Electron and proton scattering by hydrogen atoms in a coupled state approximation

Sullivan, Jan

ELECTRON AND PROTON SCATTERING BY HYDROGEN ATOMS IN A COUPLED STATE APPROXIMATION

by

Jan Sullivan

Department of Physics,
University of Durham.

This thesis is submitted to the University of Durham, September, 1972, in candidature for the Degree of Doctor of Philosophy.

Abstract.

The excitation of atomic hydrogen by electron and proton impact is examined. Some of the available theoretical methods are discussed, in particular the methods of the first and second Born approximation, the close coupling approximation and the Glauber approximation are outlined. The close coupling approximation is presented in both the wave and impact parameter formulations. The neglect of the continuum states in the eigenfunction expansion of the close coupling method is shown to be unsatisfactory and the methods of including the effects of these states described. The relationship between the two forms of close coupling approximation is explored via the eikonal approximation, and the Glauber approximation is shown to be a solution of a set of close coupled equations where all states are approximately included. A close coupling approximation that includes some eigenstates explicitly and the rest, including the continuum states, approximately is presented. The method is applied in the impact parameter approximation to electron and proton collisions with hydrogen. Results are presented for the 1s-2s and the 1s-2p excitation cross sections and are compared with the available experimental cross sections. This comparison is inconclusive and suggestions are made for further work. Comparison with other theoretical predictions suggest that the effects of charge transfer on the direct excitation process are not allowed for despite the inclusion of the continuum states.

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Preface

In this work we investigate electron and proton scattering by atomic hydrogen using a second order close coupling approximation. The method is applied to the intermediate energy range where the second order terms are thought to be important. Part I provides a brief description of the elements of scattering theory essential to this work. Part II describes some of the previous relevant work, and in part III we report our own work, the results obtained and their implications. The results obtained in part III are or will be published, Bransden et al. (1972), Sullivan et al. (1972).

It is a pleasure to express my thanks to my supervisor Dr. J. P. Coleman, and Professor B. H. Bransden for introducing me to the problem and for their expert guidance throughout this work. I should also like to thank my wife, Jennifer Sullivan, for her continuing encouragement, especially during the computational stages of this work. I acknowledge the financial support of the Science Research Council.

PART I

1. Time Dependent Scattering Theory

Quantum mechanics is thought to provide an adequate description of the interaction of charged particles with atoms. In a realistic treatment of the problem the incident particle should be represented by a wave packet, constructed from a superposition of eigenstates, to give the necessary localisations in time and space. The interaction of the particle with the atoms is then described by the time independent solutions of the Schrödinger equation. An equivalent approach, in that the same final results are obtained, is available. The incident particle is assumed to be in an eigenstate of particular energy and momentum both before and after the collision. Since this last approach is more straight forward than that utilising wave packets it is the one presented here.

Let $|\Psi^S, t_o\rangle$ be the state vector of the system at time $t = t_o$ in the Schrödinger picture. Then the Schrödinger equation of motion is

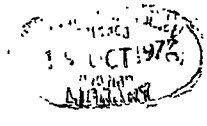
$$i \frac{\partial}{\partial t} |\Psi^S, t\rangle = H|\Psi^S, t\rangle \qquad (1.1)$$

The Hamiltonian, H, may be decomposed into an unperturbed part H_o, whose eigenfunctions and eigenvalues are in principle known, and a perturbation V. A state vector in the interaction picture may now be defined

$$|\Psi^i, t\rangle = e^{iH_o t} |\Psi^S, t\rangle \qquad (1.2)$$

Substituting equation (1.2) into the Schrödinger equation we obtain the equation of motion in the interaction picture

$$i \frac{\partial}{\partial t} |\Psi^i, t\rangle = V(t) |\Psi^i, t\rangle \qquad (1.3)$$



where

$$V(t) = e^{iH_o t} V e^{-iH_o t} \tag{1.4}$$

A time development operator, $\mu(t,t_o)$ may be defined in the interaction picture such that

$$|\Psi^i,t\rangle = \mu(t,t_o)\ |\Psi^i,t_o\rangle \tag{1.5}$$

then using equation (1.2) and

$$|\Psi^s,t\rangle = e^{-i\,H(t-t_o)}\ |\Psi^s,t_o\rangle \tag{1.6}$$

we obtain

$$\mu(t,t_o) = e^{iH_o t}\ e^{-i\,H(t-t_o)}\ e^{-iH_o t_o} \tag{1.7}$$

The operator $\mu(t,t_o)$ has the following properties:

$$\mu(0,t) = e^{iHt}\ e^{-iH_o t} \tag{1.8}$$

$$\mu^+(t,t_o) = e^{iH_o t_o}\ e^{i\,H(t-t_o)}\ e^{-iH_o t} = \mu(t_o,t) \tag{1.9}$$

$$\mu(t,t')\ \mu(t',t_o) = \mu(t,t_o) \tag{1.10}$$

To investigate a collision problem, a description of the system evolving from an initial state at $t = -\infty$ to a final state at $t = +\infty$, is required.

The scattering operator is defined as

$$S = \lim_{\substack{t_o \to -\infty \\ t \to +\infty}} \mu(t,t_o) \tag{1.11}$$

such that

$$|\Psi^i,+\infty\rangle = S|\Psi^i,-\infty\rangle \tag{1.12}$$

If there is no interaction at time t_o then

$$|\Psi^s,t_o\rangle = e^{-iE_it_o}|\psi_i\rangle \tag{1.13}$$

where $H_o|\psi_i\rangle = E_i|\psi_i\rangle$ and $|\psi_i\rangle$ is some initial state.

Since

$$|\psi_i\rangle = e^{iH_ot_o}|\Psi^s,t_o\rangle \tag{1.14}$$

then comparing this with equation (1.2) we can suppose that

$$|\Psi^i,-\infty\rangle = |\psi_i\rangle$$

The final state in the interaction picture will be a superposition of eigenstates of H_o. Thus

$$|\Psi^i,+\infty\rangle = \sum_n a_n|\psi_n\rangle$$

and

$$S|\psi_i\rangle = \sum_n S_{in}|\psi_n\rangle$$

hence the transition amplitude S_{if} is given by

$$S_{if} = \langle\psi_f|S|\psi_i\rangle \tag{1.15}$$

$$= \lim_{\substack{t_o\to-\infty \\ t\to+\infty}} \langle\psi_f|\mu(t,0)\ \mu(0,t_o)|\psi_i\rangle \tag{1.16}$$

To evaluate the limits implied by equation (1.16) we adopt a procedure due to Gell-Mann and Goldberger (1953). The limit of $f(t)$ as $t \to \pm\infty$ is defined as

$$\lim_{t\to-\infty} f(t) = \lim_{\varepsilon\to 0^+} \varepsilon \int_{-\infty}^{0} e^{\varepsilon t'} f(t')\, dt' \tag{1.17}$$

and

$$\lim_{t\to+\infty} f(t) = \lim_{\varepsilon\to 0^+} \varepsilon \int_{0}^{\infty} e^{-\varepsilon t'} f(t')\, dt' \tag{1.18}$$

If the Møller operator is defined as

$$\Omega^+ = \lim_{t\to-\infty} \mu(0,t) \tag{1.19}$$

then

$$\Omega^+|\psi_a\rangle = \lim_{\varepsilon\to 0^+} \varepsilon \int_{-\infty}^{0} e^{\varepsilon t'} e^{iHt'} e^{-iE_a t'} |\psi_a\rangle\, dt'$$

$$= \lim_{\varepsilon\to 0^+} \frac{i\varepsilon}{E_a - H + i\varepsilon} |\psi_a\rangle \tag{1.20}$$

then

$$\Omega^+|\psi_a\rangle = |\psi_a^+\rangle = \lim_{\varepsilon\to 0^+} \frac{1}{E_a - H + i\varepsilon} (i + E_a - H_o)|\psi_a\rangle$$

$$\therefore \quad |\psi_a^+\rangle = |\psi_a\rangle + \frac{1}{(E_a - H + i\varepsilon)} V|\psi_a\rangle \tag{1.21}$$

From equation (1.20) it is apparent that $(E_a - H)|\psi_a^+\rangle = 0$, thus $|\psi_a^+\rangle$ is an eigenstate of H with eigen energy E_a.

Similarly if Ω^- is defined as the $\lim_{t\to+\infty} \mu(0,t)$ and $\Omega^-|\psi_a\rangle = |\psi_a^-\rangle$ then

$$|\psi_a^-\rangle = |\psi_a\rangle + \frac{1}{E_a - H - i\varepsilon} V|\psi_a\rangle \tag{1.22}$$

and equation (1.16) becomes

$$S_{if} = \langle\psi_f^-|\psi_i^+\rangle \tag{1.23}$$

It will be seen later that $|\psi_f^-\rangle$ and $|\psi_i^+\rangle$ satisfy different boundary conditions. In equations (1.21) and (1.22) the limit $\varepsilon \to 0^+$ is implied.

The scattering matrix element may be written as

$$S_{if} = \delta_{if} - 2\pi i\, \delta(E_f - E_i)\, T_{if} \tag{1.24}$$

where

$$T_{if} = \langle \psi_f | V | \psi_i^+ \rangle \tag{1.25}$$

T_{if} is a matrix element of the operator T defined such that

$$T|\psi_i\rangle = V|\psi_i^+\rangle \tag{1.26}$$

The transition probability per unit time, denoted by W_{if}, at time t is

$$W_{if} = \lim_{t_o \to -\infty} \frac{\partial}{\partial t} \left| \langle \psi_f | \mu(t,t_o) | \psi_i \rangle \right|^2 \tag{1.27}$$

$$= 2\, \mathrm{Im}\, T_{ii}\, \delta_{if} + 2\pi\, \delta(E_i - E_f) |T_{if}|^2 \tag{1.28}$$

The singularity δ_{if} in equation (1.28) is removed by considering a transition to a group of states about $E = E_f$ instead of to a specified final state. A particular state is characterised by energy E, and momentum vector $\underline{k}$. Let the number of states with momentum vectors within $d\Omega$ and energies in the range E to E + dE be $\rho(E)\, dE\, d\Omega$.

If $|\psi_i\rangle$ does not belong to this final set of states W_{if} becomes

$$W_{if} = \int_{E_f - E}^{E_f + E} W_{if}\, \rho(E)\, dE\, d\Omega$$

$$= 2\pi\, \rho(E_f)\, |T_{if}|^2 \text{ where } E_i = E_f \tag{1.29}$$

Box normalisation gives the density of states to be

$$\rho(E) = \frac{\mu K}{8\pi^3} \tag{1.30}$$

where $E = K^2/2\mu$, and μ is the reduced mass.

$$\therefore \qquad W_{if} = \frac{\mu K_f}{4\pi^2} |T_{if}|^2 \, d\Omega \qquad (1.31)$$

W_{if} is the transition probability per unit time for an incident flux of K_i/μ, hence the differential cross section is given by

$$I(\Omega) = \frac{\mu^2}{4\pi^2} \frac{K_f}{K_i} |T_{if}|^2 \qquad (1.32)$$

and the total cross section Q,

$$Q = \frac{\mu^2}{4\pi^2} \frac{K_f}{K_i} \int |T_{if}|^2 \, d\Omega \qquad (a_o^2) \qquad (1.33)$$

The above analysis expresses the total and differential cross sections in terms of the transition matrix which in turn may be written in terms of the total wave function. All these quantities however remain undetermined except formally.

An iterative expression for the transition matrix can be obtained allowing an approximate solution to the scattering problem

$$T_{if} = \langle \psi_f | V | \psi_i^+ \rangle$$

$$= \langle \psi_f | V(1+G^+V) | \psi_i \rangle \qquad (1.34)$$

where $G^+ = \frac{1}{E-H+i\varepsilon}$.

Now consider the following identities

$$P^{-1} = Q^{-1} + P^{-1}(Q-P)\, Q^{-1} \qquad (1.35)$$

$$= Q^{-1} + Q^{-1}(Q-P)\, P^{-1} \qquad (1.36)$$

with $P = E - H + i\varepsilon$, $Q = E - H_o + i\varepsilon$. Then

$$G^+ = G_o^+ + G_o^+ V G^+ \qquad (1.37)$$

where $G_o^+ = \frac{1}{E-H_o+i\varepsilon}$.

If G^+ on the right hand side of (1.37) is successively replaced by G^+ given by (1.37), we obtain the series

$$G^+ = G_o^+ + G_o^+ V G_o^+ + G_o^+ V G_o^+ V G_o^+ + \ldots \qquad (1.38)$$

then

$$T_{if} = \langle\psi_f|V(1+G_o^+ V+G_o^+ V G_o^+ V+ \ldots)|\psi_i\rangle$$

$$= \langle\psi_f|V|\psi_i\rangle + \langle\psi_f|V G_o^+ V|\psi_i\rangle + \ldots \qquad (1.39)$$

The series obtainedfor the transition matrix element is known as the Born series. The n^{th} Born approximation is obtained by retaining the first n terms of the series. For example in the first Born approximation T_{if} becomes

$$T_{if}^B = \langle\psi_f|V|\psi_i\rangle \qquad (1.40)$$

More directly T_{if}^B can be obtained from T_{if} by replacing $|\psi_i^+\rangle$ by $|\psi_i\rangle$. This corresponds to the physical situation where the incident particle velocity is large compared with the velocities of the target particles, then the distortion of the system due to the interaction may be disregarded in calculating the scattering amplitudes. Thus the Born amplitude is expected to be the high energy limit of the Born series. This would be satisfied if the Born series were a convergent or asymptotic series. There have been no conclusive investigations of the convergence properties of the Born series. If the series is convergent then for lower energies one would expect a systematic improvement of results as more terms are included in the series.

Such an approach is impractical since only the first Born term can be evaluated exactly.

2. The Coordinate Representation

Consider a particle charge z colliding with a hydrogen atom. In figure (1) the positions of the particles are shown relative to an arbitrary origin O. Particles 1,2,3 are the incoming particle, hydrogen nucleus and the orbital electron respectively. The masses of the particles are denoted by m_1, m_2 and m_3, where $m_3 << m_2$.

The Schrödinger equation for the collision is

$$\left[-\frac{1}{2m_1}\nabla_1^2 - \frac{1}{2m_2}\nabla_2^2 - \frac{1}{2m_3}\nabla_3^2 + V(\underset{\sim}{r}_O, \underset{\sim}{R}_1, \underset{\sim}{R}_2) \right] \psi_T = E_T \psi_T \qquad (2.1)$$

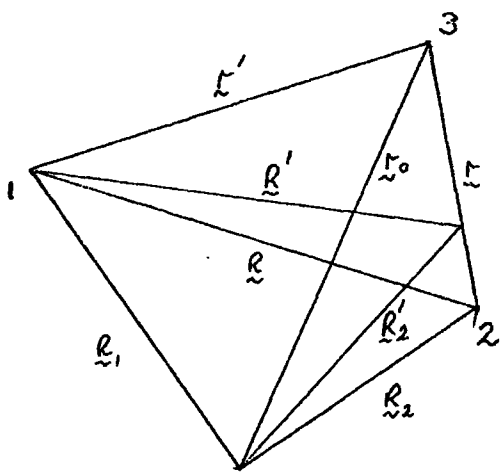


Fig (1)

The form of equation (2.1) is much simplified when the centre of mass motion is separated out.

Transform to coordinates given by

$$(m_2+m_3)\,\underset{\sim}{R}_2{}' = m_2\,\underset{\sim}{R}_2 + m_3\,\underset{\sim}{r}_O$$

and

$$\underset{\sim}{R}' = \underset{\sim}{R}_1 - \underset{\sim}{R}_2'$$

then

$$\frac{1}{2m_2} \nabla_2^2 + \frac{1}{2m_3} \nabla_3^2 = \frac{1}{2(m_2+m_3)} \nabla_{R_2'}^2 + \frac{(m_2+m_3)}{2m_2m_3} \nabla_{\underset{\sim}{r}}^2$$

where $\underset{\sim}{R}_2'$ is the position vector of the centre of mass of the target atom.

Now transform to the overall centre of mass, $\underset{\sim}{R}_{C.M.}$

$$(m_1+m_2+m_3)\, \underset{\sim}{R}_{C.M.} = m_1\, \underset{\sim}{R}_1 + (m_2+m_3)\, \underset{\sim}{R}_2'$$

and

$$\underset{\sim}{R}' = \underset{\sim}{R}_1 - \underset{\sim}{R}_2'$$

thus the Schrödinger equation becomes

$$\left[- \frac{1}{2M} \nabla_{C.M.}^2 - \frac{(m_2+m_3)}{2m_2m_3} \nabla_r^2 - \frac{M}{2m_1(m_2+m_3)} \nabla_{\underset{\sim}{R}'}^2 + V(\underset{\sim}{R}', \underset{\sim}{r}) - E_T \right] \psi_T = 0 \qquad (2.2)$$

where $M = m_1 + m_2 + m_3$.

The translational motion of the centre of mass may now be separated out to give

$$\left[- \frac{1}{2\mu'} \nabla_r^2 - \frac{1}{2\mu} \nabla_{R'}^2 + V(\underset{\sim}{R}', \underset{\sim}{r}) - E \right] \psi\, (\underset{\sim}{R}', \underset{\sim}{r}) = 0 \qquad (2.3)$$

where $\mu' = \frac{m_2m_3}{(m_3+m_2)}$ and $\mu = \frac{m_1(m_2+m_3)}{(m_1+m_2+m_3)}$.

Since for all collisions considered in this work $m_2 >> m_3$ then $\mu' \sim m_3$, $\underset{\sim}{R}' \sim \underset{\sim}{R}$ and $\mu = \frac{m_1m_2}{m_1+m_2}$ hence equation (2.3) becomes

$$\left[- \frac{1}{2\mu} \nabla_R^2 - \frac{1}{2m_3} \nabla_r^2 + V(R,r) - E \right] \psi\, (\underset{\sim}{R}, \underset{\sim}{r}) = 0 \qquad (2.4)$$

This equation holds for both proton and electron impact though the reduced mass μ will be different.

The unperturbed Hamiltonian of section I now becomes

$$H_o = -\frac{1}{2\mu}\nabla_R^2 - \frac{1}{2M_3}\nabla_r^2 + \frac{1}{|\underset{\sim}{r}|}$$

and the interaction potential

$$V = z\left(\frac{1}{|\underset{\sim}{R}|} - \frac{1}{|\underset{\sim}{R}-\underset{\sim}{r}|}\right)$$

The eigenfunction of the unperturbed Hamiltonian is

$$\psi_i(\underset{\sim}{R},\underset{\sim}{r}) = e^{i\,\underset{\sim}{K}.\underset{\sim}{R}}\,\phi_i(\underset{\sim}{r}) \qquad (2.5)$$

The scattering amplitudes may be found by considering the asymptotic form of the scattering solution given by equations (1.21) and (1.22)

$$|\psi_a^{\pm}\rangle = |\psi_a\rangle + \frac{1}{(E_a - H \pm i\varepsilon)}\,V\,|\psi_a\rangle \qquad (2.6)$$

and using the identities (1.36) and (1.37)

$$\frac{1}{E_a - H \pm i\varepsilon} = \frac{1}{E_a - H_o \pm i\varepsilon} + \frac{1}{E_a - H_o \pm i\varepsilon}\,V\,\frac{1}{E_a - H \pm i\varepsilon} \qquad (2.7)$$

then equation (2.6) becomes

$$|\psi_a^{\pm}\rangle = |\psi_a\rangle + \frac{1}{E_a - H_o \pm i\varepsilon}\,V\,|\psi_a^{\pm}\rangle \qquad (2.8)$$

In the co-ordinate representation this becomes

$$\psi_a^{\pm}(\underset{\sim}{R},\underset{\sim}{r}) = \psi_a(\underset{\sim}{R},\underset{\sim}{r}) + \int G_o^{\pm}(\underset{\sim}{R},\underset{\sim}{r};\ \underset{\sim}{R}',\underset{\sim}{r}')\,V(\underset{\sim}{R}',\underset{\sim}{r}')\,\psi_a^{\pm}(\underset{\sim}{R}',\underset{\sim}{r}')\,d\underset{\sim}{R}'\,d\underset{\sim}{r}' \qquad (2.9)$$

where

$$G_o^{\pm}(\underset{\sim}{R},\underset{\sim}{r};\ \underset{\sim}{R}',\underset{\sim}{r}') = \langle \underset{\sim}{R},\underset{\sim}{r}\left|\frac{1}{E_a - H_o \pm i\varepsilon}\right|\underset{\sim}{R}',\underset{\sim}{r}'\rangle$$

Inserting a complete set of basis states defined by equation (2.5)

$$G_o^{\pm}(\underset{\sim}{R},\underset{\sim}{r};\ \underset{\sim}{R}',\underset{\sim}{r}') = \frac{2\mu}{(2\pi)^3} \sum_n \phi_n(\underset{\sim}{r})\ \phi_n^*(\underset{\sim}{r}') \int d\underset{\sim}{K}\ \frac{e^{\pm i\ \underset{\sim}{K}.(\underset{\sim}{R}-\underset{\sim}{R}')}}{K_n^2 - K^2 \pm i\varepsilon} \qquad (2.10)$$

where $K_n^2 = 2\mu(E_a - E_n)$ and the summation over the target states Σ_n includes an integration over the continuum target states.

Performing the $\underset{\sim}{K}$ integration of equation (2.10) $G_o^{\pm}$ becomes

$$G_o^{\pm}(\underset{\sim}{R},\underset{\sim}{r};\ \underset{\sim}{R}',\underset{\sim}{r}') = -\frac{2\mu}{4\pi} \sum_n \frac{e^{\pm i\ K_n\ |\underset{\sim}{R}-\underset{\sim}{R}'|}}{|\underset{\sim}{R}-\underset{\sim}{R}'|}\ \phi_n(\underset{\sim}{r})\ \phi_n^*(\underset{\sim}{r}') \qquad (2.11)$$

thus the integral equation becomes

$$\psi_o^{\pm}(\underset{\sim}{R},\underset{\sim}{r}) = \psi_o(R,r) - \frac{1}{4\pi} \sum_n \phi_n(\underset{\sim}{r}) \int d\underset{\sim}{R}'\ d\underset{\sim}{r}'\ \frac{e^{\pm i\ K_n\ |\underset{\sim}{R}-\underset{\sim}{R}'|}}{|\underset{\sim}{R}-\underset{\sim}{R}'|}$$

$$\times\ \phi_n^*(\underset{\sim}{r}')\ \mu(\underset{\sim}{R}',\underset{\sim}{r}')\ \psi_c^{\pm}(\underset{\sim}{R}',\underset{\sim}{r}') \qquad (2.12)$$

where $\mu(\underset{\sim}{R},\underset{\sim}{r}) = 2\mu\ V(\underset{\sim}{R},\underset{\sim}{r})$.

