

impulse approximation takes some account of them as it is readily

seen that an expansion of $\omega_{13}^+ \gamma_i$ in terms of target eigenfunctions

will contain contributions from all bound and continuum states

of the target. A further satisfactory feature of the impulse

approximation is that the inclusion of V_{12} in V_f does not make

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[a]See chapter 2.2

an appreciable difference to the cross section. Pradhan[30] has shown that

$$\lim_{1/M \to 0} \left\langle \psi_f \mid V_{12} \mid \omega_{13}^+ \; \psi_i \right\rangle = 0 \qquad (2.1.16)$$

and numerical computations[31,32] have confirmed that the contribution from this term is negligible at the energies for which calculations have been carried out. It has been shown[3] that a similarity should exist between the predictions of the impulse approximation and the second Born approximation; thus the impulse approximation may be regarded as having the status of a 'second-order' approximation.

Pradhan[30] first suggested that the impulse approximation would be very suitable for describing electron capture by fast protons, and applied it to the symmetric resonant capture process

$$H^+ + H(1s) \longrightarrow H(1s) + H^+ , \qquad (2.1.17)$$

but made the simplifying approximation of replacing V_{23} in equation (2.1.15) by V_{13}, which no longer described the collision under consideration[33]. Calculations for the same process have been carried out by McDowell[34] and by Cheshire[31]; the former author made an additional approximation to simplify the analysis whereas the latter evaluated the cross section without any further approximations. Cheshire's results were later confirmed by Coleman and McDowell[32]. Calculations have also been performed for capture into higher states: Coleman and McDowell[32]; Coleman and Trelease[35]. From these, estimates for the capture cross section

$$H^+ + H(1s) \longrightarrow H^+ + H \qquad (2.1.18)$$
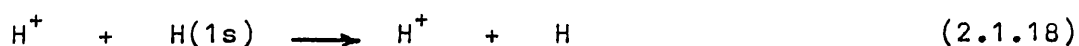
can be made. A comparison of values derived from both the first Born approximation[10] and the impulse approximation[35] with experiment[7] shows that the impulse approximation cross sections

lie about a factor of two below the observed results throughout
the energy range of the experiment, which is very puzzling since
one would expect the impulse approximation to become more accurate
as the energy range is increased. In contrast, the Born approximation
seems much more successful.

The only application of the impulse approximation to
a problem involving a target other than atomic hydrogen is the
work of Bransden and Cheshire[36] on the reaction

$$H^+ \quad + \quad He(1s^2) \quad \longrightarrow \quad H(1s) \quad + \quad He^+(1s) \;. \qquad (2.1.19)$$
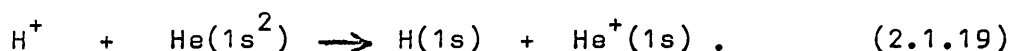
If a second electron (particle 4) is added to the configuration
described earlier in this chapter, it may be shown[a] that the
impulse approximation matrix element for the capture of electron
3 is

$$T_{if}^{IMP} = \left\langle \Psi_f \left| V_{12} + V_{23} + V_{14} + V_{34} \right| (\omega_{12}^+ + \omega_{13}^+ + \omega_{14}^+ - 2) \Psi_i \right\rangle \;.$$

$$(2.1.20)$$

If it is assumed, justifiably, that the distortion due to the
potential V_{12} is negligible, ω_{12}^+ may be replaced by unity and,
if the effect of the interaction V_{14} between the projectile and
the passive electron is treated in the same way, equation (2.1.20)
then becomes

$$T_{if}^{IMP} \simeq \left\langle \Psi_f \left| V_{12} + V_{23} + V_{14} + V_{34} \right| \omega_{13}^+ \Psi_i \right\rangle \;, \qquad (2.1.21)$$

which is the matrix element used by Bransden and Cheshire.

In calculations for reactions such as (2.1.19) there is
a source of uncertainty which is not present when the target is
hydrogenic — the exact bound state wavefunctions of the target

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[a] See chapter 2.2

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are not known. Bransden and Cheshire[36] chose, as the ground state

wavefunction of helium, the simple one-parameter variational

wavefunction

$$\Psi(\underline{r}_3, \underline{r}_4) = \frac{\lambda^3}{\pi} e^{-\lambda(r_3 + r_4)}, \quad \lambda = 1.6875 . \qquad (2.1.22)$$

They evaluated the cross section for (2.1.19) in the energy range

25 keV - 1 MeV and estimated the cross section for

$$H^+ + He(1s^2) \longrightarrow H + He^+ \qquad (2.1.23)$$
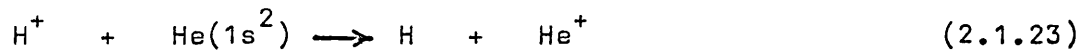
by multiplying their results by the ratio of the first Born

approximation cross section for (2.1.23) and (2.1.19) obtained

from the work of Mapleton[11]. The results obtained in this way

lie below the experimental results of Barnett and Reynolds[22],

Welsh et al[12] and Toburen et al[37], whereas the average of the

Born post and prior cross sections calculated by Mapleton[11] is

in close agreement with the measurements in the energy range

200 keV - 10 MeV. It has been suggested[3] that the use of a more

accurate wavefunction for the helium ground state may increase the

magnitude of the impulse approximation cross section at high energies,

since the high-momentum components of the bound state wavefunction

would be represented with a higher degree of accuracy.

In the present study, we systematically introduce

electron correlation into the ground state wavefunction of the

helium atom and examine the consequent effects on the impulse

approximation cross section for reaction (2.1.19), in the energy

range 25 keV - 3.5 MeV. Such an examination will reveal both

the sign and magnitude of the change in the cross section as a

function of electron correlation. In chapter 2.4, we make some

further comments on the nature of the impulse approximation in the

light of the present examination.

An alternative method of including continuum states has been introduced by Cheshire[38] in an impact parameter treatment of rearrangement collisions. It proceeds by analogy with the well known distorted wave method in the wave treatment of scattering theory[39,40], and is known as the continuum distorted wave (CDW) approximation. The method fails to take into account back-coupling to the initial state[38] and therefore can be expected to be valid only at projectile velocities greater than the typical velocity of the target electrons, which, for process (2.1.18), corresponds to proton energies above 25 keV. Detailed numerical calculations[38] show that the CDW cross section for reaction (2.1.17) lies close to, but above, the impulse approximation in the energy range 80 keV - 1 MeV. However, above 120 keV, the CDW approximation is always below the first Born approximation prediction. It is interesting to note that the CDW method has an asymptotic form at high energies which is exactly equal to that of the second Born approximation. Until recently, there had been no rigorous theoretical foundation for the CDW approximation and therefore its application to capture reactions has been viewed with some caution. However, in their work on high energy charge transfer, McCarroll and Salin[41] have shown that the CDW method is a high-energy second-order approximation. This work was later superseded by that of Gayet[42], who gave a rigorous foundation to the CDW method on the basis of a quantum three-body theory for rearrangement collisions. Salin[43] has evaluated cross sections for the process

$$H^+ + He(1s^2) \longrightarrow H(n\ell) + He^+(1s) \qquad (2.1.24)$$
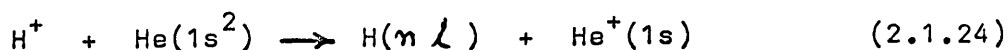
where $n\ell$ = 1s, 2s, 2p, 3s, in the energy range 400 keV - 3 MeV. For the helium ground state wavefunction he chose the two wavefunctions:

(a) The simple one-parameter variational wavefunction

$$\Psi(\underline{x}_1, \underline{x}_2) = \frac{\lambda^3}{\pi} e^{-\lambda(x_1 + x_2)}, \quad \lambda = 1.6875 . \qquad (2.1.25)$$

(b) The open shell wavefunction of Eckart[44]

$$\Psi(\underline{x}_1, \underline{x}_2) = \frac{N}{\pi} \left[e^{-(\alpha x_1 + \beta x_2)} + e^{-(\beta x_1 + \alpha x_2)} \right] \qquad (2.1.26)$$

where $\alpha = 2.1832$; $\beta = 1.1885$; $N^{-2} = 2\left[\alpha^{-3} \beta^{-3} + \left(\frac{\alpha + \beta}{2}\right)^{-6}\right]$.

The difference between the two sets of results obtained by using wavefunctions (a) and (b) was about 10% for E < 1 MeV, and up to 20% for E > 1 MeV. The discrepancy is therefore more significant than that found in Bransden and Sin Fai Lam's[19] calculations discussed earlier. The CDW cross section for capture into any state, evaluated using (2.1.25), is in reasonable agreement with experiment[12,22,37,45] throughout the energy range of the calculation. In addition, it is noted that the above theoretical results are in closer agreement with experiment than those of Bransden and Cheshire[36].

In view of the large percentage change in the electron capture cross sections due to the use of the two different wavefunctions, we have also examined, in the present study, the influence of electron correlation on the CDW approximation cross sections for reaction (2.1.24), for $n\ell$ = 1s, 2s, 2p, in the energy range 25 keV - 3 MeV. With the influence of electron correlation still in mind, we have also evaluated electron capture cross sections for

$$He^{++} + He(1s^2) \longrightarrow He^+(n\ell) + He^+(1s) \qquad (2.1.27)$$
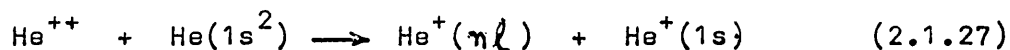
where $n\ell$ = 1s, 2s, 2p in the energy range 25 keV - 3 MeV.

Calculations within the CDW approximation for reaction (2.1.27),

using a helium ground state wavefunction of the form[46]

$$\Psi(\underline{x}_1, \underline{x}_2) = N\left[e^{-(ax_1 + bx_2)} + e^{-(bx_1 + ax_2)}\right] \quad , \qquad (2.1.28)$$

have also been reported by Belkic and Janev[47].

In chapter 2.7, we compare the fully correlated electron capture cross sections, arising from calculations based on the impulse and CDW approximations, with experimental values, as far as possible. A comparison is also made between the impulse and CDW approximations, with the emphasis being on the feasibility of using these techniques in studies involving larger atomic systems.

CHAPTER 2.2

Impulse Approximation

Formal Derivation

When considering rearrangement collisions between atomic systems it is convenient to write the total Hamiltonian H as

$$H = H_i + V_i = H_f + V_f \; . \qquad (2.2.1)$$

Here H_i and H_f are the initial and final unperturbed Hamiltonians and V_i and V_f are the corresponding perturbations. If one is interested in the probability that a system, prepared in an eigenstate $\mathcal{Y}_i$ of H_i in the remote past, will evolve, under the action of the Hamiltonian H, to a specific eigenstate $\mathcal{Y}_f$ of H_f, then it can be shown that the relevant transition matrix element is[a]

$$T_{if} = \left\langle \mathcal{Y}_f \mid V_f \mid \Psi_i^+ \right\rangle \; . \qquad (2.2.2)$$

Here Ψ_i^+ is an eigenfunction of the total Hamiltonian H representing a complete solution to the scattering problem and satisfies the integral equation

$$\Psi_i^+ = \mathcal{Y}_i + \frac{1}{E_i - H_i + i\varepsilon} \; V_i \Psi_i^+ \qquad (2.2.3a)$$

$$= \mathcal{Y}_i + \frac{1}{E_i - H + i\varepsilon} \; V_i \mathcal{Y}_i \; . \qquad (2.2.3b)$$

In deriving the impulse approximation[b] we shall restrict attention to a three-particle system consisting of a projectile (1) and a target composed of a core (2) and bound electron (3).

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[a] See appendix A.

[b] In this derivation, we follow McDowell and Coleman, reference 40.

The extension to systems of more than three particles is then straightforward. Let us assume that during the course of the collision, particle (3) is transferred to a bound state of (1, 3) and let us denote the interaction potential between any two particles (i) and (j) as V_{ij}. The initial and final unperturbed systems have Hamiltonians

$$H_i = H_o + V_{23} \quad , \quad H_f = H_o + V_{13} \quad , \qquad (2.2.4)$$

where H_o is the total kinetic energy operator and the perturbations are considered to be, respectively,

$$V_i = V_{12} + V_{13} \quad , \quad V_f = V_{12} + V_{23} \; . \qquad (2.2.5)$$

The total Hamiltonian of the system is therefore

$$H = H_o + V_{23} + V_{12} + V_{13} \quad , \qquad (2.2.6)$$

which satisfies the Schrodinger equation

$$(H - E) \; \Psi_i^+ = 0 \quad , \qquad (2.2.7)$$

where E is the total energy of the system. The initial and final unperturbed wavefunctions ψ_i and ψ_f satisfy the equations

$$(H_o + V_{23} - E)\psi_i = 0 = (H_o + V_{23} - E)\psi_f \; . \qquad (2.2.8)$$

The wavefunction for the three-particle system corresponding to an initial unperturbed state ψ_i and outgoing-wave boundary conditions can be expressed as

$$\Psi_i^+ = \Omega^+ \, \psi_i \quad , \qquad (2.2.9)$$

where

$$\Omega^+ = 1 + G^+ V_i \quad , \qquad (2.2.10)$$

and the Green's function operator G^+ is given by

$$G^+ = \frac{1}{E - H + i\varepsilon} \quad , \qquad (2.2.11)$$

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where it is understood that the limit $\varepsilon \to 0^+$ is to be taken eventually. One first expands the three-body Moller operator Ω^+ in terms of the two-body operators ω_{ij}^+ defined below and the impulse approximation is obtained by truncating this expansion.

Let χ_m be a member of the complete set of free-particle wavefunctions (plane waves), associated with an energy E_m, satisfying Schrodinger's equation

$$(H_o - E_m) \chi_m = 0 \quad . \tag{2.2.12}$$

Clearly, the χ's are the wavefunctions for the system of three particles when there are no interactions amongst them. The two-body operators $\omega_{ij}^+(m)$ $(i,j = 1, 2, 3 ; i \neq j)$ are defined by the equation

$$\omega_{ij}^+(m) \chi_m = \left[1 + \frac{1}{E_m - H_o - V_{ij} + i\varepsilon} V_{ij} \right] \chi_m \equiv \psi_m^+(i,j) \quad . \tag{2.2.13}$$

Pre-multiplying equation (2.2.13) throughout by $(H_o + V_{ij} - i\varepsilon - E_m)$, we obtain

$$(H_o + V_{ij} - E_m) \psi_m^+(i,j) - i\varepsilon \psi_m^+(i,j) = (H_o - E_m - i\varepsilon) \chi_m \quad . \tag{2.2.14}$$

Now provided that

$$\lim_{\varepsilon \to 0^+} \varepsilon \psi_m^+(i,j) = 0 \quad , \tag{2.2.15}$$

it is clear from equation (2.2.14) that $\psi_m^+(i,j)$ satisfies the differential equation

$$(H_o + V_{ij} - E_m) \psi_m^+(i,j) = 0 \quad . \tag{2.2.16}$$

It is evident that $\psi_m^+(i,j)$ is the mth member of a complete set

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of wavefunctions describing the three particles when there is an interaction between particles (i) and (j) only. If V_{ij} is a coulomb potential the condition (2.2.15) is not satisfied[48]; in that case, following McDowell and Coleman[40], equation (2.2.16) rather than equation (2.2.13) will be regarded here as the equation which defines $\Psi_m^+(i, j)$. This seems reasonable in the light of Mapleton's[48] work.[a] He has shown that if $\Psi_m^+(i, j)$ is obtained directly from equation (2.2.13), the behaviour of this wavefunction at $r \to \infty$ necessitated a non-trivial renormalization in order to achieve unit amplitude even though $\Psi_m^+(i, j)$ was originally normalized. The resultant wavefunction was then found to have the same form as $\dot{\Psi}_m^+(i, j)$ when obtained from equation (2.2.16).

If P and Q are operators for which inverse operators exist, then obviously

$$P^{-1} = Q^{-1} + P^{-1}(Q - P)Q^{-1} \qquad (2.2.17)$$

$$= Q^{-1} + Q^{-1}(Q - P)P^{-1} \qquad (2.2.18)$$

The expansion of Ψ_i^+ in terms of two-body operators is facilitated if we define $P = E - H + i\varepsilon$ and $Q = E_m - H_o - V_{ij} + i\varepsilon$; the operator identity (2.2.17) then becomes

$$G^+ \equiv \frac{1}{E-H+i\varepsilon} = \frac{1}{E_m-H_o-V_{ij}+i\varepsilon} + \frac{1}{E-H+i\varepsilon}\left[E_m-E+H-H_o-V_{ij}\right]\frac{1}{E_m-H_o-V_{ij}+i\varepsilon} \cdot$$

$$(2.2.19)$$

But from equation (2.2.6), $H - H_o = V_{23} + V_{12} + V_{13}$, and therefore we obtain

$$G^+ = \frac{1}{E_m-H_o-V_{ij}+i\varepsilon} + \frac{1}{E-H+i\varepsilon}\left[E_m-E+V_{23}+V_{12}+V_{13}-V_{ij}\right]\frac{1}{E_m-H_o-V_{ij}+i\varepsilon} \cdot$$

$$(2.2.20)$$

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[a] See also reference 53.

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Therefore,

$$G^+ V_{ij} = \frac{1}{E_m - H_o - V_{ij} + i\varepsilon} V_{ij} + \frac{1}{E - H + i\varepsilon} \left[E_m - E + V_{23} + V_{12} + V_{13} - V_{ij} \right] \frac{1}{E_m - H_o - V_{ij} + i\varepsilon} V_{ij} \cdot$$

$$(2.2.21)$$

But $G^+ \equiv \dfrac{1}{E - H + i\varepsilon}$, $(2.2.22)$

and from equation (2.2.13), if we take the plane wave basis of χ_m as understood, then

$$\omega^+_{ij}(m) - 1 \equiv \frac{1}{E_m - H_o - V_{ij} + i\varepsilon} V_{ij} \quad , \qquad (2.2.23)$$

and therefore equation (2.2.21) becomes

$$G^+ V_{ij} = b^+_{ij}(m) + G^+ \left[E_m - E + V_{23} + V_{12} + V_{13} - V_{ij} \right] b^+_{ij}(m) \ , \qquad (2.2.24)$$

where $\quad b^+_{ij}(m) = \omega^+_{ij}(m) - 1 \quad . \qquad (2.2.25)$

Let us now expand ψ_i in terms of the complete set of χ_m:

$$\psi_i = \sum_m \chi_m \langle \chi_m | \psi_i \rangle \quad . \qquad (2.2.26)$$

Operating on ψ_i by $G^+ V_{ij}$, we obtain

$$G^+ V_{ij} | \psi_i \rangle = \sum_m G^+ V_{ij} | \chi_m \rangle \langle \chi_m | \psi_i \rangle$$

$$= \sum_m \left[b^+_{ij}(m) + G^+ \left\{ (E_m - E) + V_{12} + V_{13} + V_{23} - V_{ij} \right\} b^+_{ij}(m) \right] | \chi_m \rangle \langle \chi_m | \psi_i \rangle$$

$$(2.2.27)$$

However, it is evident from equations (2.2.8) and (2.2.12) that

$$(E_m - E) \langle \chi_m | \psi_i \rangle = \langle E_m \chi_m | \psi_i \rangle - \langle \chi_m | E \psi_i \rangle$$

$$= \langle \chi_m | H_0 | \psi_i \rangle - \langle \chi_m | H_0 + V_{23} | \psi_i \rangle$$

$$= - \langle \chi_m | V_{23} | \psi_i \rangle \quad , \tag{2.2.28}$$

and consequently

$$G^+ V_{ij} | \psi_i \rangle = \sum_m b_{ij}^+(m) | \chi_m \rangle \langle \chi_m | \psi_i \rangle - \sum_m G^+ b_{ij}^+(m) | \chi_m \rangle \langle \chi_m | V_{23} | \psi_i \rangle$$

$$+ \sum_m G^+ (V_{12} + V_{13} + V_{23} - V_{ij}) b_{ij}^+(m) | \chi_m \rangle \langle \chi_m | \psi_i \rangle \; .$$

Collecting together terms containing V_{23}, we obtain

$$G^+ V_{ij} | \psi_i \rangle = \left[\sum_m b_{ij}^+(m) | \chi_m \rangle \langle \chi_m | + G^+ \sum_m \left[V_{23} b_{ij}^+(m) | \chi_m \rangle \langle \chi_m | \right. \right.$$

$$\left. \left. - b_{ij}^+(m) | \chi_m \rangle \langle \chi_m | V_{23} \right] + G^+ \sum_m (V_{12} + V_{13} - V_{ij}) b_{ij}^+(m) | \chi_m \rangle \langle \chi_m | \right] | \psi_i \rangle$$

$$\tag{2.2.29}$$

If we write

$$\sum_m b_{ij}^+(m) \; | \chi_m \rangle \langle \chi_m | \equiv b_{ij}^+ \quad , \tag{2.2.30}$$

then equation (2.2.29) is reduced to

$$G^+ V_{ij} | \psi_i \rangle = \left[b_{ij}^+ + G^+ (V_{23} b_{ij}^+ - b_{ij}^+ V_{23}) + G^+ (V_{12} + V_{13} - V_{ij}) b_{ij}^+ \right] | \psi_i \rangle \; ,$$

and if we denote the commutator of b_{ij}^+ and V_{23} as

$$V_{23} b_{ij}^+ - b_{ij}^+ V_{23} \equiv \left[V_{23} , b_{ij}^+ \right] \quad , \tag{2.2.31}$$

then

$$G^+V_{ij}|\Psi_i\rangle = \left[b^+_{ij} + G^+[V_{23},b^+_{ij}] + G^+(V_{12}+V_{13}-V_{ij})b^+_{ij}\right]|\Psi_i\rangle \ .$$

(2.2.32)

From equations (2.2.10) and (2.2.5),

$$\Omega^+ \ = \ 1 + G^+V_i \ = \ 1 + G^+V_{12} + G^+V_{13} \ .$$

But from equation (2.2.32), we see that

$$G^+V_{12} \ = \ b^+_{12} + G^+\left[V_{23},b^+_{12}\right] + G^+V_{13}b^+_{12} \ ,$$

$$G^+V_{13} \ = \ b^+_{13} + G^+\left[V_{23},b^+_{13}\right] + G^+V_{12}b^+_{13} \ ,$$

and therefore,

$$\Omega^+ = 1 + b^+_{12} + b^+_{13} + G^+\left[V_{23},(b^+_{12}+b^+_{13})\right] + G^+(V_{13}b^+_{12}+V_{12}b^+_{13}) \ .$$

That is,

$$\Omega^+ = (\omega^+_{13}+\omega^+_{12}-1) + G^+\left[V_{23},(b^+_{12}+b^+_{13})\right] + G^+(V_{13}b^+_{12}+V_{12}b^+_{13}) \ ,$$

(2.2.33)

where $\omega^+_{ij} \ = \ b^+_{ij} + 1$ (2.2.34)

$$= \sum_m \omega^+_{ij}(m)\,|\chi_m\rangle\langle\chi_m| \qquad (2.2.35)$$

Therefore, the matrix element T_{if} for the three-particle collision process under consideration may be written as

$$T_{if} \ = \ \langle\Psi_f|V_f|\Psi_i^+\rangle \ = \ \langle\Psi_f|V_f|\Omega^+\Psi_i\rangle$$

$$= \ \langle\Psi_f|V_f|(\omega^+_{13}+\omega^+_{12}-1)\Psi_i\rangle \ +$$

$$+ \ \langle\Psi_f|V_f|G^+[V_{23},(b^+_{12}+b^+_{13})]\Psi_i\rangle \ +$$

$$+ \ \langle\Psi_f|V_f|G^+(V_{13}b^+_{12}+V_{12}b^+_{13})\Psi_i\rangle \ . \qquad (2.2.36)$$

The 'impulse hypothesis' is that the binding potential V_{23} will not play an important role during the collision[28] and therefore may be neglected. This implies that the commutator involving V_{23} will vanish. Consequently, the second term on the right hand side of equation (2.2.36) vanishes, but clearly some other approximation must be made before one can calculate T_{if} – otherwise a specific knowledge of the three-body operator G^+ would be required. The simplest procedure is to neglect the expression

$$\langle \Psi_f | V_f | G^+ (V_{13}b_{12}^+ + V_{12}b_{13}^+) \Psi_i \rangle \qquad (2.2.37)$$

on the grounds that it is a contribution from multiple scattering. One then obtains as the impulse approximation to T_{if}, the matrix element

$$T_{if}^{IMP} = \langle \Psi_f | V_f | \omega_{13}^+ + \omega_{12}^+ - 1) \Psi_i \rangle . \qquad (2.2.38)$$

While multiple scattering effects are not always negligible, an argument can be put forward to justify their neglect in heavy particle collisions. Consider, for simplicity, a collision between a proton and a hydrogen atom. The time-dependent Schrodinger equation for the problem under consideration is

$$H \Psi = i \frac{\partial \Psi}{\partial t} \quad ,$$

where $H = H_0 + V_{12} + V_{13} + V_{23}$. It is possible to remove the proton-proton potential V_{12} from the Hamiltonian of the system by the transformation[a]

$$\Phi = \Psi \exp \left\{ -iv^{-1} \ln(vR - v^2 t) \right\}$$

where R is the inter-proton distance, and v is their relative velocity. This transformation holds under the condition that

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[a]See reference 40, p.297

$(1/M) \ll 1$ which, when M is the mass of a proton expressed in units of electron mass, is clearly satisfied. Since the effect of the removal of V_{12} from the Hamiltonian is merely to introduce a phase factor into the total wavefunction, it follows that when the protons are regarded as infinitely massive this potential cannot affect any electronic process. Consequently, contributions to T_{if} from the potential V_{12} can be expected to be of the order 1/M when compared with the corresponding contributions from other potentials. Therefore, neglecting V_{12} by setting it equal to zero introduces an error of order 1/M and, in addition, implies through equations (2.2.23) and (2.2.35) that $\omega_{12}^+ \rightarrow 1$; it then follows that $b_{12}^+ \rightarrow 0$. Thus, in comparison with the first term on the right hand side of equation (2.2.36), the multiple scattering expression (2.2.37) can justifiably be neglected.

The extension of the above analysis to a system of four particles is now straightforward. Let us add another electron, particle (4), to the system described earlier in this chapter. Therefore, the system now consists of a projectile (1) and a target composed of a core (2) with two bound electrons (3,4). It may easily be shown that the relevant electron-capture matrix element corresponding to (2.2.36) is given by

$$T_{if} = \langle \Psi_f | V_f | (\omega_{12}^+ + \omega_{13}^+ + \omega_{14}^+ - 2) \Psi_i \rangle +$$

$$+ \langle \Psi_f | V_f | G^+ [V_{23}, (b_{12}^+ + b_{13}^+ + b_{14}^+)] \Psi_i \rangle +$$

$$+ \langle \Psi_f | V_f | G^+ [V_{24}, (b_{12}^+ + b_{13}^+ + b_{14}^+)] \Psi_i \rangle +$$

$$+ \langle \Psi_f | V_f | G^+ \{ (V_{13}+V_{14})b_{12}^+ + (V_{12}+V_{14})b_{13}^+ + (V_{12}+V_{23})b_{14}^+ \} \Psi_i \rangle ,$$

$$(2.2.39)$$

where now,

$$V_f = V_{12} + V_{14} + V_{23} + V_{34} \quad . \qquad (2.2.39a)$$

The neglect of binding forces implies that the commutators involving V_{23} and V_{24} vanish and, as discussed previously, the multiple scattering term in equation (2.2.39) may also be neglected. Therefore,

$$T_{if}^{IMP} = \left\langle \Psi_f \left| V_f \right| \omega_{12}^{+} + \omega_{13}^{+} + \omega_{14}^{+} - 2) \Psi_i \right\rangle . \qquad (2.2.40)$$

Consider now the rearrangement in which the fast proton (1), incident on a helium atom in the ground state with nucleus (2) and electrons (3,4), captures electron (3) to give a hydrogen atom in its ground state, leaving the residual ion in its ground state. As previously indicated, the distortion of the incident proton wavefunction by the internuclear potential V_{12} is expected to be small at high energies, and the approximation $\omega_{12}^{+} \rightarrow 1$ is made (although to be consistent with the work of Bransden and Cheshire[36], we have retained V_{12} in the perturbing interaction). The interaction between the incident proton and the passive electron (4) may be treated in a similar manner by putting $\omega_{14}^{+} \rightarrow 1$. The matrix element T_{if} now becomes

$$T_{if}^{IMP} = \left\langle \Psi_f \left| V_{12} + V_{14} + V_{23} + V_{34} \right| \omega_{13}^{+} \Psi_i \right\rangle \qquad (2.2.41)$$

and no further approximation is made.