Now consider the limit of $\psi_o^{\pm}(\underset{\sim}{R},\underset{\sim}{r})$ as $\underset{\sim}{R} \to \infty$.

If $\phi_n^*(r')$ is a bound state, then $\int d\underset{\sim}{r}'\ \phi_n^*(\underset{\sim}{r}')\ \mu(\underset{\sim}{R}',\underset{\sim}{r}')\ \psi_o^{\pm}(R',r')$ is a rapidly decreasing function of $\underset{\sim}{R}'$ for large $\underset{\sim}{R}'$. Thus there is an effective upper bound on $\underset{\sim}{R}'$ outside which there is a negligible contribution to the integral with respect to $\underset{\sim}{R}'$. If $\underset{\sim}{R}$ gets larger than the upper bound on $\underset{\sim}{R}'$ we may expand $|\underset{\sim}{R}-\underset{\sim}{R}'|$ as follows

$$|\underset{\sim}{R}-\underset{\sim}{R}'| = R\left(1 - \frac{R'}{R}\ (\hat{\underset{\sim}{R}}.\hat{\underset{\sim}{R}}') + \ldots\right) \qquad \text{for } R \gg R'$$

hence

$$\psi_o^{\pm}(\underset{\sim}{R},\underset{\sim}{r}) \underset{R\to\infty}{\to} \psi_o(\underset{\sim}{R},\underset{\sim}{r}) - \frac{1}{4\pi} \sum_n \phi_n(\underset{\sim}{r})\ \frac{e^{\pm i\ K_n\ R}}{R} \int d\underset{\sim}{R}' d\underset{\sim}{r}'\ e^{-i\ \underset{\sim}{K}_n.\underset{\sim}{R}'}\ \phi_n(\underset{\sim}{r}')\mu(\underset{\sim}{R}',\underset{\sim}{r}')\psi_o^{\pm}(\underset{\sim}{R}',\underset{\sim}{r}')$$

$$- \frac{1}{4\pi} \int d\underset{\sim}{K}'\ \phi_{K'}(r) \int d\underset{\sim}{R}'\ d\underset{\sim}{r}'\ \frac{e^{\pm i\ K|\underset{\sim}{R}-\underset{\sim}{R}'|}}{|\underset{\sim}{R}-\underset{\sim}{R}'|}\ \phi_{K'}^*(\underset{\sim}{r}')\ \mu(\underset{\sim}{R}',\underset{\sim}{r}')\ \psi_o^{\pm}(\underset{\sim}{R}',\underset{\sim}{r}') \qquad (2.13)$$

The third term of this expression arises from the continuum target states included by equation (2.12) and corresponds to an ionization process where the bound electron is excited to a continuum state of the target. The first two terms of equation (2.13) may be written

$$e^{i \underset{\sim}{K}_o . \underset{\sim}{R}} \phi_o(\underset{\sim}{r}) + \sum_n \frac{e^{\pm i K_n R}}{R} f_{on}(\hat{\underset{\sim}{K}}_o, \hat{\underset{\sim}{K}}_n) \phi_n(\underset{\sim}{r}) \qquad (2.14)$$

this corresponds to a plane wave incident on a target described by $\phi_o(\underset{\sim}{r})$ being scattered into radial waves $\frac{e^{\pm i K_n R}}{R}$. The positive exponent in equation (2.14) corresponds to an outgoing radial wave and the negative exponent to an incoming radial wave. The latter situation is a time reversal of the first as would be expected from the initial derivation of $|\psi^{\pm}>$. The scattering amplitude $f_{on}(\hat{\underset{\sim}{K}}_o, \hat{\underset{\sim}{K}}_n)$ corresponds to initial and final momenta, $\underset{\sim}{K}_o$ and $\underset{\sim}{K}_n$ respectively and excitation of the target from states 0 to n.

$$f_{on}(\hat{\underset{\sim}{K}}_o, \hat{\underset{\sim}{K}}_n) = -\frac{1}{4\pi} \int d\underset{\sim}{R}' \, d\underset{\sim}{r}' \, e^{\mp i \underset{\sim}{K}_n . \underset{\sim}{R}'} \phi_n^*(r') \, \mu(\underset{\sim}{R}', \underset{\sim}{r}') \, \psi_o^{\pm}(\underset{\sim}{R}', \underset{\sim}{r}') \qquad (2.15)$$

The scattering amplitude could be obtained more directly from the transition matrix element of equation (1.25).

$$T_{if} = <\psi_f | V | \psi_i^+>$$

In the co-ordinate representation this becomes

$$T_{on}(\hat{\underset{\sim}{K}}_o, \hat{\underset{\sim}{K}}_n) = \int d\underset{\sim}{R}' \, d\underset{\sim}{r}' \, \psi_n^*(\underset{\sim}{R}', \underset{\sim}{r}') \, V(\underset{\sim}{R}', \underset{\sim}{r}') \, \psi_o^{\pm}(\underset{\sim}{R}', \underset{\sim}{r}')$$

$$= -\frac{2\pi}{\mu} f_{on}(\hat{\underset{\sim}{K}}_o, \hat{\underset{\sim}{K}}_n)$$

so that $$I(\Omega) = \frac{K_n}{K_o} |f_{on}|^2 \qquad (2.16)$$

3. Partial Wave Analysis

Partial wave analysis provides a method by which the scattering amplitudes can be calculated. The objective of this method is to convert the time-independent Schrödinger equation from a partial differential equation into a set of ordinary differential equations, for which the techniques of solution are better known.

The asymptotic form of the total wavefunctions is

$$\psi^{+}(R,r) \underset{R\to\infty}{\to} e^{i \underset{\sim}{K}_o \cdot \underset{\sim}{R}} \phi_o(\underset{\sim}{r}) + \sum_n \frac{e^{i K_n R}}{R} f_{on}(\hat{\underset{\sim}{K}}_o, \hat{\underset{\sim}{K}}_n)\, \phi_n(\underset{\sim}{r}) \qquad (3.1)$$

The incident plane wave may be expanded as

$$e^{i \underset{\sim}{K} \cdot \underset{\sim}{R}} = 4\pi \sum_{\ell=0}^{\infty} i^{\ell} j_{\ell}(KR) \sum_m Y^{*}_{\ell m}(\hat{\underset{\sim}{K}})\, Y_{\ell m}(\hat{\underset{\sim}{R}}) \qquad (3.2)$$

Here $j_{\ell}(KR)$ is the spherical Bessel function and has the following behaviour for large arguments

$$j_{\ell}(x) \underset{x\to\infty}{\to} \frac{\sin(x-\ell\pi/2)}{x} \qquad (3.3)$$

The scattering amplitudes may also be expanded in terms of the complete sets $Y^{*}_{\ell_o m_o}(\hat{\underset{\sim}{K}}_o)$ and $Y_{\ell m}(\hat{\underset{\sim}{K}}_n)$ as

$$f_{on}(\hat{\underset{\sim}{K}}_o, \hat{\underset{\sim}{K}}_n) = \frac{2\pi}{(K_o K_n)^{1/2}} \sum_{\substack{\ell_o m_o \\ \ell m}} i^{\ell_o - \ell + 1}\, T(n_o\, \ell_o\, m_o | n \ell m)$$

$$\times\, Y^{*}_{\ell_o m_o}(\hat{\underset{\sim}{K}}_o)\, Y_{\ell m}(\hat{\underset{\sim}{K}}_n) \qquad (3.4)$$

Since $\hat{\underset{\sim}{K}}_n$ is defined by $\hat{\underset{\sim}{R}}$ in the asymptotic region, the total wavefunctions may be written as

$$\psi^+(R,r) \underset{R\to\infty}{\to} 2\pi \sum_{\substack{\ell_o m_o \\ \ell m}} i^{\ell_o+1} Y_{\ell_o m_o}^*(\hat{K}_o) Y_{\ell m}(\hat{K}_n) \frac{\phi_n(r)}{R(K_o K_n)^{1/2}}$$

$$\times \left[\delta_{n_o \ell_o m_o, n\ell m} e^{-i(K_n R - \ell\pi/2)} \right.$$

$$\left. - S(n_o \ell_o m_o | n\ell m) e^{i(K_n R - \frac{1}{2}\ell\pi)} \right] \qquad (3.5)$$

where $T = \delta - S$.

This form of the wavefunction shows the incoming radial waves and outgoing scattered radial waves, the amplitudes of the latter being given by the appropriate S-matrix element. The conservation of the flux of particles requires that the S-matrix is unitary.

$$\sum_{n\ell m} |S(n_o \ell_o m_o | n\ell m)|^2 = 1 \qquad (3.6)$$

The wavefunction may also be expanded in a complete set of target states

$$\psi^+(R,r) = \sum_n F_n(R) \phi_n(r) \qquad (3.7)$$

substituting in the Schrödinger equation of the previous section we get

$$\left[\nabla_R^2 + K_n^2 \right] F_n(R) = \sum_m F_m(R) V_{nm}(R) \qquad (3.8)$$

where $V_{nm}(R) = \int \phi_n^*(r) V(R,r) \phi_m(r) \, dr$.

Now expanding

$$F_n(R) = 2\pi \sum_{\substack{\ell_o m_o \\ \ell m}} \frac{i^{\ell_o+1}}{(K_o K_n)^{1/2}} f_{\Gamma \Gamma_o}(R) Y_{\ell_o m_o}^*(\hat{K}_o) Y_{\ell m}(\hat{R}) \qquad (3.9)$$

where $\Gamma \equiv n\ell m$,

with the asymptotic conditions

$$f_{\Gamma_o\Gamma}(R) \underset{R\to\infty}{\to} \left[\delta_{\Gamma_o\Gamma} e^{-i(K_n R-\ell\pi/2)} - S_{\Gamma_o\Gamma} e^{i(K_n R-\ell\pi/2)}\right]$$

and $$f_{\Gamma_o\Gamma}(0) = 0$$

and substituting equation (3.9) in (3.8) we would obtain a set of second order ordinary differential equations for the radial functions $f_{\Gamma_o\Gamma}(R)$. If the summation on the right hand side of equation (3.8) is truncated at m = N then a set of N differential equations will result. The asymptotic forms of $f_{\Gamma_o\Gamma}(R)$ can then be calculated to yield the T-matrix elements.

From equation (2.16) the total cross-section is given by

$$Q_{on}(\hat{K}_o) = \frac{K_n}{K_o} \int d\hat{K}_n \, |f_{on}(\hat{K}_o, \hat{K}_n)|^2 \qquad (3.10)$$

using equation (3.9)

$$Q_{on}(\hat{K}_o) = \frac{4\pi^2}{K_o^2} \sum_{\substack{\ell_o m_o \ell_o' m_o' \\ \ell m}} T(n_o \ell_o m_o | n\ell m)\, T^*(n_o \ell_o' m_o' | n\ell m) \times Y^*_{\ell_o m_o}(\hat{K}_o)\, Y_{\ell_o' m_o'}(\hat{K}_o)$$

and averaging over all directions of incidence

$$Q_{on} = \frac{\pi}{(K_o)^2} \sum_{\substack{\ell_o m_o \\ \ell m}} |T(n_o \ell_o m_o | n\ell m)|^2 \qquad (3.11)$$

This type of formulation can only be applied to electron collisions since for proton collisions the partial wave expansion is only slowly convergent and a large number of cases would have to be considered.

The above analysis has been done in a completely uncoupled representation of atomic and incident particle states as the basis set. There is considerable advantage in considering a coupled representation, this is done in a later section.

4. Rearrangement Collisions

Our interest in rearrangement collisions here is restricted to their effects on elastic and excitation cross-sections. Rearrangement includes the exchange of one electron for the other in the case of the electron collision, and in the case of a proton collision the capture of the orbital electron by the incoming proton. This latter process is known as charge transfer and its effects are dealt with in some detail later.

The exact wavefunction $\psi^+(\underset{\sim}{R},\underset{\sim}{r})$ may be expanded in a complete set of basis states

$$\psi^+(\underset{\sim}{R},\underset{\sim}{r}) = \sum_n F_n(\underset{\sim}{R})\ \phi_n(\underset{\sim}{r}) + \int d\underset{\sim}{K}\ \phi_K(\underset{\sim}{r})\ F_K(\underset{\sim}{R}) \qquad (4.1)$$

the integral term is a continuous summation over the continuum states. For energetically accessible channels the expansion coefficients must have the asymptotic form

$$F_n(\underset{\sim}{R}) \underset{R\to\infty}{\to} e^{i\,\underset{\sim}{K}_o\cdot\underset{\sim}{R}}\,\delta_{on} + f_{on}(\theta)\,\frac{e^{i\,K_n\,R}}{R} \qquad (4.2)$$

To allow for the possibility of electron exchange the wavefunction $\psi^+(R,r)$ must have an additional boundary condition.

$$\psi^+(R,r) \underset{r\to\infty}{\to} \sum_n g_{on}(\theta)\,\frac{e^{i\,K_n\,r}}{r}\,\phi_n(\underset{\sim}{R}) \qquad (4.3)$$

It is not obvious how expansion (4.1) can satisfy the boundary conditions of (4.3) since from equation (4.1)

$$\psi^+(R,r) \underset{r\to\infty}{\to} \int d\underset{\sim}{K}\ \phi_K(\underset{\sim}{r})\ F_K(\underset{\sim}{R}) \qquad (4.4)$$

In general $\phi_K(\underset{\sim}{r})$ will be oscillating functions so that

$$\lim_{r\to\infty} \psi^+(R,r) = 0$$

However Castillejo et al. (1960) have shown, in the special case of elastic scattering, that $F_K(\underset{\sim}{R})$ contain singularities. Integrating around these singularities yields the correct asymptotic form of $\psi^+(R,r)$ for exchange. This implies that it is necessary to include the continuum states in expansions such as (4.1) in order to describe the exchange collision process adequately. The expansion (4.1) with boundary conditions (4.2) and (4.3) is unique. The exchange boundary condition (4.3) removes the arbitraryness introduced by the singularities of $F_K(\underset{\sim}{R})$. The singularities may be avoided by considering an overcomplete expansion

$$\psi^+(R,r) = \sum_n \phi_n(\underset{\sim}{r})\, F_n(\underset{\sim}{R}) + \sum_m \phi_m(\underset{\sim}{R})\, G_m(\underset{\sim}{r}) \qquad (4.5)$$

and choosing $F_n(\underset{\sim}{R})$ and $G_m(\underset{\sim}{r})$ to be non-singular. The expansion (4.5) then has the correct boundary conditions for large $\underset{\sim}{R}$ or $\underset{\sim}{r}$ since for large $\underset{\sim}{R}$ only the first term will contribute and for large $\underset{\sim}{r}$ only the second.

The Pauli exclusion principle requires that the overall wavefunction be antisymmetric with respect to the interchange of the space and spin coordinates of the two electrons. Such a wavefunction can be constructed since the Hamiltonian is symmetric in $\underset{\sim}{R}$ and $\underset{\sim}{r}$. Thus

$$\chi^{\pm}(R,r) = \psi^+(R,r) \pm \psi^+(r,R) \qquad (4.6)$$

The function χ^+ is associated with the singlet spin function, and χ^- with the triplet spin function. $\chi^{\pm}$ has the following asymptotic form

$$\chi^{\pm}(R,r) \underset{R\to\infty}{\to} \sum_n \left[\phi_n(\underset{\sim}{r})\, e^{i\, \underset{\sim}{K}_n \cdot \underset{\sim}{R}}\, \delta_{on} + (f \pm g)\, \frac{e^{i\, K_n R}}{R}\, \phi_n(\underset{\sim}{r}) \right] \qquad (4.7)$$

The combination of spin states of the two electrons to give spin wavefunctions of definite symmetry shows that the scattering is divided three to one between triplet and singlet modes so that for random spin orientations the differential cross section becomes

$$I_{on}(\Omega) = \frac{K_n}{K_o} \left[\tfrac{3}{4} \, |f-g|^2 + \tfrac{1}{4} \, |f+g|^2 \right] \qquad (4.8)$$

From equation (4.6) $\chi^{\pm}$ may be expanded as

$$\chi^{\pm}(R,r) = \sum_n \phi_n(\underset{\sim}{r}) \, F_n(\underset{\sim}{R}) \pm \sum_n \phi_n(\underset{\sim}{R}) \, G_n(\underset{\sim}{r}) \qquad (4.9)$$

then $\chi^{\pm}$ has the appropriate symmetry properties and F and G may be chosen to be continuous giving the correct boundary conditions in the limit of large $\underset{\sim}{R}$ or $\underset{\sim}{r}$.

P A R T I I

In the first part we reviewed the necessary elements of scattering theory. In this part the theory is applied and some existing calculations described. Since any calculations performed can only be done in a manner such that they only approximate the exact theory then we seek to isolate the components of the exact theory that are necessary for a satisfactory approximate theory. There have been a great many different attempts to describe electron and proton collisions with hydrogen. Here we only describe a few of these, selected because of their relevance to our own work.

5. The First Born Approximation

The importance of this approximation is in the belief that it is the high energy limit of the exact quantal solution to the scattering problem. Its other advantage is that it is relatively simple to evaluate compared with other approximations.

The transition matrix element for the first Born approximation is given by equation (1.40)

$$T_{if}^{B} = \langle \psi_f | V | \psi_i \rangle$$
$$= \int d\underset{\sim}{R}\, d\underset{\sim}{r}\, e^{i(\underset{\sim}{K}_i - \underset{\sim}{K}_f).\underset{\sim}{R}}\, V(\underset{\sim}{R},\underset{\sim}{r})\, \phi_f^*(\underset{\sim}{r})\, \phi_i(\underset{\sim}{r}) \qquad (5.1)$$

now consider the momentum transfer $\underset{\sim}{p} = \underset{\sim}{K}_i - \underset{\sim}{K}_f$, then since by Bethes integral we have

$$\int d\underset{\sim}{R}\, \frac{e^{i\,\underset{\sim}{p}.\underset{\sim}{R}}}{|\underset{\sim}{R}-\underset{\sim}{r}|} = \frac{4\pi}{P^2}\, e^{i\,\underset{\sim}{p}.\underset{\sim}{r}}$$

then the matrix element becomes, for $i \neq f$

$$T_{if}^{B} = \frac{4\pi z}{P^2} \int e^{i\,\underset{\sim}{p}.\underset{\sim}{r}}\, \phi_f^*(\underset{\sim}{r})\, \phi_i(\underset{\sim}{r})\, d\underset{\sim}{r} \qquad (5.2)$$

z represents the charge of the incoming particle and is ± 1.

The total cross section may be written in terms of momentum transfer so that

$$Q_{if}^{B} = \frac{1}{2\pi^2 v} \int_{P_{min}}^{P_{max}} |T_{if}^{B}|^2 \, p \, dp \qquad (\pi a_o^2) \qquad (5.3)$$

The major contribution to the integral of (5.3) comes from the region $p \sim P_{min}$, hence we may approximate $P_{max} \sim \infty$.

Conservation of energy gives

$$K_i^2 - K_f^2 = 2\mu \, \Delta E$$

where ΔE is the change in energy of the target. Thus

$$\begin{aligned} P_{min}^2 &= K_i^2 + K_f^2 - 2 K_i K_f \\ &= 2 K_i^2 - 2\mu \, \Delta E - 2 K_i (K_i^2 - 2\mu \, \Delta E)^{1/2} \\ &= \frac{\Delta E^2}{v^2} \left(1 + O\left(\frac{1}{v^2}\right)\right) \end{aligned}$$

thus $P_{min} \underset{v \to \infty}{\to} \frac{\Delta E}{v}$.

P_{max} and P_{min} are thus independent of particle mass. Hence the Born approximation suggests that in the high velocity limit the cross sections for electron and proton excitation of hydrogen are the same. This result is not confined to the case of hydrogen atoms but holds for any atomic target. Measurements of excitation cross sections for helium using protons and electrons appear to support this conclusion, though we have to rely on the velocity dependence of the cross sections instead of absolute magnitudes, Thomas and Bent (1967). It would be more satisfactory if agreement between the two cross sections could be observed above some velocity thereby indicating the range of validity of the first Born approximation.

Born approximation calculations for electron collisions are reviewed by Peterkop and Veldre (1966). In general it can be said that the total Born cross sections agree with experimental cross-sections above ten times the threshold energy of a particular transition. Bates and Griffing (1953) first applied the Born approximation to the excitation of the 2s and 2p levels of hydrogen by proton impact. Results for this process are included in figures (4) and (6).

6. The Second Born Approximation

A simplified second Born approximation has been evaluated for electron and proton scattering by Holt and Moiseiwitsch (1968). Their method is a combination of methods used by other workers Massey and Mohr (1934) and Kingston et al. (1960 a,b).