Expression for the Total Capture Cross Section.

In general, the total cross section for a rearrangement collision is[a]

$$Q_{if} = \frac{\mu_i \mu_f}{4\pi^2} \frac{k_f}{k_i} \int |T_{if}|^2 \, d\Omega \quad , \qquad (2.2.42)$$

where μ_i and μ_f are the initial and final reduced masses

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[a]See appendix A.

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such that if, as in the present case, M_1 and M_2 are the masses of the proton and helium nucleus respectively[a], then

$$\mu_f = \frac{(1 + M_1)(1 + M_2)}{2 + M_1 + M_2} \qquad (2.2.43)$$

$$\mu_i = \frac{M_1(2 + M_2)}{2 + M_1 + M_2} . \qquad (2.2.44)$$

The initial and final relative momenta $\underline{k}_i$ and $\underline{k}_f$ of the colliding systems can be written as:

$$\underline{k}_i = \mu_i \underline{v}_i \quad ; \quad \underline{k}_f = \mu_f \underline{v}_f \qquad (2.2.45)$$

where $\underline{v}_i$ and $\underline{v}_f$ are the relative velocities of the atomic systems in the initial and final states. If one chooses spherical polar coordinates (r, θ, ϕ) with the polar axis in the direction of the incident beam, equation (2.2.42) reduces to

$$Q_{if} = \frac{\mu_i \mu_f}{2\pi} \frac{k_f}{k_i} \int_{-1}^{+1} |T_{if}|^2 \, d(\cos\theta) . \qquad (2.2.46)$$

Assuming that all quantities on the right hand side of this equation are expressed in atomic units, then Q_{if} is measured in units of a_o^2. If we wish to express Q_{if} in the customary units of πa_o^2, then

$$Q_{if} = \frac{\mu_i \mu_f}{2\pi^2} \frac{k_f}{k_i} \int_{-1}^{+1} |T_{if}|^2 \, d(\cos\theta) \qquad (\pi a_o^2). \qquad (2.2.47)$$

The major contribution to the integral in equation (2.2.42) generally comes from a very narrow cone about the forward direction. For this reason, it is convenient to replace the integral with respect to $\cos\theta$ by an integral with respect to momentum transfer, in which

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[a]Units such that $m = \hbar = e = 1$ are used except where otherwise specified.

the integrand is a more slowly varying function of the variable

of integration. The relevant momentum transfer vectors $\underline{\alpha}$ and

$\underline{\beta}$ are defined by the equations

$$\underline{\alpha} = \underline{k}_f - a\,\underline{k}_i \quad , \qquad a = \frac{m_2 + 1}{m_2 + 2} \qquad (2.2.48)$$

$$\underline{\beta} = \underline{k}_i - c\,\underline{k}_f \quad , \qquad c = \frac{m_1}{m_1 + 1} \qquad . \qquad (2.2.49)$$

From equation (2.2.49),

$$\beta^2 = k_i^2 + c^2 k_f^2 - 2c\,k_i\,k_f\,\cos\Theta \qquad ,$$

therefore $\quad \sin\Theta\,d\Theta = \dfrac{\beta\,d\beta}{ck_i k_f} \qquad , \qquad (2.2.50)$

and similarly,

$$\sin\Theta\,d\Theta = \frac{\alpha\,d\alpha}{a\,k_i k_f} \qquad . \qquad (2.2.51)$$

It may readily be seen that equation (2.2.47) may be written as

$$Q_{if} = \frac{1}{2\pi^2 c\,v_i^2}\left(\frac{\mu_f}{\mu_i}\right)\int_{\beta_{min}}^{\beta_{max}} \left| T_{if} \right|^2 \beta\,d\beta \quad (\pi a_0^2), (2.2.52)$$

$$\text{or } Q_{if} = \frac{1}{2\pi^2 a\,v_i^2}\left(\frac{\mu_f}{\mu_i}\right)\int_{\alpha_{min}}^{\alpha_{max}} \left| T_{if} \right|^2 \alpha\,d\alpha \quad (\pi a_0^2). (2.2.53)$$

The integration limits are

$$\beta_{min} = \left| k_i - c\,k_f \right| \quad ; \qquad \beta_{max} = k_i + c\,k_f \qquad (2.2.54)$$

$$\alpha_{min} = \left| k_f - a\,k_i \right| \quad ; \qquad \alpha_{max} = k_f + a\,k_i \quad . \qquad (2.2.55)$$

We will normally use the form (2.2.52).

Since the total energy is conserved in the centre of mass

system, we have

$$\frac{k_f^2}{\mu_f} - \frac{k_i^2}{\mu_i} = \epsilon \qquad , \qquad (2.2.56)$$

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where $\epsilon = 2\epsilon_{He} - 2\epsilon_{H} - 2\epsilon_{He^+}$ (2.2.57)

and ϵ_{He}, ϵ_{H} and ϵ_{He^+} are the (negative) binding energies (in atomic units) of the ground state of the helium atom, the hydrogen atom and the helium ion, respectively. This equation serves as a definition for the energy defect ϵ. From the definitions of μ_i and μ_f it is clear that

$$\frac{\mu_i}{\mu_f} = \frac{m_1(m_2 + 2)}{(m_1+1)(m_2+1)} = \frac{c}{a}$$ (2.2.58)

and, consequently, from equations (2.2.54) and (2.2.56)

$$\beta^2_{min} = k_i^2(1 + ac) + ac\mu_i\epsilon - 2(ac)^{\frac{1}{2}}k_i^2 \left[1 + \frac{\mu_i\epsilon}{k_i^2}\right]^{\frac{1}{2}} .$$

(2.2.59)

The binomial expansion of $(1 + \mu_i\epsilon/k_i^2)^{\frac{1}{2}} = (1 + \epsilon/\mu_i v_i^2)^{\frac{1}{2}}$ converges rapidly if $v_i^2 \gg \epsilon/\mu_i$ and, if we retain the first three terms of the expansion, equation (2.2.59) becomes

$$\beta^2_{min} = \mu_i^2 v_i^2 \left[1 - (ac)^{\frac{1}{2}}\right]^2 - \left[1 - (ac)^{\frac{1}{2}}\right](ac)^{\frac{1}{2}}\mu_i\epsilon + \frac{(ac)^{\frac{1}{2}}\epsilon^2}{4v_i^2} ,$$

where we have made use of the relation $k_i^2 = \mu_i^2 v_i^2$.

This may be simplified further by noting that, from the definitions of a, c and μ_i,

$$1 - (ac)^{\frac{1}{2}} = \frac{1}{2\mu_i} \left[1 + O\left(\frac{1}{m_1}\right)\right] .$$

Therefore, if we neglect terms of order $1/m_1$ compared to unity, we obtain

$$\beta_{min} = \frac{(v_i^2 - \epsilon)}{2v_i} .$$ (2.2.60)

The upper limit β_{max} may be evaluated in a similar manner, but this is generally unnecessary since β_{max} may be regarded as infinite

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in most applications. An exception is the case of symmetric

resonant electron capture at very high energies; in that case,

the use of the correct value of β_{max} is essential since $M_2 = M_1$,

$k_f = k_i$ and, therefore, $\beta_{max} = (1 + c)k_i = M_1 \mathscr{V}_i$. Corresponding

expressions for α_{min} and α_{max} are easily obtainable by noting

that, from energy conservation considerations,

$$\frac{\alpha^2}{a} - \frac{\beta^2}{c} = \epsilon \ . \tag{2.2.61}$$

Another useful relation which will be required at a later stage is

$$\underline{\alpha} \cdot \underline{\beta} = \frac{1}{2} c \mathscr{V}_i^2 - \frac{1}{2} ac - \frac{(1 + ac)}{2c} \beta^2 \ . \tag{2.2.62}$$

The expression for the total capture cross section may now be

written as

$$Q_{if} = \frac{1}{4\pi^2 c \mathscr{V}_i^2} \left(\frac{\mu_f}{\mu_i}\right) \int_{\beta^2_{min}}^{\infty} \left|T_{if}\right|^2 \ d\beta^2 \ (\pi a_o^2) \ .$$

In the case of electron capture by protons in helium, before

calculating cross sections from the above formula, it is necessary

to take account of the indistinguishability of the two helium

electrons. Since these are in a singlet state, the T_{if} matrix

element corresponding to the capture of electron (3), say, must

be added to that corresponding to the capture of electron (4),

and the sum multiplied by the singlet normalization factor $2^{-\frac{1}{2}}$.

These two matrix elements are easily seen to be identical so that

the matrix element describing the capture of either electron is

$2^{\frac{1}{2}} T_{if}$. Therefore we have, finally,

$$Q_{if} = \frac{a}{2\pi^2 c^2 \mathscr{V}^2} \int_{\beta^2_{min}}^{\infty} \left|T_{if}\right|^2 \ d\beta^2 \ (\pi a_o^2) \ , \tag{2.2.63}$$

with $\beta_{min} = \dfrac{(v^2 - \epsilon)}{2v}$, (2.2.64)

where we have now dropped the subscript i of v_i.

It should be noted that if v is expressed in atomic units, the energy of the incoming proton is given by the relation $E \simeq 25v^2$ (keV).

CHAPTER 2.3

Evaluation of the Capture Cross Section

In this chapter, we evaluate the impulse approximation matrix element T_{if}^{IMP} for the reaction

$$H^+ + He(1s^2) \longrightarrow H(1s) + He^+(1s) \ . \qquad (2.3.1)$$
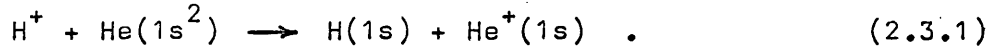
If the momentum transfer of the passive electron is neglected, the initial and final unperturbed wave functions may be written

$$\Psi_i = \bar{\Phi}(\underline{x}, \underline{t}) \, e^{i\underline{k}_i \cdot \underline{\sigma}} \qquad (2.3.2)$$

$$\Psi_f = \chi_f(\underline{s}) \, \phi_f(\underline{t}) \, e^{i\underline{k}_f \cdot \underline{\varrho}} \qquad (2.3.3.)$$

where $\bar{\Phi}(\underline{x}, \underline{t})$ is the ground state helium wavefunction, $\chi_f(\underline{s})$ the ground state wavefunction of hydrogen and $\phi_f(\underline{t})$ that of the residual helium ion; the initial and final coordinates appropriate to the present system are:

Initial: $\qquad \underline{\sigma} = a\underline{x} - \underline{s}$

$\qquad\qquad \underline{x} = \underline{r}_2 - \underline{r}_3 \qquad\qquad\qquad (2.3.4)$

$\qquad\qquad \underline{t} = \underline{r}_2 - \underline{r}_4$

Final: $\qquad \underline{\varrho} = c\underline{\sigma} + (1 - ac)\underline{x} = \underline{x} - c\underline{s}$

$\qquad\qquad \underline{s} = \underline{r}_1 - \underline{r}_3 \qquad\qquad\qquad (2.3.5)$

$\qquad\qquad \underline{t} = \underline{r}_2 - \underline{r}_4$

where $\underline{r}_i$ is the position vector of particle (i).

For the description of the helium atom in its ground state, we have employed two types of normalized wavefunction:

(1) The simple one-parameter variational function

$$\bar{\Phi}(\underline{x}, \underline{t}) = \phi_i(\underline{x}) \phi_i(\underline{t})$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad (2.3.6)$$

with $\qquad \phi_i(\underline{x}) = \left(\frac{\lambda^3}{\pi}\right)^{\frac{1}{2}} e^{-\lambda x} \ , \quad \lambda = 1.6875 \ ;$

(2) The natural expansion of the 35-configuration CI wavefunction of Weiss[a]

$$\underline{\Phi}(\underline{x}, \underline{t}) = D_{j \ell n} \, G_{j \ell}(\underline{x}) G_{jn}(\underline{t}) \quad , \tag{2.3.7a}$$

where

$$D_{j \ell n} \quad N_x \sum_{j=1}^{x} \frac{c_j}{\sqrt{2\ell_j + 1}} \sum_{\mu=-\ell_j}^{+\ell_j} \sum_{\ell=1}^{15} \sum_{n=1}^{15} b_\ell^j \, b_n^j \tag{2.3.7b}$$

$$G_{j \ell}(\underline{x}) = R_{j \ell}(\underline{x}) Y_{\ell_j, \mu}(\theta_x, \phi_x) \quad , \tag{2.3.7c}$$

$$G_{jn}(\underline{t}) = R_{jn}(\underline{t}) Y_{\ell_j, -\mu}(\theta_t, \phi_t) \quad , \tag{2.3.7d}$$

and

$$R_{j \ell}(\underline{r}) = r^{n_j - 1} e^{-\partial_{j \ell} r} \quad . \tag{2.3.7e}$$

For the hydrogen and helium ion, the eigenfunctions are

$$\chi_f(\underline{s}) = \left(\frac{1}{\pi}\right)^{\frac{1}{2}} e^{-s} \quad , \tag{2.3.8}$$

$$\phi_f(\underline{t}) = \left(\frac{8}{\pi}\right)^{\frac{1}{2}} e^{-2t} \quad . \tag{2.3.9}$$

The matrix element we wish to evaluate is given by (see equation 2.2.41)

$$T_{if} = \langle \Psi_f \, | \, V_{12} + V_{14} + V_{23} + V_{34} \, | \, \omega_{13}^+ \Psi_i \rangle \quad . \tag{2.3.10}$$

This was first evaluated for wavefunction (2.3.6) by Bransden and Cheshire[36]. We follow this derivation, but use a general wavefunction which is separable and may be written in the form (2.3.7a). It is necessary to obtain an expression for the term

$$\omega_{13}^+ \Psi_i = \sum_m \omega_{13}^+ (m) \, \chi_m \, \langle \chi_m | \Psi_i \rangle$$

$$= \sum_m \Psi_m^+ (1, 3) \, \langle \chi_m | \Psi_i \rangle \quad . \tag{2.3.11}$$

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[a] See chapter 1.3 and references therein.

The free-particle wavefunctions χ_m are given by

$$\chi_m = (2\pi)^{-9/2} \exp\left[i(\underline{k}_1\cdot\underline{s} + \underline{k}_2\cdot\underline{\rho} + \underline{k}_3\cdot\underline{t})\right] , \qquad (2.3.12)$$

where $\underline{k}_1$, $\underline{k}_2$, $\underline{k}_3$ are the momentum vectors conjugate to $\underline{s}$, $\underline{\rho}$, and $\underline{t}$, respectively. The function $\Psi_m{}^+(1,3)$ satisfies equation (2.2.16) and is given by

$$\Psi_m{}^+(1,3) = (2\pi)^{-9/2} \Psi_{\underline{k}_1}^+(\underline{s})\, e^{i(\underline{k}_2\cdot\underline{\rho} + \underline{k}_3\cdot\underline{t})} . \qquad (2.3.13)$$

$\Psi_{\underline{k}_1}^+(\underline{s})$ is a coulomb wavefunction describing the incoming proton when scattered by potential V_{13}, satisfies outgoing-wave boundary conditions, and is given by

$$\Psi_{\underline{k}_1}^+(\underline{s}) = e^{-\frac{\pi\gamma}{2}}\, \Gamma(1 + i\gamma)\, e^{i\underline{k}_1\cdot\underline{s}}\, {}_1F_1(-i\gamma, 1, ik_1 s - i\underline{k}_1\cdot\underline{s}) \qquad (2.3.14)$$

where $\gamma = -1/k_1$

Making use of equations (2.3.12) and (2.3.2), the coefficients of $\Psi_m{}^+(1,3)$ in (2.3.11) become

$$\langle\chi_m|\Psi_i\rangle = (2\pi)^{-9/2} D_{j\ell n} \iint e^{-i(\underline{k}_1\cdot\underline{s}+\underline{k}_2\cdot\underline{\rho}+\underline{k}_3\cdot\underline{t})} \times$$
$$G_{j\ell}(\underline{x})G_{jn}(\underline{t})\, e^{i\underline{k}_i\cdot\underline{\sigma}}\, d\underline{x}\ d\underline{s} . \qquad (2.3.15)$$

Therefore, since $\underline{\rho} = \underline{x} - c\,\underline{s}$,

$$\langle\chi_m|\Psi_i\rangle = (2\pi)^{-3/2} D_{j\ell n}\, \delta(c\underline{k}_2 - \underline{k}_1 - \underline{k}_i) J_{j\ell}^{(1)}(\underline{K}')G_{jn}(\underline{t})e^{-i\underline{k}_3\cdot\underline{t}} ,$$
$$(2.3.16)$$

where δ is the Dirac delta function

$$\delta(c\,\underline{k}_2 - \underline{k}_1 - \underline{k}_i) = (2\pi)^{-3} \int e^{-i(\underline{k}_i + \underline{k}_1 - c\,\underline{k}_2)\cdot\underline{s}}\, d\underline{s} ,$$
$$(2.3.17)$$

and where $J_{j\ell}^{(1)}(\underline{K}')$ is the Fourier transform of $G_{j\ell}(\underline{x})$, namely,

$$J_{j\ell}^{(1)}(\underline{K}') = \int e^{-i\underline{K}'\cdot\underline{x}}\, G_{j\ell}(\underline{x})\, d\underline{x} , \qquad (2.3.18)$$

with $\underline{K}' = \underline{k}_2 - a\,\underline{k}_i$. $\qquad$ (2.3.19)

On substituting equation (2.3.16) into (2.3.11), we obtain

$$\omega_{13}^+\Psi_i = (2\pi)^{-6}\,D_{j\ell n}\iiint \Psi_{\underline{k}_1}^+(\underline{s})\,e^{i\underline{k}_2\cdot\underline{\ell}}\,J_{j\ell}^{(1)}(\underline{k}_2 - a\,\underline{k}_i)\times$$

$$G_{jn}(\underline{t})\,\delta(c\,\underline{k}_2 - \underline{k}_1 - \underline{k}_i)\,d\underline{k}_1\,d\underline{k}_2\,d\underline{k}_3 \ , \qquad (2.3.20)$$

since $\displaystyle\sum_m$ implies integration over all values of $\underline{k}_1$, $\underline{k}_2$ amd $\underline{k}_3$.
The integrations over $\underline{k}_3$ and $\underline{k}_2$ are elementary, and therefore

$$\omega_{13}^+\Psi_i = (2\pi c)^{-3}\,D_{j\ell n}G_{jn}(\underline{t})\int\Psi_{\underline{k}_1}^+(\underline{s})\,e^{\frac{i}{c}(\underline{k}_1+\underline{k}_i)\cdot\underline{\ell}_x}$$

$$J_{j\ell}^{(1)}\left[\frac{1}{c}(\underline{k}_1 + \underline{k}_i) - a\,\underline{k}_i\right]\,d\underline{k}_1 \ . \qquad (2.3.21)$$

The substitution of equation (2.3.21) into (2.3.10) gives

$$T_{if} = (2\pi c)^{-3}\,D_{j\ell n}\iiiint \chi_f(\underline{s})\,\hat{\varphi}_f(\underline{t})\Psi_{\underline{k}}^+(\underline{s})\left[\frac{2}{|\underline{\ell} - h\,\underline{s}|} - \right.$$

$$\left.\frac{1}{|\underline{\ell} - h\,\underline{s} - \underline{t}|} - \frac{2}{|\underline{\ell} - c\,\underline{s}|} + \frac{1}{|\underline{\ell} + c\,\underline{s} - \underline{t}|}\right]e^{\frac{i}{c}(\beta+\underline{k})\cdot\underline{\ell}} \times$$

$$G_{jn}(\underline{t})\,J_{j\ell}^{(1)}\left[\left(\frac{1}{c} - a\right)\underline{k}_i + \frac{1}{c}\,\underline{k}\right]\,d\underline{k}\,d\underline{s}\,d\underline{\ell}\,d\underline{t} \ , \qquad (2.3.22)$$

where $h = (1 + M_1)^{-1}$, and where we have used $\beta = \underline{k}_i - c\,\underline{k}_f$
(see equation 2.2.49). Note that the subscript 1 of $\underline{k}_1$ has now
been dropped. The integral with respect to $\underline{\ell}$ is of the form

$$P = e^{i\underline{L}\cdot\underline{\ell}}\left[\frac{2}{|\underline{\ell} - h\,\underline{s}|} - \frac{1}{|\underline{\ell} - h\,\underline{s} - \underline{t}|} - \frac{2}{|\underline{\ell} + c\,\underline{s}|} + \frac{1}{|\underline{\ell} + c\,\underline{s} - \underline{t}|}\right]d\underline{\ell}$$

where $\underline{L} = \dfrac{1}{c}(\underline{k} + \beta)$. This type of integral may be evaluated by
making use of Bethe's[49] integral

$$\int \frac{e^{i\underline{L}\cdot\underline{\ell}}}{|\underline{\ell} - \underline{r}_j|}\,d\underline{\ell} = \frac{4\pi}{L^2}\,e^{i\underline{L}\cdot\underline{r}_j} \ , \qquad (2.3.23)$$

giving

$$P = \frac{4\pi c^2}{(\underline{k}+\underline{\beta})^2} \left[e^{i\frac{h}{c}(\underline{k}+\underline{\beta})\cdot\underline{s}} - e^{-i(\underline{k}+\underline{\beta})\cdot\underline{s}} \right] \left[2 - e^{\frac{i}{c}(\underline{k}+\underline{\beta})\cdot\underline{t}} \right] .$$

Therefore, equation (2.3.22) becomes

$$T_{if} = \frac{4\pi}{c(2\pi)^3} D_{j\ell n} \int d\underline{t} \int d\underline{k} \; \phi_f(\underline{t}) \left[2 - e^{\frac{i}{c}(\underline{k}+\underline{\beta})\cdot\underline{t}} \right] G_{jn}(\underline{t}) \; \times$$

$$(\underline{k}+\underline{\beta})^{-2} \; J_{j\ell}^{(1)} \left[(\frac{1}{c} - a)\underline{k}_i + \frac{1}{c}\underline{k} \right] \int d\underline{s} \; \chi_f(\underline{s}) \psi_{\underline{k}}^+(\underline{s}) \; \times$$

$$\left[e^{i\frac{h}{c}(\underline{k}+\underline{\beta})\cdot\underline{s}} - e^{-i(\underline{k}+\underline{\beta})\cdot\underline{s}} \right] . \hspace{2cm} (2.3.24)$$

The integral over $\underline{s}$ is of the form

$$S = \mathscr{J}\left[\underline{k}, \frac{1}{M_1}(\underline{k}+\underline{\beta})\right] - \mathscr{J}\left[\underline{k}, -(\underline{k}+\underline{\beta})\right] , \hspace{1cm} (2.3.25)$$

where $\mathscr{J}(\underline{k}, \underline{\Lambda}) = \int \chi_f(\underline{s}) \psi_{\underline{k}}^+(\underline{s}) \exp(i\underline{\Lambda}\cdot\underline{s}) d\underline{s} .$ $\hspace{1cm} (2.3.26)$

This integral has been evaluated by Massey and Mohr[50] and by McDowell[34]

It is found that

$$\mathscr{J}(\underline{k}, \underline{\Lambda}) = 8\pi^{\frac{1}{2}} e^{-\pi\gamma/2} \Gamma(1+i\gamma) \left[\frac{c_o - id}{1+\omega^2} \right]^{i\gamma} (1+\omega^2)^{-2} \; \times$$

$$(c_o^2 + d^2)^{-1} \left\{ c_o^2 + d^2 - \gamma(kc - d)(\omega^2 + 1) + i\left[\gamma(c_o^2 + d^2) - \right. \right.$$

$$\left. \gamma(c_o + kd)(1+\omega^2) \right] \right\} , \hspace{2cm} (2.3.27)$$

where

$$\gamma = -1/k , \quad d = 2k , \quad c_o = 1 + \Lambda^2 - k^2 , \quad \underline{\omega} = \underline{k} + \underline{\Lambda} ,$$

$$\underline{\Lambda} = h(\underline{k}+\underline{\beta}).$$

Note that h is a dummy which now takes on the value $h_1 = 1/M_1$ and

$h_2 = -1$ to give the first and second terms on the right hand side

of equation (2.3.25). From a computational point of view, a more convenient way of writing equation (2.3.27) is in the following form:

$$\mathcal{J}(\underline{k},\underline{A}) \equiv I\left[h(\underline{k}+\underline{\beta})\right] = \frac{8\pi^{\frac{1}{2}}e^{-\pi\gamma/2}\,\Gamma(1+i\gamma)\exp\left[\gamma\tan^{-1}d/c_0\right](C + iD)}{(c_0^2+d^2)\left\{1+\left[\underline{k}+h(\underline{k}+\underline{\beta})\right]^2\right\}^2} \quad ,$$

(2.3.28)

where

$$C = (f_1 + f_2\mu + f_3\mu^2)\cos\textcircled{H} - (f_4 + f_5\mu + f_6\mu^2)\sin\textcircled{H} \quad ,$$

(2.3.29)

$$D = (f_1 + f_2\mu + f_3\mu^2)\sin\textcircled{H} + (f_4 + f_5\mu + f_6\mu^2)\cos\textcircled{H} \quad ,$$

$$\mu = \frac{\underline{k}\cdot\underline{\beta}}{k\beta} \quad ,$$

(2.3.30)

$$\textcircled{H} = \gamma\log_e\left[\frac{(c_0^2 + d^2)^{\frac{1}{2}}}{1 + \left[\underline{k} + h(\underline{k}+\underline{\beta})\right]^2}\right] \quad ,$$

(2.3.31)

$$f_1 = 2h(h-1)k^2 + 2h(h-1)(h+1)^2k^4 + 2h^2(2h-1)(h+1)k^2\beta^2 + 2h^2(1+h^2\beta^2)\beta^2$$

$$f_2 = 2h(2h-1)k\beta + 2h(h+1)(4h^2-h-1)k^3\beta + 2h^3(4h+1)k\beta^3$$

$$f_3 = 4h^3(2h+1)k^2\beta^2$$

(2.3.32)

$$f_4 = 2h(h+1)^2k^3 + 2h^2(h+2)k\beta^2 + 2hk$$

$$f_5 = 2h(3h+1)(h+1)k^2\beta + 2h(1+h^2\beta^2)\beta$$

$$f_6 = 4h^3k\beta^2 \quad .$$

Therefore, equation (2.3.24) may now be written as

$$T_{if} = \frac{1}{2\pi^2c}\,D_{j\ell n}\int d\underline{k}\left\{I\left[h_1(\underline{k}+\underline{\beta})\right] - I\left[h_2(\underline{k}+\underline{\beta})\right]\right\}\frac{1}{(\underline{k}+\underline{\beta})^2} \times$$

$$J_{j\ell}^{(1)}(\underline{k})\,J_{jn}^{(2)}(\underline{R}) \quad ,$$

(2.3.33)

where

$$J^{(1)}_{j\ell} (\underline{K}) = \int e^{-i\underline{K}\cdot\underline{x}} \, G_{j\ell}(\underline{x}) \, d\underline{x} \quad , \tag{2.3.34}$$

$$J^{(2)}_{jn} (\underline{R}) = \int \left[2 - e^{-i\underline{R}\cdot\underline{t}} \right] G_{jn}(\underline{t}) \, \phi_f(\underline{t}) \, d\underline{t} \quad , \tag{2.3.35}$$

and if we note that $\left(\dfrac{1}{c} - a \right) \underline{k}_i = \underline{\alpha} + \dfrac{1}{c} \underline{\beta}$ (see equations (2.2.48) and (2.2.49)), then

$$\underline{K} = \underline{\alpha} + \frac{1}{c} (\underline{k} + \underline{\beta}) \quad , \tag{2.3.36}$$

$$\underline{R} = \frac{1}{c} (\underline{k} + \underline{\beta}) \quad . \tag{2.3.37}$$

In order to evaluate the transition matrix element T_{if} and, ultimately, the total cross section Q, we have adopted the following procedure:

(1) The integrands in equations (2.3.35) and (2.3.34) were evaluated by substituting the appropriate part of the helium wavefunction in place of $G_{jn}(\underline{t})$ and $G_{j\ell}(\underline{x})$, thereby giving $J^{(1)}$ and $J^{(2)}$ as functions of $\underline{k}$, $\underline{\alpha}$ and $\underline{\beta}$. We note here that $\underline{k}$ is the momentum vector conjugate to $\underline{s}$, which is the coordinate that links the incoming proton with the 'active' electron, and $\underline{\alpha}$ and $\underline{\beta}$ are the momentum transfer vectors defined in equations (2.2.48) and (2.2.47).

(2) The functions $J^{(1)}_{j\ell} (\underline{k}, \underline{\beta}, \underline{\alpha})$ and $J^{(2)}_{jn} (\underline{k}, \underline{\beta})$ were substituted into equation (2.3.33). In order to obtain the transition amplitude T_{if} it was then necessary to integrate over $\underline{k}$. Taking polar coordinates for $\underline{k}$, with $\underline{\beta}$ as axis, it was possible to perform the resulting integral over the azimuthal angle ϕ analytically, leaving the integrals over the polar variable $\mu = \dfrac{\underline{k} \cdot \underline{\beta}}{k\beta}$, and the radial variable k, to be evaluated by numerical integration procedures.

(3) Finally, the total cross section for process (2.3.1) was obtained by making use of equation (2.2.63) and performing a further numerical integration.

Numerical Methods

The expression (2.3.33) for the transition matrix element T_{if} may be written, after the analytical integration over ϕ , in the form

$$T_{if}(\beta, v^2) = \int_0^\infty dk\ \Gamma(1 - i/k) \int_{-1}^{+1} d\mu\ F(k, \beta, \mu) H(k, \beta, \mu, v^2)\ ,$$

(2.3.38)

where F contains, essentially, the expression (2.3.28) and the term $J^{(2)}(k, \beta, \mu)$, while H arises from $J^{(1)}(k, \beta, \mu, v^2)$. The symbol $\Gamma(x + iy)$ represents a gamma function with complex argument; a numerical routine was used which gave $\Gamma(x + iy)$ to an accuracy of six significant figures. All three numerical integrations were evaluated by dividing each integrand into an appropriate number of ranges, and then applying a Gaussian quadrature formula[51] to each range. The μ-integration presented the least difficulty in that it has finite limits, and a total of 32 Gaussian points ensured an accuracy of at least seven significant figures in all cases examined. The function $\Gamma\left(1 - \dfrac{i}{k}\right)$ varies smoothly for $k > 0.8$ but oscillates extremely rapidly in the region $0 < k < 0.8$. However,

$$M(k, \beta, v^2) = \int_{-1}^{+1} d\mu\ F(k, \beta, \mu) H(k, \beta, \mu, v^2) \qquad (2.3.39)$$

is a slowly varying function of k for $k < 0.8$. Accordingly, M was calculated at only 8 points in this region and interpolated to a further 240 points before integrating over k. Interpolated values were checked against calculated values of M for a large number of k and β values and were found to agree to five significant figures in all cases. In the region $0.8 < k < \infty$, a safe cut-off value k_{max} was found (which increased with

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increasing v^2) corresponding to the point beyond which there is

no significant contribution to the total area coming from the

k-integration. The region $0.8 < k < k_{max}$ was divided into 60

ranges, such that a large proportion of the ranges were concentrated

in the most significant part of the k-curve, with 4 Gaussian points

in each range. In the final β-integration, a similar technique

to that described above was used except that, in this case, only

15 ranges with 4 Gaussian points in each range were required to

give a final answer accurate to 4 significant figures.

CHAPTER 2.4

Impulse Approximation Cross Sections

Results for the total cross section Q(1s) for the

capture process

$$H^+ + He(1s^2) \longrightarrow H(1s) + He^+(1s) \quad , \qquad (2.4.1)$$
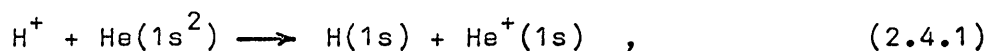
obtained within the impulse approximation, are presented in

Table 2.1. In the evaluation of these cross sections, the wave-

function of the helium atom in its ground state was represented

by (i) the simple one-parameter wavefunction (2.3.6), denoted here

by Ψ_λ, and (ii) the natural expansion of the 35-configuration

CI wavefunction (2.3.7) of Weiss[a], denoted here by Ψ_X (X = 1,2,3...15).

The symbol X is used to indicate the degree of truncation of the

natural expansion such that X = 1 can be taken as a representation

of the Hartree Fock (HF) equivalent wavefunction within the basis

set used by Weiss, while X = 15 represents the total Weiss wave-

function. In Table 2.1 we quote, after each X value, the symmetry

of the basis orbitals used to construct the X'th natural orbital.

In this discussion we denote the cross sections arising from the

use of Ψ_λ and Ψ_X in equations (2.3.33) and (2.2.63) by Q_λ and

Q_X respectively.

In our calculations, we have used the ground state

energy appropriate to the particular wavefunction being employed.

Therefore the influence of electron correlation on Q(1s) is two-fold:

(a) through improvements in the ground state energy of helium, which

appears in the formula for the energy defect ϵ

($\epsilon = -2\epsilon_{He^+} - 2\epsilon_H + 2\epsilon_{He}$, where ϵ_{He}, ϵ_H and ϵ_{He^+} are the

binding energies of the ground state of the helium atom, the

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[a]See chapter 1.3 and references therein

hydrogen atom and the helium ion respectively); (b) through

improvements in the helium wavefunction Ψ_X , which alters the

functional behaviour of the integrand in equation (2.3.33). The

nature of this dual dependence is not immediately apparent since

the energy defect ϵ appears inside the integrand for T_{if} in a way

that makes factorization of ϵ from T_{if} impossible. However,

such a two-fold dependence may be rationalized in the following

way. The terms in the probability amplitude T_{if} contain ϵ in a

factor of the form $\delta = v^2 - \epsilon$, where v is the incoming proton

velocity. The factor δ also appears in β_{min}, the lower limit

of the integrand (2.2.63). At high impact energies[a] the changes

in δ due to improvements in ϵ are minimal, since $v^2 \gg \epsilon$,

and Q(1s) is influenced only through the wavefunction. On the

other hand, at low impact energies, Q(1s) is influenced by improvements

in ϵ and in the wavefunction. At very low energies (E $<$ 50 keV),

the dominant effect on the cross section stems from ϵ in its

influence on β_{min}. Finally, from a series of pilot studies,

throughout which ϵ was held constant, it was found that improving

the ground state wavefunction (from Ψ_λ to $\Psi_{X=15}$) alone

resulted in an increase for all values of Q(1s) throughout the

projectile energy range studied here.

The effects of introducing an improved wavefunction

Ψ_X into the formula for Q(1s) may be seen more easily by examin-

ation of Table 2.2 where, for convenience, we present the percentage

changes in Q(1s) due to improvements in Ψ_X . The relative

percentage change in Q(1s), as we move from a wavefunction Ψ_ℓ to

a more accurate wavefunction Ψ_m (say), is defined here as

$$\Delta(\ell \rightarrow m) = \left[\frac{Q_m - Q_\ell}{Q_\ell} \right] \times 100\% \quad . \tag{2.4.2}$$

---

[a]Note that if v is in atomic units, then the impact energy
$E = 25\,v^2\,(keV)$.

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The first improvement over the simple non-correlated wavefunction Ψ_λ is the HF equivalent wavefunction $\Psi_{X=1}$, which is the natural expansion wavefunction truncated to include only the first (normalized) natural configuration. The percentage change $\Delta(\lambda \longrightarrow 1)$ in the cross section introduced by the replacement of Ψ_λ by $\Psi_{X=1}$ is seen to be negative for 25 keV $\leqslant E \leqslant$ 200 keV, but positive for $E \geqslant$ 400 keV. Therefore, in the light of our discussion above of the dual nature of the correlation effect, it is apparent that the use of a HF wavefunction for describing the helium atom ground state increases the capture cross section Q(1s) for all energies but, at the same time, the concomitant improvement in the ground state energy gives a reduction in Q(1s) through the energy defect ϵ , which is seen to become dominant at low impact energies. The initial introduction of electron correlation, essentially of an angular nature based on p-orbitals, causes a rather different behaviour. At low energies, the percentage change $\Delta(1 \longrightarrow 2)$ is negative, indicating that angular correlation has reduced the cross section even further. At intermediate energies (100 keV $\leqslant E \leqslant$ 400 keV) the cross-over described in the $\Delta(\lambda \longrightarrow 1)$ case has occurred and Q(1s) has consequently increased but, at high energies, the percentage increase indicated by $\Delta(1 \longrightarrow 2)$ is rapidly falling – being only +0.4% at E = 3500 keV whereas $\Delta(\lambda \longrightarrow 1) = $ +5.5% at the same energy. It is seen, therefore, that if we confine our comments to energies $E \geqslant$ 600 keV, we may conclude that Q(1s) has been further increased by the initial introduction of angular correlation, although this increase is less than that due to the introduction of the HF wavefunction. The correlation introduced into Ψ_X as we move from X = 2 $\longrightarrow$ 3 is of a purely radial nature. The consequent percentage change in

Q(1s) is shown in Table 2.2 under the column headed $\Delta(2 \rightarrow 3)$. The magnitude of $\Delta(2 \rightarrow 3)$ is greater than the magnitude of $\Delta(1 \rightarrow 2)$ throughout the energy range considered, notwithstanding the fact that the percentage change $\Delta(2 \rightarrow 3)$ is due to the introduction of a natural configuration (X = 3) which, from the point of view of the ground state energy of the target, is of less importance than the preceding natural configuration (X = 2) which, of course, gave rise to $\Delta(1 \rightarrow 2)$. Furthermore, $\Delta(2 \rightarrow 3)$ is negative throughout the energy range considered and, for E $\geqslant$ 600 keV, $\Delta(2 \rightarrow 3)$ becomes steadily greater in magnitude with increasing impact energy E, which is in direct contrast with the behaviour of $\Delta(1 \rightarrow 2)$. In other words, in the energy range 600 keV $\leqslant$ E $\leqslant$ 3500 keV, whereas angular correlation increases the cross section Q(1s) (an effect which diminishes in importance with increasing energy) radial correlation causes a decrease in the Q(1s) values which grows in importance with increasing energy. The influence on Q(1s) of total correlation within Weiss' wave-function can be examined by comparing the results for X = 15 with those for X = 1 in Table 2.1 or, alternatively, by examining the change $\Delta(1 \rightarrow 15)$ listed in Table 2.2. It is seen that the effect of the inclusion of all the correlation terms is oscillatory; decreasing Q(1s) at the extreme ends of our energy scale, but increasing Q(1s) in the middle range. A comparison between $\Delta(\lambda \rightarrow 1)$ and $\Delta(1 \rightarrow 15)$ reveals that, for E $\geqslant$ 50 keV, the improvement in the wavefunction over the simple non-correlated wavefunction and its associated energy, achieved by using the HF wavefunction, gives changes in Q(1s) which are considerably larger than those obtained due to correlation effects.

In order to make a comparison with experiment it is necessary to allow for capture into excited states and also for the possibility that the residual ion has been left in an excited state. To estimate our total cross section Q we have multiplied the results for Q(1s) obtained from the impulse approximation by the factor[a] $\sum_{n=1}^{\infty} n^{-3} = 1.202$. The results are compared with the experiments of Welsh et al[12] and of Stier and Barnett[52] in Table 2.3. Although the fully correlated results are in better agreement with experiment than the non-correlated results, it is seen that, at high energies, theoretical and experimental cross sections are diverging with increasing projectile energy. It is evident that the use of a more accurate wavefunction for the helium ground state has increased the impulse approximation cross section - thereby improving the agreement between theory and experiment, at high energies, over that obtained when using a simple non-correlated wavefunction. However, the amount of improvement is not as large as had been hoped for by Bransden[3]. This leads us to suggest that an assumption made in the impulse approximation to the scattering amplitude T_{if} is not valid at high impact energies.

In chapter 2.2 it was found possible to express the many-body operator Ω^+ in terms of the two-body operators ω_{ij}^+ in the following manner

$$\Omega^+ = (\omega_{12}^+ + \omega_{13}^+ + \omega_{14}^+ - 2) + G^+ \left[(V_{23} + V_{24}), (b_{12}^+ + b_{13}^+ + b_{14}^+) \right] +$$

$$G^+ \left\{ (V_{13} + V_{14})b_{12}^+ + (V_{12} + V_{14})b_{13}^+ + (V_{12} + V_{23})b_{14}^+ \right\} , \quad (2.4.3)$$

where
$$b_{ij}^+ = \omega_{ij}^+ - 1 . \quad (2.4.4)$$

---

[a]This is the well known Oppenheimer[4] sum rule.

Thus, T_{if} could be written as

$$T_{if} = \langle \Psi_f | V_f | (\omega_{12}^+ + \omega_{13}^+ + \omega_{14}^+ - 2) \Psi_i \rangle \quad +$$

$$\langle \Psi_f | V_f | G^+ \left[(V_{23} + V_{24}), (b_{12}^+ + b_{13}^+ + b_{14}^+) \right] \Psi_i \rangle +$$

$$\langle \Psi_f | V_f | G^+ \left\{ (V_{13} + V_{14}) b_{12}^+ + (V_{12} + V_{14}) b_{13}^+ + (V_{12} + V_{23}) b_{14}^+ \right\} \Psi_i \rangle$$

$$(2.4.5)$$

The third term of equation (2.4.5) was identified as a multiple

scattering contribution and, as such, was neglected; the second

term, which involves the binding potentials V_{23} and V_{24}, was also

neglected on the grounds of the 'impulse hypothesis'; the remaining

term represents the impulse approximation to T_{if} and, with the

added assumption that $\omega_{12}^+ = \omega_{14}^+ = 1$, was the matrix element

used to evaluate the cross sections reported here. The validity

of the expansion for Ω^+ in terms of the operators $\omega_{ij}^+(m)$

depends not only on the non-coulombic nature of the perturbation

potential $V_i = V_{12} + V_{13} + V_{14}$ but also on the non-coulombic form

of the individual contributions V_{ij} in order that the definition

of $\omega_{ij}^+(m)$, see equation (2.2.13), is strictly rigorous. Although

V_i satisfies the required condition when dealing with a neutral

target system, the individual components are coulombic and,

consequently, a modification of the impulse approximation would

appear to be required. A more satisfactory version is provided

by the extended impulse approximation where one now defines, in

place of $\omega_{ij}^+(m)$, the more complicated operators $\omega_i^+(m)$ by the

equation

$$\omega_i^+(m) \chi_m = \left[1 + \frac{1}{E_m - H_o - V_i + i\varepsilon} \right] \chi_m \equiv \Psi_m^+ (i) \quad . \qquad (2.4.6)$$

Consequently, it may be shown that

$$T_{if} = \langle \Psi_f | V_f | \omega_i^+ \Psi_i \rangle + {}^{!}\langle \Psi_f | V_f | G^+ [(V_{23} + V_{24}), b_i^+] \Psi_i \rangle \quad ,$$

$$(2.4.7)$$

where $\quad b_i^+ = \omega_i^+ - 1 \quad , \qquad\qquad (2.4.8)$

which, after invoking the 'impulse hypothesis', becomes

$$T_{if} \simeq \langle \Psi_f | V_f | \omega_i^+ \Psi_i \rangle \quad . \qquad\qquad (2.4.9)$$

Results for cross sections based on the matrix element (2.4.9),
which involves only potentials of a non-coulombic nature, have not
been reported by any authors due to difficulties associated with
the resulting integrals.

An alternative approach to the evaluation of electron
capture cross sections is provided by the continuum distorted
wave method, which was first studied by Cheshire[38] and is discussed
in the following chapters.

Summary

The initial aim of this study was to examine the effects
of electron correlation on the impulse approximation to the cross
section Q(1s) of the electron capture process (2.4.1), thereby
enabling us to comment on the consequent effects on the total
cross section Q

$$H^+ + He(1s^2) \longrightarrow H + He^+ \quad . \qquad\qquad (2.4.10)$$
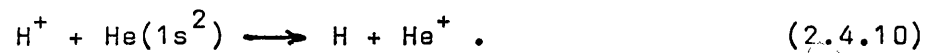
The introduction of angular and radial correlation, in that order,
showed that, at low impact energies, radial correlation is the
more important and, for energies well below 400 keV, both effects
work together to reduce the cross section Q(1s) whereas, at about
400 keV, the effects almost cancel since they now oppose - angular
correlation giving an increase in Q(1s) and radial correlation still
giving a reduction. At larger impact energies (E $\simeq$ 1000 keV),

the reduction in Q(1s) due to radial correlation was found to predominate over the increase which arose from the angular correlation effect. As the degree of truncation X within the natural expansion of the ground state wavefunction for the target is increased, correlation effects drop off fairly rapidly and, at X = 5, we have converged on to the X = 15 (totally correlated) result to within about 1%.

To evaluate the total cross section Q it is necessary to allow for the possibility of capture into any state; i.e. $Q = \sum_{n\ell} Q(n\ell)$. This was achieved by making use of the Oppenheimer[4] sum rule, Q = 1.202 Q(1s). A comparison of the evaluated cross section Q with experiment revealed that, at high energies, although the correlated results are an improvement over the non-correlated results, experimental and theoretical values still diverged as the projectile energy was increased. Thus, the increase in magnitude of the cross section due to the introduction of electron correlation, within the impulse approximation, was not sufficient to produce the expected convergence between theory and experiment at high impact energies. It is thought that this situation must presumably arise because of the presence of the <u>coulomb</u> potential V_{13} in the two-body Moller operator $\omega_{13}^{+}(m)$, which was subsequently used to evaluate Q(1s).

TABLE 2.1   Impulse approximation total cross section $Q(1s)$ (in units of πa_o^2) for the reaction $H^+ + He(1s^2) \rightarrow H(1s) + He^+(1s)$, evaluated using the non-correlated (λ) and the natural expansion (X-terms) helium wavefunctions – see equations (2.3.6) and (2.3.7) of text.

E(keV)	λ	X = 1(s)	X = 2(p)	X = 3(s)	X = 4(d)	X = 5(p)	X = 6(s)	X = 15(s)
25	3.952^0 [a]	3.693^0	3.569^0	3.352^0	3.350^0	3.339^0	3.333^0	3.375^0
50	1.168^0	1.112^0	1.100^0	1.051^0	1.053^0	1.052^0	1.051^0	1.066^0
100	2.088^{-1}	2.031^{-1}	2.042^{-1}	1.975^{-1}	1.983^{-1}	1.985^{-1}	1.985^{-1}	2.014^{-1}
150	5.931^{-2}	5.849^{-2}	5.928^{-2}	5.766^{-2}	5.797^{-2}	5.807^{-2}	5.812^{-2}	5.892^{-2}
200	2.174^{-2}	2.168^{-2}	2.203^{-2}	2.150^{-2}	2.163^{-2}	2.169^{-2}	2.172^{-2}	2.200^{-2}
400	1.374^{-3}	1.403^{-3}	1.431^{-3}	1.402^{-3}	1.412^{-3}	1.418^{-3}	1.422^{-3}	1.437^{-3}
600	2.262^{-4}	2.334^{-4}	2.376^{-4}	2.330^{-4}	2.346^{-4}	2.357^{-4}	2.364^{-4}	2.388^{-4}
800	5.876^{-5}	6.099^{-5}	6.199^{-5}	6.076^{-5}	6.112^{-5}	6.142^{-5}	6.162^{-5}	6.226^{-5}
1000	2.000^{-5}	2.082^{-5}	2.133^{-5}	2.070^{-5}	2.082^{-5}	2.091^{-5}	2.098^{-5}	2.122^{-5}
1500	2.656^{-6}	2.775^{-6}	2.807^{-6}	2.746^{-6}	2.759^{-6}	2.769^{-6}	2.777^{-6}	2.811^{-6}
2500	1.900^{-7}	1.995^{-7}	2.008^{-7}	1.961^{-7}	1.968^{-7}	1.973^{-7}	1.978^{-7}	1.999^{-7}
3500	3.187^{-8}	3.382^{-8}	3.375^{-8}	3.288^{-8}	3.298^{-8}	3.306^{-8}	3.314^{-8}	3.340^{-8}

(a) The superscript denotes the power of ten by which the entry should be multiplied.

TABLE 2.2   The relative percentage change $\Delta(\ell \to m)$ in Q(1s), as we move from a wavefunction $\tilde{\Psi}_\ell$ to a more accurate wavefunction $\tilde{\Psi}_m$, defined as $\Delta(\ell \to m) = \left\{ \dfrac{Q_m - Q_\ell}{Q_\ell} \right\} \times 100\%$

E(keV)	$\Delta(\lambda \to 1)$	$\Delta(1 \to 2)$	$\Delta(2 \to 3)$	$\Delta(3 \to 4)$	$\Delta(4 \to 5)$	$\Delta(5 \to 6)$	$\Delta(1 \to 15)$	$\Delta(\lambda \to 15)$
25	—	-3.4%	-6.1%	-0.1%	-0.3%	-0.2%	-8.6%	-14.6%
50	-4.8%	-1.1%	-4.5%	+0.2%	-0.1%	-0.1%	-4.1%	-8.7%
100	-2.7%	+0.5%	-3.3%	+0.4%	+0.1%	+0.0%	-0.8%	-3.5%
150	-1.4%	+1.4%	-2.7%	+0.5%	+0.2%	+0.1%	+0.7%	-0.7%
200	-0.3%	+1.6%	-2.4%	+0.6%	+0.3%	+0.1%	+1.5%	+1.2%
400	+2.1%	+2.0%	-2.0%	+0.7%	+0.4%	+0.3%	+2.4%	+4.6%
600	+3.2%	+1.8%	-1.9%	+0.7%	+0.5%	+0.3%	+2.3%	+5.6%
800	+3.8%	+1.6%	-2.0%	+0.6%	+0.5%	+0.3%	+2.1%	+6.0%
1000	+4.1%	+1.5%	-2.0%	+0.6%	+0.4%	+0.3%	+1.9%	+6.1%
1500	+4.5%	+1.2%	-2.2%	+0.5%	+0.4%	+0.3%	+1.3%	+5.5%
2500	+5.0%	+0.7%	-2.3%	+0.4%	+0.3%	+0.3%	+0.2%	+5.2
3500	+5.5%	+0.4%	-2.6%	+0.3%	+0.2%	+0.2%	-0.7%	+4.8%
% of correlation energy recovered	—	48.4%	36.7%	4.3%	4.0%	1.9%	100%(a)	—

(a) By definition.

TABLE 2.3   Impulse approximation total cross section Q (in units of πa_0^2) for the reaction $H^+ + He(1s^2) \rightarrow H + He^+$, evaluated using the non-correlated (λ) and the natural expansion (X-terms) helium wavefunctions — see equations (2.3.6) and (2.3.7) of text.

E(keV)	λ	X = 1	X = 15	Experiment
100	2.510^{-1} (a)	2.441^{-1}	2.421^{-1}	3.4^{-1} (b)
440	1.093^{-3}	1.120^{-3}	1.146^{-3}	$(1.8 \pm 0.2)^{-3}$ (c)
654	1.825^{-4}	1.887^{-4}	1.930^{-4}	$(3.3 \pm 0.4)^{-4}$ (c)
851	5.255^{-5}	5.461^{-5}	5.570^{-5}	$(9.4 \pm 1.1)^{-5}$ (c)
1063	1.783^{-5}	1.857^{-5}	1.900^{-5}	$(3.3 \pm 0.4)^{-5}$ (c)
2450	2.540^{-7}	2.665^{-7}	2.672^{-7}	$(3.6 \pm 0.4)^{-7}$ (c)
2990	8.874^{-8}	9.337^{-8}	9.151^{-8}	$(1.4 \pm 0.1)^{-7}$ (c)

(a)   The superscript denotes the power of ten by which the entry should be multiplied.

(b)   Stier and Barnett, reference 52.

(c)   Welsh et al., reference 12.

CHAPTER 2.5

Continuum Distorted Wave Method

In recent years, a certain amount of interest has arisen in the continuum distorted wave (CDW) method since it may be easily applied to electron capture scattering reactions, with a high degree of accuracy, at large impact energies. The CDW method, which has the advantage of being a second-order approximation, has been introduced by Cheshire[38], who applied it to the resonant charge transfer process

$$H^+ + H(1s) \longrightarrow H(1s) + H^+ \ . \qquad\qquad (2.5.1)$$

Detailed numerical calculations[38] have shown that the CDW cross sections for reaction (2.5.1) lie close to, but above, the impulse approximation cross sections in the energy range 80 keV – 1 MeV and are therefore found to be in closer agreement with experiment. However, until recently, there had been no rigorous theoretical foundation for the CDW method and consequently its application to other capture reactions has been viewed with some caution. In their work on high energy charge transfer, McCarroll and Salin[41] have shown that the CDW method is a high energy second-order approximation. This work was later superseded by that of Gayet[42], who gave a rigorous foundation to the CDW method on the basis of a quantum three-body theory for rearrangement collisions and, in addition, suggested that it would be interesting to compare the cross sections calculated by means of this method with available experimental data down to about 25 keV. Salin[43] has evaluated cross sections for the process

$$H^+ + He(1s^2) \longrightarrow H(n\ell) + He^+(1s) \ , \qquad\qquad (2.5.2a)$$
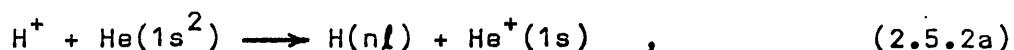
where $n\ell$ = 1s, 2s, 2p, 3s, in the energy range 400 keV - 3 MeV.

The difference between his two sets of results - obtained using the

helium wavefunctions (2.1.25) and (2.1.26) - was up to 20% for

impact energies greater than 1 MeV. In view of this large percentage

change in the electron capture cross section which, after all,

was due to a change in the basis set $1s^2$ to $1s1s'$, we examine here

the influence of the systematic introduction of electron correlation

on the CDW approximation cross section $Q(n\ell)$ for reaction (2.5.2a)

for $n\ell$ = 1s, 2s, 2p, in the energy range 25 keV - 3 MeV. In

particular, it will be of interest to compare our results for the

cross sections $Q(n\ell)$ obtained by using the simple one-parameter

target wavefunction with those we obtained by using the HF descrip-

tion of the target. It will be recalled that, within the impulse

approximation, it was the introduction of the HF wavefunction which

had the greatest effect on the magnitude of $Q(1s)$. Also considered,

are similar effects for the reaction which involves alpha-particles

as projectiles, namely,

$$He^{++} + He(1s^2) \longrightarrow He^+(n\ell) + He^+(1s) \quad , \qquad (2.5.2b)$$
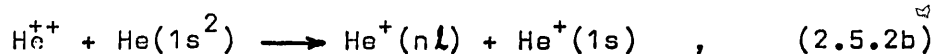
where $n\ell$ = 1s, 2s, 2p, in the energy range 25 keV - 3 MeV.

Derivation of the Transition Amplitude

Consider an encounter in which a nucleus A, of charge Z_A,

is incident on an atom or ion consisting of two electrons (1) and

(2) bound to a nucleus B, charge Z_B. Let $\underline{x}_1$ and $\underline{x}_2$ be the position

vectors of electron (1) and (2) with respect to the nucleus of B

and $\underline{s}_1$, $\underline{s}_2$ be the corresponding vectors relative to the nucleus A.

Then the process we are considering is of the type

$$Z_A + \left[Z_B, e(1), e(2)\right]_i \longrightarrow \left[Z_A, e(1)\right]_{f_1} + \left[Z_B, e(2)\right]_{f_2} \quad ,$$

$$(2.5.3)$$

where i and f denote initial and final states, respectively. This treats the electrons as being distinguishable; the cross section for single electron capture is then twice the cross section for capture of either electron. Let $\underline{R}$ be the position vector of A relative to B. Let us assume that the velocity $\underline{v}$ of A, relative to the fixed nucleus B, remains constant and that the impact parameter of the collision is $\underline{b}$. Therefore

$$\underline{R} = \underline{b} + \underline{v} \, t, \tag{2.5.4}$$

where t is the time chosen such that, at t = 0, the nuclei A and B have a minimum separation $\underline{b}$. Let 0 be an arbitrary origin along AB, such that $p\underline{R} + q\underline{R} = \underline{R}$, and let $\underline{r}_1$ and $\underline{r}_2$ be the position vectors of electron (1) and (2) with respect to the origin 0. The complete Schrodinger equation describing the motion of the electrons during collision is

$$\left[\frac{1}{2}\nabla^2_{\underline{r}_1} + \frac{1}{2}\nabla^2_{\underline{r}_2} + \frac{Z_B}{x_1} + \frac{Z_B}{x_2} + \frac{Z_A}{s_1} + \frac{Z_A}{s_2} - \frac{1}{x_{12}} - \frac{Z_A Z_B}{R} \right] \Psi(\underline{r}_1, \underline{r}_2, t) =$$

$$- i \frac{\partial \Psi}{\partial t}(\underline{r}_1, \underline{r}_2, t) \quad , \tag{2.5.5}$$

where x_{12} is the distance between electrons (1) and (2).