The transition matrix element corresponding to the second Born approximation may be written using equation (1.39) as

$$T_{if}^{B_2} = T_{if}^{1} + T_{if}^{2} \tag{6.1}$$

where

$$T_{if}^{1} = \int e^{i(\underset{\sim}{K}_i - \underset{\sim}{K}_f).\underset{\sim}{R}} V_{fi}(\underset{\sim}{R})\, d\underset{\sim}{R}$$

and

$$T_{if}^{2} = \langle \psi_f | V\, G_o^{+}\, V | \psi_i \rangle$$

$$= \frac{1}{4\pi} \sum_n \int d\underset{\sim}{R}\, d\underset{\sim}{R}'\, e^{i(\underset{\sim}{K}_i.\underset{\sim}{R} - \underset{\sim}{K}_f.\underset{\sim}{R}')} \frac{e^{i K_n |\underset{\sim}{R} - \underset{\sim}{R}'|}}{|\underset{\sim}{R} - \underset{\sim}{R}'|}$$

$$\times V_{fn}(\underset{\sim}{R}')\, V_{ni}(\underset{\sim}{R}) \tag{6.2}$$

$$V_{nm}(\underset{\sim}{R}) = z \int \phi_n^*(\underset{\sim}{r}) \left[\frac{1}{R} - \frac{1}{|R-r|}\right] \phi_m(\underset{\sim}{r})\, d\underset{\sim}{r}$$

But

$$\frac{e^{i K |\underset{\sim}{R}-\underset{\sim}{R}'|}}{4\pi |\underset{\sim}{R}-\underset{\sim}{R}'|} = \lim_{\varepsilon\to 0} \frac{1}{(2\pi)^3} \int \frac{e^{i \underset{\sim}{q}.(\underset{\sim}{R}-\underset{\sim}{R}')}}{q^2-K^2-i\varepsilon}\, d\underset{\sim}{q}$$

and

$$\int \frac{e^{i \underset{\sim}{K}.\underset{\sim}{R}'}}{|\underset{\sim}{R}-\underset{\sim}{R}'|}\, d\underset{\sim}{R}' = \frac{4\pi}{K^2} e^{i \underset{\sim}{K}.\underset{\sim}{R}} \qquad \text{(Bethes integral)}$$

then if

$$T_{if}^2 = \sum_n T_n^2 \tag{6.3}$$

we have

$$T_n^2 = \lim_{\varepsilon\to 0} \frac{z}{\pi} \int \frac{I(f,n,\underset{\sim}{q}-\underset{\sim}{K}_f)\, I(n,i,\underset{\sim}{K}_i-\underset{\sim}{q})\, d\underset{\sim}{q}}{(q^2-K_n^2-i\varepsilon)\,(\underset{\sim}{q}-\underset{\sim}{K}_f)^2\,(\underset{\sim}{q}-\underset{\sim}{K}_i)^2} \tag{6.4}$$

where

$$I(n,m,\underset{\sim}{s}) = \int \phi_n^*(\underset{\sim}{r})\, \phi_m(\underset{\sim}{r}) \left[e^{i \underset{\sim}{s}.\underset{\sim}{r}} - 1\right] d\underset{\sim}{r}$$

The summation of equation (6.3) may be performed by utilising an approximation due to Massey and Mohr (1934) i.e. set $K_n = K_i$ for all n and use the closure relation to remove the infinite sum. Holt and Moiseiwitsch retain the first N terms of (6.3) exactly and then for $n \geq N+1$ K_n is replaced by K_{N+1} and the summation from N+1 extending over the continuum states is done by closure. Thus

$$T_{if}^2 = T_2^N = \bar{T}_2^N + \sum_{n=N+1} T_2^{N+1,n} \tag{6.5}$$

The total cross section for the i → f transition is given by

$$Q_{if} = \frac{\mu^2}{4\pi^2} \frac{K_f}{K_i} \int |T_{if}|^2 \, d\Omega$$

$$= \frac{\mu^2}{2\pi} \frac{K_f}{K_i} \int_{-1}^{+1} |T_{if}|^2 \, d(\cos\theta)$$

$$\sim \frac{\mu^2}{2\pi} \frac{K_f}{K_i} \int_{-1}^{+1} |T_{if}^1 + T_{if}^2|^2 \, d(\cos\theta)$$

Retaining only the terms that include up to third order terms in the potential v we have

$$Q_{if} \sim \frac{\mu^2}{2\pi} \frac{K_f}{K_i} \int_{-1}^{+1} |T_{if}^1|^2 \left(1+2 \, \mathrm{Re} \frac{T_{if}^2}{T_{if}^1}\right) d(\cos\theta) \qquad (6.6)$$

The integrals arising from equation (6.4) are in general extremely complicated. However considerable simplification is possible if the real part of the forward scattering amplitude is evaluated. Then it is possible to compare the effects of including and omitting the continuum states for N up to N = 100. Table I shows the results of Holt and Moiseiwitsch for K_i = 2 a.u. and for θ = 0.

Table I

N	Re $\bar{T}_2^N$	Re T_2^N
2	.850	1.791
5	1.053	1.796
10	1.085	1.797
100	1.096	1.798

The convergence of $\bar{T}_2^N$ for increasing N is quite good, N = 5 being satisfactory, however the convergence is much improved by including all states even if most are only included by the closure approximation. The

discrepancy between the limits of Re $\bar{T}_2^N$ and Re T_2^N for large N shows the importance of including the contribution from the continuum.

The approximation (6.5) has been applied to electron collisions for the 1s-1s, 1s-2s and 1s-2p processes. In the case of the elastic collision the second Born approximations gives cross sections higher than those of the first Born approximations, reasonable agreement between the two being attained for v ~ 5 a.u.. For the excitation cross sections agreement between first and second Born approximations is achieved for v > 3 a.u. For proton collisions the first Born approximation seriously underestimates the 2s excitation cross section in comparison with the second Born approximation. The discrepancy is such that agreement is not reached until the proton energy exceeds 300 KEV. The reason for the difference is the strong long range 2s-2p coupling that is included by the second Born approximation. The 1s-2p transition cross sections are in quite good agreement for energies above 200 KEV. The comparison of the first and second Born approximations in this manner affords no definite indication as to the reliability of the first Born approximation.

7. The Close Coupling Approximation

In this approach to the scattering problem the techniques of partial wave analysis are applied using a coupled representation. This leads to a set of second order ordinary integro-differential equations that may be solved in a truncated eigenfunction expansion approximation. Such a procedure is only applicable to the electron scattering problem. The electron co-ordinates are defined as $\underset{\sim}{r}_1$ and $\underset{\sim}{r}_2$ relative to the centre of mass, in this case the hydrogen atom nucleus.

The quantum numbers identifying the collision channel are specified by

$$n,\lambda,\mu,\ell,m,L,M$$

where $n\lambda\mu$ - identify the target atomic state

ℓm - the orbital angular momentum and its z-component of the scattered electron

and L,M - the total angular momentum and its z-component

L must obey the triangular relation

$$|\ell - \lambda| \leq L \leq \ell + \lambda$$

The possibility of exchange scattering is included by explicitly symmetrising the approximate wave-function used.

Eigenfunctions of total angular momentum may be constructed

$$\gamma_\Gamma(\hat{\underset{\sim}{r}}_1, \underset{\sim}{r}_2) = \frac{\mu_{n\lambda}(r_2)}{r_2} \sum_{m,\mu} \tau(\lambda,\ell,L;\ \mu,m,M)\ Y_{\lambda\mu}(\hat{\underset{\sim}{r}}_2)\ Y_{\ell,m}(\hat{\underset{\sim}{r}}_1) \qquad (7.1)$$

where the target eigenfunction $\phi_n(\underset{\sim}{r}_2) = \frac{\mu_{n\lambda}(r_2)}{r_2} Y_{\lambda\mu}(\hat{\underset{\sim}{r}}_2)$ and $\tau(\lambda,\ell,L;\ \mu,m,M)$ are Clebsh-Gordan coefficients defined in Rose (1957). The symbol Γ represents the quantum numbers $n\lambda\ell LM$, and Γ_o represents the incident channel quantum numbers, $\Gamma_o \equiv n_o\lambda_o\ell_o LM$. The total wave-function for a given incident channel Γ_o is

$$\psi_{\Gamma_o}(\underset{\sim}{r}_1, \underset{\sim}{r}_2) = \sum_{n,\ell,\lambda} \frac{F_{\Gamma\Gamma_o}(r_1)}{r_1} \gamma_\Gamma(\hat{\underset{\sim}{r}}_1, \underset{\sim}{r}_2) \pm \sum_{n\ell\lambda} \frac{F_{\Gamma\Gamma_o}(r_2)}{r_2} \gamma_\Gamma(\hat{\underset{\sim}{r}}_2, \underset{\sim}{r}_1) \qquad (7.2)$$

The asymptotic form of the radial functions may be assumed to be

$$F_{\Gamma\Gamma_o}(r) \underset{r\to\infty}{\to} (K_n)^{-1/2} \left[\delta_{\Gamma_o\Gamma}\, e^{-i\,(K_n r - \ell\pi/2)} - S_{\Gamma_o\Gamma}\, e^{i(K_n r - \ell\pi/2)}\right] \qquad (7.3)$$

We require to find the scattering amplitudes in terms of the scattering matrix element $S_{\Gamma_o\Gamma}$. The total wavefunction ψ_{K_o} has the asymptotic form

$$\psi_{K_o}(\underset{\sim}{r}_1,\underset{\sim}{r}_2) \underset{r_1\to\infty}{\to} e^{i\,\underset{\sim}{K}_o\cdot\underset{\sim}{r}_1}\,\phi_o(\underset{\sim}{r}_2) + \sum_{n\lambda\mu} \frac{e^{i\,K_n\,r_1}}{r_1} f_{on}\,\phi_n(\underset{\sim}{r}_1) \qquad (7.4)$$

But $e^{i\,\underset{\sim}{K}_o\cdot\underset{\sim}{r}}$ may be expanded as

$$e^{i\,\underset{\sim}{K}_o\cdot\underset{\sim}{r}_1} = 4\pi \sum_{\ell_o=0}^{\infty} i^{\ell_o}\, j_{\ell_o}(K_o r_1) \sum_{m_o} Y^*_{\ell_o m_o}(\hat{\underset{\sim}{K}}_o)\, Y_{\ell_o m_o}(\hat{\underset{\sim}{r}}_1) \qquad (7.5)$$

and from equation (7.1) using the orthogonality properties of Clebsch-Gordan coefficients

$$Y_{\ell_o m_o}(\hat{\underset{\sim}{r}}_1)\,\phi_o(\underset{\sim}{r}_2) = \sum_{L,M} \tau(\lambda_o\,\ell_o\,L,\mu_o\,m_o\,M)\,\gamma_{\Gamma_o}(\hat{\underset{\sim}{r}}_1,\underset{\sim}{r}_2) \qquad (7.6)$$

Using results (7.6) and (7.5) the incident wave in (7.4) becomes

$$e^{i\,\underset{\sim}{K}_o\cdot\underset{\sim}{r}_1}\,\phi_o(\underset{\sim}{r}_2) = 4\pi \sum_{\substack{L\,M\\ \ell_o m_o}} i^{\ell_o}\, j_{\ell_o}(K_o r_1)\, Y^*_{\ell_o m_o}(\hat{\underset{\sim}{K}}_o)\,\tau(\lambda_o\ell_o L,\mu_o m_o M)\,\gamma_{\Gamma_o}(\hat{\underset{\sim}{r}}_1,\underset{\sim}{r}_2)$$

$$\underset{r_1\to\infty}{\to} 2\pi \sum_{\substack{L\,M\\ \ell_o m_o}} i^{\ell_o - l}\, Y^*_{\ell_o m_o}(\hat{\underset{\sim}{K}}_o)\,(\lambda_o\,\ell_o\,L,\mu_o\,m_o\,M)\,\gamma_{\Gamma_o}(\hat{\underset{\sim}{r}}_1,\underset{\sim}{r}_2)$$

$$X\ \frac{1}{K_o r_1}\left[e^{i(K_o r_1 - \ell_o \pi/2)} - e^{-i(K_o r_1 - \ell_o \pi/2)}\right] \qquad (7.7)$$

The total wavefunction may be expanded as

$$\psi_{K_o}(\underset{\sim}{r}_1,\underset{\sim}{r}_2) = \sum_{\substack{L\,M\\ \ell_o m_o}} B(\ell_o\,m_o\,\Gamma_o)\, Y^*_{\ell_o m_o}(\hat{\underset{\sim}{K}}_o)\,\psi_{\Gamma_o}(\underset{\sim}{r}_1,\underset{\sim}{r}_2)$$

Using equation (7.2) and the asymptotic form of $F_{\Gamma_o\Gamma}$, ψ_{K_o} becomes

$$\psi_{K_o}(\underset{\sim}{r}_1,\underset{\sim}{r}_2) \underset{r_1\to\infty}{\to} \sum_{\substack{L\,M\\ \ell_o m_o}} B(\ell_o\,m_o\,\Gamma_o)\, Y^*_{\ell_o m_o}(\hat{\underset{\sim}{K}}_o) \sum_{n\ell\lambda} \gamma_\Gamma(\underset{\sim}{r}_1,\underset{\sim}{r}_2)$$

$$X\ \frac{1}{K_n^{1/2}\, r_1}\left[\delta_{\Gamma_o\Gamma}\, e^{-i(K_n r_1 - \ell\pi/2)} - S_{\Gamma_o\Gamma}\, e^{i(K_n r_1 - \ell\pi/2)}\right] \qquad (7.8)$$

Comparing the incident waves of (7.7) and (7.8) i.e. compare the coefficients of $Y^*_{\ell_o m_o}(\hat{K}_o)\, \gamma_{\Gamma_o}(\hat{r}_1, r_2)\, e^{-i(K_o r_1 - \ell_o \pi/2)}$, we get

$$B(\ell_o\ m_o\ \Gamma_o) = 2\pi\, i^{\ell_o+1}\, (K_o)^{-1/2}\, \tau(\lambda_o\ \ell_o\ L, \mu_o\ m_o\ M) \qquad (7.9)$$

thus

$$\psi_{K_o}(r_1, r_2) \underset{r_1\to\infty}{\to} 2\pi \sum_{\substack{L\,M \\ \ell_o m_o}} i^{\ell_o+1}\, \tau(\lambda_o\ \ell_o\ L, \mu_o\ m_o\ M)\, Y^*_{\ell_o m_o}(\hat{K}_o) \sum_{n\lambda\ell} \frac{\gamma_\Gamma(\hat{r}_1, r_2)}{r_1}$$

$$X\ \frac{1}{(K_o\ K_n)^{1/2}} \left[\delta_{\Gamma_o\Gamma}\, e^{-i(K_n r_1 - \ell\,\pi/2)} - S_{\Gamma_o\Gamma}\, e^{i(K_n r_1 - \ell\,\pi/2)}\right] \qquad (7.10)$$

The total wavefunction ψ_{K_o} may be decomposed into two parts, the incident wave ψ_{INC} and the scattered wave ψ_{SCAT}. ψ_{INC} is given by equation (7.7). Hence combining equations (7.7) and (7.10) we get

$$\psi_{SCAT} = 2\pi i \sum_{\substack{L\,M \\ \ell_o m_o}} i^{\ell_o-\ell}\, \tau(\lambda_o\ \ell_o\ L, \mu_o\ m_o\ M) \sum_{n\ell\lambda} \gamma_\Gamma(\hat{r}_1, r_2)\, \frac{e^{i K_n r_1}}{r_1}$$

$$X\ \frac{Y^*_{\ell_o m_o}(\hat{K}_o)}{(K_o\ K_n)^{1/2}} \left[\delta_{\Gamma_o\Gamma} - S_{\Gamma_o\Gamma}\right] \qquad (7.11)$$

Comparing this with the asymptotic form of the scattered wave, equation (7.4), the scattering amplitude becomes

$$f_{on} = 2\pi i \sum_{\substack{L\,M \\ \ell_o m_o \\ \ell, m}} \frac{i^{\ell_o-\ell}}{(K_o\ K_n)^{1/2}}\, \tau(\lambda_o\ \ell_o\ L, \mu_o\ m_o\ M)\, \tau(\lambda\ \ell\ L, \mu\ m\ M)$$

$$X\ Y^*_{\ell_o m_o}(\hat{K}_o)\, Y_{\ell m}(\hat{K}_n)\, T_{\Gamma_o\Gamma} \qquad (7.12)$$

where $\underset{\sim}{T} = \delta - \underset{\sim}{S}$.

When this expression is compared with scattering amplitude defined in the uncoupled representation, equation (3.4), the relation between the two

representations is such that

$$T(n_o\ \ell_o\ m_o|n\ \ell\ m) = \sum_{LM} \tau(\lambda_o\ \ell_o\ L,\mu_o\ m_o\ M)\ \tau(\lambda\ \ell\ L,\mu\ m\ M)$$

$$\times\ T_{\Gamma_o\Gamma} \qquad (7.13)$$

where the quantum numbers n_o and n in the expression $T(n_o\ \ell_o\ m_o|n\ \ell\ m)$ implicitly contain $\lambda_o\ \mu_o$ and $\lambda\mu$ respectively.

The expression for the total cross section is then given by equation (3.11). Using the orthogonality conditions of the Clebsch-Gordan coefficients and averaging over the μ_o states we have

$$Q_{n_o\lambda_o\to n\lambda} = \frac{\pi}{(2\lambda_o+1)\ K_o^2} \sum_{L,\ell,\ell_o} (2L+1)\ |T_{\Gamma_o\Gamma}|^2 \qquad (7.14)$$

Here we have assumed that $T_{\Gamma_o\Gamma}$ is independent of M, the z-component of total angular momentum. This must be so since the physics of the collision is independent of the axes used to describe it.

The equations satisfied by the radial function $F_{\Gamma_o\Gamma}$ are derived by substituting the expansion (7.2) into the Schrödinger equation. This yields

$$\left[\frac{d^2}{dr_1^2} - \frac{\ell(\ell+1)}{r_1^2} + K_n^2\right] F_{\Gamma_o\Gamma}(r_1)$$

$$= 2\mu \int d\hat{\underset{\sim}{r}}_1\ d\underset{\sim}{r}_2\ \gamma_\Gamma^*(\hat{\underset{\sim}{r}}_1,\underset{\sim}{r}_2)\ V(\underset{\sim}{r}_1,\underset{\sim}{r}_2) \sum_{\Gamma'} F_{\Gamma_o\Gamma'}(r_1)\ \gamma_{\Gamma'}(\hat{\underset{\sim}{r}}_1,\underset{\sim}{r}_2)$$

$$\pm 2\mu\ r_1 \int d\hat{\underset{\sim}{r}}_1\ d\underset{\sim}{r}_2\ \gamma_\Gamma^*(\hat{\underset{\sim}{r}}_1,\underset{\sim}{r}_2) \sum_{\Gamma'} \left[H_o(\underset{\sim}{r}_2) + V(\underset{\sim}{r}_2,\underset{\sim}{r}_1) - E - E_{n'}\right]$$

$$\times\ \frac{F_{\Gamma_o\Gamma'}(r_2)}{r_2}\ \gamma_{\Gamma'}(\hat{\underset{\sim}{r}}_2,\underset{\sim}{r}_1) \qquad (7.15)$$

Equation (7.15) has the more compact form, Burke (1969)

$$\left[\frac{d^2}{dr_1^2} - \frac{\ell(\ell+1)}{r_1^2} + K_n^2\right] F_{\Gamma_o\Gamma}(r_1) = \sum_{\Gamma'} \left[V_{\Gamma\Gamma'} \pm W_{\Gamma\Gamma'}\right] F_{\Gamma_o\Gamma'}(r_1) \qquad (7.16)$$

where $V_{\Gamma\Gamma'}$ and $W_{\Gamma\Gamma'}$ are defined below, $W_{\Gamma\Gamma'}$ being an integral operator.

$$V_{\Gamma\Gamma'} = 2\mu\left[-\frac{1}{r_1}\delta_{nn'}\,\delta_{\lambda\lambda'}\,\delta_{\ell\ell'} + \sum_{\alpha=0} y_\alpha(\mu_{n\lambda},\mu_{n'\lambda'}|r_1)\, f_\alpha(\lambda\ell,\lambda'\ell';L)\right] \tag{7.17}$$

and

$$W_{\Gamma\Gamma'} = 2\mu\,(-1)^{\lambda+\ell-L} \sum_{\alpha=0}^{\infty} f_\alpha(\lambda\ell',\lambda'\ell;L)\left[\left[E_n + E_{n'} - E\right]\delta_{\alpha o}\,\Delta(\mu_{n\lambda},F_{\Gamma_o\Gamma'}) + y_\alpha(\mu_{n\lambda},F_{\Gamma_o\Gamma'}|r_1)\right]\mu_{n'\lambda'}(r_1) \tag{7.18}$$

where $y_\alpha(A,B|r_1) = \int_o^\infty dr_2\; A(r_2)\; B(r_2)\; q_\alpha(r_1,r_2)$

$$q_\alpha(r_1,r_2) = r_1{}^\alpha/r_2{}^{\alpha+1} \qquad r_1 \leqslant r_2$$

$$= r_2{}^\alpha/r_1{}^{\alpha+1} \qquad r_2 \leqslant r_1$$

$$f_\alpha(\lambda\ell,\lambda'\ell';L) = \frac{4\pi}{(2\alpha+1)} \sum_{\substack{m\mu \\ m\mu' \\ \beta}} \tau(\lambda\;\ell\;L,\mu\;m\;M)\;\tau(\lambda'\;\ell'\;L,\mu'\;m'\;M) \times \int d\hat{\underset{\sim}{r}}_1\; Y_{\ell m}^*(\hat{\underset{\sim}{r}}_1)\; Y_{\ell' m'}(\hat{\underset{\sim}{r}}_1)\; Y_{\alpha\beta}(\hat{\underset{\sim}{r}}_1) \times \int d\hat{\underset{\sim}{r}}_2\; Y_{\lambda\mu}^*(\hat{\underset{\sim}{r}}_2)\; Y_{\lambda'\mu}(\hat{\underset{\sim}{r}}_2)\; Y_{\alpha\beta}^*(\hat{\underset{\sim}{r}}_2)$$

and $\Delta(A,B)$ is the overlap integral

$$\int_o^\infty dr\; A(r)\; B(r)$$

Equations (7.16) are solved numerically the number of states included in the initial expansion being truncated for some n = N. This yields S-matrix elements that are variationally of 'second-order accuracy'.

The close coupling equations have been solved by several workers. Burke, Shey and Smith (1963) calculated cross sections in the energy range 11 → 54.4 eV, including only the 1s, 2s and 2p states in the expansion (7.2). The agreement of these results with the experimental results of Hils et al.

(1966), Stebbings et al. (1960) and Lichten and Shulty (1959) is poor in this overall energy range. This is possibly due to the limited number of states included in the approximate wavefunction. Burke et al. (1967) have solved the close coupling equations retaining only the 1s,2s,2p,3d and 3p states in the energy range 10-12.5 eV. The results of these calculations show the effects of resonances associated with the n = 2 and n = 3 threshold energies on the total cross sections. The fact that the 1s, 2s and 2p calculation does not give the resonance for the n = 3 threshold indicates the importance of including at least all the open channels for a particular energy in the approximate wavefunction.

The problem of convergence of close coupled calculations has been investigated by Burke and Shey (1962). They calculated the s-wave phase shift for 1,2,3,5 and 6 state wavefunctions. Their results are displayed in table (2).

Table (2)

INCLUDED STATES	K^2 = 0.55	K^2 = 0.60
1s	.700	.670
1s-2s	.735	.711
1s-2s-2p	.785	.771
1s-2s-2p-3s	.789	.774
1s-2s-2p-3s-3p	.798	.781

The convergence of the phase shifts is obviously poor particularly since the obvious region of application of close coupling calculations is in the range considered in table (2). A reason for this slow convergence is not hard to find. Castilejo et al. (1960) show that for electron

hydrogen collisions the 2p state contributes only 66% of the ground state polarisation while all bound states contribute 81.4% and the continuum states contribute the remainder. This means that the long range polarisation potential is poorly represented in a close coupled approximation that only includes a small number of target states. Hence such a method must be inaccurate when the polarisation potential is important. Polarisation effects may be included in the close coupling approximation by including extra terms in the initial expansion that account for part of the optical potential. The optical potential may be defined in the following way, initially due to Feshbach (1962).

Consider the projection operators P and Q, such that $P + Q = I$ and $PQ = QP = 0$. The Schrödinger equation may be written as

$$P(H-E)\ (P+Q)\psi = 0 \qquad (7.19a)$$

and

$$Q(H-E)\ (P+Q)\psi = 0 \qquad (7.19b)$$

from equation (7.19b) we have

$$Q\psi = -Q \frac{1}{Q(H-E)Q} QHP\psi$$

and hence (7.19a) becomes

$$P\left(H-PHQ \frac{1}{Q(H-E)Q} QHP-E\right) P\psi = 0$$

The close coupling equation may be written as

$$P(H-E)\ P\psi = 0$$

Hence the terms omitted by the close coupling approximation are

$$V_{opt} = - PHQ \frac{1}{Q(H-E)Q} QHP \qquad (7.20)$$

V_{opt} thus represents the effects of the terms omitted from the close coupled expansion. Part of the optical potential can be included by writing the wavefunction, neglecting symmetry properties, as

$$\psi(\underset{\sim}{r}_1,\underset{\sim}{r}_2) = \sum_n F_n(\underset{\sim}{r}_1)\,\phi_n(\underset{\sim}{r}_1) + \sum_i \alpha_i\,\chi(\underset{\sim}{r}_1,\underset{\sim}{r}_2) \qquad (7.21)$$

the first summation corresponds to $P\psi$ and the second to $Q\psi$. A variational principle applied to a trial function of this type gives the usual set of close coupled equations coupled to a set of linear equations arising from the variation of the a_i coefficients. This procedure has been applied by Taylor and Burke (1967) who include the 1s, 2s and 2p states exactly and twenty extra terms. The calculations were done in the energy range 10-11.5 eV. Good agreement is reached between this calculation and the previous 1s-2s-2p and 1s-2s-2p-3s-3p close coupling calculations. This implies that the close coupling approximation is reliable beneath the threshold of the first omitted channel.

A comparison of these three calculations and the experimental results of Litchen and Shulty (1959) is made by Burke, Taylor and Ormonde (1967). The 2p cross sections in the energy range 10-11.8 eV agree well with the experimental cross sections for the 1s-2p transition, the normalisation being consistent with the Born approximation results at high energies. The 2s cross sections, however, are almost a factor of 2 higher than the experimental cross sections normalised to the first Born results at 300 eV. Renormalisation of the 2s experimental results produces good agreement with all three calculations. This conflict of high and low energy data for the 2s cross sections remains unresolved. However Damburg and Propin (1972) have solved the close coupling approximation for a model interaction; retaining only the 1s-2p and 2s-2p coupling. The resulting equations are solved exactly and compared with the Born approximation; obtained by neglect-

ing the 2s-2p coupling in the same model. Their results for the 2p excitation total cross section show that the coupling between channels of fixed total angular momentum increases with an increase in the incident electron energy and that consequently the close coupling result tends to the Born result more slowly than expected. Such an effect on the 2s transition cross section is likely to be relatively larger since the 1s-2s transition is not optically allowed. The discrepancy between the two results lends support to the conjectures of Burke et al. (1967) and Geltman and Burke (1970) that the normalization of 2s and 2p experimental data to the Born approximation at 300 eV is unsatisfactory.

When the incident energy is above the threshold energy of the first omitted state the effects of the omitted states can be included by expanding the total wavefunction in a discrete set of states that are not target eigenfunctions. This so called Sturmian expansion was first suggested by Rotenberg (1962). The Sturmian functions $T_{n\lambda\mu}$ may be written

$$T_{n\lambda\mu}(\underset{\sim}{r}) = \frac{1}{r} S_{n\lambda}(r)\, Y_{\lambda\mu}(\underset{\sim}{\hat{r}}) \tag{7.22}$$

where the radial part satisfies

$$\left[\frac{d^2}{dr^2} + \frac{\alpha_n^{\lambda}}{r} - \frac{\lambda(\lambda+1)}{r^2}\right] S_{n\lambda}(r) = \varepsilon\, S_{n\lambda}(r) \tag{7.23}$$

$\varepsilon_\lambda = \frac{1}{(\lambda+1)^2}$ and $\alpha_{n\ell}$ is the required eigenvalue. With this choice of ε_λ the 'lowest' eigenfunction for $S_{n\lambda}$ coincides with the lowest radial hydrogenic eigenfunction $\mu_{n\lambda}$. By making the transformation $x = \alpha_{n\lambda}\, r$, it can be seen that each higher Sturmian function is related to a corresponding hydrogenic function by

$$S_{n\lambda}(r) = N_{n\lambda}\, \mu_{n\lambda}(\alpha_{n\lambda}\, r) \tag{7.24}$$

where $\alpha_{n\lambda} = n/(\lambda+1)$.

Since $n \geq \lambda + 1$, $\alpha_{n\lambda} \geq 1$ the higher Sturmian functions are more compact than the corresponding hydrogenic functions. The Sturmian eigenfunctions are all denumerable, there is no continuum. Thus a finite number of Sturmian functions may partly represent the continuum states of the hydrogen atom.

The possible improvement afforded by the use of Sturmian functions is achieved at the expense of the simplicity of the asymptotic boundary conditions.

Burke and Shey (1962) suggested an expansion in functions similar to the Sturmian functions. Neglecting symmetry the total wavefunction may be written

$$\psi_{\Gamma_0}(\underset{\sim}{r}_1,\underset{\sim}{r}_2) = \sum_{\Gamma} \frac{F_{\Gamma_0\Gamma}(r_1)}{r_1} \gamma_{\Gamma}(\hat{\underset{\sim}{r}}_1,\underset{\sim}{r}_2) + \sum_{\Gamma'} \frac{G_{\Gamma_0\Gamma'}(r_1)}{r_1} R_{\Gamma'}(\hat{\underset{\sim}{r}}_1,\underset{\sim}{r}_2) \quad (7.25)$$

where Γ' represents the quantum numbers $n'\ell'\lambda'LM$ and

$$R_{\Gamma'}(\hat{\underset{\sim}{r}}_1,\underset{\sim}{r}_2) = \frac{V_{n'\lambda'}(r_2)}{r_2} \sum_{M'\mu'} \tau(\lambda'\ell'L,\ m'\mu'M) \times Y_{\ell'M'}(\hat{\underset{\sim}{r}}_1)\ Y_{\lambda'\mu'}(\hat{\underset{\sim}{r}}_2) \quad (7.26)$$

The functions $V_{n\lambda}(r)$ are constructed to be normalised to unity and orthogonal to each other and to the hydrogen radial functions $\mu_{n\lambda}(r)$ for the same angular momentum quantum numbers. Apart from this the functions $V_{n\lambda}(r)$ are arbitrary but have the following boundary conditions.

$$V_{n\lambda}(r) \to r^{\lambda+1} \qquad \text{for small } r$$
$$\to 0 \qquad \text{for large } r$$

The coefficients $F_{\Gamma_0\Gamma}$ and $G_{\Gamma_0\Gamma'}$ satisfy a set of coupled integro-differential equations whose form is similar to equation (7.16) when exchange is

allowed for. If only one F and one G function is retained in the initial expansion the equation satisfied by F_{ls} has the asymptotic form

$$\left[\frac{d^2}{dr^2} + K^2 + \frac{\alpha}{r^2}\right] F_{ls}(r) = 0 \qquad (7.27)$$

where α is a function that depends on $V_{n\lambda}(r)$ and α/r^2 represents the polarization potential. Damburg and Karule (1967) show that the correct polarizability can be achieved if V is chosen to be

$$V_{21} = \frac{8}{\sqrt{129}} (2r^2+r^3)\, e^{-r} \qquad (7.28)$$

Burke et al. (1969) utilise this pseudo state in a 1s-2s-$\overline{2p}$ calculation. The $\overline{2p}$ state being the pseudo state given in equation (7.28). The addition of a 2s hydrogenic state will not affect the long range behaviour in the 1s channel since the 1s-2s coupling is short range only. Hence the polarization potential is correctly described in this calculation. The results obtained show considerable improvement over those of previous close coupled calculations when compared to the variational calculation of Swartz (1961).

The method of pseudo state expansions has been applied to electron scattering in the energy range 16-54 eV, Burke and Webb (1970). The expansion includes the 1s, 2s and 2p hydrogenic states exactly and two pseudo states, $\overline{3s}$ and $\overline{3p}$. The pseudo states are chosen so as to have approximately the same range as the 2s and 2p atomic eigenstates, and also so that their threshold energies coincide with each other and with the ionisation threshold. The 2s and 2p cross sections calculated show surprisingly good agreement with experiment, see figures (9,11). The normalisation of the experiments are however still in doubt so that this agreement may be fortuitous. The convergence of this method at these energies has still to be investigated but is expected to be good.

In summary the close coupling method appears to be adequate where the incident energy is below the threshold energy of the first omitted state. Above these energies it is important to include the effects of omitted bound and continuum states.

8. The Impact Parameter Approximation

The impact parameter method assumes a rectilinear trajectory for the incident particle. The interaction of the incident particle with the target may then be treated as a time dependent perturbation and the resulting ordinary differential equations solved accordingly. The assumption of a rectilinear trajectory implies that the incoming particle is distinguishable from the target particles so that the effects of electron exchange for electron collisions and of nuclear identity for proton collisions are neglected.

The Schrödinger equation may be written

$$\left[-\frac{1}{2\mu} \nabla_R^2 - \tfrac{1}{2} \nabla_r^2 + V(\underset{\sim}{R},\underset{\sim}{r}) - E \right] \Psi(\underset{\sim}{R},\underset{\sim}{r}) = 0 \qquad (8.1)$$

μ is the reduced mass of the incident particle and the co-ordinates are defined in figure (2).

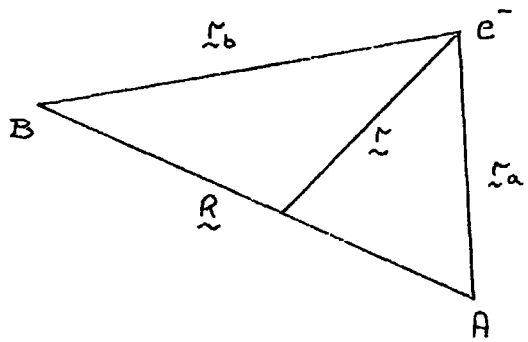


Figure (2)

Equation (8.1) is readily deduced from equation (2.3) on the interchange of

particles 1 and 3 and relabelling of the co-ordinates. Following a procedure due to Wilets and Wallace (1968) we can write

$$\Psi = e^{i\mu VZ}\,\psi \tag{8.2}$$

and assuming $E \sim \frac{1}{2}\,\mu V^2$, equation (8.1) becomes

$$\left[-\frac{1}{2\mu}\,\nabla_R^{\,2} - iV\,\frac{\partial}{\partial Z} + H(\underset{\sim}{r},\underset{\sim}{R})\right]\psi(\underset{\sim}{r},\underset{\sim}{R}) = 0 \tag{8.3}$$

where $H(\underset{\sim}{r},\underset{\sim}{R}) = -\frac{1}{2}\,\nabla_r^{\,2} + V(\underset{\sim}{R},\underset{\sim}{r}b)$.

Equation (8.3) may be solved by neglecting the components of $\nabla_R^{\,2}$ associated with the motion of the particle perpendicular to the projectile velocity. This is equivalent to assuming $\underset{\sim}{R} = \underset{\sim}{\rho} + \underset{\sim}{Z}$, where $\underset{\sim}{\rho}$ is a vector in the X-Y plane perpendicular to the $\hat{\underset{\sim}{Z}}$ direction. Then we have

$$\left[-\frac{1}{2\mu}\,\frac{\partial^2}{\partial Z^2} - iV\,\frac{\partial}{\partial Z} + H(\underset{\sim}{R},\underset{\sim}{r})\right]\psi(\underset{\sim}{r},\underset{\sim}{R}) = 0 \tag{8.4}$$

The standard impact parameter equation of motion is obtained by considering the limit as $\mu \to \infty$ while the projectile velocity remains finite. Then equation (8.4) becomes

$$\left[-iV\,\frac{\partial}{\partial Z} + H(\underset{\sim}{R},\underset{\sim}{r})\right]\psi(\underset{\sim}{r},\underset{\sim}{R}) = 0 \tag{8.5}$$

writing $\underset{\sim}{Z} = \underset{\sim}{V}t$ where $\underset{\sim}{V}$ is the velocity of the incident particle we have

$$i\,\frac{\partial}{\partial t}\,\psi(\underset{\sim}{R},\underset{\sim}{r}) = H(\underset{\sim}{r},\underset{\sim}{R})\,\psi(\underset{\sim}{R},\underset{\sim}{r}) \tag{8.6}$$

where $\underset{\sim}{R} = \underset{\sim}{\rho} + \underset{\sim}{V}t$.

The electron Hamiltonian $H(\underset{\sim}{r},\underset{\sim}{R})$ may be written as

$$H(\underset{\sim}{r},\underset{\sim}{R}) = H_o + V(\underset{\sim}{R},\underset{\sim}{r}_b)$$

where

$$H_o = -\tfrac{1}{2} \nabla_{\underset{\sim}{r}}^2 + \frac{1}{|\underset{\sim}{r}_a|}$$

and $V(\underset{\sim}{R},\underset{\sim}{r}_b) = \frac{\eta}{|\underset{\sim}{r}_b|} - \frac{\eta}{|\underset{\sim}{R}|}$, η is the charge of the incoming particle, ± 1. H_o describes the unperturbed target electron and the target eigenfunctions are solutions of

$$H_o \, \phi_n(\underset{\sim}{r}_a,t) = i \frac{\partial}{\partial t} \phi_n(\underset{\sim}{r}_a,t) \tag{8.7}$$

where $\phi_n(\underset{\sim}{r}_a,t) = \phi_n(\underset{\sim}{r}_a) \, e^{-i\alpha_n t}$,

and α_n is the eigenenergy of the n^{th} target state. The total wavefunction may be expanded in a complete set of target states

$$\psi_n(\underset{\sim}{R},\underset{\sim}{r}) = \sum_s a_{ns}(t) \, \phi_s(\underset{\sim}{r}_a) \, e^{-i\alpha_s t} \tag{8.8}$$

here the summation includes an integration over the continuum target states. The probability that the target will be in the m^{th} state after a collision is then given by $|a_{nm}(+\infty)|^2$ and the total cross section for excitation from the n^{th} to m^{th} state is given by

$$Q_{nm} = 2 \int_o^\infty |a_{nm}(\infty)|^2 \, \rho \, d\rho \quad (\pi a_o^2) \tag{8.9}$$

McCarrol and Salin (1966) have shown that this result is equivalent to the exact quantum theory result under the following conditions:

$$\begin{aligned} & K_i >> 1 \\ & K_i \sim K_f >> (2\mu \, \Delta E)^{1/2} \\ & \cos^{-1} (\hat{\underset{\sim}{K}}_i . \hat{\underset{\sim}{K}}_f) << 1 \end{aligned} \tag{8.10}$$

where $\underset{\sim}{K}_i$ and $\underset{\sim}{K}_f$ are the relative momenta of the scattered particle and target nuclei when the target atom is in its initial and final states

respectively. ΔE is the inelasticity of the collision. The conditions of (8.10) are well satisfied for proton impact for energies above 1 KEV. For electron impact above 20 eV the conditions are at best only marginally satisfied. The usefulness of the impact parameter approximation for treating electron collisions is discussed in section (9).

Substituting the expansion (8.8) in the equation of motion (8.6) we obtain an infinite set of coupled differential equations

$$i \frac{\partial}{\partial t} a_{nm}(t) = \sum_s a_{ns}(t) V_{ms}(t) e^{i(\alpha_m - \alpha_s)t} \qquad (8.11)$$

where

$$V_{nm}(t) = \int \phi_n^*(\underset{\sim}{r}_a) V(\underset{\sim}{R},\underset{\sim}{r}) \phi_m(\underset{\sim}{r}_a) d\underset{\sim}{r}$$

A solution may be attempted by retaining only a few of the terms of the summation. The impact parameter Born approximation, or I.P.B., is obtained by retaining the elastic amplitude only. i.e.

$$a_{ns}(t) = \delta_{ns}$$

then

$$i \dot{a}_{nm}(t) = V_{mn}(t) e^{i(\alpha_m - \alpha_n)t}$$

and

$$a_{nm}(t) = -i \int_{-\infty}^{t} V_{mn}(t') e^{i(\alpha_m - \alpha_n)t'} dt' + \delta_{nm} \qquad (8.12)$$

The equivalence of (8.12) and the wave treatment Born approximation has been shown by Moiseiwitsch (1966). This author also shows the equivalence of successive terms of the Born series in the two approaches.

The distortion approximation of Bates (1959) allows explicitly for the final state. Equation (8.11) is approximated to

$$i\,\dot{a}_{nm}(t) = a_{nn}(t)\,V_{mn}(t)\,e^{i(\alpha_m-\alpha_n)t} + a_{nm}(t)\,V_{mm}(t) \qquad (8.13)$$

In the weak perturbation approximation we have $a_{ns}(t) = 0$ for $n \neq s$, thus

$$a_{nn}(t) = \exp\left[-\,i\int_{-\infty}^{t} V_{nn}(t')\,dt'\right]$$

hence

$$i\,\dot{a}_{nm}(t) = V_{mn}(t)\exp\left[-\,i\int_{-\infty}^{t} V_{nn}(t')\,dt'\right] e^{i(\alpha_m-\alpha_n)t} + a_{nm}(t)\,V_{mm}(t) \qquad (8.14)$$

now transforming a_{nm} to c_{nm} such that

$$c_{nm}(t) = a_{nm}(t)\exp\left[i\int_{-\infty}^{t} V_{mm}(t')\,dt'\right] \qquad (8.15)$$

we have

$$i\,\dot{c}_{nm}(t) = V_{mn}(t)\,e^{i(\alpha_m-\alpha_n)t}\exp\left[-\,i\int_{-\infty}^{t}(V_{nn}(t')-V_{mm}(t'))\,dt'\right]$$

thus

$$c_{nm}(t) = \delta_{nm} - i\int_{-\infty}^{t} V_{mn}(t')\,e^{i(\alpha_m'-\alpha_n')t'}\,dt' \qquad (8.16)$$

where

$$\alpha_n' = \alpha_n + \int_{-\infty}^{t} V_{nn}(t')\,dt'$$

Equation (8.16) has the same form as the I.P.B. approximation, but the energy levels of the target have been perturbed by the incoming particle. More complex approximations to the initial set of equations (8.11) have to be solved numerically, but since they include more coupling terms than the I.P.B. or distortion approximations, they are thought to describe the collision process more exactly. One such approximation is due to Flannery

(1969). In this work equations (8.11) were truncated so that only the $1s, 2s, 2p_0, 2p_{\pm 1}$ states were retained. The four resulting coupled differential equations were then solved numerically. The results of this work are discussed at the end of this section.

For a proton hydrogen collision there is always the possibility of a rearrangement collision, where the electron forms a bound state with the incoming proton; particle B in figure (2). In principle this type of process is included by the eigenfunction expansion (8.8) in particular by the continuum states of this expansion. Castilejo et al. (1960) have shown that the coefficients of the states above the ionization threshold contain singularities. However it is these continuum states that are required to describe the rearrangement channels. No procedures have been developed to deal with these singularities. The problems associated with the singularities are avoided if a truncated eigenfunction expansion is considered. This leaves us with a new problem in how to describe rearrangement collisions. One obvious way is to project out from the approximate wavefunction the final rearranged state. We shall see that this is unsatisfactory since it allows ambiguities in the final expression for the rearrangement amplitudes.

The rearranged eigenfunction is given by $\phi_n(\underset{\sim}{r}_b, t)$ such that

$$\phi_n(\underset{\sim}{r}_b, t) = \phi_n(\underset{\sim}{r}_b)\, e^{-i\beta_n t} \tag{8.17}$$

where β_n are the rearranged eigenenergies.