In a frame of reference with origin at a point which divides the internuclear line AB in the ratio p : q, the active electron (1) has, in addition to its orbital motion about the target nucleus B, a velocity $-p\,\underline{v}$ by virtue of being bound to B. Similarly, an electron bound to the nucleus A would have a velocity $q\,\underline{v}$. If a collision results in the excitation of the target atom, the active electron continues to move with the nucleus B, and its translational motion remains unchanged since $\underline{v}$ is assumed constant. However, in the case of a rearrangement collision, the electron,

which was originally moving with B, is captured by A and must therefore acquire the linear velocity of A. The consequent change in momentum of the electron might be expected to have an increasingly important effect on the electron capture cross section as the projectile energy is increased. It was therefore suggested by Bates and McCarroll[54] that a set of wavefunctions which take into account the energy and momentum associated with the translational motion of the active electron should be used as the basis for the expansion of the electronic wavefunction $\Psi(\underline{r}_1, \underline{r}_2, t)$.

Following Bates[15] we write $\Psi(\underline{r}_1, \underline{r}_2, t)$ in terms of the function

$$\Phi_i(\underline{r}_1, \underline{r}_2, t) = \phi_i(\underline{x}_1, \underline{x}_2)\exp\left\{-i\left[p\ \underline{v}\cdot\underline{r}_1 + p\ \underline{v}\cdot\underline{r}_2 + p^2 v^2 t + \epsilon_i t\right]\right\} \quad (2.5.6)$$

or alternatively,

$$\Phi_f(\underline{r}_1, \underline{r}_2, t) = \Psi_{f_1}(\underline{s}_1)\chi_{f_2}(\underline{x}_2)\exp\left\{i\left[q\ \underline{v}\cdot\underline{r}_1 - p\ \underline{v}\cdot\underline{r}_2 - \right.\right.$$

$$\left.\left.\frac{1}{2}p^2 v^2 t - \frac{1}{2}q^2 v^2 t - (\epsilon_{f_1} + \epsilon_{f_2})t\right]\right\} , \quad (2.5.7)$$

where $\phi_i(\underline{x}_1, \underline{x}_2)$, $\Psi_{f_1}(\underline{s}_1)$, $\chi_{f_2}(\underline{x}_2)$ are the helium atom, hydrogen atom and helium ion electronic wavefunctions with corresponding eigenenergies ϵ_i, ϵ_{f_1}, ϵ_{f_2}, such that

$$\left(\frac{1}{2}\nabla^2_{\underline{r}_1} + \frac{1}{2}\nabla^2_{\underline{r}_2} + \frac{Z_B}{x_1} + \frac{Z_B}{x_2} - \frac{1}{x_{12}} + \epsilon_i\right)\phi_i(\underline{x}_1, \underline{x}_2) = 0 \quad (2.5.8)$$

$$\left(\frac{1}{2}\nabla^2_{\underline{r}_1} + \frac{Z_A}{s_1} + \epsilon_{f_1}\right)\Psi_{f_1}(\underline{s}_1) = 0 \quad (2.5.9)$$

$$\left(\frac{1}{2}\nabla^2_{\underline{r}_2} + \frac{Z_B}{x_2} + \epsilon_{f_2}\right)\chi_{f_2}(\underline{x}_2) = 0 . \quad (2.5.10)$$

In the limit of infinite internuclear separation, the functions Φ_i and Φ_f satisfy the equations

$$\left[\frac{1}{2}\nabla^2_{\underline{r}_1} + \frac{1}{2}\nabla^2_{\underline{r}_2} + \frac{Z_B}{x_1} + \frac{Z_B}{x_2} - \frac{1}{x_{12}} + \frac{i\partial}{\partial t}\right] \Phi_i(\underline{r}_1, \underline{r}_2, t) = 0 \quad (2.5.11)$$

and

$$\left[\frac{1}{2}\nabla^2_{\underline{r}_1} + \frac{1}{2}\nabla^2_{\underline{r}_2} + \frac{Z_B}{x_2} + \frac{Z_A}{s_1} + \frac{i\partial}{\partial t}\right] \Phi_f(\underline{r}_1, \underline{r}_2, t) = 0 \quad , \qquad (2.5.12)$$

respectively. The above is easily seen to be true by substituting equation (2.5.6) or (2.5.7) for Ψ in equation (2.5.5), and then, after some manipulation, taking the limit $t \longrightarrow \pm\infty$. Bates and McCarroll[54] have shown that the results of the theory are independent of the choice of origin O; therefore we shall always take O to be the mid-point of the line AB which corresponds to making the choice $p = q = \frac{1}{2}$. This means that equations (2.5.6) and (2.5.7) become

$$\Phi_i(\underline{r}_1, \underline{r}_2, t) = \phi_i(\underline{x}_1, \underline{x}_2)\exp\left\{-i\left[\frac{1}{2}\underline{v}\cdot(\underline{r}_1 + \underline{r}_2) + \frac{1}{4}v^2 t + \epsilon_i t\right]\right\}$$

$$(2.5.13)$$

$$\Phi_f(\underline{r}_1, \underline{r}_2, t) = \Psi_{f_1}(\underline{s}_1)\chi_{f_2}(\underline{x}_2)\exp\left\{i\left[\frac{1}{2}\underline{v}\cdot(\underline{r}_1 - \underline{r}_2) - \frac{1}{4}v^2 t - (\epsilon_{f_1} + \epsilon_{f_2})t\right]\right\} \quad .$$

$$(2.5.14)$$

We now introduce the distorted waves χ_i and χ_f, defined as solutions of the equations

$$\left[\frac{1}{2}\nabla^2_{\underline{r}_1} + \frac{1}{2}\nabla^2_{\underline{r}_2} + \frac{Z_B}{x_1} + \frac{Z_B}{x_2} - \frac{1}{x_{12}} + \frac{i\partial}{\partial t} + U_i\right] \chi_i(\underline{r}_1, \underline{r}_2, t) = 0$$

$$(2.5.15)$$

$$\left[\frac{1}{2}\nabla^2_{\underline{r}_1} + \frac{1}{2}\nabla^2_{\underline{r}_2} + \frac{Z_B}{x_2} + \frac{Z_A}{s_1} + \frac{i\partial}{\partial t} + U_f\right] \chi_f(\underline{r}_1, \underline{r}_2, t) = 0 \quad ,$$

$$(2.5.16)$$

with the boundary conditions

$$\chi_i \xrightarrow[t \to -\infty]{} \Phi_i \quad ; \quad \chi_f \xrightarrow[t \to +\infty]{} \Phi_f \quad . \qquad (2.5.17)$$

Clearly the distorting potentials U_i and U_f will vanish in the limit

of large internuclear separation.

Let Ψ_i and Ψ_f be the solutions of equation (2.5.5) with boundary conditions

$$\Psi_i \xrightarrow[t \to -\infty]{} \Phi_i \quad ; \quad \Psi_f \xrightarrow[t \to +\infty]{} \Phi_f \quad . \qquad (2.5.18)$$

The transition amplitude a_{if} is obtained by projecting the initial state on the complete wavefunction Ψ_f. Therefore

$$a_{if} = \lim_{t \to -\infty} \int d\underline{r}_1 \, d\underline{r}_2 \, \Psi_f^* \, \Phi_i$$

$$= \lim_{t \to -\infty} \int d\underline{r}_1 \, d\underline{r}_2 \, \Psi_f^* \, \chi_i \quad . \qquad (2.5.19)$$

Now consider the term

$$\frac{d}{dt} \int d\underline{r}_1 \, d\underline{r}_2 \, \Psi_f^* \, \chi_i = \int d\underline{r}_1 \, d\underline{r}_2 \left[\frac{\partial \Psi_f^*}{\partial t} \chi_i + \Psi_f^* \frac{\partial \chi_i}{\partial t} \right] \quad .$$

Using equation (2.5.15), this becomes

$$\frac{d}{dt} \int d\underline{r}_1 \, d\underline{r}_2 \, \Psi_f^* \, \chi_i = \frac{1}{i} \int d\underline{r}_1 \, d\underline{r}_2 \left[i \frac{\partial \Psi_f^*}{\partial t} \chi_i + \Psi_f^* \left(-\frac{1}{2} \nabla_{\underline{r}_1}^2 - \right. \right.$$

$$\left. \left. \frac{1}{2} \nabla_{\underline{r}_2}^2 - \frac{Z_B}{x_1} - \frac{Z_B}{x_2} + \frac{1}{x_{12}} - U_i \right) \chi_i \right] \quad . \qquad (2.5.20)$$

By noting the relation that, if an operator Q is Hermitian, then

$$\int \gamma_a^* \, Q \, \gamma_b \, d\underline{r} = \int Q^* \, \gamma_a^* \, \gamma_b \, d\underline{r} \quad , \qquad (2.5.21)$$

and also making use of equation (2.5.5), we find that (2.5.20) becomes

$$\frac{d}{dt} \int d\underline{r}_1 \, d\underline{r}_2 \, \Psi_f^* \, \chi_i = \frac{1}{i} \int d\underline{r}_1 \, d\underline{r}_2 \, \Psi_f^* \left(\frac{Z_A}{s_1} + \frac{Z_A}{s_2} - \frac{Z_A Z_B}{R} - U_i \right) \chi_i \quad .$$

$$(2.5.22)$$

Consider the integral

$$J_{if} = -\frac{1}{i} \lim_{t \to -\infty} \int_t^\infty dt \int d\underline{r}_1 \, d\underline{r}_2 \, \Psi_f^* \left(\frac{Z_A}{s_1} + \frac{Z_A}{s_2} - \frac{Z_A Z_B}{R} - U_i \right) \chi_i$$

$$(2.5.23)$$

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which, by equation (2.5.22), is

$$J_{if} = -\lim_{t \to -\infty} \int_t^\infty dt \left[\frac{d}{dt} \int d\underline{r}_1 \, d\underline{r}_2 \, \Psi_f^* \, \chi_i \right] \,. \qquad (2.5.24)$$

Now provided

$$\lim_{t \to +\infty} \int d\underline{r}_1 \, d\underline{r}_2 \, \Psi_f^* \, \chi_i = 0 \,, \qquad (2.5.25)$$

we can integrate equation (2.5.24) to obtain

$$J_{if} = \lim_{t \to -\infty} \int d\underline{r}_1 \, d\underline{r}_2 \, \Psi_f^* \, \chi_i = a_{if} \,. \qquad (2.5.26)$$

Therefore we have shown that, provided condition (2.5.25) holds,

$$a_{if} = i \int_{-\infty}^\infty dt \int d\underline{r}_1 \, d\underline{r}_2 \, \Psi_f^* \left(\frac{Z_A}{s_1} + \frac{Z_A}{s_2} - \frac{Z_A Z_B}{R} - U_i \right) \chi_i \,.$$

$$(2.5.27)$$

Alternatively, we can consider the time reversed reaction to obtain the transition amplitude in the form b_{if} :

$$b_{if} = i \int_{-\infty}^\infty dt \int d\underline{r}_1 \, d\underline{r}_2 \left[\left(\frac{Z_B}{x_1} + \frac{Z_A}{s_2} - \frac{1}{x_{12}} - \frac{Z_A Z_B}{R} - U_f^* \right) \chi_f^* \right] \Psi_i \,,$$

$$(2.5.28)$$

provided $\quad \lim_{t \to -\infty} \int \chi_f^* \, \Psi_i \, d\underline{r}_1 \, d\underline{r}_2 = 0 \,. \qquad (2.5.29)$

The total cross section Q_{if} is obtained by integrating over all possible impact parameters

$$Q_{if} = 2 \int_0^\infty b \, |a_{if}|^2 \, db \, (\pi a_0^2) = 2 \int b \, |b_{if}|^2 \, db \, (\pi a_0^2) \,. \quad (2.5.30)$$

The Distorted Wave Functions.

We represent the solutions Ψ_i and Ψ_f in the form

$$\Psi_i(\underline{r}_1, \underline{r}_2, t) = \Phi_i(\underline{r}_1, \underline{r}_2, t) \, \mathcal{I}_i(\underline{s}_1, \underline{s}_2, t) \qquad (2.5.32a)$$

$$\Psi_f(\underline{r}_1, \underline{r}_2, t) = \Phi_f(\underline{r}_1, \underline{r}_2, t) \, \mathcal{I}_f(\underline{x}_1, \underline{s}_2, t) \,. \qquad (2.5.32b)$$

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Clearly, $\lim_{t \to -\infty} \mathcal{I}_i = \lim_{t \to +\infty} \mathcal{I}_f = 1$. (2.5.33)

Substituting for Ψ_i or Ψ_f into equation (2.5.5), we see

that $\mathcal{I}_i$ and $\mathcal{I}_f$ are solutions of

$$\left[\tfrac{1}{2}\nabla_{\underline{r}_1}^2 + \tfrac{1}{2}\nabla_{\underline{r}_2}^2 + \frac{Z_A}{s_1} + \frac{Z_A}{s_2} - \frac{Z_A Z_B}{R} - \frac{i}{2}\,\underline{v}\cdot\nabla_{\underline{r}_1} - \frac{i}{2}\,\underline{v}\cdot\nabla_{\underline{r}_2} + \right.$$

$$\left. i\frac{\partial}{\partial t}\right] \mathcal{I}_i(\underline{s}_1,\underline{s}_2,t) = -\sum_{j=1}^{2}\left[\nabla_{\underline{r}_j} \log_e \phi_i(\underline{x}_1,\underline{x}_2)\right]\cdot\left[\nabla_{\underline{r}_j}\mathcal{I}_i(\underline{s}_1,\underline{s}_2,t)\right] ,$$

(2.5.34)

$$\left[\tfrac{1}{2}\nabla_{\underline{r}_1}^2 + \tfrac{1}{2}\nabla_{\underline{r}_2}^2 + \frac{Z_B}{x_1} + \frac{Z_A}{s_2} - \frac{1}{x_{12}} - \frac{Z_A Z_B}{R} + \frac{i}{2}\,\underline{v}\cdot\nabla_{\underline{r}_1} - \frac{i}{2}\,\underline{v}\cdot\nabla_{\underline{r}_2} + i\frac{\partial}{\partial t}\right] \times$$

$$\mathcal{I}_f(\underline{x}_1,\underline{s}_2,t) = -\sum_{j=1}^{2}\left[\nabla_{\underline{r}_j}\log_e\left\{\Psi_{f_1}(\underline{s}_1)\,X_{f_2}(\underline{x}_2)\right\}\right]\cdot\left[\nabla_{\underline{r}_j}\mathcal{I}_f(\underline{x}_1,\underline{s}_2,t)\right]$$

(2.5.35)

Equations (2.5.34) and (2.5.35) are exact. The exact solution to

$\mathcal{I}_i$ and $\mathcal{I}_f$ cannot be obtained without solving the complete

scattering problem. First-order approximations to $\mathcal{I}_i$ and $\mathcal{I}_f$,

denoted by $\mathcal{I}_i'$ and $\mathcal{I}_f'$, are obtained by neglecting the right

hand sides of equations (2.5.34) and (2.5.35). In solving such

equations for $\mathcal{I}_i'$ and $\mathcal{I}_f'$ attention should be paid to the

fact that the dominant contribution to the single electron capture

amplitude in reaction (2.5.3) comes from the region of small values

of $|\underline{x}_2|$. This implies that in the equations for $\mathcal{I}_i'$ and $\mathcal{I}_f'$

we can replace $1/s_2$ by $1/R$ and $1/x_{12}$ by $1/x_1$ to a good approximation.

In this way the coordinate s_2 of the 'passive' electron disappears

from these equations; $\mathcal{I}_i'$ and $\mathcal{I}_f'$ then become solutions of

$$\left(\tfrac{1}{2}\nabla_{\underline{r}_1}^2 + \frac{Z_A}{s_1} - \frac{Z_A(Z_B - 1)}{R} - \frac{i}{2}\,\underline{v}\cdot\nabla_{\underline{r}_1} + i\frac{\partial}{\partial t}\right) \mathcal{I}_i'(\underline{s}_1, t) = 0$$

(2.5.36a)

$$\left(\frac{1}{2}\nabla_{\underline{r}_1}^2 + \frac{(Z_B-1)}{x_1} - \frac{Z_A(Z_B-1)}{R} + \frac{i}{2}\underline{v}\cdot\nabla_{\underline{r}_1} + i\frac{\partial}{\partial t}\right)\mathcal{I}'_f(\underline{x}_1,t) = 0 \quad ,$$

(2.5.36b)

with boundary conditions

$$\lim_{t\to-\infty}\mathcal{I}'_i = \lim_{t\to+\infty}\mathcal{I}'_f = 1 \quad . \tag{2.5.37}$$

Solving for $\mathcal{I}'_i$ and $\mathcal{I}'_f$, we obtain

$$\mathcal{I}'_i(\underline{s}_1,t) = N_A(v)\,{}_1F_1\left[i\gamma_1;\ 1;\ i(vs_1+\underline{v}\cdot\underline{s}_1)\right]\exp\left\{\frac{iZ_A(Z_B-1)}{v}\ell n(vR-v^2t)\right\}$$

(2.5.38)

$$\mathcal{I}'_f(\underline{x}_1,t) = N_B^*(v)\,{}_1F_1\left[-i\gamma_2;\ 1;\ -i(vx_1+\underline{v}\cdot\underline{x}_1)\right]\exp\left\{-\frac{iZ_A(Z_B-1)}{v}\ell n(vR+v^2t)\right\} \quad ,$$

(2.5.39)

where

$$N_A(v) = e^{\pi\gamma_1/2}\,\Gamma(1-i\gamma_1) \tag{2.5.40a}$$

$$\gamma_1 = Z_A/v \tag{2.5.40b}$$

$$N_B^*(v) = e^{\pi\gamma_2/2}\,\Gamma(1+i\gamma_2) \tag{2.5.41a}$$

$$\gamma_2 = (Z_B-1)/v \quad . \tag{2.5.41b}$$

If we now choose to define the distorted wavefunctions as [a]

$$\chi_i(\underline{r}_1,\underline{r}_2,t) = \Phi_i(\underline{r}_1,\underline{r}_2,t)\mathcal{I}'_i(\underline{s}_1,t) \tag{2.5.42}$$

$$\chi_f(\underline{r}_1,\underline{r}_2,t) = \Phi_f(\underline{r}_1,\underline{r}_2,t)\mathcal{I}'_f(\underline{x}_1,t) \quad , \tag{2.5.43}$$

and the corresponding distortion potentials as

$$U_i = \frac{Z_A}{s_1} + \frac{Z_A}{s_2} - \frac{Z_AZ_B}{R} + A_i \tag{2.5.44}$$

---

[a]It is not difficult to show that conditions (2.5.25) and (2.5.29) are satisfied with the present choice of χ_i and χ_f.

$$U_f = \frac{Z_B}{x_1} + \frac{Z_A}{s_2} - \frac{1}{x_{12}} - \frac{Z_A Z_B}{R} + A_f \quad , \tag{2.5.45}$$

then equation (2.5.15) is of the form (2.5.36a) and equation
(2.5.16) is of the form (2.5.36b) provided we take

$$A_i \, \chi_i = - \, \bar{\Phi}_i \Big[\nabla_{\underline{r}_1} \log_e \phi_i (\underline{x}_1, \underline{x}_2) \Big] \cdot \Big[\nabla_{\underline{r}_1} \mathcal{I}'_i \, (\underline{s}_1, t) \Big] \tag{2.5.46}$$

and

$$A_f \, \chi_f = - \, \bar{\Phi}_f \Big[\nabla_{\underline{r}_1} \log_e \Big\{ \Psi_{f_1} (\underline{s}_1) \, \chi_{f_2} (\underline{x}_2) \Big\} \Big] \cdot \Big[\nabla_{\underline{r}_1} \mathcal{I}'_f (\underline{x}_1, t) \Big] \quad . \tag{2.5.47}$$

Substituting for U_i and U_f in equations (2.5.27) and (2.5.28), we
obtain

$$a_{if} = - \, i \int_{-\infty}^{\infty} dt \int d\underline{r}_1 \, d\underline{r}_2 \, A_i \, \chi_i \, \Psi_f^* \tag{2.5.48}$$

$$b_{if} = - \, i \int_{-\infty}^{\infty} dt \int d\underline{r}_1 \, d\underline{r}_2 \, A_f^* \, \chi_f^* \, \Psi_i \quad . \tag{2.5.49}$$

The continuum distorted wave approximation consists of the
replacement of Ψ_i , Ψ_f in equations (2.5.49) and (2.5.48)
by χ_i , χ_f respectively. It is easily seen that in this
approximation the distorted wavefunctions χ_i and χ_f have the
correct asymptotic conditions: from equations (2.5.42) and (2.5.43),
we have that $\chi_i = \bar{\Phi}_i \, \mathcal{I}'_i$ and $\chi_f = \bar{\Phi}_f \, \mathcal{I}'_f$; therefore,
by virtue of equations (2.5.37) and (2.5.18),

$$\chi_i \xrightarrow[t \to -\infty]{} \Phi_i \xrightarrow[t \to -\infty]{} \Psi_i \quad \text{and} \quad \chi_f \xrightarrow[t \to +\infty]{} \Phi_f \xrightarrow[t \to +\infty]{} \Psi_f \quad , \text{ which}$$

are the required conditions.

CHAPTER 2.6

Evaluation of the Transition Amplitude

We are interested in evaluating the transition amplitude $a_{if} \equiv a(n\ell)$ for the reactions

$$H^+ + He(1s^2) \longrightarrow H(n\ell) + He^+(1s) \qquad (2.6.1)$$

$$He^{++} + He(1s^2) \longrightarrow He^+(n\ell) + He^+(1s) \quad , \qquad (2.6.2)$$
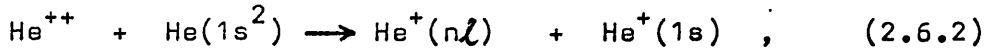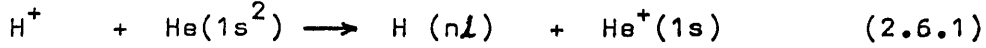
for $n\ell$ = 1s, 2s and 2p. As before, the ground state wavefunction of the helium atom is represented by:

(a) The simple one-parameter variational function

$$\Psi_\lambda(\underline{x}_1, \underline{x}_2) = \phi_i(\underline{x}_1)\phi_i(\underline{x}_2) \quad ,$$

with $\qquad \phi_i(\underline{x}) = \left(\frac{\lambda^3}{\pi}\right)^{\frac{1}{2}} e^{-\lambda x} \quad , \quad \lambda = 1.6875 \quad ;$ $\qquad\qquad (2.6.3)$

(b) The natural expansion of the 35-configuration CI wavefunction of Weiss

$$\Psi_\chi(\underline{x}_1, \underline{x}_2) = D_{\alpha\beta\gamma} \, G_{\alpha\beta}(\underline{x}_1) \, G_{\alpha\gamma}(\underline{x}_2) \quad , \qquad (2.6.4)$$

where $D_{\alpha\beta\gamma}$, $G_{\alpha\beta}$ and $G_{\alpha\gamma}$ are defined in an equivalent manner to equation (2.3.7) — see also chapter 1.3. The following analysis is general for a helium wavefunction which is separable into the form (2.6.4). The transition amplitude we wish to evaluate is given by (see equation (2.5.48))

$$a(n\ell) = -i \int_{-\infty}^{\infty} dt \int d\underline{r}_1 \, d\underline{r}_2 \; A_i \, \chi_i \, \Psi_f^* \quad , \qquad (2.6.5)$$

where $A_i \chi_i = -\oint_i \left[\nabla_{\underline{r}_1} \log_e \Psi_\chi(\underline{x}_1, \underline{x}_2)\right] \cdot \left[\nabla_{\underline{r}_1} \mathcal{I}_i'(\underline{s}_1, t)\right] \cdot$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (2.6.6)$

The integral representation for the coulomb function[55] is given by

$${}_1F_1(i\gamma; 1; iq) = \frac{1}{2\pi i} \oint \frac{d\omega}{\omega} \left(1 + \frac{1}{\omega}\right)^{-i\gamma} e^{-i\omega q} \quad , \qquad (2.6.7)$$

where the contour encloses the points 0 and -1. Substituting for χ'_i from equation (2.5.38) and making use of the representation (2.6.7), equation (2.6.6) then becomes

$$A_i \chi_i = -\Phi_i \nabla_{\underline{r}_1} \log_e \Psi_x(\underline{x}_1,\underline{x}_2) \nabla_{\underline{r}_1} \left\{ \frac{N_A(v)}{2\pi i} \oint \frac{d\omega}{\omega} \left(1 + \frac{1}{\omega}\right)^{-i\gamma} \times \right.$$
$$\left. e^{-i\omega(vs_1 + \underline{v}\cdot\underline{s}_1)} \exp\left[\frac{iZ}{v} \ell n(vR - v^2 t)\right]\right\} , \qquad (2.6.8)$$

where $Z = Z_A(Z_B - 1)$. Therefore,

$$a(n\ell) = -i \int_{-\infty}^{\infty} dt \int d\underline{r}_1 \int d\underline{r}_2 \left\{\frac{v}{2\pi} N_A(v) \exp\left[\frac{iZ}{v} \ell n(vR - v^2 t)\right]\Phi_i \times \right.$$

$$\left[\frac{\underline{s}_1\cdot\underline{x}_1}{s_1 x_1} + \frac{\underline{v}\cdot\underline{x}_1}{v x_1}\right] \frac{\partial}{\partial x_1} \left[\log_e \Psi_x(\underline{x}_1,\underline{x}_2)\right] \oint d\omega \left(1 + \frac{1}{\omega}\right)^{-i\gamma_i} \times$$

$$\left. e^{-i\omega(vs_1 + \underline{v}\cdot\underline{s}_1)} \right\} \Psi_f^* . \qquad (2.6.9)$$

Replacing Ψ_f^* by $\chi_f^* = \Phi_f^* \chi_f'^*$, and substituting for Φ_f^* and Φ_i, we obtain

$$a(n\ell) = -\frac{vN_A(v)N_B(v)}{4\pi^2} (bv)^{2iZ/v} \int_{-\infty}^{\infty} dt\, e^{-i\epsilon t} \oint d\omega \oint \frac{d\zeta}{\zeta} \times$$

$$\left(1 + \frac{1}{\omega}\right)^{-i\gamma_i}\left(1 + \frac{1}{\zeta}\right)^{-i\gamma_2} \int d\underline{r}_1 \int d\underline{r}_2\; \Psi_{n\ell}^*(\underline{s}_1) \chi_{1s}^*(\underline{x}_2) \frac{\partial}{\partial x_1} \Psi_x(\underline{x}_1,\underline{x}_2) \times$$

$$e^{-i\underline{v}\cdot\underline{r}_1} e^{-i\omega(vs_1 + \underline{v}\cdot\underline{s}_1)} e^{-i\zeta(vx_1+\underline{v}\cdot\underline{x}_1)}\left[\frac{\underline{s}_1\cdot\underline{x}_1}{s_1 x_1} + \frac{\underline{v}\cdot\underline{x}_1}{v x_1}\right] , \qquad (2.6.10)$$

where $\Psi_x(\underline{x}_1, \underline{x}_2)$, $\Psi_{n\ell}(\underline{s}_1)$, $\chi_{1s}(\underline{x}_2)$ are the helium atom, hydrogen atom and helium ion electronic wavefunctions with corresponding eigenenergies $\epsilon_B(1s^2)$, $\epsilon_A(n\ell)$, $\epsilon_B(1s)$ and where $\epsilon = \epsilon_B(1s^2) - \epsilon_A(n\ell) - \epsilon_B(1s)$. Equation (2.6.10) may be re-written in the form

$$a(n\ell) = -\frac{vN_A(v)N_B(v)}{4\pi^2}(bv)^{2iZ/v} \, D_{\alpha\beta\gamma} \int_{-\infty}^{\infty} dt \, e^{i\epsilon t} \oint d\omega \oint \frac{d\xi}{\xi} \times$$

$$\left(1 + \frac{1}{\omega}\right)^{-i\nu_1} \left(1 + \frac{1}{\xi}\right)^{-i\nu_2} \quad I_{\alpha\gamma} \quad R_{\alpha\beta} \qquad (2.6.11a)$$

where $I_{\alpha\gamma} = \int d\underline{r}_2 \; \chi_{1s}^*(\underline{x}_2) \, G_{\alpha\gamma}(\underline{x}_2)$ (2.6.11b)

and $R_{\alpha\beta} = \int d\underline{r}_1 \; \psi_{n\ell}^*(\underline{s}_1) \frac{\partial}{\partial x_1} G_{\alpha\beta}(\underline{x}_1) e^{-i\underline{v}\cdot\underline{r}_1} \, e^{-i\omega(vs_1 + \underline{v}\cdot\underline{s}_1)} \times$

$$e^{-i\xi(vx_1 + \underline{v}\cdot\underline{x}_1)} \left[\frac{\underline{v} \cdot \underline{x}_1}{v \, x_1} + \frac{\underline{s}_1 \cdot \underline{x}_1}{s_1 \, x_1}\right] . \qquad (2.6.11c)$$