The Schrödinger equation is, in the impact parameter approximation for proton collisions

$$\left[-\tfrac{1}{2} \nabla_r^2 + \frac{1}{r_a} + \frac{1}{r_b} - \frac{1}{R} \right] \psi(\underset{\sim}{R}, \underset{\sim}{r}) = i \frac{\partial}{\partial t} \psi(\underset{\sim}{R}, \underset{\sim}{r}) \tag{8.18}$$

The total wavefunction may be expanded in a complete set of rearranged states.

$$\psi_n(\underset{\sim}{R},\underset{\sim}{r}) = \sum_q b_{nq}\, \phi_q(\underset{\sim}{r}_b)\, e^{-i\beta_q t} \tag{8.19}$$

then substituting in the Schrödinger equation we obtain

$$i\, \dot{b}_{nm}(t) = \sum_q b_{nq}(t)\, V_{mq}(t)\, e^{i(\beta_m-\beta_q)t} \tag{8.20}$$

where in this case $V_{mq}(t) = \int d\underset{\sim}{r}\, \phi_m^*(\underset{\sim}{r}_b)\, V(\underset{\sim}{r}_b,\underset{\sim}{R})\, \phi_q(\underset{\sim}{r}_b)$, but

$$\begin{aligned} i\, \dot{b}_{nm}(t) &= \int d\underset{\sim}{r}\, \phi_m^*(\underset{\sim}{r}_b)\, V(\underset{\sim}{r}_b,\underset{\sim}{R})\, \psi_n(\underset{\sim}{R},\underset{\sim}{r}) \\ &= \sum_q a_{nq}(t) \int d\underset{\sim}{r}\, \phi_m^*(\underset{\sim}{r}_b)\, V(\underset{\sim}{r}_b,\underset{\sim}{R})\, \phi_q(\underset{\sim}{r}_a) \end{aligned} \tag{8.21}$$

Since $\phi_n(\underset{\sim}{r}_b)$ and $\phi_m(\underset{\sim}{r}_a)$ are not orthogonal then $b'_{nm}(t)$ is dependent upon the internuclear potential. This is contradictory to the initial assumptions of rectilinear trajectories for the incoming particle, since within this assumption no choice of internuclear potential can affect the cross section. This difficulty is overcome by considering a two centred expansion, first suggested by Bates (1958).

$$\psi(R,r) = \sum_n a_n(t)\, \phi_n(\underset{\sim}{r}_a,t) + \sum_m b_m(t)\, \phi_m(\underset{\sim}{r}_b,t) \tag{8.22}$$

where the initial channel index has now been dropped. This expansion is overcomplete, but has the advantage of producing rearrangement amplitudes that are independent of the internuclear potential, to within a phase factor. This property is retained when the n and m summations are truncated, provided all coupling terms implied by (8.22) are retained.

The expansion (8.22) takes no explicit account of the relative colliding velocities of the incident particle with the target particles. In order that capture may take place the electron must acquire the same linear

velocity as the incoming proton. The larger this velocity is, the greater its affect will be on the capture cross sections. This velocity dependence may be included by considering a two centred expansion in travelling orbitals i.e. bound state wavefunctions with an overall translational movement included. Such wavefunctions were first introduced by Bates and McCarrol (1958) and have the form

$$\bar{\phi}_n(\underset{\sim}{r}_a,t) = \phi_n(\underset{\sim}{r}_a,t)\exp\left[-\text{ipvz} - \tfrac{1}{2}\,\text{i}\,p^2v^2t\right] \qquad (8.23)$$

and

$$\bar{\phi}_n(\underset{\sim}{r}_b,t) = \phi_n(\underset{\sim}{r}_b,t)\exp\left[\text{iqvz} + \tfrac{1}{2}\,\text{i}\,q^2v^2t\right]$$

where the target nucleus has the velocity $-p\underset{\sim}{v}$ relative to the origin and the incident proton has velocity $q\underset{\sim}{v}$ relative to the origin. The quantities p and q are defined by figure (3). The origin O divides the internuclear

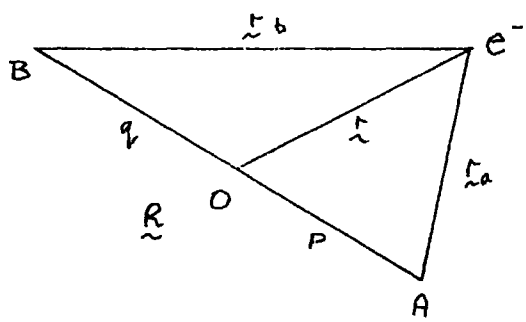


Figure (3)

line $\underset{\sim}{R}$ in the ratio p:q such that p + q = 1. Using the following results

$$z = \underset{\sim}{R}.\underset{\sim}{\hat{v}},\quad z = \underset{\sim}{r}.\underset{\sim}{\hat{v}},\quad z_a = \underset{\sim}{r}_a.\underset{\sim}{\hat{v}},\quad z_b = \underset{\sim}{r}_b.\underset{\sim}{\hat{v}}$$

and

$$z - vt = z_a - z - pvt = z_b - z + qvt = 0$$

then it can be shown that $\bar{\phi}_n(r_{a,b},t)$ satisfies

$$\left[H_o - i\frac{\partial}{\partial t}\right] \bar{\phi}_n(r,t) = V(r,R)\, \bar{\phi}_n(r,t) \qquad (8.24)$$

so that $\bar{\phi}_n(r,t)$ are eigenfunctions of the unperturbed Hamiltonian and can be used as a basis for an eigenfunction expansion. Bates and McCarrol (1958) have shown this result to be indepdendent of the origin O so if we assume O to coincide with the centre of gravity then $p = q = \frac{1}{2}$ and

$$\psi(\underset{\sim}{r},\underset{\sim}{R}) = \sum_n a_n(t)\, \bar{\phi}_n(r_a,t) + \sum_m b_m(t)\, \bar{\phi}_m(r_b,t) \qquad (8.25)$$

Substituting (8.25) into the Schrödinger equation and utilising the result (8.24) it may be seen that

$$i\left[\dot{a}_n(t) + \sum_m \dot{b}_m(t)\, S_{nm}(t)\, e^{-i(\beta_m-\alpha_n)t}\right] = \sum_m b_m(t)\, R_{nm}(t)\, e^{-i(\beta_m-\alpha_n)t} + \sum_m a_m(t)\, P_{nm}(t)\, e^{-i(\alpha_m-\alpha_n)t} \qquad (8.25)$$

and

$$i\left[\dot{b}_m(t) + \sum_n \dot{a}_n(t)\, S_{mn}(t)\, e^{-i(\alpha_n-\beta_m)t}\right] = \sum_n a_n(t)\, Q_{mn}(t)\, e^{-i(\alpha_n-\beta_m)t} + \sum_n b_n(t)\, T_{mn}(t)\, e^{-i(\beta_n-\beta_m)t}$$

where

$$S_{nm}(t) = \int \phi_n^*(\underset{\sim}{r}_a)\, \phi_m(r_b)\, e^{ivz}\, d\underset{\sim}{r}$$

$$S_{mn}(t) = \int \phi_m^*(r_b)\, \phi_n(\underset{\sim}{r}_a)\, e^{-ivz}\, d\underset{\sim}{r}$$

$$R_{nm}(t) = \int \phi_n^*(\underset{\sim}{r}_a)\, V(\underset{\sim}{r}_b, \underset{\sim}{R})\, \phi_m(\underset{\sim}{r}_b)\, e^{ivz}\, d\underset{\sim}{r}$$

$$P_{nm}(t) = \int \phi_n^*(\underset{\sim}{r}_a)\, V(\underset{\sim}{r}_a, \underset{\sim}{R})\, \phi_m(\underset{\sim}{r}_a)\, d\underset{\sim}{r}$$

$$Q_{mn}(t) = \int \phi_m^*(\underset{\sim}{r}_b)\, V(\underset{\sim}{r}_a, \underset{\sim}{R})\, \phi_n(\underset{\sim}{r}_a)\, e^{-ivz}\, d\underset{\sim}{r}$$

$$T_{mn}(t) = \int \phi_m^*(\underset{\sim}{r}_b)\, V(\underset{\sim}{r}_b, \underset{\sim}{R})\, \phi_n(\underset{\sim}{r}_b)\, d\underset{\sim}{r}$$

If in equation (8.26) charge exchange is neglected by considering $b_n(t)$ and $\dot{b}_n(t) = 0$ the equations reduce to those obtained in the single centred expansion case and also contain no reference to the relative velocity of the incident particle and target. The effects of including the velocity factors can be seen in the matrix elements of (8.26). When the velocity is large the exp(±ivz) factors produce rapid oscillations in the integrands giving cancellation that reduces the size of the various couplings. This effect has been explored quantitatively by McDowell and Coleman (1970), they consider a two state approximation i.e. retaining only the ground state of the target and of the rearranged atom, and evaluate the charge transfer amplitudes in the high velocity limit for the process

$$P + H(1s) \rightarrow H(1s) + P$$

The work was further simplified by assuming a weak perturbation approximation. In the case where the velocity factors were included the charge transfer probability P_{if} was found to be

$$P_{if}(\rho) \underset{v\to\infty}{\rightarrow} \frac{64\pi\,\rho^3}{v^4}\, e^{-\rho v} \qquad (8.27)$$

whereas in the case where the velocity factors were omitted

$$P_{if}^{o}(\rho) \underset{v\to\infty}{\rightarrow} \frac{2\pi\,\rho^3}{v^2}\, e^{-2\rho} \qquad (8.28)$$

Equations (8.27) and (8.28) give the following behaviour for the total cross sections

$$Q_{if} \propto v^{-12} \tag{8.29}$$

and

$$Q_{if}^{o} \propto v^{-2} \tag{8.30}$$

The high velocity behaviours of these charge transfer cross sections are significantly different. Comparison with experiment, in the energy range up to 250 KeV shows that (8.29) is close to the experimental behaviour but that (8.30) is in error, Witthower et al. (1966).

Calculations of direct and charge transfer excitation cross sections for proton hydrogen collisions using the two centre expansion (8.25) have been carried out by Wilets and Gallaher (1966). They retained the 1s, 2s, $2p_o$ and $2p_{\pm 1}$ states of both target and rearranged atom. The results obtained are shown to be in error, particularly at low energies, by Cheshire et al. (1970) who repeated the calculation. A comparison of direct excitation cross sections calculated using a two centre expansion with those calculated using a single centred expansion, Flannery (1969) shows the important effect the rearrangement channels have on direct excitation cross sections. The results of our own four state single centre calculations and the results of the two centre calculations of Cheshire are shown in table (3). The two sets of results are in reasonable agreement for energies above 100 KEV, showing that the effects of charge exchange on direct excitation can only be neglected above this energy.

ENERGY	1s - 2s		1s - 2p	
(KEV)	a	b	a	b
10	3.58(-1)	1.15(-1)	2.96(-1)	1.78(-1)
15	5.98(-1)	1.51(-1)	5.91(-1)	1.28(-1)
20	6.59(-1)	1.21(-1)	8.36(-1)	2.04(-1)
25	6.39(-1)	1.27(-1)	1.01	3.86(-1)
30	5.89(-1)	1.40(-1)	1.11	5.32(-1)
40	4.84(-1)	1.79(-1)	1.22	7.76(-1)
60	3.28(-1)	1.95(-1)	1.22	9.32(-1)
100	1.85(-1)	1.54(-1)	1.04	9.68(-1)
300	4.89(-2)	4.83(-1)	5.53(-1)	5.61(-1)

Table 3. Excitation cross sections in units of (πa_o^2)
(a) Single centred 4-state expansion.
(b) Wilets and Gallaher (1966) corrected by Cheshire et al. (1970).

In their original calculations Wilets and Gallaher (1966) attempted to check the convergence of the eight state calculation by comparing a few results with those obtained using a sixteen state calculation. In this calculation all states up to the $3p_{\pm1}$ level were retained for both centres. This difference between the two calculations is small. This is interpreted as evidence that the convergence of the initial comparison is slow and that the continuum states must also be taken into account. This is particularly evident if we require that the united atom limit, corresponding to $\underset{\sim}{R} = 0$ and $\underset{\sim}{r}_a = \underset{\sim}{r}_b$, is well represented by the approximate wavefunction. In the work of Wilets and Gallaher (1966) the ground state wavefunctions of the He^+ atom were expanded in a complete set of hydrogen wavefunctions. The overlap probability with the ground state was found to be 0.70, and with all the bound states 0.76. This leaves 0.24 for the continuum states, and indicates

the relative importance of including the effects of continuum states in an eigenfunction expansion.

In an attempt to represent the continuum states Gallaher and Wilets (1967) expanded the total wavefunction in a Sturmian basis set. Further work, Gallaher and Wilets (1968) showed that this basis also had poor convergence properties. Cheshire et al. (1970) attempt to account for the effects of the continuum states by considering a pseudo state expansion. The 1s, 2s and 2p hydrogenic states were retained exactly and pseudo s_{11}, s_{21} states were also added. The pseudo states were chosen so that the He^+ 1s, 2s and 2p states were well represented by the approximate wavefunctions. In fact the overlap probabilities of the approximate wavefunction with the He^+ states were 0.997, 0.996 and 0.966 respectively.

A comparision of the above calculations with available experimental data for both direct and charge exchange excitation cross sections shows the pseudo state method of Cheshire et al. to have the closest agreement. However this agreement is not conclusive since there is still discrepancies between experiment and theory. As yet no work has been reported that investigates the convergence of the pseudo state method.

The implications of the above is clear. In order to calculate satisfactory direct excitation cross sections it is necessary to allow for the charge exchange process and in the case of eigenfunction expansions to allow for the effects of the omitted continuum states. At best the inclusion of the continuum states of the target should implicitly allow for the charge exchange process.

9. The Eikonal Approximation and Glauber Theory

Direct excitation collision can be treated approximately by assuming a semi-classical formulation of the operator equation (2.6). This is the Eikonal approximation, Byron (1971) has shown how this can lead to a semi-

classical close coupling approximation, equivalent to an impact parameter treatment yet comparable the close coupling approximation of Burke et al. (1963). If a complete set of target eigenstates is included in the close coupling approximation the expression obtained for the scattering amplitudes is identical to that derived by Franco (1966) in the the Glauber approximation. The significance of this work is that the Glauber approximation can then be placed in context with the work of previous sections.

The conditions for the validity of the Glauber approximation are

$$K_i \, a_o \gg 1$$

and

$$E_i \gg \bar{v} \qquad (9.1)$$

$$a_o \, \Delta E / v_i \ll 1 \qquad (9.2)$$

where ΔE is a typical energy difference between eigenstates of the target. The conditions expressed in equation (9.1) are those usually demanded by the Eikonal approximation and that of equation (9.2) is required to derive the usual form of the Glauber scattering amplitudes from the semi-classical close coupling approximation. In particular $K_i \, a_o \gg 1$ implies that the incident particle wavelength is much smaller than the typical potential width a_o, a_o is the first Bohr radius and is equal to one in atomic units, and $E \gg \bar{v}$ implies that the incident particle energy is much greater than an average interaction potential. Under these conditions scattering will be mainly in the forward direction and the momentum transfer correspondingly small when compared with the incident particle momentum. These conditions are well satisfied for proton impact of energy where 1 KEV. For electron impact the conditions are at best only marginally satisfied. The validity of the eikonal approximation for electron scattering is examined heuristically later.

The total wavefunction for the collision satisfies the integral equation

$$\psi_n(\underset{\sim}{R},\underset{\sim}{r}) = e^{i\,\underset{\sim}{K}_i.\underset{\sim}{R}}\,\phi_n(\underset{\sim}{r}) + \int G_n^{+}(\underset{\sim}{R}\,\underset{\sim}{r},\underset{\sim}{R'}\underset{\sim}{r'})\, V(\underset{\sim}{R'},\underset{\sim}{r'})\, \psi_n(\underset{\sim}{R'},\underset{\sim}{r'})\, d\underset{\sim}{R'}\, d\underset{\sim}{r'} \tag{9.3}$$

where

$$G_n^{+}(\underset{\sim}{R}\,\underset{\sim}{r},\underset{\sim}{R'}\underset{\sim}{r'}) = \frac{2\mu}{(2\pi)^3} \sum_m \phi_m^*(\underset{\sim}{r'})\, \phi_m(\underset{\sim}{r}) \int d\underset{\sim}{K}\, \frac{e^{-i\,\underset{\sim}{K}.(\underset{\sim}{R'}-\underset{\sim}{R})}}{\left[2\mu(\varepsilon_n-\varepsilon_m)+K_i^2-K^2+i\varepsilon\right]}$$

$$= \sum_m \phi_m^*(\underset{\sim}{r'})\, \phi_m(\underset{\sim}{r})\, g_n(\underset{\sim}{R}\,\underset{\sim}{R'},m) \tag{9.4}$$

and

$$g_n(\underset{\sim}{R}\,\underset{\sim}{R'},m) = \frac{2\mu}{(2\pi)^3} \int d\underset{\sim}{K}\, \frac{e^{-i\,\underset{\sim}{K}.(\underset{\sim}{R'}-\underset{\sim}{R})}}{\left[2\mu(\varepsilon_n-\varepsilon_m)+K_i^2-K^2+i\varepsilon\right]} \tag{9.5}$$

μ is the reduced mass for the collision. The exact wavefunction may be expanded as

$$\psi_n(\underset{\sim}{R},\underset{\sim}{r}) = \sum_m F_{nm}(\underset{\sim}{R})\, \phi_m(\underset{\sim}{r}) \tag{9.6}$$

and using equation (9.3) we have

$$F_{nm}(\underset{\sim}{R}) = e^{i\,\underset{\sim}{K}_i.\underset{\sim}{R}}\,\delta_{nm} + \sum_{m'} \int g_n(\underset{\sim}{R}\,\underset{\sim}{R'},m)\, V_{mm'}(\underset{\sim}{R'})\, F_{nm'}(\underset{\sim}{R'})\, d\underset{\sim}{R'} \tag{9.7}$$

where $$V_{nm}(\underset{\sim}{R}) = \int \phi_n^*(\underset{\sim}{r})\, V(\underset{\sim}{R},\underset{\sim}{r})\, \phi_m(\underset{\sim}{r})\, d\underset{\sim}{r}$$

Following Glauber (1959) we can write

$$F_{nm}(\underset{\sim}{R}) = e^{i\,\underset{\sim}{K}_i.\underset{\sim}{R}}\,\chi_{nm}(\underset{\sim}{R}) \tag{9.8}$$

thus from equation (9.7) we have

$$\chi_{nm}(\underset{\sim}{R}) = \delta_{mn} + \sum_{m'} \int g_n(\underset{\sim}{R}\,\underset{\sim}{R}',m)\, V_{mm'}(\underset{\sim}{R}')\, \chi_{nm'}(\underset{\sim}{R}')\, e^{-i\,\underset{\sim}{K}_i.(\underset{\sim}{R}-\underset{\sim}{R}')}\, d\underset{\sim}{R}' \tag{9.9}$$

if $Q_{nm} = 2\mu(\epsilon_n - \epsilon_m)$

then

$$g_n(\underset{\sim}{R}\,\underset{\sim}{R}',m) = \frac{2\mu}{(2\pi)^3} \int d\underset{\sim}{K}\, \frac{e^{-i\,\underset{\sim}{K}.(\underset{\sim}{R}'-\underset{\sim}{R})}}{\left[Q_{nm}+K_i^2-K^2+i\varepsilon\right]} \tag{9.10}$$

making the change of variable $\underset{\sim}{K} = \underset{\sim}{K}_i + \underset{\sim}{\eta}$, $\underset{\sim}{\eta}$ is the momentum transfer and is such that $\eta << K_i$ under the conditions of (9.1) thus

$$K^2 \sim K_i^2 + 2\underset{\sim}{\eta}.\underset{\sim}{K}_i$$

and

$$g_n(\underset{\sim}{R}\,\underset{\sim}{R}',m) \sim -\frac{2\mu}{(2\pi)^3} \int d\underset{\sim}{K}\, \frac{e^{-i\,\underset{\sim}{K}.(\underset{\sim}{R}'-\underset{\sim}{R})}}{\left[Q_{nm}+2\underset{\sim}{\eta}.\underset{\sim}{K}_i-i\varepsilon\right]} \tag{9.11}$$

The integral of (9.11) may be calculated by the method of appendix I to give

$$g_n(\underset{\sim}{R}\,\underset{\sim}{R}',m) = -\frac{2\mu i}{2K_i}\, \delta^2(\underset{\sim}{b}-\underset{\sim}{b}')\, \theta(z-z')\, e^{i\,Q_{nm}(z-z')/2K_i}\, e^{-i\,\underset{\sim}{K}_i.(\underset{\sim}{R}'-\underset{\sim}{R})} \tag{9.12}$$

where $\underset{\sim}{b}$ is a vector in the X-Y plane perpendicular to the Z direction.

Equation (9.9) now becomes

$$\chi_{nm}(\underset{\sim}{R}) = \delta_{mn} - \frac{i\mu}{K_i} \sum_{m'} \int_{-\infty}^{z} e^{-q_{mn}(z-z')}\, V_{mm'}(X,Y,Z')\, \chi_{nm'}(X,Y,Z')\, dZ' \tag{9.13}$$

where $q_{nm} = Q_{nm}/2K_i$

If $\chi_{nm}(\underset{\sim}{R})$ is written as $e^{-i\,q_{mn}z}\, \alpha_{nm}(\underset{\sim}{R})$ then equation (9.13) reduces to

$$\alpha_{nm}(\underset{\sim}{R}) = \delta_{mn} - \frac{i\mu}{K_i} \sum_{m'} \int_{-\infty}^{z} V_{mm'}(\underset{\sim}{b},z')\, e^{-i\,q_{m'm}z'}\, \alpha_{nm'}(\underset{\sim}{b},z')\, dz' \tag{9.14}$$

and thus

$$\frac{\partial}{\partial z}\alpha_{nn}(\underset{\sim}{R}) = -\frac{i\mu}{K_i}\sum_{m'} V_{nm'}(\underset{\sim}{b},z)\, e^{-i\,q_{m'm}z}\,\alpha_{nm'}(\underset{\sim}{b},z) \qquad (9.15)$$

If we identify z with vt where v is the incident particle velocity and t is time, then equation (9.15) reduces to equation (8.11) which was 'derived' directly in the impact parameter approximation.