Using the Fourier transform method of evaluating two-centre integrals[a], it is easily shown that

$$a(n\ell) = -\frac{vN_A(v)N_B(v)}{4\pi^2(2\pi)^6}(bv)^{2iZ/v} \, D_{\alpha\beta\gamma} \int_{-\infty}^{\infty} dt \, e^{-i\epsilon t} \oint d\omega \oint \frac{d\xi}{\xi} \times$$

$$\left(1 + \frac{1}{\omega}\right)^{-i\nu_1} \left(1 + \frac{1}{\xi}\right)^{-i\nu_2} I_{\alpha\gamma} \int d\underline{r}_1 \, e^{-i\underline{v}\cdot\underline{r}_1} \int d\underline{K} \int d\underline{k} \, F_{n\ell}^*(\underline{k}) H_{\alpha\beta}(\underline{K}) \times$$

$$e^{i\underline{k} \cdot \underline{s}_1} \, e^{-i\underline{K} \cdot \underline{x}_1} \qquad (2.6.12a)$$

where $F_{n\ell}^*(\underline{k}) \, H_{\alpha\beta}(\underline{K}) = \int d\underline{s}_1 \int d\underline{x}_1 \, \psi_{n\ell}^*(\underline{s}_1) \, e^{-i\omega(vs_1 + \underline{v}\cdot\underline{s}_1)} \times$

$$e^{-i\underline{k}\cdot\underline{s}_1} \frac{\partial}{\partial x_1} G_{\alpha\beta}(\underline{x}_1) \, e^{-i\xi(vx_1 + \underline{v}\cdot\underline{x}_1)} \, e^{i\underline{K}\cdot\underline{x}_1} \left[\frac{\underline{v} \cdot \underline{x}_1}{v \, x_1} + \frac{\underline{s}_1 \cdot \underline{x}_1}{s_1 \, x_1}\right] .$$

$$(2.6.12b)$$

From the coordinate system described in chapter 2.5 we have the relationships $\underline{x}_1 = \underline{r}_1 + \frac{1}{2} \underline{R}$ and $\underline{s}_1 = \underline{r}_1 - \frac{1}{2} \underline{R}$ when $p = q = \frac{1}{2}$. Using these relations the integrations over $\underline{r}_1$ and $\underline{k}$ in equation (2.6.12a) may be performed with little difficulty. A further substitution, $u = vt$, enables us to evaluate the integral over time

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[a] See reference 40, p.213.

t. Taking cartesian coordinates for $\underline{K}$, with $\underline{v}$ defining the z-direction, it is found that another integration, that over K_z, may easily be performed. The result achieved is:

$$a(n\ell) = - \frac{N_A(v)N_B(v)}{4\pi^2(2\pi)^2} (bv)^{2iZ/v} D_{\alpha\beta\gamma} \oint d\omega \oint \frac{d\xi}{\xi} \left(1 + \frac{1}{\omega}\right)^{-i\gamma_1} \times$$

$$\left(1 + \frac{1}{\xi}\right)^{-i\gamma_2} I_{\alpha\gamma} \int_{-\infty}^{\infty} dK_x e^{-i bK_x} \int_{-\infty}^{\infty} dK_y \; F_{n\ell}^*\left(K_x,K_y,\frac{v}{2}-\delta\right) H_{\alpha\beta}\left(K_x,K_y,-\frac{v}{2}-\delta\right) ,$$

$$\text{(2.6.13)}$$

where $\qquad \delta = \epsilon/v .$ $\hspace{4cm}$ (2.6.14)

The quantity $I_{\alpha\gamma}$ defined in equation (2.6.11b) is the overlap between the orbitals of the electron which is not captured. This is easily seen, since it may be shown (again using the Fourier transform technique) that

$$I_{\alpha\gamma} = \int d\underline{r}_2 \; \chi_{1s}^*(\underline{x}_2) \; G_{\alpha\gamma}(\underline{x}_2) = h_{\alpha\gamma}^*(\underline{L} = 0) ,$$

where, generally, $\quad h_{\alpha\gamma}(\underline{L}) = \int \chi_{1s}(\underline{x}_2) \; G_{\alpha\gamma}(\underline{x}_2) \; e^{i \underline{L}\cdot\underline{x}_2} d\underline{x}_2 ,$

which means

$$I_{\alpha\gamma} = \int \chi_{1s}^*(\underline{x}_2) \; G_{\alpha\gamma}(\underline{x}_2) \; d\underline{x}_2 , \qquad \text{(2.6.15)}$$

where χ_{1s} is the wavefunction of the residual helium ion and, in our case, $G_{\alpha\gamma}(\underline{x}_2)$ is the natural expansion description of the 'passive' electron in the helium atom. From a correlation point of view, the behaviour of $I_{\alpha\gamma}$ has a very significant effect on the transition amplitude $a(n\ell)$. The wavefunction of the helium ion, left in the 1s state, is given by

$$\chi_{1s}(\underline{x}_2) = \left(\frac{8}{\pi}\right)^{\frac{1}{2}} e^{-2x_2} . \qquad \text{(2.6.16)}$$

Therefore,

$$I_{\alpha\gamma} = \left(\frac{8}{\pi}\right)^{\frac{1}{2}} \int e^{-2x_2} G_{\alpha\gamma}(\underline{x}_2) \, d\underline{x}_2$$

$$= \left(\frac{8}{\pi}\right)^{\frac{1}{2}} \int e^{-2x_2} R_{\alpha\gamma}(\underline{x}_2) Y_{\ell_\alpha, -\mu}(\Theta_{x_2}, \phi_{x_2}) \, d\underline{x}_2 ,$$

(2.6.17)

where we have made use of equation (2.3.7d). Consider the integral

over the azimuthal angle ϕ_{x_2} ; the integral will be of the form

$$\int_0^{2\pi} e^{-i\mu\phi_{x_2}} \, d\phi_{x_2} = \begin{cases} 2\pi & \text{if } \mu = 0 \\ \\ 0 & \text{if } \mu = 1, 2, 3 \ldots \end{cases}$$

(2.6.18)

Therefore μ is restricted to zero irrespective of ℓ_α values.

This means that equation (2.6.17) becomes

$$I_{\alpha\gamma} = 2\pi \left(\frac{8}{\pi}\right)^{\frac{1}{2}} \int_0^\infty dx_2 \, e^{-2x_2} x_2^2 R_{\alpha\gamma}(\underline{x}_2) \int_0^\pi Y_{\ell,0}(\Theta_{x_2}, \phi_{x_2}) \sin\Theta_{x_2} d\Theta_{x_2}$$

Using $\quad Y_{\ell,0}(\Theta, \phi) = \left(\frac{2\ell + 1}{4\pi}\right)^{1/2} P_\ell(\cos\Theta) \quad ,$

$$I_{\alpha\gamma} = 2\pi \left(\frac{8}{\pi}\right)^{\frac{1}{2}} \left(\frac{2\ell_\alpha + 1}{4\pi}\right)^{\frac{1}{2}} \int_0^\infty dx_2 e^{-2x_2} x_2^2 R_{\alpha\gamma}(\underline{x}_2) \int_0^\pi P_{\ell_\alpha}(\cos\Theta_{x_2}) \sin\Theta_{x_2} d\Theta_{x_2} .$$

(2.6.19)

But $\displaystyle\int_0^\pi P_0(\cos\Theta) P_{\ell_\alpha}(\cos\Theta) \sin\Theta \, d\Theta = \frac{2}{2\ell_\alpha + 1}$ if $\ell_\alpha = 0$,

(2.6.20)

$$= 0 \text{ otherwise.}$$

Therefore, due to the orthogonality between $\chi_{1s}(\underline{x}_2)$ and the

angular parts of $G_{\alpha\gamma}(\underline{x}_2)$, the contribution to $a(n\ell)$ from all

natural configurations using basis functions with $\ell_\alpha \neq 0$ will be

zero. This, in turn, means that only pure radial correlation will

have any effect on $a(n\ell)$ and consequently on the total cross section.

It is also evident that if we were considering, for example, the

process

$$H^+ + He(1s^2) \longrightarrow H(n\ell) + He^+(2p) \quad , \tag{2.6.21}$$
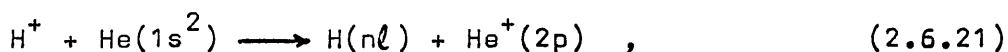
then only configurations involving $\ell_\alpha = 1$ would contribute to

the cross section. Therefore, within the present approximation, a zero cross section for process (2.6.21) would be predicted unless angular correlation is included in the description of the helium ground state. The orthogonality condition in $I_{\alpha\gamma}$ has arisen because, in equation (2.5.36), we have eliminated the 'passive' electron from the distorted wavefunctions χ'_i and χ'_f. If this had not been done, an operator of the type $e^{i\omega'(v \, s_2 + \underline{v}\cdot\underline{s}_2)}$ would have been introduced into $I_{\alpha\gamma}$ — destroying the orthogonality condition in (2.6.20) and therefore retaining contributions from all angular-type correlation terms.

Returning to equation (2.6.13), it was found that, on further integration, the expression for $a(n\ell)$ may be reduced to the form

$$a(n\ell) = \int_0^\infty \eta^{m+1} \, J_m(b\eta) \, W_{n\ell}(\eta) \, d\eta \quad , \qquad (2.6.22)$$

where: $m = 0$ for $n\ell \equiv 1s, 2s, 2p_z$; $m = 1$ for $n\ell \equiv 2p_x$; $J_m(b\eta)$ is a Bessel function of order m; $W_{n\ell}(\eta)$ is a complicated function which depends not only on the quantum numbers $n\ell$ for the hydrogen-like atom but also on the type of wavefunction used for the helium atom ground state. With $n\ell = 1s, 2s$ and $2p$, $W_{n\ell}(\eta)$ was evaluated analytically for both types of helium wavefunction employed here — see equations (2.6.3) and (2.6.4). In the evaluation of the integrals in equation (2.6.12), the polar axis z is defined as being in the direction of the velocity $\underline{v}$ of the incident projectile and the impact parameter $\underline{b}$ has been chosen to specify the x-axis. Consequently, if, as in this case, it is of interest to compute the total cross section Q for capture into the 2p state of the hydrogen-like system, then $Q(2p)$ is given by

$$Q(2p) = Q(2p_z) + Q(2p_x) \quad ,$$

since, in the present mathematical framework, $Q(2p_y)$ is identically
zero.

Fortunately, there is no need to perform the integration
in (2.6.22) since, by substituting equation (2.6.22) into (2.5.30)
and noting that[56]

$$\sqrt{\eta \eta'} \int J_m(b\eta) \, J_m(b\eta')b \, db = \delta(\eta - \eta'),$$ (2.6.24)

where m is arbitrary, we obtain finally

$$Q(n\ell) = \int_0^\infty \eta^{2m} \left| W_{n\ell}(\eta) \right|^2 d\eta^2,$$ (2.6.25)

which leaves only one numerical integration to be performed in order
to obtain the total cross section $Q(n\ell)$. This numerical integration
has been evaluated by dividing the integrand into an appropriate
number of ranges R and then applying a four-point Gaussian
quadrature formula to each range. A safe cut-off η_{max} was
determined for each value of impact velocity considered. The
values of R and η_{max} were chosen to give cross sections accurate
to at least five significant figures.

CHAPTER 2.7

Continuum Distorted Wave Approximation Cross Sections.

        In this chapter we discuss our results for the capture

cross sections $Q(n\ell)$, obtained within the continuum distorted

wave (CDW) method, for the processes

$$H^+ + He(1s^2) \longrightarrow H(n\ell) + He^+(1s), \quad n\ell = 1s,2s,2p \quad (2.7.1)$$

and $He^{++} + He(1s^2) \longrightarrow He^+(n\ell) + He^+(1s), \quad n\ell = 1s,2s,2p. \quad (2.7.2)$
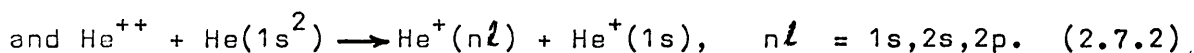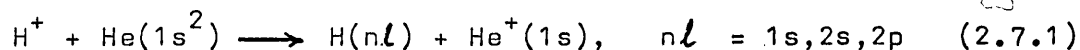
The calculations were carried out using not only a simple non-

correlated description for the ground state of the helium atom

but also we employed a series of truncated functions Ψ_X obtained

from the natural expansion of a CI wavefunction. At high impact

energies, the major contribution to the capture cross section arises

from small impact parameters which corresponds to a region close

to the target nucleus. Therefore, any improvements in the description

of the innermost region of the target wavefunction are likely to

be of most importance in their effect on the total cross section

$Q(n\ell)$. We may further suppose, as is physically reasonable, that

at high impact energies the target electron is most likely to be

captured if the trajectories of the incident projectile and target

electron almost coincide (at the same point in time) in the vicinity

of the target nucleus. It is evident, therefore, that the cross

section is determined by a quantity which involves the orbital of

the 'active' electron in the helium target, a coulombic operator,

and the orbital of the captured electron in the hydrogen-like

system. An examination of the 1s, 2s and 2p hydrogen-like orbitals[57]

reveals that, at small nucleus-electron separations ($0 \leqslant r \leqslant 1$),

the radial parts of the 1s and 2s orbitals are remarkably similar,

but both are radically different from the radial part of the 2p orbital (the 2p wavefunction is zero at $r = 0$ whereas the 1s and 2s wavefunctions are non-zero at $r = 0$). Therefore it is expected that, at high energies, the _percentage_ changes in $Q(n\ell)$, arising from the use of an improved helium wavefunction, will be very similar in the case of capture into the 1s and 2s states of the hydrogen-like atom, but will be fundamentally different from the percentage changes derived in the case of capture into the 2p state.

We examine first the results for a proton projectile-reaction (2.7.1). The cross sections $Q(n\ell)$ were evaluated at impact energies E ranging from 25 keV to 3 MeV using the following descriptions of the helium atom:

(a) the simple wavefunction Ψ_λ (equation (2.6.3)) and

(b) the natural expansion wavefunction Ψ_X (equation (2.6.4)) for various orders X of truncation. Therefore, as X is increased incrementally from X = 1 (the HF-equivalent wavefunction) to X = 15 (equal to the Weiss total wavefunction) electron correlation is introduced systematically by virtue of the decreasing importance, energetically, of each additional natural configuration. For the reasons discussed in chapter 2.6, configurations composed of angular-type orbitals do not contribute to the cross sections; only X = 1, 3, 6, 10 and 15, each composed of s-type orbitals, make a non-zero contribution. The cross sections Q(1s) and Q(2s) are given in Tables 2.4 and 2.5 for various values of impact energy. The cross section Q(2p) for capture into the 2p state, given in Table 2.8, is composed of a contribution from capture into the $2p_z$ orbital and a contribution from capture into a $2p_x$ orbital, i.e., $Q(2p) = Q(2p_z) + Q(2p_x)$. Values for $Q(2p_z)$ and $Q(2p_x)$ are given in

Tables 2.6 and 2.7. For convenience, we have shown in Table 2.9 the percentage changes $\Delta(\lambda \to 1)$ and $\Delta(1 \to 15)$ in $Q(n\ell)$(for $n\ell$ = 1s, 2s and 2p) due to improving the basic wavefunction Ψ_λ to the HF wavefunction $\Psi_{X=1}$ and those due to improving the HF wavefunction $\Psi_{X=1}$ to the totally correlated wavefunction $\Psi_{X=15}$, respectively. Inspection of Table 2.9 reveals that, as expected, the percentage change $\Delta(\lambda \to 1)$ in $Q(1s)$ and $Q(2s)$ is virtually the same in each case throughout the energy range considered whereas, in contrast, $\Delta(\lambda \to 1)$ in $Q(2p)$ displays a completely different behaviour. This observation also holds when comparing $\Delta(1 \to 15)$ for $Q(1s)$, $Q(2s)$ and $Q(2p)$. Furthermore, we observe that the $\Delta(\lambda \to 1)$ results for $Q(2p_x)$ and $Q(2p_z)$ are different in behaviour as the energy is increased; a corresponding observation holds for $\Delta(1 \to 15)$. This is due to the fact that the different angular parts in the $2p_z$ and $2p_x$ orbitals give rise to differing forms of equation (2.6.22) for the transition amplitude.

As we move from the simple wavefunction Ψ_λ, describing the helium ground state, to the more sophisticated HF description $\Psi_{X=1}$, a large percentage change is observed in each of the capture cross sections $Q(1s)$, $Q(2s)$ and $Q(2p)$, throughout the energy range considered. At energies greater than 300 keV, $\Delta(\lambda \to 1)$ is greater for $Q(2p)$ than it is for $Q(1s)$ and $Q(2s)$, which means that a HF description of the helium wavefunction is more important when considering capture into excited states of an angular nature than it is when the excited state is spherically symmetric. However, it should be noted that, even in the case of $Q(1s)$ and $Q(2s)$, $\Delta(\lambda \to 1)$ is about 36% at E = 3000 keV, and is therefore very significant. It is also important to note that at high energies the difference between the values for $Q(1s)$, $Q(2s)$

and Q(2p), derived from the use of Ψ_λ and $\Psi_{X=1}$ respectively, is becoming greater with increasing energy. In addition Table 2.9 reveals that the effect of the HF wavefunction over and above the one-parameter wavefunction is first to reduce and then to increase the cross sections Q(1s) and Q(2s) as we move from low to high impact energies, the cross-over occurring at E $\simeq$ 600 keV. In general, this behaviour is followed in the case of $Q(2p_z)$, but the cross-over occurs at E $\simeq$ 400 keV. However, in $Q(2p_x)$, the effect of the HF wavefunction is to increase the cross section everywhere, except at E = 25 keV. Therefore, in the energy range 50 keV $\leqslant$ E $<$ 400 keV, the changes in Q(2p) are small in spite of the significant changes which occur for $Q(2p_x)$ and $Q(2p_z)$ since they are of opposite sign, whereas, at E $\geqslant$ 400 keV, the changes in the individual components are now additive. The resultant effect is that, at impact energies greater than 50 keV, a relatively small increase in Q(2p) is observed due to the introduction of the HF wavefunction. However, this increase grows rapidly in importance with increasing energy and is as large as 86% at E = 3000 keV.

Turning now to the effect due to the inclusion of all the electron correlation terms within the total helium wavefunction $\Psi_{X=15}$ we see that, as shown in Table 2.9, the percentage change $\Delta(1 \rightarrow 15)$ in Q(1s), Q(2s) and Q(2p), is negative for all energies E $\geqslant$ 50 keV. This means that all the cross sections have been reduced by introducing total electron correlation over and above our approximate HF wavefunction. The magnitude of this decrease, however, is far less important, at high energies, than the increase arising from the use of the HF wavefunction. At high energies, therefore, the overall effect due to improving Ψ_λ to $\Psi_{X=15}$

is a large _increase_ in the cross sections Q($n\ell$), for all $n\ell$

considered. Although not shown in Table 2.9, it is easily seen

from Tables 2.4, 2.5 and 2.8 that the percentage change $\Delta(1 \rightarrow 3)$

gives the greatest contribution to $\Delta(1 \rightarrow 15)$ in all cases

($\Delta(3 \rightarrow 15)$ gives small variations of an oscillatory nature).

Thus, the initial introduction of radial correlation gives the most

important contribution to the cross sections when compared with

subsequent radial correlation contributions (X = 6, 10 and 15).

At this stage, it is of interest to compare the relative

effects of electron correlation within the impulse and continuum

distorted wave approximations when applied to the process

$$H^+ + He(1s^2) \longrightarrow H(1s) + He^+(1s).\qquad\qquad (2.7.3)$$
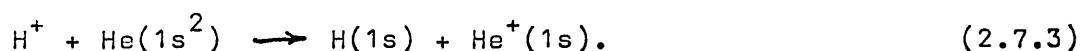
Tables 2.2 and 2.9 reveal that the trends in Q(1s), introduced by

the use of an improved helium wavefunction, are different for the

two methods. The most striking difference is the high energy

behaviour of $\Delta(\lambda \rightarrow 1)$ which, in the CDW method, rises steeply

with increasing E and is 32% at E = 2500 keV, whereas, in the

impulse approximation, the rise is very gradual and is only 5%

at E = 2500 keV. The trends introduced by the introduction of all

electron correlation terms, $\Delta(1 \rightarrow 15)$, are also quite different

in the two methods – in fact, for most of the energy range, they are

of opposite sign. It is interesting to note, however, that the

initial introduction of _radial_ correlation has the same effect in

both cases; that is, to reduce the cross section – the reduction

being the greater in the CDW method (cf Tables 2.1 and 2.4). In

the impulse approximation, this reduction is largely compensated

for by the increase due to the initial introduction of _angular_

correlation. Of course, no such compensation exists within the

CDW approximation - see chapter 2.6.

The total cross section Q, which includes capture into any state, may be obtained from the relation[43]

$$Q = \sum_{n,\ell} Q(n\ell) \simeq Q(1s) + 1.616 \left[Q(2s) + Q(2p) \right] . \qquad (2.7.4)$$

Values for the CDW approximation total cross section Q are presented in Table 2.10; also given are the experimental results of Stier and Barnett[52] and of Welsh et al.[12] It is quite clear that for $E \geqslant 654$ keV, the fully correlated (X = 15) results are in better agreement with experiment than are the simple non-correlated (λ) results. At impact energies greater than about 1500 keV, the X = 15 results are in agreement with experimental values, within experimental error. This is in direct contrast with the situation found in the impulse approximation, where the correlated results were seen to diverge from the experimental values at high energies - cf Table 2.3.

We now turn our attention to the electron capture by alpha-particles in helium, reaction (2.7.2). Calculations within the CDW approximation for this reaction, using a helium ground state wavefunction of the form[46]

$$\Psi(\underline{x}_1, \underline{x}_2) = N \left[e^{-(ax_1 + bx_2)} + e^{-(bx_1 + ax_2)} \right] , \qquad (2.7.5)$$

have been reported by Belkic and Janev[47]. They conclude that above 600 keV their results are in good agreement with experiment[58]. We have also evaluated cross sections for reaction (2.7.2) in the energy range 25 keV - 3 MeV, using wavefunctions (2.6.3) and (2.6.4), and examine the consequent effects on the capture cross sections. It should be noted that the velocity of an alpha-particle is 0.5 times the velocity of a proton with the same kinetic energy.

Therefore, in this discussion, it should be kept in mind that we are not in the same high velocity region as was the case when discussing proton-helium collisions, and the high velocity arguments used in that case cannot be used here. Calculated values for $Q(1s)$, $Q(2s)$, $Q(2p_z)$, $Q(2p_x)$ and $Q(2p)$ are given in Tables 2.11 - 2.15 respectively. It is seen that the effects of introducing a HF wavefunction for helium are quite different at these low velocities. At most energies considered here, the cross sections for capture into the 1s and 2s states of the helium ion, when evaluated using $\Psi_{X=1}$, were considerably reduced relative to those evaluated using Ψ_λ. This is more easily seen by examination of Table 2.16, where we present the relative percentage changes in $Q(n\ell)$ due to using the improved wavefunctions $\Psi_{X=1}$ and $\Psi_{X=15}$. Also reduced by the HF wavefunction were the $Q(2p_z)$ cross sections, whereas $Q(2p_x)$ were mostly increased. The resultant cross sections, $Q(2p)$, were reduced everywhere except at energies $E \lesssim 50$ keV and $E \gtrsim 2$ MeV. The effect of total correlation was, as in the case of proton projectiles, to reduce all the cross sections $Q(n\ell)$ considered for all energies $E \gtrsim 300$ keV. As before, the greatest contribution to $\Delta(1 \rightarrow 15)$ arose from the initial introduction of radial correlation, $\Delta(1 \rightarrow 3)$.

The total cross section Q was obtained with the aid of equation (2.7.4) and the corresponding values for a particular impact energy are given in Table 2.17. Also shown, for comparison, are the experimental results of Pivovar et al[58]. At low energies, the fully correlated results give better agreement with experiment than the simple non-correlated (λ) results. However, in the higher energy region, the correlated results are in worse agreement with experiment than the non-correlated (λ) results, although the

overall agreement with experiment is still good. It is expected
that if the energy range of the calculation were extended to include
alpha-particle velocities of comparable magnitude to proton velocities
corresponding to proton energies E = 3 MeV, then the correlated
results would give the better agreement with experiment. For such
a comparison it would be necessary to extend the energy range of the
alpha-particle reaction to 12 MeV. Unfortunately, no experimental
data exists for E > 1.5 MeV.

Conclusion

Including electron correlation in the helium atom
wavefunction, over and above the HF description, has a small effect
on the total capture cross section Q when compared with the effect
of using a HF wavefunction rather than the one-parameter wavefunction;
the latter effect gives an increase in Q as large as 37% at E = 2990 keV
when considering electron capture by protons incident on a helium
target. However, although by comparison the total correlation
effect may be small, it is also significant, causing a decrease
in Q of as much as 7% at intermediate energies. Nevertheless,
we may conclude that if the CDW method were applied to larger
atomic systems, then the use of HF wavefunctions for the description
of the initial and final states should be adequate to give reliable
results. From a computational viewpoint, it is anticipated that the
cross sections $Q(n\ell)$ for charge transfer reactions involving large
atomic systems will still only require one final numerical integration
if the target is described by a HF-type wavefunction.

Perhaps, in the above, a note of caution should be added.
In the application of the CDW method to reactions (2.7.1) and
(2.7.2) an approximation was made which was to replace $1/x_{12}$ by

$1/x_1$ and $1/s_2$ by $1/R$ in equations (2.5.34) and (2.5.35) (see chapters 2.5 and 2.6) thereby removing the coordinates of the 'passive' electron from the problem. This caused a simplification which meant that only purely radial correlation terms would contribute to the cross sections. In effect, we have eliminated electron correlation from within the method itself, but have included it in the atomic wavefunction. It would be of considerable interest to see the difference made to the theory, and the consequent difference in the cross sections, if we left the term $1/s_2$ as it is, and replaced $1/x_{12}$ by an expansion[59] in terms of x_1 and x_2:

$$\frac{1}{x_{12}} = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{+\ell} \frac{(\ell - |m|)!}{(\ell + |m|)!} P_\ell^{|m|}(\cos\theta_1) P_\ell^{|m|}(\cos\theta_2) e^{im(\phi_1-\phi_2)} \frac{x_<^\ell}{x_>^{\ell+1}} \quad,$$

(2.7.6)

where (x_1, θ_1, ϕ_1); (x_2, θ_2, ϕ_2) are the polar coordinates of electrons (1) and (2) respectively, $x_<$ and $x_>$ are respectively the lesser and greater of x_1 and x_2, and $P_\ell^{|m|}$ is an associated Legendre function. The expansion (2.7.6) cannot be used as it stands because it has an infinite number of terms. However, instead of restricting the summation over ℓ to $\ell = 0$, as we have done in the present study, a second-order term could be included by allowing $\ell = 1$ and an attempt made to solve the resulting differential equation which would replace (2.5.36). The distorted wavefunctions $\mathcal{X}'_i$ and $\mathcal{X}'_f$ would now include electron correlation, thereby modifying the CDW approach from within the structure of the method.

With reference to the capture reaction

$$H^+ + He(1s^2) \longrightarrow H(1s) + He^+(1s) \quad,$$
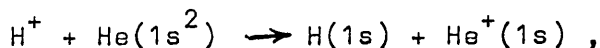
we have seen that, for the impulse approximation, the cross sections

are very cumbersome to evaluate since they involve a triple numerical integration for each impact energy. Furthermore, the validity of the impulse approximation is uncertain due to the presence of the coulomb potential V_{13} in the two-body operator $\omega_{13}^{+}(m)$ (see chapter 2.4) which is subsequently used to evaluate the transition amplitude. In contrast, the CDW cross sections are easy to evaluate and are more reliable since they are based on a rigorous theoretical foundation[42]. In the light of our experience, extension of the impulse method to charge transfer reactions involving large atomic systems would be extremely difficult, if not impossible, due to numerical complications. On the other hand, a real possibility exists that the CDW method may be extended to charge transfer reactions of the type

$$X^{n+} + A \longrightarrow X^{(n-1)+} + A^{+} ,$$
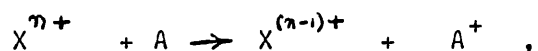
where X^{n+} is a structureless projectile and A is a many-electron system.

In summary, although the impulse approximation gave somewhat disappointing results for a helium target, the application of the CDW method yielded very satisfactory values. Furthermore, the latter method has the added advantage of possessing a rigorous theoretical foundation and is easily applied to high-energy electron capture reactions.

TABLE 2.4   Continuum distorted wave approximation total cross section Q(1s) (in units of πa_0^2) for the reaction $H^+ + He(1s^2) \longrightarrow H(1s) + He^+(1s)$, evaluated using the non-correlated (λ) and the natural expansion (X-terms) helium wavefunctions - see equations (2.6.3) and (2.6.4) of text.

E(keV)	λ	X = 1	X = 3	X = 6	X = 15
25	7.552^0 [a]	7.254^0	6.632^0	6.554^0	6.527^0
50	1.806^0	1.711^0	1.640^0	1.631^0	1.628^0
100	2.958^{-1}	2.701^{-1}	2.637^{-1}	2.631^{-1}	2.629^{-1}
200	3.055^{-2}	2.733^{-2}	2.664^{-2}	2.661^{-2}	2.661^{-2}
300	6.445^{-3}	5.853^{-3}	5.668^{-3}	5.666^{-3}	5.665^{-3}
400	1.936^{-3}	1.807^{-3}	1.740^{-3}	1.740^{-3}	1.740^{-3}
500	7.228^{-4}	6.954^{-4}	6.668^{-4}	6.670^{-4}	6.671^{-4}
600	3.131^{-4}	3.104^{-4}	2.967^{-4}	2.969^{-4}	2.969^{-4}
700	1.512^{-4}	1.542^{-4}	1.471^{-4}	1.472^{-4}	1.472^{-4}
800	7.935^{-5}	8.306^{-5}	7.909^{-5}	7.918^{-5}	7.919^{-5}
900	4.448^{-5}	4.769^{-5}	4.535^{-5}	4.542^{-5}	4.542^{-5}
1000	2.630^{-5}	2.882^{-5}	2.739^{-5}	2.744^{-5}	2.744^{-5}
1500	3.284^{-6}	3.920^{-6}	3.721^{-6}	3.731^{-6}	3.731^{-6}
2000	7.152^{-7}	9.052^{-7}	8.603^{-7}	8.631^{-7}	8.629^{-7}
2500	2.145^{-7}	2.833^{-7}	2.697^{-7}	2.706^{-7}	2.705^{-7}
3000	7.922^{-8}	1.081^{-7}	1.030^{-7}	1.034^{-7}	1.034^{-7}

[a] The superscript denotes the power of ten by which the entry should be multiplied.

TABLE 2.5   Continuum distorted wave approximation total cross section $Q(2s)$ (in units of πa_o^2) for the reaction $H^+ + He(1s^2) \longrightarrow H(2s) + He^+(1s)$, evaluated using the non-correlated (λ) and the natural expansion (X-terms) helium wavefunctions - see equations (2.6.3) and (2.6.4) of text.

E(keV)	λ	X = 1	X = 3	X = 6	X = 15
25	5.583^{-1} [a]	5.118^{-1}	4.481^{-1}	4.412^{-1}	4.389^{-1}
50	2.132^{-1}	2.026^{-1}	1.900^{-1}	1.884^{-1}	1.878^{-1}
100	4.228^{-2}	3.907^{-2}	3.794^{-2}	3.781^{-2}	3.777^{-2}
200	4.519^{-3}	4.052^{-3}	3.952^{-3}	3.947^{-3}	3.946^{-3}
300	9.395^{-4}	8.505^{-4}	8.246^{-4}	8.241^{-4}	8.240^{-4}
400	2.776^{-4}	2.576^{-4}	2.484^{-4}	2.483^{-4}	2.483^{-4}
500	1.022^{-4}	9.768^{-5}	9.375^{-5}	9.376^{-5}	9.377^{-5}
600	4.374^{-5}	4.309^{-5}	4.122^{-5}	4.124^{-5}	4.124^{-5}
700	2.092^{-5}	2.121^{-5}	2.024^{-5}	2.025^{-5}	2.025^{-5}
800	1.089^{-5}	1.134^{-5}	1.080^{-5}	1.081^{-5}	1.081^{-5}
900	6.065^{-6}	6.468^{-6}	6.154^{-6}	6.163^{-6}	6.163^{-6}
1000	3.566^{-6}	3.889^{-6}	3.697^{-6}	3.703^{-6}	3.703^{-6}
1500	4.368^{-7}	5.196^{-7}	4.934^{-7}	4.947^{-7}	4.947^{-7}
2000	9.414^{-8}	1.188^{-7}	1.129^{-7}	1.133^{-7}	1.133^{-7}
2500	2.804^{-8}	3.695^{-8}	3.518^{-8}	3.530^{-8}	3.529^{-8}
3000	1.031^{-8}	1.404^{-8}	1.338^{-8}	1.343^{-8}	1.343^{-8}

(a) The superscript denotes the power of ten by which the entry should be multiplied.

TABLE 2.6   Continuum distorted wave approximation total cross section $Q(2p_z)$ (in units of πa_o^2) for the reaction $H^+ + He(1s^2) \rightarrow H(2p_z) + He^+(1s)$, evaluated using the non-correlated (λ) and the natural expansion (X-terms) helium wavefunctions - see equations (2.6.3) and (2.6.4) of text.

E(keV)	λ	X = 1	X = 3	X = 6	X = 15
25	3.759^{-1} (a)	3.432^{-1}	3.195^{-1}	3.167^{-1}	3.157^{-1}
50	7.801^{-2}	7.114^{-2}	6.800^{-2}	6.771^{-2}	6.760^{-2}
100	1.086^{-2}	9.812^{-3}	9.406^{-3}	9.376^{-3}	9.365^{-3}
200	8.368^{-4}	7.696^{-4}	7.366^{-4}	7.356^{-4}	7.352^{-4}
300	1.392^{-4}	1.342^{-4}	1.277^{-4}	1.277^{-4}	1.277^{-4}
400	3.468^{-5}	3.528^{-5}	3.344^{-5}	3.346^{-5}	3.345^{-5}
500	1.113^{-5}	1.193^{-5}	1.128^{-5}	1.129^{-5}	1.129^{-5}
600	4.257^{-6}	4.785^{-6}	4.516^{-6}	4.523^{-6}	4.523^{-6}
700	1.851^{-6}	2.172^{-6}	2.048^{-6}	2.052^{-6}	2.052^{-6}
800	8.881^{-7}	1.083^{-6}	1.021^{-6}	1.023^{-6}	1.023^{-6}
900	4.606^{-7}	5.812^{-7}	5.480^{-7}	5.495^{-7}	5.494^{-7}
1000	2.544^{-7}	3.312^{-7}	3.124^{-7}	3.133^{-7}	3.132^{-7}
1500	2.487^{-8}	3.643^{-8}	3.449^{-8}	3.462^{-8}	3.460^{-8}
2000	4.658^{-9}	7.385^{-9}	7.018^{-9}	7.045^{-9}	7.041^{-9}
2500	1.263^{-9}	2.119^{-9}	2.021^{-9}	2.028^{-9}	2.027^{-9}
3000	4.344^{-10}	7.609^{-10}	7.275^{-10}	7.301^{-10}	7.296^{-10}

(a) The superscript denotes the power of ten by which the entry should be multiplied.

TABLE 2.7   Continuum distorted wave approximation total cross
section $Q(2p_x)$ (in units of πa_0^2) for the reaction
$H^+ + He(1s^2) \longrightarrow H(2p_x) + He^+(1s)$, evaluated using
the non-correlated (λ) and the natural expansion
(X-terms) helium wavefunctions - see equations
(2.6.3) and (2.6.4) of text.

E(keV)	λ	X = 1	X = 3	X = 6	X = 15
25	5.787^{-1} (a)	4.680^{-1}	4.741^{-1}	4.745^{-1}	4.767^{-1}
50	7.153^{-2}	7.873^{-2}	7.826^{-2}	7.841^{-2}	7.869^{-2}
100	8.535^{-3}	9.746^{-3}	9.398^{-3}	9.411^{-3}	9.429^{-3}
200	6.494^{-4}	7.776^{-4}	7.334^{-4}	7.351^{-4}	7.360^{-4}
300	1.124^{-4}	1.447^{-4}	1.354^{-4}	1.359^{-4}	1.360^{-4}
400	2.937^{-5}	4.043^{-5}	3.774^{-5}	3.790^{-5}	3.792^{-5}
500	9.898^{-6}	1.439^{-5}	1.345^{-5}	1.352^{-5}	1.352^{-5}
600	3.968^{-6}	6.031^{-6}	5.652^{-6}	5.682^{-6}	5.682^{-6}
700	1.804^{-6}	2.842^{-6}	2.673^{-6}	2.688^{-6}	2.687^{-6}
800	9.032^{-7}	1.464^{-6}	1.382^{-6}	1.390^{-6}	1.390^{-6}
900	4.875^{-7}	8.095^{-7}	7.670^{-7}	7.714^{-7}	7.711^{-7}
1000	2.796^{-7}	4.736^{-7}	4.504^{-7}	4.530^{-7}	4.527^{-7}
1500	3.198^{-8}	5.771^{-8}	5.573^{-8}	5.603^{-8}	5.598^{-8}
2000	6.739^{-9}	1.257^{-8}	1.228^{-8}	1.233^{-8}	1.232^{-8}
2500	2.001^{-9}	3.810^{-9}	3.750^{-9}	3.766^{-9}	3.761^{-9}
3000	7.401^{-10}	1.428^{-9}	1.414^{-9}	1.420^{-9}	1.418^{-9}

(a) The superscript denotes the power of ten by which the entry
   should be multiplied.

TABLE 2.8 Continuum distorted wave approximation total cross section $Q(2p)$ (in units of πa_0^2) for the reaction $H^+ + He(1s^2) \rightarrow H(2p) + He^+(1s)$, evaluated using the non-correlated (λ) and the natural expansion (X-terms) helium wavefunctions - see equations (2.6.3) and (2.6.4) of text.

$E(keV)$	λ	$X = 1$	$X = 3$	$X = 6$	$X = 15$
25	9.546^{-1} [a]	8.112^{-1}	7.936^{-1}	7.912^{-1}	7.924^{-1}
50	1.495^{-1}	1.499^{-1}	1.463^{-1}	1.461^{-1}	1.463^{-1}
100	1.940^{-2}	1.956^{-2}	1.880^{-2}	1.879^{-2}	1.879^{-2}
200	1.486^{-3}	1.547^{-3}	1.470^{-3}	1.471^{-3}	1.471^{-3}
300	2.516^{-4}	2.789^{-4}	2.631^{-4}	2.636^{-4}	2.637^{-4}
400	6.405^{-5}	7.571^{-5}	7.118^{-5}	7.136^{-5}	7.137^{-5}
500	2.103^{-5}	2.632^{-5}	2.473^{-5}	2.481^{-5}	2.481^{-5}
600	8.225^{-6}	1.082^{-5}	1.017^{-5}	1.021^{-5}	1.021^{-5}
700	3.655^{-6}	5.014^{-6}	4.721^{-6}	4.740^{-6}	4.739^{-6}
800	1.791^{-6}	2.547^{-6}	2.403^{-6}	2.413^{-6}	2.413^{-6}
900	9.481^{-7}	1.391^{-6}	1.315^{-6}	1.321^{-6}	1.321^{-6}
1000	5.340^{-7}	8.048^{-7}	7.628^{-7}	7.663^{-7}	7.659^{-7}
1500	5.685^{-8}	9.414^{-8}	9.022^{-8}	9.065^{-8}	9.058^{-8}
2000	1.140^{-8}	1.996^{-8}	1.930^{-8}	1.938^{-8}	1.936^{-8}
2500	3.264^{-9}	5.929^{-9}	5.771^{-9}	5.794^{-9}	5.788^{-9}
3000	1.175^{-9}	2.189^{-9}	2.142^{-9}	2.150^{-9}	2.148^{-9}

(a) The superscript denotes the power of ten by which the entry should be multiplied.

TABLE 2.9   The relative percentage change $\Delta(i \to j)$ in $Q(n\ell)$, as we move from a wavefunction $\tilde{\psi}_i$ to a more accurate wavefunction $\tilde{\psi}_j$, defined as $\Delta(i \to j) = \left\{ \dfrac{Q_j - Q_i}{Q_i} \right\} \times 100\%$

H^+ PROJECTILE

E(keV)	Q(1s)		Q(2s)		Q(2p$_x$)		Q(2p$_z$)		Q(2p)	
	$\Delta(\lambda \to 1)$	$\Delta(1 \to 15)$	$\Delta(\lambda \to 1)$	$\Delta(1 \to 15)$	$\Delta(\lambda \to 1)$	$\Delta(1 \to 15)$	$\Delta(\lambda \to 1)$	$\Delta(1 \to 15)$	$\Delta(\lambda \to 1)$	$\Delta(1 \to 15)$
25	-3.9%	-10.0%	-8.3%	-14.2%	-19.1%	+1.9%	-8.7%	-8.0%	-15.0%	-2.3%
50	-5.3%	-4.9%	-5.0%	-7.3%	+10.1%	-0.1%	-8.8%	-5.0%	+0.3%	-2.4%
100	-8.7%	-2.7%	-7.6%	-3.3%	+14.2%	-3.3%	-9.7%	-4.6%	+0.8%	-3.9%
200	-10.5%	-2.6%	-10.3%	-2.6%	+19.7%	-5.3%	-4.8%	-4.5%	+4.1%	-4.9%
400	-6.7%	-3.7%	-7.2%	-3.6%	+37.7%	-6.2%	+1.7%	-5.2%	+18.2%	-5.7%
600	-0.9%	-4.3%	-1.5%	-4.3%	+52.0%	-5.8%	+12.4%	-5.5%	+31.6%	-5.6%
800	+4.7%	-4.7%	+4.1%	-4.7%	+62.1%	-5.1%	+21.9%	-5.5%	+42.2%	-5.3%
1000	+9.6%	-4.8%	+9.1%	-4.8%	+69.4%	-4.4%	+30.2%	-5.4%	+50.7%	-4.8%
1500	+19.4%	-4.8%	+19.0%	-4.8%	+80.5%	-3.0%	+46.5%	-5.0%	+65.6%	-3.8%
2000	+26.6%	-4.7%	+26.2%	-4.6%	+86.5%	-2.0%	+58.5%	-4.7%	+75.1%	-3.0%
2500	+32.1%	-4.5%	+31.8%	-4.5%	+90.4%	-1.3%	+67.8%	-4.3%	+81.6%	-2.4%
3000	+36.5%	-4.3%	+36.2%	-4.3%	+92.2%	-0.7%	+75.2%	-4.1%	+86.3%	-1.9%

TABLE 2.10   Continuum distorted wave approximation total cross section Q (in units of πa_0^2) for the process $H^+ + He(1s^2) \longrightarrow H + He^+$, evaluated using the non-correlated (λ) and the natural expansion (X-terms) helium wavefunctions – see equations (2.6.3) and (2.6.4) of text.

E(keV)	λ	X = 1	X = 3	X = 6	X = 15	Experiment
100	3.955^{-1}(a)	3.648^{-1}	3.554^{-1}	3.546^{-1}	3.544^{-1}	3.4^{-1} (b)
440	1.637^{-3}	1.562^{-3}	1.450^{-3}	1.450^{-3}	1.450^{-3}	$(1.8 \pm 0.2)^{-3}$(c)
654	2.643^{-4}	2.868^{-4}	2.563^{-4}	2.565^{-4}	2.565^{-4}	$(3.3 \pm 0.4)^{-4}$(c)
851	7.367^{-5}	7.881^{-5}	7.497^{-5}	7.509^{-5}	7.509^{-5}	$(9.4 \pm 1.1)^{-5}$(c)
1063	2.418^{-5}	2.707^{-5}	2.571^{-5}	2.577^{-5}	2.577^{-5}	$(3.3 \pm 0.4)^{-5}$(c)
2450	2.959^{-7}	3.921^{-7}	3.734^{-7}	3.747^{-7}	3.746^{-7}	$(3.6 \pm 0.4)^{-7}$(c)
2990	9.959^{-8}	1.367^{-7}	1.304^{-7}	1.309^{-7}	1.308^{-7}	$(1.4 \pm 0.1)^{-7}$(c)

(a) The superscript denotes the power of ten by which the entry should be multiplied.

(b) Stier and Barrett, reference 52.

(c) Welsh et al., reference 12.

TABLE 2.11 Continuum distorted wave approximation total cross section $Q(1s)$ (in units of πa_0^2) for the reaction $He^{++} + He(1s^2) \longrightarrow He^+(1s) + He^+(1s)$, evaluated using the non-correlated (λ) and the natural expansion (X-terms) helium wavefunctions — see equations (2.6.3) and (2.6.4) of text.

E(keV)	λ	$X = 1$	$X = 3$	$X = 6$	$X = 15$
25	9.005^{+1} [a]	9.084^{+1}	9.064^{+1}	9.105^{+1}	9.118^{+1}
50	2.464^{+1}	2.497^{+1}	2.476^{+1}	2.493^{+1}	2.498^{+1}
100	1.420^{+1}	1.355^{+1}	1.383^{+1}	1.394^{+1}	1.397^{+1}
200	6.233^{0}	5.653^{0}	5.636^{0}	5.654^{0}	5.660^{0}
300	2.925^{0}	2.629^{0}	2.593^{0}	2.597^{0}	2.599^{0}
400	1.536^{0}	1.381^{0}	1.354^{0}	1.355^{0}	1.356^{0}
500	8.788^{-1}	7.935^{-1}	7.745^{-1}	7.751^{-1}	7.754^{-1}
600	5.363^{-1}	4.870^{-1}	4.738^{-1}	4.741^{-1}	4.742^{-1}
700	3.439^{-1}	3.144^{-1}	3.050^{-1}	3.051^{-1}	3.052^{-1}
800	2.294^{-1}	2.112^{-1}	2.045^{-1}	2.045^{-1}	2.046^{-1}
900	1.580^{-1}	1.466^{-1}	1.416^{-1}	1.417^{-1}	1.417^{-1}
1000	1.118^{-1}	1.045^{-1}	1.008^{-1}	1.009^{-1}	1.009^{-1}
1500	2.651^{-2}	2.575^{-2}	2.468^{-2}	2.469^{-2}	2.470^{-2}
2000	8.610^{-3}	8.667^{-3}	8.276^{-3}	8.283^{-3}	8.284^{-3}
2500	3.401^{-3}	3.536^{-3}	3.368^{-3}	3.372^{-3}	3.372^{-3}
3000	1.538^{-3}	1.646^{-3}	1.565^{-3}	1.568^{-3}	1.568^{-3}

(a) The superscript denotes the power of ten by which the entry should be multiplied.

TABLE 2.12   Continuum distorted wave approximation total cross
section Q(2s) (in units of πa_o^2) for the reaction
$He^{++} + He(1s^2) \rightarrow He^+(2s) + He^+(1s)$, evaluated using
the non-correlated (λ) and the natural expansion
(X-terms) helium wavefunctions - see equations
(2.6.3) and (2.6.4) of text.

E(keV)	λ	X = 1	X = 3	X = 6	X = 15
25	1.194^{+2} [a]	1.042^{+2}	8.223^{+1}	7.993^{+1}	7.916^{+1}
50	4.401^{+1}	4.170^{+1}	3.788^{+1}	3.738^{+1}	3.721^{+1}
100	1.247^{+1}	1.189^{+1}	1.150^{+1}	1.144^{+1}	1.142^{+1}
200	2.902^{0}	2.696^{0}	2.658^{0}	2.653^{0}	2.651^{0}
300	1.098^{0}	1.001^{0}	9.876^{-1}	9.867^{-1}	9.863^{-1}
400	5.133^{-1}	4.623^{-1}	4.554^{-1}	4.551^{-1}	4.550^{-1}
500	2.713^{-1}	2.428^{-1}	2.386^{-1}	2.384^{-1}	2.384^{-1}
600	1.557^{-1}	1.391^{-1}	1.363^{-1}	1.362^{-1}	1.362^{-1}
700	9.488^{-2}	8.482^{-2}	8.289^{-2}	8.286^{-2}	8.285^{-2}
800	6.061^{-2}	5.433^{-2}	5.297^{-2}	5.295^{-2}	5.294^{-2}
900	4.020^{-2}	3.619^{-2}	3.520^{-2}	3.519^{-2}	3.519^{-2}
1000	2.750^{-2}	2.489^{-2}	2.416^{-2}	2.416^{-2}	2.416^{-2}
1500	5.740^{-3}	5.378^{-3}	5.178^{-3}	5.178^{-3}	5.178^{-3}
2000	1.712^{-3}	1.665^{-3}	1.595^{-3}	1.595^{-3}	1.595^{-3}
2500	6.357^{-4}	6.405^{-4}	6.114^{-4}	6.119^{-4}	6.120^{-4}
3000	2.744^{-4}	2.854^{-4}	2.719^{-4}	2.722^{-4}	2.722^{-4}

(a) The superscript denotes the power of ten by which the entry
should be multiplied.

TABLE 2.13   Continuum distorted wave approximation total cross section $Q(2p_z)$ (in units of πa_0^2) for the reaction $He^{++} + He(1s^2) \rightarrow He^+(2p_z) + He^+(1s)$, evaluated using the non-correlated (λ) and the natural expansion (X-terms) helium wavefunctions - see equations (2.6.3) and (2.6.4) of text.

E(keV)	λ	X = 1	X = 3	X = 6	X = 15
25	1.137^{+2}(a)	1.479^{+2}	1.396^{+2}	1.386^{+2}	1.383^{+2}
50	3.525^{+1}	3.625^{+1}	3.472^{+1}	3.463^{+1}	3.460^{+1}
100	1.046^{+1}	8.891^{0}	8.270^{0}	8.213^{0}	8.193^{0}
200	2.469^{0}	1.948^{0}	1.834^{0}	1.822^{0}	1.818^{0}
300	8.801^{-1}	6.867^{-1}	6.540^{-1}	6.509^{-1}	6.498^{-1}
400	3.806^{-1}	2.975^{-1}	2.851^{-1}	2.840^{-1}	2.836^{-1}
500	1.857^{-1}	1.462^{-1}	1.405^{-1}	1.400^{-1}	1.399^{-1}
600	9.873^{-2}	7.844^{-2}	7.544^{-2}	7.525^{-2}	7.518^{-2}
700	5.600^{-2}	4.498^{-2}	4.326^{-2}	4.317^{-2}	4.313^{-2}
800	3.344^{-2}	2.718^{-2}	2.613^{-2}	2.608^{-2}	2.606^{-2}
900	2.082^{-2}	1.714^{-2}	1.646^{-2}	1.644^{-2}	1.643^{-2}
1000	1.343^{-2}	1.120^{-2}	1.075^{-2}	1.073^{-2}	1.073^{-2}
1500	2.191^{-3}	1.948^{-3}	1.861^{-3}	1.860^{-3}	1.859^{-3}
2000	5.402^{-4}	5.095^{-4}	4.848^{-4}	4.849^{-4}	4.848^{-4}
2500	1.720^{-4}	1.708^{-4}	1.622^{-4}	1.623^{-4}	1.622^{-4}
3000	6.527^{-5}	6.779^{-5}	6.424^{-5}	6.432^{-5}	6.431^{-5}

(a) The superscript denotes the power of ten by which the entry should be multiplied.

TABLE 2.14   Continuum distorted wave approximation total cross section $Q(2p_x)$ (in units of πa_0^2) for the reaction $He^{++} + He^+(1s^2) \rightarrow He^+(2p_x) + He^+(1s)$, evaluated using the non-correlated (λ) and the natural expansion (X-terms) helium wavefunctions - see equations (2.6.3) and (2.6.4) of text.

E(keV)	λ	X = 1	X = 3	X = 6	X = 15
25	8.336^{+1}(a)	7.068^{+1}	7.348^{+1}	7.399^{+1}	7.444^{+1}
50	1.387^{+1}	1.373^{+1}	1.342^{+1}	1.343^{+1}	1.342^{+1}
100	3.458^{0}	3.699^{0}	3.450^{0}	3.530^{0}	3.529^{0}
200	8.479^{-1}	9.170^{-1}	8.878^{-1}	8.859^{-1}	8.853^{-1}
300	3.167^{-1}	3.417^{-1}	3.327^{-1}	3.322^{-1}	3.321^{-1}
400	1.421^{-1}	1.529^{-1}	1.491^{-1}	1.490^{-1}	1.490^{-1}
500	7.146^{-2}	7.677^{-2}	7.481^{-2}	7.480^{-2}	7.479^{-2}
600	3.898^{-2}	4.183^{-2}	4.071^{-2}	4.071^{-2}	4.071^{-2}
700	2.261^{-2}	2.427^{-2}	2.357^{-2}	2.358^{-2}	2.358^{-2}
800	1.378^{-2}	1.481^{-2}	1.435^{-2}	1.436^{-2}	1.436^{-2}
900	8.738^{-3}	9.419^{-3}	9.108^{-3}	9.116^{-3}	9.117^{-3}
1000	5.731^{-3}	6.202^{-3}	5.985^{-3}	5.991^{-3}	5.992^{-3}
1500	1.002^{-3}	1.119^{-3}	1.070^{-3}	1.072^{-3}	1.073^{-3}
2000	2.608^{-4}	3.033^{-4}	2.890^{-4}	2.898^{-4}	2.898^{-4}
2500	8.708^{-5}	1.055^{-4}	1.004^{-4}	1.007^{-4}	1.007^{-4}
3000	3.448^{-5}	4.343^{-5}	4.132^{-5}	4.146^{-5}	4.146^{-5}

(a) The superscript denotes the power of ten by which the entry should be multiplied.

TABLE 2.15   Continuum distorted wave approximation total cross
             section Q(2p) (in units of πa_0^2) for the reaction
             $He^{++} + He(1s^2) \rightarrow He^+(2p) + He^+(1s)$, evaluated using
           . the non-correlated (λ) and the natural expansion
             (X-terms) helium wavefunctions — see equations
             (2.6.3) and (2.6.4) of text.

E(keV)	λ	X = 1	X = 3	X = 6	X = 15
25	1.971^{+2} (a)	2.186^{+2}	2.131^{+2}	2.126^{+2}	2.127^{+2}
50	4.912^{+1}	4.998^{+1}	4.814^{+1}	4.806^{+1}	4.807^{+1}
100	1.392^{+1}	1.259^{+1}	1.172^{+1}	1.174^{+1}	1.172^{+1}
200	3.317^{0}	2.865^{0}	2.722^{0}	2.708^{0}	2.703^{0}
300	1.197^{0}	1.028^{0}	9.867^{-1}	9.831^{-1}	9.819^{-1}
400	5.227^{-1}	4.504^{-1}	4.342^{-1}	4.330^{-1}	4.326^{-1}
500	2.572^{-1}	2.230^{-1}	2.153^{-1}	2.148^{-1}	2.147^{-1}
600	1.377^{-1}	1.203^{-1}	1.162^{-1}	1.160^{-1}	1.159^{-1}
700	7.861^{-2}	6.925^{-2}	6.683^{-2}	6.675^{-2}	6.671^{-2}
800	4.722^{-2}	4.199^{-2}	4.048^{-2}	4.044^{-2}	4.042^{-2}
900	2.956^{-2}	2.656^{-2}	2.557^{-2}	2.556^{-2}	2.555^{-2}
1000	1.916^{-2}	1.740^{-2}	1.674^{-2}	1.672^{-2}	1.672^{-2}
1500	3.193^{-3}	3.067^{-3}	2.931^{-3}	2.932^{-3}	2.932^{-2}
2000	8.010^{-4}	8.128^{-4}	7.738^{-4}	7.747^{-4}	7.746^{-4}
2500	2.591^{-4}	2.763^{-4}	2.626^{-4}	2.630^{-4}	2.629^{-4}
3000	9.975^{-5}	1.112^{-4}	1.056^{-4}	1.058^{-4}	1.058^{-4}

(a) The superscript denotes the power of ten by which the entry
    should be multiplied.

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TABLE 2.16   The relative percentage change $\Delta(i \to j)$ in $Q(n\ell)$, as we move from a wavefunction Ψ_i to a more accurate wavefunction Ψ_j, defined as $\Delta(i \to j) = \left\{ \dfrac{Q_j - Q_i}{Q_i} \right\} \times 100\%$.