The scattering amplitude from equation (1.25) is

$$T_{if} = \langle\psi_f|V|\psi_i^{+}\rangle$$

where $$\psi_f = e^{i\,\underset{\sim}{K}_f.\underset{\sim}{R}}\,\phi_{n'}(\underset{\sim}{r})$$

and $$\psi_i^{+}(\underset{\sim}{R},\underset{\sim}{r}) = e^{i\,\underset{\sim}{K}_i.\underset{\sim}{R}}\sum_m e^{-i\,q_{nm}z}\,\alpha_{nm}(\underset{\sim}{R})\,\phi_m(\underset{\sim}{r})$$

thus

$$T_{if} = \int e^{i(\underset{\sim}{K}_i-\underset{\sim}{K}_f).\underset{\sim}{R}}\sum_m e^{-i\,q_{nm}z}\,V_{n'm}(\underset{\sim}{R})\,\alpha_{nm}(\underset{\sim}{R})\,d\underset{\sim}{R} \qquad (9.16)$$

This expression for the scattering amplitude can be considerably simplified by making kinematic approximations

$$T_{if} = \int e^{i(\underset{\sim}{K}_i-\underset{\sim}{K}_f).\underset{\sim}{R}}\, e^{-i\,q_{n'n}z}\sum_m e^{-i\,q_{mn'}z}\,V_{n'm}(R)\,\alpha_{nm}(\underset{\sim}{R})\,d\underset{\sim}{R} \qquad (9.17)$$

but $$\underset{\sim}{K}_i.\underset{\sim}{R} + q_{nn'}z = (K_i+q_{nn'})z$$

conservation of energy gives $\frac{K_i^2}{2\mu} + \epsilon_n = \frac{K_f^2}{2\mu} + \epsilon_{n'}$ thus

$$K_f = K_i(1+q_{nn'}/2K_i)^{1/2}$$

$$\sim K_i - q_{n'n}$$

$$= K_i'$$

then $$\underset{\sim}{K}_i.\underset{\sim}{R} + q_{nn'}z = \underset{\sim}{K}_i'.\underset{\sim}{R}$$

where $\underset{\sim}{K_i}'$ is a vector in the z direction with magnitude K_f thus

$$T'_{if} = \int e^{i(\underset{\sim}{K_i}'-\underset{\sim}{K_f}).\underset{\sim}{R}} \sum_m e^{i q_{n'm} z} V_{n'm}(\underset{\sim}{R})\, \alpha_{nm}(\underset{\sim}{R})\, d\underset{\sim}{R} \qquad (9.18)$$

since $K_i' \sim K_f$, then for small scattering angles

$$(\underset{\sim}{K_i}'-\underset{\sim}{K_f}).\underset{\sim}{R} \sim (\underset{\sim}{K_i}'-\underset{\sim}{K_f}).\underset{\sim}{b}$$

and $$T_{if} = \int e^{i(\underset{\sim}{K_i}'-\underset{\sim}{K_f}).\underset{\sim}{b}} \sum_m \int_{-\infty}^{\infty} e^{i q_{n'm} z} V_{n'm}(\underset{\sim}{b},z)\, \alpha_{nm}(\underset{\sim}{b},z)\, dz\, d\underset{\sim}{b}$$

using equation (9.14) we have

$$T_{if} = \frac{i K_i}{\mu} \int e^{i(\underset{\sim}{K_i}'-\underset{\sim}{K_f}).\underset{\sim}{b}} \left[\alpha_{nn'}(\underset{\sim}{b},\infty) - \delta_{nm'}\right] d\underset{\sim}{b} \qquad (9.19)$$

The total cross section for the $n \to n'$ transition is then

$$\sigma_{nn'} = \frac{\mu^2}{4\pi^2} \frac{K_f}{K_i} \int |T_{if}|^2\, d\Omega$$

and using equation (9.19) this becomes

$$\sigma_{nn'} = \frac{K_i}{K_f} \int |\alpha_{nn'}(\underset{\sim}{b},\infty) - \delta_{nn'}|^2\, d\underset{\sim}{b} \qquad (9.20)$$

The validity of the approximation made for electron scattering has been examined by Byron (1971). The derivation of the scattering amplitude (9.19) involved two distinct stages of approximation; firstly the eikonal approximation of equation (9.11) and secondly the kinematic approximation of equation (9.19). If equation (9.15) is solved in the first Born approximation and the eikonal-Born amplitude calculated, using equation (9.19), and compared with the exact first Born approximation then the difference between the two results is due to the kinematic approximation only. Calculations show that the kinematic approximation can have effects of up to 20% on the total cross section results. In order to test the eikonal approximation

alone it is essential to use the scattering amplitudes given directly by equation (9.16). Byron solved equations (9.15) by retaining only the 1s, 2s, $2p_o$ and $2p_{\pm 1}$ states in the summation and produced transition amplitudes that were directly comparable to the results of the close coupling approximation of Burke et al. (1963). The results show agreement to within about 10%. Burke et al. (1963) allow for electron exchange but at the energy considered, 54.4 eV, this is assumed to be negligible. Since equations (9.15) and (9.19) are precisely those that appear in the impact parameter approximation it would appear that one can expect to obtain qualitative results only from an impact parameter treatment of electron collisions with hydrogen. However such results could well be an improvement over other approximations.

The familiar Glauber approximation as utilised by Tai et al. (1970) for electron hydrogen scattering and by Franco and Thomas (1971) for proton hydrogen scattering is obtained by including a complete set of states in the solution of equation (9.15).

Assuming that the important values of z in equation (9.15) are of order a_o then $q_{mn}z$ is small since then

$$q_{mn}z \sim a_o \, \Delta E/v_i << 1$$

hence $e^{i q_{mn} z} \sim 1$

thus equation (9.15) becomes

$$\frac{\partial}{\partial z} \alpha_{nm}(\underset{\sim}{R}) = - \frac{i\mu}{K_i} \sum_{m'} V_{mm'}(\underset{\sim}{b},z) \, \alpha_{nm'}(\underset{\sim}{b},z) \qquad (9.21)$$

using closure equation (9.21) may be solved exactly

$$\alpha_{nm}(\underset{\sim}{R}) = \int d\underset{\sim}{r} \, \phi_m^*(\underset{\sim}{r}) \, \phi_n(\underset{\sim}{r}) \exp\left[- \frac{i\mu}{K_i} \int_{-\infty}^{z} V(\underset{\sim}{b},z',\underset{\sim}{r}) \, dz' \right] \qquad (9.22)$$

and the scattering amplitude becomes

$$T_{if} = i \frac{K_i}{\mu} \int e^{i(\underset{\sim}{K}_i - \underset{\sim}{K}_f).\underset{\sim}{b}} \phi_{n'}^{*}(\underset{\sim}{r}) \phi_n(\underset{\sim}{r}) \left[\exp\left(- \frac{i\mu}{K_i} \int_{-\infty}^{\infty} V(\underset{\sim}{b}, z', \underset{\sim}{r}) \, dz' \right) - 1 \right] d\underset{\sim}{b} \, d\underset{\sim}{r} \qquad (9.23)$$

This expression for the scattering amplitudes has two undesirable features. Franco (1968) shows that in the case of elastic scattering the transition amplitude $T_{nn}(\underset{\sim}{q})$, where $\underset{\sim}{q}$ is the momentum transfer, contains a logarithmic singularity. Tai et al. (1970) show from their explicit calculations for electron collisions that the transition from an s state to a p_o state is strictly forbidden. Both of these features result from the kinematic approximations made to the momentum transfer factor. The effects of these on the total cross sections for excitation are small. Byron (1971) has evaluated an expression for the scattering amplitudes that does not include the kinematic approximation.

Again assuming $q_{mn} z << 1$ equation (9.16) becomes

$$T_{if} = \int e^{i(\underset{\sim}{K}_i - \underset{\sim}{K}_f).\underset{\sim}{R}} \sum_m V_{n'm}(\underset{\sim}{R}) \, \alpha_{nm}(\underset{\sim}{R}) \, d\underset{\sim}{R} \qquad (9.24)$$

using the Glauber expression for α_{nm} and also closure we obtain

$$T_{if} = \int e^{i(\underset{\sim}{K}_i - \underset{\sim}{K}_f).\underset{\sim}{R}} \int \phi_{n'}^{*}(\underset{\sim}{r}) \, \phi_n(\underset{\sim}{r}) \, V(\underset{\sim}{R}, \underset{\sim}{r}) \times \exp\left[- \frac{i\mu}{K_i} \int_{-\infty}^{z} V(\underset{\sim}{b}, z', \underset{\sim}{r}) \, dz' \right] d\underset{\sim}{r} \, d\underset{\sim}{R} \qquad (9.25)$$

A comparison of the results for excitation cross sections to the 2s and 2p states for electron hydrogen collisions evaluated using equation (9.25) with the Glauber approximation results of Tai et al. (1970) shows the two sets

of cross sections to be in good agreement. The two methods diverge however on the question of polarization of reemitted radiation and excitation to the 2p state, the more exact treatment of Byron being closer to the experimental results. Thus under the Glauber approximation the approximation of the momentum transfer is acceptable if cross sections only are required. Since the eikonal approximation gave quite good results for electron collisions in the close coupling approximation it appears satisfactory to evaluate transition cross sections for electron collisions using the Glauber approximation. Proton collision should of course also be well described by the Glauber approximation.

The 2s and 2p excitation cross sections calculated in the Glauber approximation, Tai et al. (1970), for electron hydrogen collisions are in good accord with experiment for energies greater than 30 eV. It is thought that the discrepancy below 30 eV may be due to the neglect of electron exchange and also to the failure of the eikonal approximation. No such direct comparison with experiment can be made for proton hydrogen collisions since very little experimental data is available. However where data are available the calculations of Franco and Thomas (1971) agree quite well. Perhaps of more significance though is the comparison of the Glauber results with the pseudo state results of Cheshire et al. (1970). The total cross sections for 2s and 2p transitions as functions of the incident proton energy are very much alike above 10 KEV, in both shape and magnitude. This is not surprising since the Glauber approximation implicitly includes the continuum states of the target so that the rearrangement channels, shown to have important effects on the direct excitation processes, are represented. The failure of the Glauber approximation below 10 KEV can be attributed to the fact that the target electron velocity is very similar to the incident proton velocity contrary to the condition of equation (9.2). The success of Glauber theory in describing electron and proton collisions shows that

it is unnecessary to include strongly coupled states exactly provided that transitions between such states are implicitly allowed. It is however, difficult to see a way of systematically improving the Glauber approximation.

PART III

10.1 Present Work

The previous sections have shown how the close coupling approximation can be applied to atomic collision processes, both in the wave formulation and in the impact parameter approximation. In general the description afforded by the close coupling approximation in the intermediate energy range has not been good. This is due to the neglect of all but the first few states in the eigenfunction expansion. Where attempts have been made to represent the neglected states considerable improvement of the results has been seen. In this work an alternative method is presented to include the effects of all states not explicitly included in a close coupling approximation. The method is due to Bransden and Coleman (1972). The inclusion of the neglected states is done by means of a closure approximation. This leaves a free parameter that is chosen so that the correct polarization potential is obtained in the ground state channel. The method is applied to direct collisions of electrons and protons with a hydrogen atom.

The Schrödinger equation, from equation (2.4), is

$$\left[-\frac{1}{2\mu} \nabla_R^2 + H_o + V(\underset{\sim}{R},\underset{\sim}{r}) - E \right] \psi_n(\underset{\sim}{R},\underset{\sim}{r}) = 0 \qquad (10.1)$$

where H_o is the target Hamiltonian. Expanding the exact wavefunction into a complete set of target states gives

$$\psi_n(\underset{\sim}{R},\underset{\sim}{r}) = \sum_m F_{nm}(\underset{\sim}{R})\, \phi_m(\underset{\sim}{r}) \qquad (10.2)$$

combining this with the Schrödinger equation (10.1) we get

$$\left[\nabla_R^2 + K_m^2\right] F_{nm}(\underset{\sim}{R}) = 2 \sum_{m'} V_{mm'}(\underset{\sim}{R})\, F_{nm'}(\underset{\sim}{R}) \qquad (10.3)$$

where $V_{nm}(\underset{\sim}{R})$ has been defined previously and

$$K_m^2 = 2\mu(E-\varepsilon_m)$$

The total wavefunction satisfies the integral equation

$$\psi_n(\underset{\sim}{R},\underset{\sim}{r}) = e^{i\,\underset{\sim}{K}_i.\underset{\sim}{R}}\,\phi_n(\underset{\sim}{r}) + \int G_n^{+}(\underset{\sim}{R},\underset{\sim}{r};\underset{\sim}{R}',\underset{\sim}{r}')\, V(\underset{\sim}{R}',\underset{\sim}{r}')\, \psi_n(\underset{\sim}{R}',\underset{\sim}{r}')\, d\underset{\sim}{R}'\, d\underset{\sim}{r}' \tag{10.4}$$

where

$$G_n^{+}(\underset{\sim}{R},\underset{\sim}{r};\underset{\sim}{R}',\underset{\sim}{r}') = \frac{2\mu}{(2\pi)^3} \sum_m \phi_m^*(\underset{\sim}{r}')\, \phi_m(\underset{\sim}{r}) \int d\underset{\sim}{K}\, \frac{e^{-i\,\underset{\sim}{K}.(\underset{\sim}{R}'-\underset{\sim}{R})}}{\left[K_m^2-K^2-i\varepsilon\right]}$$

defining the function g_n as

$$g_n(\underset{\sim}{R},\underset{\sim}{R}',m) = \frac{2\mu}{(2\pi)^3} \int d\underset{\sim}{K}\, \frac{e^{-i\,\underset{\sim}{K}.(\underset{\sim}{R}'-\underset{\sim}{R})}}{\left[K_m^2-K^2-i\varepsilon\right]} \tag{10.5}$$

and substituting the expansion (10.2) in (10.4) we obtain

$$F_{nm}(\underset{\sim}{R}) = e^{i\,\underset{\sim}{K}_i.\underset{\sim}{R}}\,\delta_{nm} + \sum_{m'} \int g_n(\underset{\sim}{R},\underset{\sim}{R}',m)\, V_{mm'}(\underset{\sim}{R}')\, F_{nm'}(\underset{\sim}{R}')\, d\underset{\sim}{R}' \tag{10.6}$$

If in expansion (10.2) only the first N states are retained then for $n > N$

$$F_{nm}(R) = \sum_{m'=0}^{N} \int g_n(\underset{\sim}{R},\underset{\sim}{R}',m)\, V_{mm'}(\underset{\sim}{R}')\, F_{nm'}(\underset{\sim}{R}')\, d\underset{\sim}{R}' \tag{10.7}$$

Then in equation (10.3) the first N states are treated exactly and the others approximated using (10.7) we obtain

$$\left[\nabla_R^2 + K_m^2\right] F_{nm}(\underset{\sim}{R}) = 2 \sum_{m'=0}^{N} V_{mm'}(\underset{\sim}{R})\, F_{nm'}(\underset{\sim}{R}) + 2 \sum_{m'=0}^{N} \int d\underset{\sim}{R}'\, K_{mm'}(\underset{\sim}{R},\underset{\sim}{R}')\, F_{nm'}(\underset{\sim}{R}') \tag{10.8}$$

$$m = 0,N$$

where

$$K_{nn'}(\underset{\sim}{R},\underset{\sim}{R}') = \sum_{j=N+1}^{\infty} V_{nj}(\underset{\sim}{R})\, V_{jn'}(\underset{\sim}{R}')\, g_n(\underset{\sim}{R},\underset{\sim}{R}',j) \qquad (10.9)$$

the summation in this latter expression includes the continuum states also. The summation is now removed by closure. For $n > N$ the eigenenergies ϵ_n are replaced by an average energy $\bar{\epsilon}$ which corresponds to $\bar{K}^2$ where

$$\bar{K}^2 = 2\mu(E-\bar{\epsilon})$$

then

$$K_{nn'}(\underset{\sim}{R},\underset{\sim}{R}') = g(\underset{\sim}{R},\underset{\sim}{R}') \sum_{j=N+1}^{\infty} V_{nj}(\underset{\sim}{R})\, V_{jn'}(\underset{\sim}{R}') \qquad (10.10)$$

where

$$g(\underset{\sim}{R},\underset{\sim}{R}') = \frac{2\mu}{(2\pi)^3} \int d\underset{\sim}{K}\, \frac{e^{-i\,\underset{\sim}{K}.(\underset{\sim}{R}'-\underset{\sim}{R})}}{\left[\bar{K}^2-K^2-i\epsilon\right]}$$

The closure relation is

$$\sum_j \phi_j(\underset{\sim}{r})\, \phi_j^*(\underset{\sim}{r}') = \delta(\underset{\sim}{r}-\underset{\sim}{r}')$$

using this in equation (10.10) $K_{nn'}$ becomes

$$K_{nn'}(\underset{\sim}{R},\underset{\sim}{R}') = g(\underset{\sim}{R},\underset{\sim}{R}') \left[\mu_{nn'}(\underset{\sim}{R},\underset{\sim}{R}') - \sum_{j=0}^{N} V_{nj}(\underset{\sim}{R})\, V_{jn'}(\underset{\sim}{R}')\right] \qquad (10.11)$$

where

$$\mu_{nn}(\underset{\sim}{R},\underset{\sim}{R}') = \int \phi_n^*(\underset{\sim}{r})\, V(\underset{\sim}{R},\underset{\sim}{r})\, V(\underset{\sim}{R}',\underset{\sim}{r})\, \phi_m(\underset{\sim}{r})\, d\underset{\sim}{r} \qquad (10.12)$$

The equations (10.8) can then be reduced to a form suitable for numerical solution by expanding the coefficients F_{nn} into partial waves.

Alternatively we can apply the same approximate procedures directly to the impact parameter approximation previously derived in section (8) and also in section (9). Considering transitions from the incident channel

ground state only, we have

$$i \frac{\partial}{\partial t} a_n(t) = \sum_{m=0}^{\infty} a_m(t)\, V_{nm}(t)\, \exp\left[-i(\varepsilon_n-\varepsilon_m)t\right] \qquad (10.13)$$

Again only retaining the first N states we have for $n > N$

$$i \dot{a}_n(t) = \sum_{m=0}^{N} a_m(t)\, V_{nm}(t)\, \exp\left[-i(\varepsilon_n-\varepsilon_m)t\right] \qquad (10.14)$$

then if the first N states of equation (10.13) are included explicitly and the states for $n > N$ are included using equation (10.14) we get

$$\begin{aligned} i \dot{a}_n(t) = & \sum_{m=0}^{N} a_m(t)\, V_{nm}(t)\, \exp\left[-i(\varepsilon_n-\varepsilon_m)t\right] \\ & - i \sum_{m=0}^{N} \int_{-\infty}^{t} a_m(t') \sum_{j=N+1}^{\infty} \bar{V}_{nj}(t)\, \bar{V}_{jm}(t')\, \exp\left[-i(\varepsilon_n-\varepsilon_j)t \right. \\ & \qquad \left. + i(\varepsilon_j-\varepsilon_m)t'\right] \\ & \qquad n = 0,N \end{aligned} \qquad (10.15)$$

where

$$\bar{V}_{nj}(t) = \int d\underset{\sim}{r}\, \phi_n^*(\underset{\sim}{r})\, \frac{1}{|\underset{\sim}{R}-\underset{\sim}{r}|}\, \phi_j(\underset{\sim}{r})$$

The 'internuclear' potential term has been omitted from the definition of $\bar{V}_{nj}$ since $\bar{V}_{nj}$ only occurs when $n \neq j$. The infinite summation of (10.15) is removed by closure; ε_j is replaced by $\bar{\varepsilon}$ for all $j > N$. This gives

$$\begin{aligned} i \dot{a}_n(t) = & \sum_{m=0}^{N} \left[a_m(t)\, V_{nm}(t)\, \exp\left[-i(\varepsilon_n-\varepsilon_m)t\right] \right. \\ & \left. - i \exp\left[-i(\varepsilon_n-\bar{\varepsilon})t\right] \int_{-\infty}^{t} a_m(t')\, K_{nm}(t,t')\, dt' \right] \\ & \qquad n = 0,N \end{aligned} \qquad (10.16)$$

where

$$K_{nm}(t,t') = \exp\left[-i(\bar{\varepsilon}-\varepsilon_m)t'\right] \left(\mu_{nm}(t,t') - \sum_{j=0}^{N} \bar{V}_{nj}(t)\, \bar{V}_{jm}(t') \right) \qquad (10.17a)$$

and

$$\mu_{nm}(t,t') = \int \phi_n^*(\underset{\sim}{r}) \frac{1}{|\underset{\sim}{R}-\underset{\sim}{r}|} \frac{1}{|\underset{\sim}{R}'-\underset{\sim}{r}|} \phi_m(\underset{\sim}{r})\, d\underset{\sim}{r}$$

with

$$\underset{\sim}{R} = \underset{\sim}{\rho} + \underset{\sim}{v}t \qquad \text{and} \qquad \underset{\sim}{R}' = \underset{\sim}{\rho} + \underset{\sim}{v}t'$$

Some of the energies ε_j within the sum of equation (10.15) could be included exactly. Then ε_j is replaced by $\bar{\varepsilon}'$ for $j > M > N+1$ and the exact energies used for values of j between M and N. The kernal of equation (10.16) is then replaced by

$$K_{nm}(t,t') + \sum_{j=N+1}^{M} \bar{V}_{nj}(t)\, \bar{V}_{jm}(t') \left[\exp\left[i(\bar{\varepsilon}'-\varepsilon_j)t + i(\varepsilon_j-\varepsilon_m)t' \right] - \exp\left[i(\bar{\varepsilon}'-\varepsilon_m)t' \right] \right] \qquad (10.17b)$$

The effective energies $\bar{\varepsilon}$ or $\bar{\varepsilon}'$ are chosen so that the correct polarization potential is obtained in the incident channel; where the polarization potential is such that

$$i\,\dot{a}_o(t) \underset{t\to-\infty}{\sim} V^{POL}\, a_o(t)$$

For the ground state of the hydrogen atom, Castillejo et al. (1960) have shown that

$$V^{POL} \sim -\frac{\alpha}{R^4} \qquad \text{where} \qquad \alpha = 2.25 \qquad (10.18)$$

The N coupled integro-differential equation (10.16) can now be solved with the kernal K_{nm} given either by (10.17a) or by (10.17b). To calculate transition amplitudes for excitation from the 1s state of hydrogen the boundary conditions are

$$a_n(-\infty) = \delta_{on}$$

The amplitudes for excitation to a state n for n > N can be calculated using equation (10.14), or allowing for distortion in the final state from

$$i\,\dot{a}_n(t) = \sum_{m=0}^{N} a_m(t)\, V_{nm}(t)\, \exp\left[-i(\varepsilon_n - \varepsilon_m)t\right] + a_n(t)\, V_{nn}(t) \qquad (10.19)$$

The approximation has been applied to both proton and electron scattering in the impact parameter formulation, the 1s, the 1s and 2s, and the 1s, 2s and 2p states being retained explicitly. These three forms of the approximation are known as the one, two and four channel approximations respectively.

The excitation cross-sections are given by

$$Q_{on} = 2 \int_o^\infty \rho\, |a_n(\rho)|^2\, d\rho \qquad (\pi a_o^{\,2}) \qquad (10.20)$$

The differential cross sections can be deduced from the transition amplitudes in the impact parameter approximation using an expression derived by McCarrol and Salin (1968)

$$I_{on}(\theta) = 2v^2 \left| \int_o^\infty \rho\, J_m(2\mu v \rho \sin\theta/_2) \left[a_n(\infty) - \delta_{on}\right] d\rho \right|^2 \qquad (10.21)$$

where m is the magnetic quantum number of the nth state.

The impact parameter formulation is a good approximation for proton scattering above 1 KeV. The range of application to electron scattering is not so clear, however it may be adequate above 50 eV. Below 50 eV not only is the impact parameter method suspect but also exchange scattering becomes important. Our approximation neglects exchange scattering so that the comparison of our electron scattering results with other work particularly with experimental results must be made with caution.

10.2 The One Channel Approximation

In the one channel approximation equation (10.16) is solved retaining only the 1s hydrogen eigenstate. The excitation amplitudes are obtained by applying equation (10.19) with N = 0. Equation (10.16) becomes

$$i\,\dot{a}_o(t) = a_o(t)\,V_{oo}(t) - i\,\exp\left[-i(\varepsilon_o-\bar{\varepsilon})t\right]\int_{-\infty}^{t} a_o(t')\,K_{oo}(t,t')\,dt' \tag{10.22}$$

where in the first instance

$$K_{oo}(t,t') = \exp\left[-i(\bar{\varepsilon}-\varepsilon_o)t'\right]\,(\mu_{oo}(t,t')-\bar{V}_{oo}(t)\,\bar{V}_{oo}(t'))$$

In order to choose $\bar{\varepsilon}$ to give the correct polarization potential consider equation (10.22) in the limit $t \to -\infty$. Since $V_{oo}(t)$ decreases exponentially we have

$$i\,\dot{a}_o(t) \sim -i\,\exp\left[-i(\varepsilon_o-\bar{\varepsilon})t\right]\int_{-\infty}^{t} a_o(t')\,K_{oo}(t,t')\,dt' \tag{10.23}$$

In general $a_n(t) \underset{t\to-\infty}{\to} \delta_{on} + c/R^K$ for $K > 0$ and c is a constant. So that to first order

$$i\,\dot{a}_o(t) \sim -i\,\exp\left[-i(\varepsilon_o-\bar{\varepsilon})t\right]\,a_o(t)\int_{-\infty}^{t} K_{oo}(t,t')\,dt' \tag{10.24}$$

but

$$K_{oo}(t,t') = \exp\left[-i(\bar{\varepsilon}-\varepsilon_o)t'\right]\sum_{j=1}^{\infty}\bar{V}_{oj}(t)\,\bar{V}_{jo}(t')$$

Castillejo et al. (1960) have shown that $V_{nm}(R) \underset{R\to\infty}{\to} R^{-K}$ where $n \neq m$ and $K \geq 2$. So that integration by parts in equation (10.24) yields an asymptotic series in inverse powers of R the leading term being

$$-\,a_o(t)\sum_{j=1}^{\infty}\frac{\bar{V}_{oj}(t)\,\bar{V}_{jo}(t)}{(\bar{\varepsilon}-\varepsilon_o)}$$

thus

$$i\,\dot{a}_o(t) \sim -\frac{a_o(t)}{(\bar{\varepsilon}-\varepsilon_o)}\left[\mu_{oo}(t,t) - |\bar{V}_{oo}(t)|^2\right] \qquad (10.25)$$

The two centred matrix elements $\mu_{oo}(t,t')$ may be expanded to yield an asymptotic series, in the case $t = t'$, as $t \to \pm\infty$ by the method shown in Appendix II. Combining the two asymptotic forms of μ_{oo} and $|V_{oo}|^2$ then

$$i\,\dot{a}_o(t) \sim -\frac{a_o(t)}{(\bar{\varepsilon}-\varepsilon_o)\,R^4} \qquad (10.26)$$

Comparing this with equation (10.18) then

$$\alpha = \frac{1}{(\bar{\varepsilon}-\varepsilon_o)} \qquad \text{and} \qquad \bar{\varepsilon} = -1/18 \text{ a.u.}$$

With this choice of effective energy equation (10.22) was solved numerically for both electron and proton impact. The transition amplitude for 2s, $2p_o$ and $2p_{\pm 1}$ excitation were evaluated using (10.19). The azimuthal dependence of the $2p_{\pm 1}$ states is removed by making the transformation

$$a_n(t) = c_n(t)\, e^{-i\, m_n \phi}$$

where m_n is the magnetic quantum number of the nth state.
Then from the explicit forms of the single matrix elements $\bar{V}_{ns}(t)$, evaluated in Appendix IV, it can be seen that the product

$$e^{-i(m_s-m_n)\phi}\,\bar{V}_{ns}(t)$$

is independent of ϕ. Thus the ϕ dependence of $\bar{V}_{ns}(t)$ may be omitted, then $\bar{V}_{ns}(t) = \bar{V}_{sn}(t)$.

Using the notation that 1s → 1, 2s → 2, $2p_o$ → 3, $2p_{+1}$ → 4 and $2p_{-1}$ → 5 then

$$\bar{V}_{14} = -\bar{V}_{15} \qquad \text{and} \qquad \bar{V}_{44} = \bar{V}_{55}$$

then

$$i(\dot{c}_4(t)+\dot{c}_5(t)) = V_{44}(t)\ (c_4(t)+c_5(t))$$

since

$$c_4(-\infty) + c_5(-\infty) = 0 \quad \text{then} \quad c_4(t) + c_5(t) = 0$$

and

$$c_4(t) = -c_5(t)$$

Thus the equations for c_4 and c_5 may be replaced by a single equation for $\frac{1}{\sqrt{2}}(c_4(t)-c_5(t))$. The one channel case then reduces to the solution of the following set of partially coupled equations

$$i\,\dot{a}_1(t) = a_1(t)\,V_{11}(t) - i\exp\left[-i(\varepsilon_1-\bar{\varepsilon})t\right]\int_{-\infty}^{t} a_1(t')\,K_{11}(t,t')\,dt'$$

$$i\,\dot{a}_2(t) = a_1(t)\,V_{21}(t)\exp\left[-i(\varepsilon_2-\varepsilon_1)t\right] + a_2(t)\,V_{22}(t)$$

$$i\,\dot{a}_3(t) = a_1(t)\,V_{31}(t)\exp\left[-i(\varepsilon_3-\varepsilon_1)t\right] + a_3(t)\,V_{33}(t)$$

$$i\,\dot{a}_4(t) = \sqrt{2}\,a_1(t)\,V_{41}(t)\exp\left[-i(\varepsilon_4-\varepsilon_1)t\right] + a_4(t)\,V_{44}(t) \qquad (10.27)$$

with $\bar{\varepsilon} = -1/18$ a.u. The probability of a transition to the 2p state is then given by

$$|a_3(\infty)|^2 + |a_4(\infty)|^2$$

The single channel case was also solved using the modified kernel given in equation (10.17b). Using the same procedure as above the effective energy is found to be $\bar{\varepsilon}' = 0.078$ a.u., summation to M includes $2s$, $2p_{0,\pm1}$ states.

10.3 The Two Channel Approximation

Retaining the 1s and 2s target states explicitly we solved the two coupled equations

$$i\,\dot{a}_1(t) = a_1(t)\,V_{11}(t) + a_2(t)\,V_{12}(t)\,\exp\left[-i(\varepsilon_1-\varepsilon_2)t\right] - i\,\exp\left[-i(\varepsilon_1-\bar{\varepsilon})t\right]\int_{-\infty}^{t}\left(a_1(t')\,K_{11}(t,t')+a_2(t')\,K_{12}(t,t')\right)dt'$$

$$i\,\dot{a}_2(t) = a_1(t)\,V_{21}(t)\,\exp\left[-i(\varepsilon_2-\varepsilon_1)t\right] + a_2(t)\,V_{22}(t) - i\,\exp\left[-i(\varepsilon_2-\bar{\varepsilon})t\right]\int_{-\infty}^{t}\left(a_1(t')\,K_{21}(t,t') + a_2(t')\,K_{22}(t,t')\right)dt' \qquad (10.28)$$

where K_{nm} is defined by (10.17a).

Since it is unrealistic to include the 2s state but not the 2p states explicitly, we did not evaluate the excitation amplitudes to the 2p states. Such a procedure would have omitted the important long range 2s-2p coupling from the initial calculation of the 2s amplitude. The effective energy $\bar{\varepsilon}$ is unaltered from the one channel approximation since the 1s-2s coupling is of short range only. The two channel approximation was also evaluated, at a few selected energies, with the effective energy altered to $\bar{\varepsilon} = 0$. This was done to check the sensitivity of the approximation to the choice of the effective energy.

10.4 The Four Channel Approximation

When the 1s, 2s, $2p_o$ and $2p_{\pm1}$ states are retained we obtain five coupled equations. Again from the explicit forms of both the V_{nm} and μ_{nm} matrix elements it is clear that the products

$$e^{i(m_n-m_s)\phi}\,V_{nm}(t) \quad \text{and} \quad e^{i(m_n-m_s)\phi}\,\mu_{nm}(t,t')$$

are independent of ϕ the orientation of the scattering plane $(\underset{\sim}{p},\underset{\sim}{v})$. Hence using the transformation

$$c_n(t) = e^{i m_n \phi} a_n(t)$$

the ϕ dependence of the scattering amplitudes is removed. Noting that

$$V_{14} = -V_{15},\ V_{24} = -V_{25},\ V_{34} = -V_{35},\ V_{44} = V_{55} \text{ and } V_{45} = V_{54}$$

and similarly for the corresponding $\underset{\sim}{\mu}$ matrix elements the equation for the $2p_{\pm 1}$ amplitudes may be combined. Summing the equations for $\dot{c}_4(t)$ and $\dot{c}_5(t)$ we get

$$i\,\dot{d}(t) = (V_{44}(t)+V_{45}(t))\,d(t)$$

$$- i \exp\left[i(\epsilon_4-\bar{\epsilon})t\right] \int_{-\infty}^{t} d(t') \exp\left[i(\bar{\epsilon}-\epsilon_4)t'\right]$$

$$\times \left[\mu_{44}(t,t') + \mu_{45}(t,t') - (V_{44}(t)+V_{45}(t))(V_{44}(t')+V_{45}(t'))\right] dt'$$

where $$d(t) = c_4(t) + c_5(t)$$

but $$d(-\infty) = 0, \text{ then } d(t) = 0$$

hence $c_4(t) = -c_5(t)$ and the two equations for c_4 and c_5 can now be replaced by one i.e. $c_4 \rightarrow \frac{1}{\sqrt{2}}(c_4-c_5)$. The differential equations for the 1s, 2s and $2p_o$ amplitudes are similar, the equation for the 1s amplitude has the form

$$i\,\dot{a}_1(t) = a_1 V_{11} + a_2 V_{12} e^{i\alpha_{12}t} + a_3 V_{13} e^{i\alpha_{13}t} + \sqrt{2}\, a_4 V_{14} e^{i\alpha_{14}t}$$

$$- i\, e^{-i\bar{\alpha}_1 t} \int_{-\infty}^{t} a_1 e^{i\bar{\alpha}_1 t'} \left[\mu_{11} - \bar{V}_{11}\bar{V}'_{11} - \bar{V}_{12}\bar{V}'_{21} - \bar{V}_{13}\bar{V}'_{31} - 2\,\bar{V}_{14}\bar{V}'_{41}\right] dt'$$

$$- i\, e^{-i\bar{\alpha}_1 t} \int_{-\infty}^{t} a_2 e^{i\bar{\alpha}_2 t'} \left[\mu_{12} - \bar{V}_{11}\bar{V}'_{12} - \bar{V}_{12}\bar{V}'_{22} - \bar{V}_{13}\bar{V}'_{32} - 2\,\bar{V}_{14}\bar{V}'_{42}\right] dt'$$

$$- i\, e^{-i\bar{\alpha}_1 t} \int_{-\infty}^{t} a_3 e^{i\bar{\alpha}_3 t'} \left[\mu_{13} - \bar{V}_{11}\bar{V}'_{13} - \bar{V}_{12}\bar{V}'_{23} - \bar{V}_{13}\bar{V}'_{33} - 2\,\bar{V}_{14}\bar{V}'_{43}\right] dt'$$

$$- i\sqrt{2}\, e^{-i\alpha_1 t} \int_{-\infty}^{t} a_4 e^{i\bar{\alpha}_4 t'} \left[\mu_{14} - \bar{V}_{11}\bar{V}'_{14} - \bar{V}_{12}\bar{V}'_{24} - \bar{V}_{13}\bar{V}'_{34} - \bar{V}_{14}(\bar{V}_{44}-\bar{V}'_{45})\right] dt'$$

(10.29a)

where $\alpha_{nm} = \varepsilon_n - \varepsilon_m$, $\bar{\alpha}_n = \bar{\varepsilon} - \varepsilon_n$

and $\bar{V}_{nm} \equiv \bar{V}_{nm}(t)$, $\bar{V}'_{nm} \equiv \bar{V}_{nm}(t')$

The equation for the $2p_{\pm 1}$ amplitude has the form

$$\begin{aligned} i\,\dot{a}_4(t) = {} & \sqrt{2}\, a_1 V_{41} e^{i\alpha_{41}t} + \sqrt{2}\, a_2 V_{42} e^{i\alpha_{42}t} + \sqrt{2}\, a_3 V_{43} e^{i\alpha_{43}t} + a_4(V_{44}-V_{45}) \\ & - i\, e^{i\bar{\alpha}_4 t}\Big[\sqrt{2}\int_{-\infty}^{t} a_1\, e^{-i\bar{\alpha}_1 t'}\big[\mu_{41}-\bar{V}_{41}\bar{V}'_{11}-\bar{V}_{42}\bar{V}'_{21}-\bar{V}_{43}\bar{V}'_{31}-(\bar{V}_{44}-\bar{V}_{45})\bar{V}'_{41}\big]\,dt' \\ & + \sqrt{2}\int_{-\infty}^{t} a_2\, e^{-i\bar{\alpha}_2 t'}\big[\mu_{42}-\bar{V}_{41}\bar{V}'_{12}-\bar{V}_{42}\bar{V}'_{22}-\bar{V}_{43}\bar{V}'_{32}-(\bar{V}_{44}-\bar{V}_{45})\bar{V}'_{42}\big]\,dt' \\ & + \sqrt{2}\int_{-\infty}^{t} a_3\, e^{-i\bar{\alpha}_3 t'}\big[\mu_{43}-\bar{V}_{41}\bar{V}'_{13}-\bar{V}_{42}\bar{V}'_{23}-\bar{V}_{43}\bar{V}'_{33}-(\bar{V}_{44}-\bar{V}_{45})\bar{V}'_{43}\big]\,dt' \\ & + \int_{-\infty}^{t} a_4\, e^{-i\bar{\alpha}_4 t'}\big[\mu_{44}-\mu_{45}-2\,\bar{V}_{41}\bar{V}'_{14}-2\,\bar{V}_{42}\bar{V}'_{24}-2\,\bar{V}_{43}\bar{V}'_{34} \\ & \qquad -(\bar{V}_{44}-\bar{V}_{45})(\bar{V}'_{44}-\bar{V}'_{45})\big]\,dt'\Big] \qquad (10.29b) \end{aligned}$$

and the 2p transition probability is given by

$$|a_3(+\infty)|^2 + |a_4(+\infty)|^2$$

In the four channel case the choice of effective energy is complicated by contributions from both the strongly coupled states and the non-local integral terms. The behaviour of

$$\int_{-\infty}^{t} a_m(t')\, e^{i(\bar{\varepsilon}-\varepsilon_m)t'}\Big[\mu_{lm}(t,t') - \sum_{j=1}^{4} \bar{V}_{lj}(t)\, V_{jm}(t')\Big]$$

in the limit of $t \to -\infty$ may be seen from the single channel case, to first order to be

$$\frac{a_m(t)}{i(\bar{\varepsilon}-\varepsilon_m)}\Big[\mu_{lm}(t,t') - \sum_{j=1}^{4} \bar{V}_{lj}(t)\, \bar{V}_{jm}(t)\Big]$$

Since in general $a_m(t) \underset{t\to-\infty}{\to} \delta_{lm} + c/R^K$, where $K > 0$ and c is a constant, and

$$\mu_{nm}(t,t) - \sum_{j=1}^{4} \bar{V}_{nj}(t)\,\bar{V}_{jm}(t) \underset{t\to-\infty}{\to} O\left(\frac{1}{R^4}\right)$$

the asymptotic form of the equation for the elastic scattering amplitude is

$$i\,\dot{\bar{a}}_1(t) \underset{t\to-\infty}{\to} a_3(t)\,V_{13}(t)\exp\left[i(\varepsilon_1-\varepsilon_3)t\right] + \sqrt{2}\,a_4(t)\,V_{14}(t)\exp\left[i(\varepsilon_1-\varepsilon_4)t\right]$$
$$- \frac{a_1(t)}{(\bar{\varepsilon}-\varepsilon_1)}\left[\mu_{11}(t,t) - |\bar{V}_{11}(t)|^2 - |\bar{V}_{13}(t)|^2 - 2|V_{14}(t)|^2\right] \qquad (10.30)$$

where only terms of order R^{-4} have been retained.

To order R^{-2} the amplitudes a_3 and a_4 satisfy the following equations for $t \to -\infty$

$$i\,\dot{\bar{a}}_3(t) \sim a_1(t)\,V_{31}(t)\exp\left[i(\varepsilon_3-\varepsilon_1)t\right]$$

and
$$i\,\dot{\bar{a}}_4(t) \sim \sqrt{2}\,a_1(t)\,V_{41}(t)\exp\left[i(\varepsilon_4-\varepsilon_1)t\right] \qquad (10.31)$$

Integrating by parts, we have to order R^{-2}

$$a_3(t) \sim -\frac{V_{31}(t)}{(\varepsilon_3-\varepsilon_1)}\,a_1(t)\exp\left[i(\varepsilon_3-\varepsilon_1)t\right]$$

and
$$a_4(t) \sim -\sqrt{2}\,\frac{V_{41}(t)}{(\varepsilon_4-\varepsilon_1)}\,a_1(t)\exp\left[i(\varepsilon_4-\varepsilon_1)t\right] \qquad (10.32)$$

Substituting the results of (10.32) into (10.30) and using the asymptotic forms of the $\underline{\mu}$ and $\underline{v}$ matrix elements we get

$$i\,\dot{\bar{a}}_1(t) \sim -\frac{a_1(t)}{R^4}\left[\frac{K^2}{(\varepsilon_2-\varepsilon_1)} + \frac{1-K^2}{(\bar{\varepsilon}-\varepsilon_1)}\right] \qquad (10.33)$$

where $K = 8 \times 0.093117$.

Comparing this result with equation (10.18) we obtain

$$\bar{\varepsilon} = \varepsilon_1 + \frac{1-K^2}{\alpha - K^2/(\varepsilon_2-\varepsilon_1)}$$

so that $\bar{\varepsilon} = 0.0778$ a.u.

The four coupled equations are then solved with this value of effective energy.

11. Numerical Methods

The coupled differential equations were solved using a difference scheme due to Hamming (1962). This method has the advantage that the error at each step can be estimated so that the step length can be adjusted according to some predetermined error bound. The non-local integrals appearing in the expression for the derivatives were calculated using the Simpson quadrature rule. Since the amplitudes appearing in these integrals were only known at finite intervals, the step length of the quadrature rule was determined by the step length for the solution of the differential equations. Because of this it was found necessary to place an upper limit, h^{μ}, on the solution step length. The effect of altering the mesh size of the integration routine for the non-local terms on the overall solution could then be determined by successively reducing h^{μ} and comparing the results. To reduce the time of execution of the program the bound was set as large as possible within the overall error constraint, a typical value of h^{μ} was $h^{\mu} = 1.0$. The single centred potential matrix elements $\underset{\sim}{V}$ that appear in the kernal are elementary, the expressions used for these elements are shown in Appendix IV. The two centred matrix elements have not so far been evaluated in closed form and have to be evaluated numerically. They fall into two distinct classes, those that are spherically symmetric and those which are not. The spherically symmetric type are of the form

$$N \int \frac{f(r)}{|\underset{\sim}{R}-\underset{\sim}{r}|\,|\underset{\sim}{R}'-\underset{\sim}{r}|}\, d\underset{\sim}{r} \qquad (11.1)$$

where N is a normalisation factor. This type occur between s-states and can be reduced to a form suitable for numerical computation by a method due to

Coleman (1970).

$$\int \frac{f(r)}{|\underset{\sim}{R}-\underset{\sim}{r}|\ |\underset{\sim}{R}'-\underset{\sim}{r}|}\, d\underset{\sim}{r} = \frac{4\pi}{R^2} \int_0^1 \frac{A(yR_1, R_2/y)}{(1-2xy^2\cos\theta+x^2y^4)^{1/2}} \qquad (11.2)$$

where $A(\alpha,\beta) = \int_\alpha^\beta f(r)\, rdr$, $x = R_1/R_2$ and $\cos\theta = \hat{\underset{\sim}{R}}_1.\hat{\underset{\sim}{R}}_2$. R_1 is the smaller and R_2 the larger of $|\underset{\sim}{R}|$ and $|\underset{\sim}{R}'|$. For the second class of matrix elements, notably those containing at least one p-state wavefunction, the situation is more complex though the same final form of result as the symmetric case can be obtained. The details of the method applied to the $1s\text{-}2p_{o,\pm1}$, $2s\text{-}2p_{o,\pm1}$, and $2p_{o\pm1}\text{-}2p_{o\pm1}$ matrix elements, due to Coleman (1972) are given in Appendix III. The one dimensional integrals in the interval $[0,1]$ are evaluated in both cases by Gaussian quadrature. A total of 32 points were required to give the matrix elements to six significant figures. The range of integration was divided into four unequal parts: $[0,0.1]$, $[0.1,0.2]$, $[0.2,0.6]$, and $[0.6,1.0]$, since in general the integrands varied more sharply at the lower end of the interval. The accuracy was determined by comparing with the results obtained using a total of 64 Gaussian points.