He^{++} PROJECTILE

E(keV)	Q(1s)		Q(2s)		Q(2p$_x$)		Q(2p$_z$)		Q(2p)	
	$\Delta(\lambda \to 1)$	$\Delta(1 \to 15)$	$\Delta(\lambda \to 1)$	$\Delta(1 \to 15)$	$\Delta(\lambda \to 1)$	$\Delta(1 \to 15)$	$\Delta(\lambda \to 1)$	$\Delta(1 \to 15)$	$\Delta(\lambda \to 1)$	$\Delta(1 \to 15)$
25	+0.9%	+0.4%	-12.7%	-24.0%	-15.2%	+5.3%	+30.1%	-6.5%	+10.9%	-2.7%
50	+1.3%	+0.0%	-5.2%	-10.8%	-1.0%	-1.9%	+2.8%	-4.5%	+1.8%	-3.8%
100	-4.6%	+3.1%	-4.7%	-4.0%	+7.0%	-4.6%	-15.0%	-7.8%	-9.6%	-6.9%
200	-9.3%	+0.1%	-7.1%	-1.7%	+8.1%	-3.5%	-21.1%	-6.7%	-13.6%	-5.7%
400	-10.1%	-1.8%	-9.9%	-1.6%	+7.6%	-2.6%	-21.8%	-4.7%	-13.8%	-4.0%
600	-9.2%	-2.6%	-10.7%	-2.1%	+7.3%	-2.7%	-20.6%	-4.2%	-12.6%	-3.7%
800	-7.9%	-3.1%	-10.4%	-2.6%	+7.5%	-3.0%	-18.7%	-4.1%	-11.1%	-3.7%
1000	-6.5%	-3.4%	-9.5%	-2.9%	+8.2%	-3.4%	-16.6%	-4.2%	-9.2%	-3.9%
1500	-2.9%	-4.1%	-6.3%	-3.7%	+11.7%	-4.1%	-11.1%	-4.6%	-3.9%	-4.4%
2000	+0.7%	-4.4%	-2.7%	-4.2%	+16.3%	-4.5%	-5.7%	-4.8%	+1.4%	-4.7%
2500	+4.0%	-4.6%	+0.8%	-4.4%	+21.2%	-4.6%	-0.7%	-5.0%	+6.6%	-4.8%
3000	+7.0%	-4.7%	+4.0%	-4.6%	+26.0%	-4.5%	+3.9%	-5.1%	+11.5%	-4.9%

TABLE 2.17 Continuum distorted wave approximation total cross section Q (in units of πa_0^2) for the process $He^{++} + He(1s^2) \longrightarrow He^+ + He^+$ evaluated using the non-correlated (λ) and the natural expansion (X-terms) helium wavefunctions — see equations (2.6.3) and (2.6.4) of text.

E(keV)	λ	X = 1	X = 3	X = 6	X = 15	Experiment[a]
300	6.634^0 [b]	5.908^0	5.783^0	5.781^0	5.779^0	3.0^0
400	3.210^0	2.856^0	2.792^0	2.790^0	2.798^0	1.8^0
500	1.733^0	1.546^0	1.508^0	1.507^0	1.508^0	1.1^0
600	1.010^0	9.062^{-1}	8.818^{-1}	8.817^{-1}	8.816^{-1}	7.2^{-1}
700	6.243^{-1}	5.634^{-1}	5.469^{-1}	5.469^{-1}	5.466^{-1}	6.0^{-1}
800	4.036^{-1}	3.669^{-1}	3.561^{-1}	3.554^{-1}	3.555^{-1}	3.9^{-1}
900	2.707^{-1}	2.480^{-1}	2.398^{-1}	2.399^{-1}	2.399^{-1}	2.3^{-1}
1000	1.872^{-1}	1.728^{-1}	1.669^{-1}	1.670^{-1}	1.670^{-1}	2.2^{-1}
1100	1.329^{-1}	1.237^{-1}	1.193^{-1}	1.193^{-1}	1.193^{-1}	1.3^{-1}
1200	9.640^{-2}	9.049^{-2}	8.711^{-2}	8.711^{-2}	8.711^{-2}	1.1^{-1}
1300	7.129^{-2}	6.749^{-2}	6.487^{-2}	6.489^{-2}	6.488^{-2}	7.4^{-2}
1400	5.362^{-2}	5.118^{-2}	4.915^{-2}	4.916^{-2}	4.917^{-2}	6.0^{-2}
1500	4.095^{-2}	3.940^{-2}	3.778^{-2}	3.780^{-2}	3.781^{-2}	5.5^{-2}

(a) Pivovar et al., reference 58.

(b) The superscript denotes the power of ten by which the entry should be multiplied.

APPENDIX A

Formal Time-Dependent Theory of Scattering

The Interaction Representation

The equation of motion of a system, in the Schrodinger representation, is given by

$$i \frac{\partial \Psi}{\partial t}(t) = H \Psi(t) \quad , \qquad (A.1)$$

where H denotes the Hamiltonian for the system, with units such that $\hbar = 1$. If the state of the system at time t_0 is denoted by $\Psi(t_0)$, equation (A.1) may be formally integrated to give

$$\Psi(t) = e^{-iH(t - t_0)} \Psi(t_0) \quad . \qquad (A.2)$$

Thus the causal development of the system from time t_0 to time t is specified by the unitary operator[a] $\exp\left[-iH(t - t_0)\right]$.

We now suppose that the Hamiltonian H may be decomposed into two parts; an unperturbed Hamiltonian H_0, whose eigenfunctions and eigenvalues are known, and a perturbation V:

$$H = H_0 + V \qquad (A.3)$$

The wavefunction in the interaction representation is defined by

$$\Psi_I(t) = e^{iH_0t} \Psi(t) \quad . \qquad (A.4)$$

Differentiating equation (A.4) with respect to time leads to

$$i \frac{\partial \Psi_I}{\partial t}(t) = i e^{iH_0t} \frac{\partial \Psi}{\partial t}(t) - H_0 e^{iH_0t} \Psi(t)$$

which, by using equations (A.1), (A.3) and (A.4), becomes

$$i \frac{\partial \Psi_I}{\partial t}(t) = V(t) \Psi_I(t) \quad , \qquad (A.5)$$

---

[a] An operator, say $a(t)$, satisfying $a(t)a^{\dagger}(t) = E$, where E is the identity matrix, is said to be unitary.

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where

$$V(t) = e^{iH_0 t} V e^{-iH_0 t} \quad . \qquad (A.6)$$

Therefore, in the interaction representation, both the wavefunction $\Psi_I(t)$ and the operator $V(t)$ are explicit functions of time.

If there is no interaction at time t_0 , the wavefunction in the Schrodinger representation is

$$\Psi(t_0) = e^{-iE_i t_0} \psi_i \quad , \qquad (A.7)$$

where ψ_i is an eigenfunction of the unperturbed Hamiltonian H_0 and E_i is the corresponding eigenenergy. Therefore the formal solution (A.2) to equation (A.1) may be written as

$$\Psi_i(t) = e^{-iH(t-t_0)} \Psi_i(t_0) = e^{-iH(t-t_0)} e^{-iE_i t_0} \psi_i \quad ,$$

$$(A.8)$$

where the subscript i in $\Psi_i(t)$ corresponds to the i in E_i. Now equation (A.2) above implies that at t_0 (when the system is in the state $\Psi_i(t_0)$ of H_0), the system is suddenly subjected to the interaction V. A more physical picture and a better mathematical formulation of the collision problem is to require that, as $t_0 \longrightarrow -\infty$, the Hamiltonian H approaches H_0 , and $\Psi_i(t)$ approaches the stationary state ψ_i asymptotically. In this view, it is convenient to introduce the artifice of assuming the interaction V to be 'switched on' adiabatically from V $\longrightarrow$ 0 as $t_0 \longrightarrow -\infty$ to the full strength V at t = 0, and to V $\longrightarrow$ 0 as t $\longrightarrow +\infty$. The $\Psi_i(t)$ at time t is then the result of the $\exp\left[-iH(t-t_0)\right]\Psi_i(t_0)$ of equation (A.8) for all t_0 ranging from $-\infty$ to 0. This is most conveniently represented by the average[60]

$$\Psi_i(t) = \varepsilon \int_{-\infty}^{0} dt_0 \; e^{\varepsilon t_0} \; e^{-iH(t-t_0)} \Psi_i(t_0) \, dt_0 \quad , \quad t > 0$$

$$(A.9)$$

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$$= e^{-iHt} \, \epsilon \int_{-\infty}^{0} dt_0 \, e^{\epsilon t_0} \, e^{i(H - E_i)t_0} \, \psi_i \qquad (A.10)$$

$$= e^{-iHt} \, \frac{i\epsilon}{E_i - H + i\epsilon} \, \psi_i \qquad (A.11)$$

Therefore,

$$\Psi_i^+ (0) = \frac{i\epsilon}{E_i - H + i\epsilon} \, \psi_i \quad , \qquad (A.12)$$

where it is understood that the limit $\epsilon \rightarrow 0$ will be taken eventually, and that the superscript + signifies outgoing wave boundary conditions. If we make use of the fact that

$$(H_0 - E_i)\psi_i = 0 = (H - V - E_i)\psi_i \quad , \qquad (A.13)$$

then equation (A.12) becomes

$$\Psi_i^+ = \psi_i + \frac{1}{E_i - H + i\epsilon} \, V \, \psi_i \quad . \qquad (A.14)$$

In an entirely analogous manner, we can obtain

$$\Psi_i^- = \psi_i + \frac{1}{E_i - H - i\epsilon} \, V \, \psi_i \quad , \qquad (A.15)$$

where Ψ_i^+ , Ψ_i^- are, respectively, the outgoing and ingoing wave eigenfunctions of H corresponding to the initial wave ψ_i. Note that the above is also true in the interaction representation, since, by equation (A.4), $\Psi_I(0) \equiv \Psi(0)$.

As in the Schrodinger representation, the time development of the dynamical state of the system may be represented by the action of a unitary linear operator on the wavefunction describing the system at some arbitrary time t_0. If this operator is denoted by $U(t, t_0)$, then

$$\Psi_I(t) = U(t, t_0)\Psi_I(t_0) \quad . \qquad (A.16)$$

Making use of equations (A.2) and (A.4), we have

$$\Psi_I(t) = e^{iH_0 t}\, e^{-iH(t - t_0)}\, e^{-iH_0 t_0}\, \Psi_I(t_0) \quad . \tag{A.17}$$

Comparing equation (A.17) with (A.16), then

$$U(t, t_0) = e^{iH_0 t}\, e^{-iH(t - t_0)}\, e^{-iH_0 t_0} \quad . \tag{A.18}$$

On substituting the expression (A.16) for $\Psi_I(t)$ in equation
(A.5), it is evident that $U(t, t_0)$ satisfies the differential
equation

$$\frac{i \partial U}{\partial t}(t, t_0) = V(t)\, U(t, t_0) \quad , \tag{A.19}$$

a result which may also be obtained by differentiating (A.18).
If we note that

$$U(t_0, t_0) = 1 \quad , \tag{A.20}$$

then integration of the expression (A.19) yields the integral
equation

$$U(t, t_0) = 1 + \frac{1}{i}\int_{t_0}^{t} V(t')\, U(t', t_0)\, dt' \quad . \tag{A.21}$$

A number of other results, which will be useful later, may also be
obtained from equation (A.18); in particular

$$U(0, t) = e^{iHt}\, e^{-iH_0 t} \tag{A.22}$$

$$U^{\dagger}(t, t_0) = e^{iH_0 t_0}\, e^{-iH(t - t_0)}\, e^{-iH_0 t} = U(t_0, t) \tag{A.23}$$

$$U(t, t')\, U(t', t_0) = U(t, t_0) \quad . \tag{A.24}$$

The S Matrix

In discussing a collision problem, one is interested
in the evolution of a system prepared in a specific state $\Psi_I(-\infty)$
in the remote past. At time $t = +\infty$, the system will have
evolved to a state

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$$\Psi_I(+\infty) = S \, \Psi_I(-\infty) \quad , \tag{A.25}$$

where the scattering operator S is defined to be

$$S = \lim_{\substack{t_o \to -\infty \\ t \to +\infty}} U(t, t_o) \quad , \tag{A.26}$$

provided the double limit exists. At the time $t_o \to -\infty$, there

is no interaction present in the system and we suppose, therefore,

that

$$\Psi_I(-\infty) = \Psi_i \quad , \tag{A.27}$$

where, as before, Ψ_i is an eigenfunction of the unperturbed

Hamiltonian H_o. The final state $\Psi_I(+\infty)$ will be a superposition

of eigenstates of H_o and consequently the amplitude for a transition

from the initial state Ψ_i to any eigenstate Ψ_f of H_o is simply

the coefficient of Ψ_f in the expansion of $\Psi_I(+\infty)$ in terms

of the eigenfunctions of H_o. Thus the required amplitude for a

transition from Ψ_i to Ψ_f is

$$S_{if} = \langle \Psi_f \mid S \mid \Psi_i \rangle \tag{A.28}$$

$$= \lim_{\substack{t_o \to -\infty \\ t \to +\infty}} \langle \Psi_f \mid U(t, t_o) \mid \Psi_i \rangle$$

$$= \lim_{\substack{t_o \to -\infty \\ t_o \to +\infty}} \langle U(o, t) \Psi_f \mid U(o, t_o) \Psi_i \rangle , \tag{A.29}$$

where we have used equations (A.26), (A.24) and (A.23). The

aggregate of the quantities S_{if} is called the scattering or S

matrix. In order to evaluate S_{if} one must first examine the

effect of U(o,t) operating on an eigenfunction of H_o, and then

consider what happens in the limit as $t \to \pm\infty$.

Let Ψ_a be an arbitrary continuum eigenfunction of H_0,
and E_a the corresponding eigenenergy. Then, from equation (A.22),
it is evident that

$$U(o,t)\Psi_a = e^{iHt} e^{-iE_a t} \Psi_a \qquad (A.30)$$

This result, in its present form, is of little use if we wish to
investigate the limits $t \to \pm \infty$. Difficulties which arise in
these limits are most easily seen by examining the integral equation
(A.21). Each term in the Neumann solution of this equation involves
an oscillatory integral, and the limits as $t \to \pm \infty$ are not
defined (see reference 61, pp 308-315). These oscillations must
somehow be damped out to achieve a meaningful limiting process.
To remove the difficulties associated with the limits $t \to \pm \infty$
we adopt the method of adiabatic switching. This treatment is
due originally to Gell-Mann and Goldberger[62]. We define the limits
of a function $f(t)$ as $t \to \pm \infty$ by the equations

$$\lim_{t \to -\infty} f(t) = \lim_{\varepsilon \to o^+} \varepsilon \int_{-\infty}^{o} e^{\varepsilon t'} f(t') \, dt' \qquad (A.31)$$

$$\lim_{t \to +\infty} f(t) = \lim_{\varepsilon \to o^+} \varepsilon \int_{o}^{\infty} e^{-\varepsilon t'} f(t') \, dt' . \qquad (A.32)$$

If the functions $f(t)$ possess limits in the ordinary sense as
$t \to \pm \infty$, then by integrating by parts we can see that these
limits coincide with

$$\lim_{t \to -\infty} f(t) = f(-\infty)$$

$$\lim_{t \to +\infty} f(t) = f(+\infty)$$

as it should be. On the other hand, if $f(t)$ is an oscillatory
function, the above procedure provides the required damping of the
oscillations.

Introducing the Moller operator Ω^+, defined by the equation

$$\Omega^+ = \lim_{t \to -\infty} U(o, t) \quad , \tag{A.33}$$

and using the limiting process prescribed by (A.31), one obtains

$$\Omega^+ \psi_a = \lim_{\varepsilon \to o^+} \varepsilon \int_{-\infty}^{o} e^{\varepsilon t'} U(o, t') \psi_a \, dt' \quad .$$

$$= \lim_{\varepsilon \to o^+} \frac{i\varepsilon}{(E_a - H + i\varepsilon)} \psi_a \quad , \tag{A.34}$$

where we have made use of equation (A.30). Since

$$(E_a - H_o)\psi_a = 0 = (E_a - H + V)\psi_a, \tag{A.35}$$

equation (A.34) reduces to

$$\Omega^+ \psi_a = \lim_{\varepsilon \to o^+} \left\{ \psi_a + \frac{1}{E_a - H + i\varepsilon} V \psi_a \right\} = \Psi_a^+ , \tag{A.36}$$

(by A.14) with

$$\Psi_a^+ = \psi_a + \frac{1}{E_a - H + i\varepsilon} V \psi_a \tag{A.37}$$

where, as usual, it is understood that the limit as $\varepsilon \to o^+$ is to be taken eventually. This establishes the important fact that the Moller operator Ω^+ acting on a continuum eigenfunction of H_o generates the continuum eigenfunction of H which has the same energy and which satisfies outgoing-wave boundary conditions. Likewise, if the operator Ω^- is defined by

$$\Omega^- = \lim_{t \to +\infty} U(o,t) \tag{A.38}$$

it is easily seen that

$$\Omega^- \psi_a = \Psi_a^- \quad , \tag{A.39}$$

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with
$$\Psi_a^- = \psi_a + \frac{1}{E_a - H - i\epsilon} V \psi_a \quad , \qquad (A.40)$$

which is the continuum eigenfunction of H with energy E_a , and satisfies incoming-wave boundary conditions.

If P and Q are operators for which inverse operators exist, then obviously

$$P^{-1} = Q^{-1} + P^{-1}(Q - P)Q^{-1} \qquad (A.41)$$

$$= Q^{-1} + Q^{-1}(Q - P)P^{-1} \quad . \qquad (A.42)$$

Taking
$$P^{-1} = \frac{1}{E_a - H + i\epsilon} \qquad (A.43)$$

and
$$Q^{-1} = \frac{1}{E_a - H_0 + i\epsilon} \quad , \qquad (A.44)$$

then using the identity (A.42) it is relatively easy to show that

$$\Psi_a^+ = \psi_a + \frac{1}{E_a - H_0 + i\epsilon} V \Psi_a^+ \quad . \qquad (A.45)$$

Similarly, it may also be shown that

$$\Psi_a^- = \psi_a + \frac{1}{E_a - H_0 + i\epsilon} V \Psi_a^- \quad . \qquad (A.46)$$

It is now evident from equations (A.33), (A.36), (A.38) and (A.39) that the S matrix element S_{if}, defined by (A.29) takes the form

$$S_{if} = \left\langle \Psi_f^- \mid \Psi_i^+ \right\rangle$$

$$= \left\langle \Psi_f^+ \mid \Psi_i^+ \right\rangle + \left\langle \Psi_f^- - \Psi_f^+ \mid \Psi_i^+ \right\rangle .$$

$$(A.47)$$

However, Ψ_i^+ and Ψ_f^+ are continuum eigenfunctions of the same Hamiltonian and have the same normalization as ψ_i and ψ_f ; consequently

$$\left\langle \Psi_f^+ \mid \Psi_i^+ \right\rangle = \delta_{if} \qquad (A.48)$$

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where δ_{if} contains a Dirac delta function for the energies and Kronecker deltas for other quantum numbers. Also, from equations (A.37) and (A.40),

$$\Psi_f^- - \Psi_f^+ = \left[\frac{1}{E_f - H - i\epsilon} - \frac{1}{E_f - H + i\epsilon}\right] V \Psi_f . \qquad (A.49)$$

Consequently,

$$S_{if} = \delta_{if} + \left\langle \Psi_f \left| V \left[\frac{1}{E_f - H - i\epsilon} - \frac{1}{E_f - H + i\epsilon}\right] \Psi_i^+ \right\rangle \right.$$

$$= \delta_{if} + \left[\frac{1}{E_f - E_i - i\epsilon} - \frac{1}{E_f - E_i + i\epsilon}\right] \left\langle \Psi_f \left| V \right| \Psi_i^+ \right\rangle$$

$$= \delta_{if} - \frac{2i\epsilon}{\left[(E_f - E_i)^2 + \epsilon^2\right]} \left\langle \Psi_f \left| V \right| \Psi_i^+ \right\rangle . \qquad (A.50)$$

At this point we recall that the limit $\epsilon \to 0^+$ is implied in equation (A.50), and using the result[63]

$$\lim_{\epsilon \to 0^+} \left[\frac{\epsilon}{(E_f - E_i)^2 + \epsilon^2}\right] = \pi \delta(E_f - E_i) , \qquad (A.51)$$

we obtain

$$S_{if} = \delta_{if} - 2\pi i \, \delta(E_f - E_i) T_{if} \qquad (A.52)$$

where $T_{if} = \left\langle \Psi_f \left| V \right| \Psi_i^+ \right\rangle .$ $\qquad (A.53)$

The expression T_{if} may be regarded as a matrix element of the operator T defined by

$$T \Psi_i = V \Psi_i^+ . \qquad (A.54)$$

Alternatively, if we write

$$S_{if} = \left\langle \Psi_f^- \left| \Psi_i^- \right\rangle + \left\langle \Psi_f^- \left| \Psi_i^+ - \Psi_i^- \right\rangle , \qquad (A.55)$$

it follows that

$$S_{if} = \delta_{if} - 2\pi i \, \delta(E_f - E_i) \langle \Psi_f^- | V | \Psi_i \rangle \quad . \quad (A.56)$$

Therefore, on the energy shell, that is when $E_i = E_f$,

$$\langle \Psi_f | V | \Psi_i^+ \rangle = \langle \Psi_f^- | V | \Psi_i \rangle \quad . \quad (A.57)$$

This result may also be obtained directly by using the formal

expressions for Ψ_i^+ and Ψ_f^- in terms of Ψ_i and Ψ_f , and from

this derivation it is seen that (A.57) is not, in general, valid off

the energy shell.

Transition Probability for Direct Collisions.

The quantity $|S_{if}|^2$ is the probability for all time

of finding the system in a state Ψ_f if it was prepared in a state Ψ_i.

However, the duration of any experiment is necessarily finite.

The physically meaningful quantity is therefore the transition

probability per unit time, which will be denoted by W_{if}. Thus, at

time t, we have

$$W_{if} = \lim_{t_0 \to -\infty} \frac{\partial}{\partial t} |S_{if}|^2$$

$$= \lim_{t_0 \to -\infty} \frac{\partial}{\partial t} |\langle \Psi_f | U(t, t_0) | \Psi_i \rangle|^2 \quad . \quad (A.58)$$

From equations (A.4) and (A.27)

$$\Psi_I(t) = U(t, t_0) \Psi_i \quad , \quad t_0 \to -\infty \quad . \quad (A.59)$$

Therefore,

$$W_{if} = \frac{d}{dt} |\langle \Psi_f | \Psi_I(t) \rangle|^2$$

$$= \langle \Psi_f | \Psi_I(t) \rangle \langle \Psi_f | \frac{\partial}{\partial t} \Psi_I(t) \rangle^* + \text{c.c.} \quad (A.60)$$

where the abbreviation c.c. is used to denote the complex conjugate

of the first term in the expression. Using equations (A.5), (A.16),

(A.18), (A.24) and the fact that $\Psi_I(0) = \Psi_i^+$ we obtain

$$\left\langle \Psi_f \left| \frac{\partial}{\partial t} \Psi_I(t) \right.\right\rangle = - i \left\langle \Psi_f \left| e^{iH_o t} V e^{-iH_o t} U(t,t_o) \Psi_I(t_o) \right.\right\rangle$$

$$= - i \left\langle \Psi_f \left| e^{iH_o t} V e^{-iHt} \Psi_i^+ \right.\right\rangle$$

$$= - i\, e^{iE_f t} \left\langle \Psi_f \left| V e^{-iHt} \Psi_i^+ \right.\right\rangle$$

$$= - i\, e^{i(E_f - E_i)t} \left\langle \Psi_f \left| V \right| \Psi_i^+ \right\rangle$$

$$= - i\, e^{i(E_f - E_i)t} \, T_{if} \quad , \qquad (A.61)$$

where T_{if} is the same as given in equation (A.53). Also, proceeding as before,

$$\left\langle \Psi_f \mid \Psi_I(t) \right\rangle = e^{i(E_f - E_i)t} \left\langle \Psi_f \mid \Psi_i^+ \right\rangle . \qquad (A.62a)$$

Using the integral equation (A.45) for Ψ_i^+ , this becomes

$$\left\langle \Psi_f \mid \Psi_I(t) \right\rangle = e^{i(E_f - E_i)t} \left[\left\langle \Psi_f \mid \Psi_i \right\rangle + \left\langle \Psi_f \left| \frac{1}{E_i - H_o + i\epsilon} V \right| \Psi_i^+ \right\rangle \right]$$

$$= e^{i(E_f - E_i)t} \left[\delta_{if} + \frac{1}{E_i - E_f + i\epsilon} T_{if} \right] \quad , \quad (A.62b)$$

where δ_{if} has the same meaning as in (A.48).
Therefore

$$W_{if} = \lim_{\epsilon \to 0^+} \left[e^{i(E_f - E_i)t} \left\{ \delta_{if} + \frac{1}{E_i - E_f + i\epsilon} T_{if} \right\} i\, e^{-i(E_f - E_i)t} T_{if}^* + c.c. \right]$$

$$= \lim_{\epsilon \to 0^+} \left[i \left\{ \delta_{if} + \frac{1}{E_i - E_f + i\epsilon} T_{if} \right\} T_{if}^* + c.c. \right]$$

which, using equation (A.51), becomes

$$W_{if} = 2I_m \, T_{if}^* \, S_{if} + 2\pi \, \delta(E_i - E_f) \, |T_{if}|^2 \qquad (A.63)$$

which is obviously independent of time.

The Dirac delta function in equation (A.63) arises because W_{if} is the probability of a transition to a specified continuum state. This apparent singularity disappears if one considers instead the probability of transitions to a group of states centered at $E = E_f$. Let the density of these states be $\rho(E)$ per unit solid angle; in other words, the number of states, with momentum vectors lying within $d\Omega$ and with energies in the range E to $E + dE$, is $\rho(E) \, dE \, d\Omega$. Then, if ψ_i does not belong to the group of final states under consideration, the transition probability per unit time from ψ_i to some state of the group is

$$\omega_{if} = \int_{E_f - \Delta E}^{E_f + \Delta E} W_{if} \, \rho(E) \, dE \, d\Omega$$

$$= \int_{E_f - \Delta E}^{E_f + \Delta E} \left[2 \, I_m T_{if}^* \, S_{if} + 2\pi \, \delta(E_i - E) |T_{if}|^2 \right] \rho(E) \, dE \, d\Omega$$

$$= 2\pi \, \rho(E_f) \, |T_{if}|^2 \, d\Omega \qquad (A.64)$$

and in the final expression $E_f = E_i$.

An expression for the density of final states is readily obtained by considering the possible states of a free particle in a box with periodic boundary conditions. Let the box be a cube of volume L^3 with edges parallel to the axes of a system of

cartesian coordinates (x, y, z). The wavefunction for a free

particle with momentum $\underline{k}$ is

$$\phi_{\underline{k}}(x, y, z) = e^{i(xk_x + yk_y + zk_z)}$$

and the periodic boundary conditions require that

$$\phi_{\underline{k}}(x + L, y + L, z + L) = \phi_{\underline{k}}(x, y, z).$$

Thus the allowed values of the components of $\underline{k}$ are

$$k_x = \frac{2\pi N_x}{L} \quad ; \quad k_y \frac{2\pi N_y}{L} \quad ; \quad k_z \frac{2\pi N_z}{L} \quad ,$$

where N_x, N_y, N_z are positive or negative integers or zero.

Consequently the total number of states with momenta in the range

$\underline{k}$ to $\underline{k} + d\underline{k}$ is $(L/2\pi)^3 d\underline{k}$, and the number of states per unit

volume in this range is

$$(2\pi)^{-3} d\underline{k} = (2\pi)^{-3} k^2 d\Omega \, dk.$$

From the definition of $\rho(E)$ it follows that

$$\rho(E) \, dE d\Omega = (2\pi)^{-3} k^2 d\Omega \, dk$$

and, since $E = k^2/2\mu$, the required expression for the density of

states is

$$\rho(E) = \frac{\mu k}{8\pi^3} \quad . \tag{A.65}$$

When this result is applied to a collision problem, E is the

energy associated with the relative motion of the colliding systems

and μ is their reduced mass. Therefore equation (A.64) becomes

$$\omega_{if} = \frac{\mu k_f}{4\pi^2} |T_{if}|^2 \, d\Omega \tag{A.66}$$

where k_f is the final relative momentum. In order to relate this

quantity to the differential cross section $I(\theta, \phi)$, one notes

that, for an incident flux of N particles per unit area per unit

time, the number of particles per unit time which cause the required

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transition, and are scattered into an element of solid angle $d\Omega$,
is $N\,I(\theta ,\phi)\,d\Omega$. Since ω_{if} is the transition probability
per unit time corresponding to an incident flux of magnitude
k_i/μ , it follows that

$$I(\theta ,\phi) = \frac{\mu^2}{4\pi^2}\ \frac{k_f}{k_i}\ |T_{if}|^2 \qquad\qquad (A.67)$$

and the total cross section for a transition from an initial state
i to a final state f is

$$Q_{if} = \frac{\mu^2}{4\pi^2}\ \frac{k_f}{k_i}\ \int |T_{if}|^2\ d\Omega \ . \qquad\qquad (A.68)$$

The results in equations (A.67) and (A.68) are identical to those

obtained in the time-independent approach.

Rearrangement Collisions.

When considering rearrangement collisions, it is convenient
to express the total Hamiltonian H as

$$H = H_i + V_i = H_f + V_f \ , \qquad\qquad (A.69)$$

where H_i and H_f are the initial and final unperturbed Hamiltonians
and V_i and V_f are the corresponding perturbations. If one is
interested in direct transitions from one eigenstate of H_i to
another eigenstate of the same Hamiltonian, it follows from the
analysis preceding equation (A.53) that the relevant transition
matrix element is

$$T_{if} = \left\langle \Psi_f \left| V_i \right| \Psi_i^+ \right\rangle \qquad\qquad (A.70)$$

where

$$\Psi_i^+ = \Psi_i + \frac{1}{E_i - H_i + i\epsilon}\ V_i\, \Psi_i^+ \qquad\qquad (A.71)$$

$$= \Psi_i + \frac{1}{E_i - H + i\epsilon}\ V_i\, \Psi_i \qquad\qquad (A.72)$$

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and Ψ_i and Ψ_f are both eigenfunctions of H_i corresponding to the same total energy E_i. Although the wavefunction Ψ_i^+ was introduced for the discussion of direct collisions only, it is nevertheless clear that, being an eigenfunction of the total Hamiltonian H, it represents a complete solution of the scattering problem. Therefore Ψ_i^+ contains the description of all possible reactions and the only remaining problem is the extraction from Ψ_i^+ of the information which refers specifically to rearrangements. It is evident that for rearrangement transitions, the quantity of interest is the probability that a system, prepared in an eigenstate Ψ_i of H_i in the remote past, will evolve, under the action of the Hamiltonian H, to a specific eigenstate Ψ_f of H_f. It is convenient to re-write the initial Green's function operator

$$G_i^+ (E_i) = \frac{1}{E_i - H_i + i\epsilon} \quad , \quad (A.73)$$

which occurs in equation (A.71), in a form which includes explicit reference to the decomposition of H in terms of H_f and V_f , the object being to facilitate the expansion of Ψ_i^+ in terms of the complete set of eigenstates of H_f. To this end we define the final state Green's function for arbitrary E

$$G_f^+ (E) = \frac{1}{E - H_f + i\epsilon} \quad . \quad (A.74)$$

Using the operator identity (A.42) and setting

$$P^{-1} \equiv \frac{1}{E_i - H_i + i\epsilon} = G_i^+ (E_i) \quad (A.75)$$

$$Q^{-1} \equiv \frac{1}{E_i - H_f + i\epsilon} = G_f^+ (E_i) \quad , \quad (A.76)$$

we obtain

$$G_i^+(E_i) = G_f^+(E_i) + G_f^+(E_i)(H_i - H_f)G_i^+(E_i)$$

$$= G_f^+(E_i)\left[1 + (V_f - V_i)G_i^+(E_i)\right] \quad . \qquad (A.77)$$

The integral equation (A.71) now becomes

$$\Psi_i^+ = \Psi_i + G_f^+(E_i)\left[1 + (V_f - V_i)G_i^+(E_i)\right] V_i \Psi_i^+$$

$$= \Psi_i + G_f^+(E_i)\left[V_i \Psi_i^+ + (V_f - V_i)(\Psi_i^+ - \Psi_i)\right]$$

$$= \left[1 - G_f^+(E_i)(V_f - V_i)\right]\Psi_i + G_f^+(E_i)V_f\Psi_i^+ \quad .$$

However,

$$\left[1 - G_f^+(E_i)(V_f - V_i)\right]\Psi_i = G_f^+(E_i)\left[E_i - H_i + i\epsilon\right]\Psi_i$$

$$= i\epsilon G_f^+(E_i)\Psi_i$$

since $(H_i - E_i)\Psi_i = 0$,

and therefore

$$\Psi_i^+ = i\epsilon G_f^+(E_i)\Psi_i + G_f^+(E_i) V_f\Psi_i^+$$

$$= \frac{i\epsilon}{E_i - H_f + i\epsilon} \Psi_i + \frac{1}{E_i - H_f + i\epsilon} V_f\Psi_i^+ \qquad (A.78)$$

This expression may now be used to expand Ψ_i^+ in terms of the complete set of solutions Ψ_f of the equation

$$(H_f - E_f) \Psi_f = 0 \qquad (A.79)$$

and the expansion takes the form

$$\Psi_i^+ = \sum_f \frac{i\epsilon \Psi_f \langle \Psi_f | \Psi_i \rangle}{E_i - E_f + i\epsilon} + \sum_f \frac{\Psi_f \langle \Psi_f | V_f | \Psi_i^+ \rangle}{E_i - E_f + i\epsilon} \quad .$$

$$(A.80)$$

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When endeavouring to obtain a scattering amplitude, one is interested in the asymptotic form of $\Psi_i{}^+$ as the separation between the interacting systems tends to infinity. Under these conditions the bound states within the set Ψ_f are irrelevant since they vanish asymptotically, and we may therefore confine our attention to those states of Ψ_f which lie in the continuum. If $E_f \neq E_i$, the ε dependent factor in the first term of (A.80) tends to zero as $\varepsilon \rightarrow 0$, whereas for $E_f = E_i$ this factor tends to unity. Thus the effect of the ε dependent factor is to project out of Ψ_i only those states Ψ_f for which $E_f = E_i$. Since the states of interest lie in the continuum, the sum over all states f involves a sum over discrete quantum numbers and an integral over the energy E_f. The ε dependent factor ensures that the integrand vanishes except at one value of E_f and, therefore, this integral can be non-zero only if the integrand contains the delta function $\delta(E_i - E_f)$.

To show that such a delta function does not normally arise we consider a rearrangement collision of the form

$$1 + (2 + 3) \longrightarrow (1 + 3) + 2$$

where initially particle 1 is free and particles 2 and 3 are bound whereas, finally, particles 1 and 3 are bound and particle 2 is free. If the independent coordinates are chosen to be the position vectors $\underline{r}_1$ and $\underline{r}_2$ of the exchanged particle 3 with respect to 1 and 2, the scalar product $\langle \Psi_f \mid \Psi_i \rangle$ involves integration over the spaces of $\underline{r}_1$ and $\underline{r}_2$. The $\underline{r}_1$ integral involves a plane wave from Ψ_i and a bound state wavefunction from Ψ_f ; the $\underline{r}_2$ integral involves a plane wave from Ψ_f and a bound state wavefunction from Ψ_i. It is therefore clear that for collisions

of this type $\langle \Psi_f \mid \Psi_i \rangle$ does not involve a delta function. In fact, a delta function could arise only if all three particles were unbound before and after the collision. Since such situations are of no interest in the present context, they will be ignored from now on.

We have now shown that the first term in equation (A.80) vanishes asymptotically and consequently

$$\langle \Psi_f \mid \Psi_i^+ \rangle = \frac{\langle \Psi_f \mid V_f \mid \Psi_i^+ \rangle}{E_i - E_f + i\varepsilon} \quad . \tag{A.81}$$

The transition probability for rearrangement is given by

$$W_{if} = \frac{d}{dt} \mid \langle \Psi_f \mid \Psi_I(t) \rangle \mid^2 \tag{A.82}$$

as in equation (A.60), but in this case the appropriate interaction picture wavefunction is

$$\Psi_I(t) = e^{i H_f t} \Psi(t) \tag{A.83}$$

and therefore

$$\frac{\partial \Psi}{\partial t}_I(t) = i e^{i H_f t} (H_f - H) \Psi(t)$$

$$= i e^{i H_f t} V_f e^{-i H t} \Psi_i^+ \quad . \tag{A.84}$$

Consequently, proceeding as before in the direct transition case,

$$W_{if} = \lim_{\varepsilon \to 0^+} \left[\frac{i}{E_i - E_f + i\varepsilon} \mid \langle \Psi_f \mid V_f \mid \Psi_i^+ \rangle \mid^2 + c.c. \right]$$

$$= 2\pi \mid \langle \Psi_f \mid V_f \mid \Psi_i^+ \rangle \mid^2 \delta(E_i - E_f) \quad . \tag{A.85}$$

This may be written as

$$W_{if} = 2\pi \mid T_{if} \mid^2 \delta(E_i - E_f) \tag{A.86}$$

where now

$$T_{if} = \langle \Psi_f \mid V_f \mid \Psi_i^+ \rangle \quad . \tag{A.87}$$

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The arguments concerning the use and evaluation of the density of final states follow through precisely as before, and we obtain

$$I(\theta, \phi) = \frac{\mu_i \mu_f}{4\pi^2} \quad \frac{k_f}{k_i} \quad |T_{if}|^2 \tag{A.88}$$

and

$$Q = \frac{\mu_i \mu_f}{4\pi^2} \quad \frac{k_f}{k_i} \quad \int |T_{if}|^2 \quad d\Omega \quad , \tag{A.89}$$

where μ_i and μ_f are the reduced masses before and after the collision.

In the foregoing analysis the expression for the cross section is obtained by examining the expansion of Ψ_i^+ in terms of the complete set of eigenfunctions of H_f. Alternatively, one may proceed by expanding the wavefunction

$$\Psi_f^- = \Psi_f + \frac{1}{E - H - i\varepsilon} V_f \Psi_f \quad , \tag{A.90}$$

where $E = E_i = E_f$, in terms of the eigenfunctions of H_i to obtain

$$T_{if} = \left\langle \Psi_f^- \middle| V_i \middle| \Psi_i \right\rangle . \tag{A.91}$$

The Born Series.

In the evaluation of cross sections based on the formulae derived above, the use of approximate expressions for the matrix elements T_{if} is inevitable because, irrespective of the type of collision under consideration, the relevant matrix element takes the form

$$T_{if} = \left\langle \Psi_f \middle| V_f \middle| \Psi_i^+ \right\rangle = \left\langle \Psi_f \middle| V_f (1 + G^+ V_i) \middle| \Psi_i \right\rangle ,$$

$$\tag{A.92}$$

where

$$G^+ = \frac{1}{E - H + i\varepsilon} \quad , \tag{A.93}$$

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since for direct collisions $V_f = V_i$, and tractable expressions
for the matrix elements of operators involving the Green's function
G^+ are not available. Physical arguments suggest that, if the
relative velocity of two colliding systems is sufficiently large,
the distortion of the systems due to their interaction may be
disregarded in calculating scattering amplitudes, which leads to
the expectation that the first Born approximation matrix element

$$T_{if}^{B} = \langle \Psi_f | V_f | \Psi_i \rangle \qquad (A.94)$$

is the high-energy limit of the exact matrix element, and that in
some range of large finite energies T_{if}^{B} provides an adequate
representation of T_{if}. The matrix element T_{if}^{B} may be regarded as
the first term in a Born series for T_{if} obtained by expanding the
Green's function G^+ in terms of a simpler Green's function. Use of
the identity (A.42) shows that G^+ satisfies the integral equations

$$G^+ = G_i^+ + G_i^+ V_i G^+ \qquad (A.95)$$

and

$$G^+ = G_o^+ + G_o^+ V G^+ \qquad (A.96)$$

where

$$G_o^+ = \frac{1}{E - H_o + \iota \epsilon} \quad , \quad V = H - H_o \quad ,$$

and H_o is the sum of kinetic energy operators for all the particles
present. By splitting the Hamiltonian in different ways many other
integral equations for G^+ may be obtained, and the iterative
solution of any of these leads to a Born series for T_{if}. For
example from equations (A.95) and (A.96)

$$G^+ = G_i^+ + G_i^+ V_i G_i^+ + G_i^+ V_i G_i^+ V_i G_i^+ + \ldots \qquad (A.97)$$

$$= G_o^+ + G_o^+ V G_o^+ + G_o^+ V G_o^+ V G_o^+ + \ldots \qquad (A.98)$$

and substitution of these in equation (A.92) yields

$$T_{if} = T_{if}^B + \langle \Psi_f | V_f G_i^+ V_i | \Psi_i \rangle + \langle \Psi_f | V_f G_i^+ V_i G_i^+ V_i | \Psi_i \rangle + \dots$$

<div align="right">(A.99)</div>

and

$$T_{if} = T_{if}^B + \langle \Psi_f | V_f G_o^+ V | \Psi_i \rangle + \langle \Psi_f | V_f G_o^+ V G_o^+ V | \Psi_i \rangle + \dots$$

<div align="right">(A.100)</div>

The nth Born approximation is obtained by retaining the first n terms of either of these expansions. It is obvious by examination of equations (A.99) and (A.100) that, unlike the first Born approximation, the second and higher order Born approximations are not uniquely defined, but depend on the particular series used for G^+.

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Ground-state correlation effects in He–He inelastic scattering

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Abstract. The previous analysis concerning the influence of electron correlation in the ground-state description of He when evaluating inelastic scattering cross sections via the first Born approximation is applied here to an examination of He–He scattering. Excitations of one or both atoms to either a $2\,^1P$ or $3\,^1P$ state are considered along with the example of a mixed $(2\,^1P, 3\,^1P)$ transition. Correlation effects were found to be most important when both atoms were excited, the cross sections being reduced by about a quarter at low impact energies. For the description of angular correlation within He $(1\,^1S)$, configurations based on p orbitals were always the most significant thus reflecting the symmetry of the excited states. A brief comment is made regarding the elastic cross sections at large impact energies.

1. Introduction

Ground-state correlation effects are known to be of considerable significance when evaluating generalized oscillator strengths and inelastic scattering cross sections for closed-shell target systems; see, for example, Banyard and Seddon (1974), Banyard and Taylor (1974), and Seddon and Banyard (1974). For He and Li^+ we have already examined, within the first Born approximation, cross sections for the $1\,^1S \rightarrow 2\,^1P$ and $1\,^1S \rightarrow 3\,^1P$ excitations arising from the scattering of e^-, H^+ and H. Electron correlation was introduced into the description of the ground states in a systematic and well ordered manner by using configuration-interaction (CI) wavefunctions (Weiss 1961) expressed in the form of natural expansions (Löwdin 1955). In the present work we extend our analysis of ground-state correlation effects to a consideration of He–He scattering where both the projectile and target atoms may be excited from their ground states to the excited states $2\,^1P$ or $3\,^1P$ giving, in total, five possible inelastic reactions. A brief comment is also made regarding the elastic scattering cross sections.

2. Calculations and results

The theory of the first Born approximation is well known and we quote the expression for the total scattering cross section $Q(T)$ essentially to establish definitions for the purposes of discussion. For a collision between identical atoms we may write

$$Q(T) = \frac{4\pi M}{T} \int_{K_{min}}^{K_{max}} |\delta_{pq}Z - \epsilon_{pq}(-K)|^2 |\delta_{mn}Z - \epsilon_{mn}(K)|^2 K^{-3}\, dK \qquad (1)$$

where M is the mass of the projectile with kinetic energy T and K is the momentum

transfer. The limits K_{max} and K_{min} are determined from the kinematics of the reaction. The projectile and target atoms, of atomic number Z, are assumed to undergo excitations from states $p \to q$ and $m \to n$, respectively, and the corresponding form factors are denoted by $\epsilon_{pq}(-K)$ and $\epsilon_{mn}(K)$, these being determined here within the velocity formulation. Throughout the present work the atoms are initially in their ground states and the excited states are 2 ^{1}P and 3 ^{1}P. The latter are described, as before, in terms of anti-symmetrized products of hydrogen-like orbitals which, for such states, represent close approximations to Hartree–Fock (HF) orbitals; see Bell et al (1968). Equation (1) describes elastic scattering under the condition that the Kroenecker deltas are unity; K_{min} then becomes zero. At sufficiently high T the value for K_{max} is effectively infinite and the elastic cross section $Q(T)$ then behaves as BT^{-1} where the constant B can be referred to as the cross section coefficient. The natural expansion of the Weiss CI wavefunction was used to describe the ground state of He and $Q(T)$ values were determined for various orders, X, of truncation. Thus, as X is increased from unity (approximating the HF equivalent wavefunction) to fifteen (equal to Weiss' total wavefunction), electron correlation is introduced into the ground state through configurations which are well ordered by virtue of their energetically decreasing importance.

Results for the 3 ^{1}P excitation of both atoms and for a single atom are given in tables 1 and 2, respectively. For reasons of space, only selected results for the double and

Table 1. Cross sections $Q(T)$ (in units of 10^{-24} m^2) for He(1 ^{1}S)+He(1 ^{1}S) → He(3 ^{1}P)+ He(3 ^{1}P) for various orders of truncation, X, in the natural expansion of the ground-state wavefunction. Quoted after each X value is the symmetry of the basis orbitals used to form the additional natural configuration.

T(keV) \ X =	1(s)	2(p)	3(s)	4(d)	5(p)	6(s)	15(s)
100	0·1386	0·1171	0·0959	0·0938	0·0889	0·0880	0·0867
200	0·7202	0·6720	0·5881	0·5786	0·5570	0·5530	0·5466
400	1·432	1·418	1·294	1·278	1·242	1·235	1·225
600	1·568	1·587	1·469	1·454	1·417	1·411	1·400
1000	1·417	1·461	1·369	1·356	1·326	1·320	1·312
2000	0·9707	1·015	0·9597	0·9517	0·9318	0·9286	0·9236
4000	0·5693	0·5999	0·5694	0·5650	0·5536	0·5518	0·5491
8000	0·3084	0·3262	0·3103	0·3079	0·3019	0·3010	0·2995
12000	0·2112	0·2237	0·2129	0·2113	0·2072	0·2066	0·2056

Table 2. As in table 1, for He(1 ^{1}S)+He(1 ^{1}S) → He(1 ^{1}S)+He(3 ^{1}P).

T(keV) \ X =	1(s)	2(p)	3(s)	4(d)	5(p)	6(s)	15(s)
100	96·24	97·04	94·44	94·07	92·61	92·45	92·29
200	56·60	57·82	56·81	56·64	55·87	55·80	55·76
400	29·86	30·65	30·22	30·14	29·75	29·72	29·70
600	20·13	20·69	20·42	20·37	20·10	20·08	20·07
1000	12·16	12·50	12·34	12·31	12·15	12·14	12.14
2000	6·095	6·270	6·191	6·175	6·096	6·090	6·088
4000	3·050	3·137	3·098	3·090	3·051	3·048	3·047
8000	1·525	1·569	1·549	1·546	1·526	1·524	1·524
12000	1·017	1·046	1·033	1·030	1·017	1·016	1·016

single 2 ^{1}P excitations and the (2 ^{1}P, 3 ^{1}P) mixed excitation are presented in table 3. The symmetry of the basis orbitals used to construct each additional natural configuration as X is increased is given by Banyard and Baker (1969); however, for convenience, they are also quoted in the tables after each X value. Values for $Q(T)$, when $X = 15$, are compared graphically in figure 1.

Table 3. Cross sections $Q(T)$ (in units of 10^{-24} m^2) for $X = 1$ and 15 for the scattering products: the double excitation He(2 ^{1}P)+He(2 ^{1}P); He(1 ^{1}S)+He(2 ^{1}P); and the mixed double excitation He(2 ^{1}P)+He(3 ^{1}P).

	(2 ^{1}P, 2 ^{1}P)		(2 ^{1}P)		(2 ^{1}P, 3 ^{1}P)	
T(keV)	$X = 1$(s)	$X = 15$(s)	$X = 1$(s)	$X = 15$(s)	$X = 1$(s)	$X = 15$(s)
100	2·360	1·482	314·2	301.8	0·5692	0·3569
200	10·53	7·945	181·3	178·5	2·737	2·073
400	19·53	16·51	95·05	94·47	5·257	4·471
600	21·05	18·55	64·02	63·76	5·712	5·070
1000	18·89	17·25	38·62	38·52	5·149	4·735
2000	12·93	12·14	19·36	19·32	3·528	3·335
4000	7·596	7·232	9·686	9·666	2·072	1·986
8000	4·121	3·952	4·843	4·834	1·124	1·085
12000	2·824	2·714	3·229	3·223	0·7699	0·7448

3. Discussion

Our analysis is concerned with ground-state correlation effects. Therefore, our discussion will concentrate on results for transitions to the excited state which should, intuitively, be least influenced by correlation, namely the 3 ^{1}P state.

Correlation effects influence $Q(T)$ through improvements in (i) the transition energy, and (ii) the wavefunction used in the evaluation of the form factor. The nature of this dual dependence as X is increased has already been discussed (Seddon and Banyard 1974). Table 1 shows that for low impact energies the non-correlated result ($X = 1$) is reduced by about a quarter when using the total CI wavefunction ($X = 15$). However, as T increases, the results for $X = 1$ and 15 are seen to converge. The initial introduction of correlation, based on p orbitals and therefore of an essentially angular nature, causes a drop in the value of $Q(T)$ at low T and an increase at large T which results in an improvement and worsening, respectively, of the agreement with the $X = 15$ values. The addition of purely radial correlation through the inclusion of a configuration based on s orbitals as $X = 2 \rightarrow 3$ causes a reduction in $Q(T)$ for all T. However, at high energy the results are still inferior to the non-correlated values when compared with $X = 15$, even though we have accounted for 85 % of the correlation energy at $X = 3$. At low energies, on the other hand, a significant improvement has occurred. Table 1 also reveals that, relative to $X = 1$, the point of crossover of the $X = 3$ values occurs at a higher energy than that observed for $X = 2$. This latter trend continues as X increases, and when $X = 6$ the crossover point is in excess of 35 000 keV. In the energy range considered here, the results for $6 \leqslant X \leqslant 15$ exhibited a general convergence towards $X = 15$ as a consequence of being dependent essentially on the transition energy. Overall, p-based configurations were found to be of greater relative significance than other angular-based
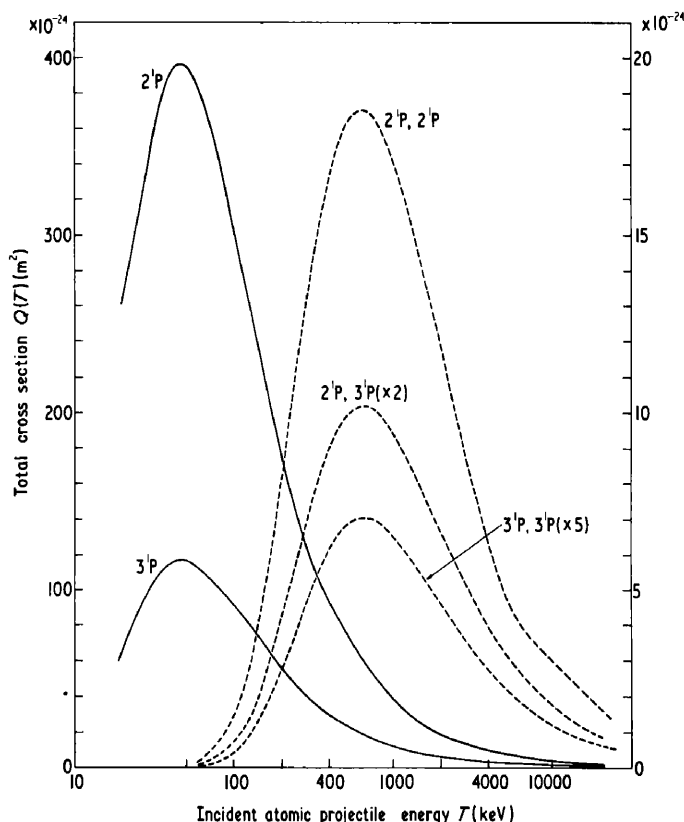
Figure 1. Comparisons of the single and double excitation cross sections $Q(T)$ (measured in units of 10^{-24} m^2) against T. The left-hand scale refers to the full curves and the right-hand scale is for the double excitations shown by broken curves.

configurations in their influence on $Q(T)$, irrespective of their ordering in X. Such a feature, reflecting the symmetry of the excited states, may well be modified if the 2 ^{1}P and 3 ^{1}P wavefunctions were of correlated form.

Inspection of table 2 shows that, as expected, the $Q(T)$ values for the single-atom excitation to the 3 ^{1}P state are larger than those for the double excitation. However, from a percentage point of view, correlation effects are seen to be of less importance. As X increases, the trends in relative magnitudes shown in table 2 follow those for the double excitation but the crossover points, with respect to $X = 1$, were found to occur at lower energies. As before, p-based configurations gave rise to the greatest change when introducing angular correlation. In passing, we note that the influence of correlation in the present case is less than that determined for the 3 ^{1}P excitation of He by He$^+$ ions although, in that instance, the $Q(T)$ values are larger due to the long-range nature of the interaction forces—cf table 4 of Seddon and Banyard (1974). A further comparison with table 4 of the earlier work indicates that at comparable velocities the present results are in close agreement with those for H–He (1 ^{1}S → 3 ^{1}P) scattering.

Cross sections for the double and single 2 ^{1}P excitation reactions are, of course, considerably larger than their 3 ^{1}P counterparts. For the single 2 ^{1}P excitation the trends in $Q(T)$ as X increased were found to parallel those observed for 3 ^{1}P. This also holds for comparisons between the double excitations except that, in contrast with (3 ^{1}P, 3 ^{1}P), the cross sections for the (2 ^{1}P, 2 ^{1}P) excitation for $X = 3$ were found to be superior to those for $X = 1$ over the whole energy range when compared with $X = 15$ as a reference. Although not shown in table 3, the influence of angular correlation on $Q(T)$

was once again dominated by the p-based configurations. For the mixed $(2\,^1P, 3\,^1P)$ excitation, $Q(T)$ corresponds most closely in magnitude with $(3\,^1P, 3\,^1P)$. This feature arises not only because of the nature of the integrand in equation (1) but also from the size of the lower limit K_{min}. Consequently, as X increases, the trends in $Q(T)$ at high energy follow those for the double $3\,^1P$ excitation.

The energy dependence of the single, double and mixed excitation cross sections for $X = 15$ can be compared by inspection of figure 1. We note that double and mixed excitations peak at a common T value; a similar observation holds for the single excitations. This behaviour has been rationalized in earlier work (Banyard and Seddon 1974, Seddon and Banyard 1974).

For elastic scattering the non-correlated $(X = 1)$ and correlated $(X = 15)$ values for B are 4·734 and 4·747, respectively (measured in units of $10^{-18}\,\text{m}^2\,\text{keV}^{-1}$). Such small changes for the elastic cross sections arise from the fact that, within the first Born approximation, we are evaluating a one-particle expectation property over a pure state and therefore it is easily shown that correlation effects are second order. However, for inelastic scattering, where we are dealing with transitions between different states, correlation can make a first-order contribution which, as seen, is clearly significant.

4. Summary

The influence of an ordered introduction of ground-state correlation has been examined for He–He scattering within the first Born approximation when one or both atoms are excited to low-lying $n\,^1P$ states. Electron correlation proved to be most significant at low projectile energies. For the double excitations, where correlation effects were of greatest importance, the cross sections were reduced by about a quarter at low T values. As observed earlier, correlation gave rise to similar trends irrespective of whether the excited state was $2\,^1P$ or $3\,^1P$—the cross sections possessing a maximum at approximately the same impact energy. The initial introduction of correlation for He was of an angular character and accounted for nearly half the total correlation energy; this resulted in a sizeable improvement over the non-correlated cross sections only for low-energy double excitations. In all other cases the agreement with the total correlated result was worse. A general improvement over the non-correlated results was not achieved until approximately 93 % of the ground-state correlation energy had been recovered. The observation regarding the relative importance of p-based angular correlation effects in the ground state when determining $Q(T)$ suggests an extension of our analysis to include correlation effects in the excited states.

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ABSTRACT

Part I

Total cross sections for high-energy inelastic collisions
between helium atoms originally in their ground state have been
obtained within the framework of the first Born approximation.
The ground state of the helium atoms was described by the 35-
configuration CI wavefunction of Weiss expressed in the form of
a natural expansion, thereby facilitating an examination of the
influence of ground state correlation effects on the scattering
cross sections.

Part II

The natural expansion of the Weiss 35-configuration
CI wavefunction for helium was used to assess the behaviour
of high-energy electron-capture cross sections for the reaction
$H^+ + He(1s^2) \rightarrow H(n\ell) + He^+(1s)$ when the target is described
by wavefunctions of varying sophistication. The impulse approxi-
mation and the continuum distorted wave approximation were used to
evaluate the above cross sections for proton impact energies
ranging from 25 keV to 3.5 MeV. It was found that, in contrast
with the impulse approximation, the continuum distorted wave
(CDW) method is easily applied to electron capture reactions
and overall gave the better agreement with experiment. The CDW
method was also used to obtain capture cross sections for alpha
particles impinging on a helium target.