To calculate transition cross sections with an error of less than 2%, the absolute error in the calculated amplitudes must be of order 10^{-4}. The solution to the equations is calculated in the range t_i to t_f where t_i is large and negative and t_f large and positive. The smallest values of t_i and t_f compatible with the overall error requirement on the solutions may be found by considering the asymptotic forms of the equations and their solutions as $t \to \pm\infty$. As an example we will consider the four channel calculations only. The methods required for the one and two channel calculations are contained therein.

Assuming that $a_n(t) \underset{t\to-\infty}{\to} \delta_{1n} + O(R^{-K})$ where $K > 0$ the four channel equations may be uncoupled in the limit of $t \to -\infty$ to the order of R^{-4}. Using the asymptotic forms of the matrix elements $\underset{\sim}{v}$ and neglecting terms of

order R^{-4} we have

$$i\,\dot{a}_1(t) \sim 0$$

$$i\,\dot{a}_2(t) \sim 0$$

$$i\,\dot{a}_3(t) \sim a_1(t)\,V_{31}(t)\,\exp\left[i(\varepsilon_3-\varepsilon_1)t\right]$$

$$i\,\dot{a}_4(t) \sim \sqrt{2}\,a_1(t)\,V_{41}(t)\,\exp\left[i(\varepsilon_4-\varepsilon_1)t\right] \qquad (11.3)$$

integrating by parts, for $t \to -\infty$ we have to order R^{-4}

$$a_1(t) \sim 1.0$$

$$a_2(t) \sim 0$$

$$a_3(t) \sim \pm K_1 \frac{\cos\theta}{R^2} \frac{\exp\left[i(\varepsilon_3-\varepsilon_1)t\right]}{(\varepsilon_3-\varepsilon_1)}$$

$$a_4(t) \sim \pm K_1 \frac{\sin\theta}{R^2} \frac{\exp\left[i(\varepsilon_4-\varepsilon_1)t\right]}{(\varepsilon_3-\varepsilon_1)} \qquad (11.4)$$

where $K = 8 \times 0.093117$, and the precise sign of these asymptotic amplitudes will depend on whether electron or proton scattering is being considered.

In starting the solution at a value $t = t_i$ the contribution between the limits $\left[-\infty, t_i\right]$ to the non-local integral terms is neglected. This would result in an error of the order R_i^{-2}, where

$$R_i^2 = \rho^2 + v^2 t_i^2$$

However an asymptotic series can be found so that this error may be corrected for. Consider

$$\int_{-\infty}^{t_i} a_m(t') \exp\left[i(\bar{\varepsilon}-\varepsilon_m)t'\right] \sum_{j=N+1}^{\infty} \bar{V}_{nj}(t)\,\bar{V}_{jm}(t')\,dt' \qquad (11.5)$$

where t may have any value in the interval $\left[t_i, t_f\right]$.

Expression (11.5) may be written

$$\sum_j \bar{V}_{nj}(t) \int_{-\infty}^{t_i} a_m(t') \exp\left[i(\bar{\varepsilon}-\varepsilon_m)t'\right] \bar{V}_{jm}(t')\, dt' \qquad (11.6)$$

Since $\bar{V}_{nj}(t) \underset{t\to\pm\infty}{\to} R^{-K}$, $K \geq 2$, Castillejo et al. (1960), integration by parts gives

$$\sum_{j=N+1}^{\infty} \bar{V}_{nj}(t) \left[\frac{\exp\left[i(\bar{\varepsilon}-\varepsilon_m)t_i\right]}{(\bar{\varepsilon}-\varepsilon_m)} a_m(t_i)\, \bar{V}_{jm}(t_i) + O(R_i^{-3})\right] \qquad (11.7)$$

thus the integration over the interval $[-\infty,t_i]$ of the non-local terms may be approximated by

$$a_m(t_i) \frac{\exp\left[i(\bar{\varepsilon}-\varepsilon_m)t_i\right]}{(\bar{\varepsilon}-\varepsilon_m)} \left[\mu_{nm}(t,t_i) - \sum_{j=1}^{N} \bar{V}_{nj}(t)\, \bar{V}_{jm}(t_i)\right] \qquad (11.8)$$

Thus the most restrictive error in starting the solution at $t = t_i$, after implementing the results (11.4) and (11.8) is of order R_i^{-3}. Thus

$$R_i \sim V t_i \sim -(10^{+4})^{1/3} \quad \text{a.u.}$$

$$\sim -21.5 \quad \text{a.u.}$$

$$\therefore \quad t_i \sim -21.5/V \quad \text{a.u.}$$

As $t \to +\infty$ the asymptotic forms are more complex, the non-local times contribute terms of order R_f^{-2} to the derivatives. Consider

$$I = \int_{-\infty}^{t_f} a_m(t') \exp\left[i(\bar{\varepsilon}-\varepsilon_m)t'\right] \sum_{j=N+1}^{\infty} \bar{V}_{nj}(t_f)\, \bar{V}_{jm}(t')\, dt' \qquad (11.9)$$

where t_f is large and positive, thus t' takes on a wide range of values, at worst $t' = 0$, making I largest. But

$$I = \sum_{j=N+1}^{\infty} \bar{V}_{nj}(t_f) \int_{-\infty}^{t_f} a_m(t') \exp\left[i(\bar{\varepsilon}-\varepsilon_m)t'\right] \bar{V}_{jm}(t')\, dt'$$

$$= \sum_{j=N+1}^{\infty} \bar{V}_{nj}(t_f) \left[\int_{-\infty}^{\infty} a_m(t') \exp\left[i(\bar{\varepsilon}-\varepsilon_m)t'\right] \bar{V}_{jm}(t')\, dt' \right.$$

$$\left. - \int_{t_f}^{\infty} a_m(t') \exp\left[i(\bar{\varepsilon}-\varepsilon_m)t'\right] V_{jm}(t')\, dt' \right] \qquad (11.10)$$

From previous discussion it is apparent that

$$\sum_j \bar{V}_{nj}(t_f) \int_{t_f}^{\infty} a_m(t') \exp\left[i(\bar{\varepsilon}-\varepsilon_m)t'\right] \bar{V}_{jm}(t')\, dt'$$

behaves as R_f^{-4} for large t_f so that

$$I \sim \sum_{j=N+1}^{\infty} \bar{V}_{nj}(t_f) \int_{-\infty}^{\infty} a_m(t') \exp\left[i(\bar{\varepsilon}-\varepsilon_m)t'\right] \bar{V}_{jm}(t')\, dt' + O(R_f^{-4})$$

$$\sim \sum_{j=N+1}^{\infty} \bar{V}_{nj}(t_f)\, K_j + O(R_f^{-4}) \qquad (11.11)$$

where K_j is a constant, independent of t_f. From the asymptotic behaviour of $\bar{V}_{nj}(t)$, $n \neq j$, it is clear that

$$I \underset{t\to\infty}{\sim} O(R_f^{-2}) \qquad (11.12)$$

Since the expression for I appears in the amplitude derivatives in the form of $e^{i\alpha t} I$, for α real, then the error resulting in the amplitudes in stopping the solution at t_f is of order R_f^{-2}. Now consider the strong coupling terms in the limit as $t \to +\infty$

$$i\begin{bmatrix}\dot{a}_1\\ \dot{a}_2\\ \dot{a}_3\\ \dot{a}_4\end{bmatrix} = \begin{bmatrix} 0 & 0 & -\frac{\cos\theta\, e^{-i\varepsilon t}\, K_1}{R^2} & \frac{\sin\theta\, K_1\, e^{-i\varepsilon t}}{R^2} \\ 0 & 0 & \frac{\cos\theta\, K_2}{R^2} & -\frac{\sin\theta\, K_2}{R^2} \\ -\frac{\cos\theta\, K_1\, e^{i\varepsilon t}}{R^2} & \frac{\cos\theta\, K_2}{R^2} & \frac{(1-3\cos^2\theta)K_3}{R^3} & \frac{\sin\theta\cos\theta\, K_4}{R^3} \\ \frac{\sin\theta\, K_1\, e^{i\varepsilon t}}{R^2} & -\frac{\sin\theta\, K_2}{R^2} & \frac{\sin\theta\cos\theta\, K_4}{R^3} & \frac{(3\cos^2\theta-1)K_3-\sin^2\theta K_5}{R^3} \end{bmatrix}\begin{bmatrix}a_1\\ a_2\\ a_3\\ a_4\end{bmatrix} \qquad (11.13)$$

assuming that $a_n(t) \underset{t\to\infty}{\sim} a_n(\infty) + c/R^K$, where $K > 0$ and c is a constant w.r.t. t, the equations of (11.13) may be uncoupled. Neglecting terms of order R^{-3} we have

$$i\,\dot{a}_2(t) \sim \frac{\cos\theta\, K_2}{R^2}\, a_3(t)$$

and

$$i\,\dot{a}_3(t) \sim \frac{\cos\theta\, K_2}{R^2}\, a_2(t) \qquad (11.14)$$

thus

$$i\,a_2(\infty) \sim a_3(\infty)\, K_2 \int_{t_f}^{\infty} \frac{\cos\theta}{R^2}\, dt + i\,a_2(t_f)$$

$$i\,a_2(\infty) \sim a_3(t_f)\,\frac{K_2}{V R_f} + i\,a_2(t_f) + O(R_f^{-2})$$

and

$$i\,a_3(\infty) \sim a_2(t_f)\,\frac{K_2}{V R_f} + i\,a_3(t_f) + O(R_f^{-2}) \qquad (11.15)$$

where $K_2 = \pm 3.0$. Thus provided the asymptotic corrections of equation (11.15) are made the error incurred by stopping the solution at $t = t_f$ is of order R_f^{-2}. Thus t_f is chosen such that

$$R_f^{-2} \sim 2 \times 10^{-4}$$

i.e.

$$R_f \sim 65 \quad \text{thus} \quad t_f \sim 65/v$$

The validity of the above procedures for approximating the infinite limits of the overall integration were checked empirically by comparing

solutions obtained with vt_i = -100,-30 and -21; and vt_f = 40,65 and 120 a.u. In all cases the differences obtained were within the theoretical error bounds for these particular values.

A constraint on the solution due to unitarity provided a valuable check on the numerical procedures. Since

$$\sum_{n=0}^{\infty} |a_n(-\infty)|^2 = 1$$

then unitarity is preserved throughout the solution if

$$\sum_{n=0}^{\infty} \frac{\partial}{\partial t} |a_n(t)|^2 = 0$$

for our particular approximation. Consider

$$\frac{\partial}{\partial t} |a_n(t)|^2 = a_n(t)\, \dot{a}_n^*(t) + a_n^*(t)\, \dot{a}_n(t) \qquad (11.15)$$

for $n > N$ $\quad \dot{a}_n(t) = -i \sum_{m=0}^{N} a_m(t)\, V_{nm}(t) \exp\left[i(\epsilon_n - \epsilon_m)t\right]$

Thus (11.16) becomes

$$\frac{\partial}{\partial t} |a_n(t)|^2 = -i\, a_n(t) \sum_{m=0}^{N} a_m^*(t)\, V_{nm}^*(t) \exp\left[-i(\epsilon_n - \epsilon_n)t\right]$$

$$+ i\, a_n^*(t) \sum_{m=0}^{N} a_m(t)\, V_{nm}(t) \exp\left[i(\epsilon_n - \epsilon_m)t\right]$$

But

$$\sum_{n=N+1}^{\infty} a_n(t)\, V_{mn}(t) \exp\left[i(\epsilon_n - \epsilon_m)t\right]$$

$$= i\, \dot{a}_m(t) - \sum_{s=0}^{N} a_s(t)\, V_{ms}(t) \exp\left[i(\epsilon_m - \epsilon_s)t\right]$$

thus

$$\sum_{n=N+1}^{\infty} \frac{\partial}{\partial t} |a_n(t)|^2 = -i \sum_{n=0}^{N} \left[i\, a_m^*(t)\dot{a}_m(t) - a_m^*(t) \sum_{s=0}^{N} a_s(t) V_{ms}(t) \exp\left[i(\epsilon_m - \epsilon_s)t\right] \right]$$

$$+ i \sum_{m=0}^{N} \left[-i\, a_m(t)\dot{a}_m^*(t) - a_m(t) \sum_{s=0}^{N} a_s^*(t) V_{ms}^*(t) \exp\left[-i(\epsilon_m - \epsilon_s)t\right] \right]$$

$$= - \sum_{m=0}^{N} \left[\dot{a}_m(t)\, a_m^*(t) + a_m(t)\, \dot{a}_m^*(t) \right]$$

$$= - \sum_{n=0}^{N} \frac{\partial}{\partial t} |a_n(t)|^2$$

thus $\sum_{n=0}^{\infty} \frac{\partial}{\partial t} |a_n(t)|^2 = 0$ and unitarity is preserved in our approximation. Since in our calculations we only consider amplitudes up to n = M we expect the condition $\sum_{n=0}^{M} |a_n(t)|^2 \leq 1$ to hold for all t. Because for the states M > n > M we also allowed for back coupling the unitarity condition becomes

$$\sum_{n=0}^{N} |a_n(t)|^2 \leq 1 \qquad (11.17)$$

The calculated amplitudes obeyed the condition, for all values of t, to within the errors of the amplitudes.

The total cross sections were evaluated using equation (10.20). The infinite limit of the integral was replaced by the value of the impact parameter ρ_{max} for which $\rho_{max} |a_n(\rho_{max})|^2 < 10^{-4}$. The integration was done by Simpsons rule. The long range interaction associated with the p-states of hydrogen required ρ_{max} to be $\rho_{max} = 25$ a.u. Differential cross sections were evaluated for electron impact only using equation (10.21). Again the range of integration was $[0, \rho_{max}]$, the results remaining unaltered when ρ_{max} was extended to greater values.

The results of the calculations carried out in the manner described above are given in Section 12.

12.1 Excitation by Proton Impact

The methods of section 10 have been used to evaluate total cross sections for the 1s-2s, and 1s-2p transitions in atomic hydrogen in the energy range 15 to 200 KeV. The second order potential terms were constructed using the kernel given by equation (10.17a) and the equation (10.16) solved in the one, two and four channel approximations by the methods of section 11. The one channel case was also solved using the kernel given by equation (10.17b). The results for the 2s transition are given in table 4 and are also displayed in figure 4 where they are compared with the results of the Born approximation and the four state approximation. The one channel results evaluated using kernel (10.17b), method b, are not

E(KEV)	ONE CHANNEL	TWO CHANNEL	E	FOUR CHANNEL
15	5.50(-2)	7.12(-2)		
20	7.40(-2)	9.00(-2)		
30	9.20(-2)	1.01(-1)	25	4.25(-1)
40	9.57(-2)	1.01(-1)	35	4.11(-1)
50	-	9.58(-2)	50	3.40(-1)
70	8.47(-2)	8.52(-2)	70	2.50(-1)
100	7.16(-2)	7.05(-2)	100	1.67(-1)
200	4.38(-2)	4.38(-2)	200	7.48(-2)

Table 4 - 1s-2s total cross sections in units of (πa_o^2).

shown since they are almost identical to the tabulated one channel results evaluated using kernal (10.17a), method a. In figure 4 the one, two and four channel results show no obvious trend towards convergence, though the one and two channel calculations are in reasonable agreement. The four

channel approximation appears to be dominated by the 2s-2p strong coupling terms; the second order terms provide little correction to the established four state calculation of Flannery (1969). The two channel results and the two state results are related in a similar way. The choice of effective energy and its effect on the total cross sections has been investigated by calculating one channel results by methods a and b and comparing, and also by repeating the two channel calculations with an effective energy coincident with the ionization threshold i.e. $\bar{\varepsilon} = 0$ (a.u.). The results of this calculation we also shown in figure 4, and it can be seen that the new choice of effective energy makes little difference to the calculated cross sections. Thus the total cross sections appear to be insensitive to value of the effective energy and to how it is included in the approximation.

The 2s excitation cross sections are compared with the results of the Glauber approximation, Franco and Thomas (1970) and the pseudo state calculation of Cheshire et al. (1970) in figure 5. The one channel and Glauber results are in close agreement over the whole energy range considered. Below 40 KeV the pseudo state calculation gives results close to the Glauber approximation, while the peak of the pseudo state cross section, at about 60 KeV, passes through the curve through the four channel results. The maximum of the four channel results occurs almost at the same energy as the minimum of the pseudo state results, which in turn coincides with the maximum of the resonant charge transfer cross section as measured by Bayfield (1969). Since the pseudo state calculations take explicit account of the rearrangement channels thereby removing flux from the direct channels, it could be implied that the four channel wavefunction does not represent the rearrangement channels very well. The one channel approximation does not allow adequately for the 2s-2p strong coupling and hence gives rather low results for the 2s transition. The close agreement between the

one channel and the Glauber results is probably due to the similar structure of the approximations, only the elastic channel being properly represented. In view of this similarity, in particular as to how the continuum states are included it seems that it is unlikely that allowance is made for rearrangement collisions in the Glauber approximation.

The results for the 2p transition are given in table 5 and are also displayed in figure 6 where the one and four channel approximations are compared with the Born and four state approximations. The one channel

E(KeV)	ONE CHANNEL	E	FOUR CHANNEL
15	6.69(-1)		
20	9.35(-1)		
30	1.17	25	8.93(-1)
40	1.25	35	8.13(-1)
50	1.23	50	8.53(-1)
70	1.17	70	8.81(-1)
100	1.03	100	8.71(-1)
200	7.24	200	6.73(-1)

Table 5 - 1s-2p total cross sections in units of (πa_o^2).

results and the four state results are very similar in direct contrast with the same comparison for the 2s transition. The four channel results lie beneath the one channel results but the difference between the two is much less than in the 2s case, reflecting that the 2p transition is optically allowed and is thus less sensitive than the 2s transition to the type of approximate wavefunctions employed. The 2p results are compared with the results of the pseudo state and Glauber approximations in figure 7. The

four channel results and the Glauber results are in reasonable agreement, and the one channel results pass through the maximum of the pseudo state results. The experimental results for the 2p transition of Stebbing et al. (1965), not shown in figure 7, overlap our results in the range 20 to 30 KeV only. In this range they agree closely with the Glauber approximation. Gaily (1968) has cast some doubt on the reliability of the normalisation of the experimental results, combining this with their limited range they are of little value in determining the relative merits of the various approximations.

12.2 Excitation by Electron Impact

(a) Total Cross Sections

The methods of sections 10 and 11 have also been applied to electron impact with hydrogen to evaluate the 1s-2s, 1s-2p and 1s-3p total cross sections. The 2s excitation results are shown in table 6. Both versions of the one channel approximation were used. It can be seen that, as in the case of proton impact, they yield almost identical results.

E(eV)	ONE CHANNEL METHOD a	ONE CHANNEL METHOD b	TWO CHANNEL	Ė	FOUR CHANNEL
20	2.00(-1)	2.06(-1)	1.32(-1)		
30	1.50(-1)	1.52(-1)	1.06(-1)	25	3.47(-2)
40	1.20(-1)	1.21(-1)	8.84(-2)	35	4.25(-2)
54	9.40(-1)	9.42(-1)	7.19(-2)	54	4.88(-2)
70	7.50(-1)	7.53(-2)	5.93(-2)	70	4.79(-2)
100	5.46(-1)	-	4.52(-2)	100	4.22(-2)
200	2.87(-2)	-	2.54(-2)	200	2.67(-2)

Table 6 - 1s-2s total cross sections in units of (πa_o^2).

The one, two and four channel approximations are compared with the Born approximation and the close coupling calculations of Burke et al. (1963) in figure 8. The latter two calculations are almost identical over the energy range 25-54 eV. The one channel calculation also lies close to the Born approximation, but as more states are explicitly included the total cross section decreases at any one energy. Again the one, two and four channel results show no sign of convergence, but the effects of adding in explicitly higher states must be small if only because of the greater energy difference between the higher and the initial ground state. The close coupling results and the four channel results differ widely in direct contrast with the 2s excitation by protons.

The results for the 2p transition are given in table 7 and are also displayed in figure 10. The one and four channel results are both very

E(eV)	ONE CHANNEL METHOD a	METHOD b	E	FOUR CHANNEL
20	1.45	1.46		
30	1.28	1.30	25	1.26
40	1.14	1.15	35	1.23
54	9.92(-1)	9.94(-1)	54	1.06
70	8.76(-1)	8.78(-1)	70	9.53(-1)
100	7.21(-1)	-	100	7.75(-1)
200	4.63(-1)	-	200	4.88(-1)

Table 7 - 1s-2p total cross sections in units of (πa_o^2).

similar to the Born approximation results except that the maximum in the Born cross sections does not occur until lower energies. The close coupling approximation also gives values that are not far from the Born results. As

in the case of proton impact the 2p excitation process appears insensitive to the approximate wave function employed.

The 2s and 2p excitation cross sections in the one and four channel approximations are compared with the results of the Glauber approximation of Tai et al. (1970) and the pseudo state calculation of Burke and Webb (1971) in figures 10 and 11. Experimental results are available in the energy range considered for both the 2s and 2p cross sections. The 2s results of Kaupilla (1970) include the cascade contribution from the 3p state. This has been estimated to be 0.23 of the total 3p cross section, Hummer and Seaton (1961). The results of Tai et al. and Burke and Webb have been corrected accordingly and are displayed in figure 12 along with our own results and the experimental results of Kaupilla. In our work the 3p excitation cross sections were calculated only in the one channel case, see table 8. It is thought that the one channel approximation provides an adequate estimate for the cascade contribution. The 3p cross sections at

E(eV)	ONE CHANNEL
20	3.23(-1)
30	2.62(-1)
40	2.24(-1)
54	1.88(-1)
70	1.59(-1)
100	1.26(-1)
200	7.86(-2)

Table 8 - 1s-3p total cross sections in units of (πa_o^2).

25 and 35 eV were obtained by graphical interpolation. As discussed previously the Glauber results and the pseudo state results are in good agreement with the experimental points. Our four channel results are also in excellent agreement with the experiment down to about 25 eV where exchange should be a significant factor. This agreement should be treated with caution for two reasons; firstly the one channel approximation may not provide a satisfactory estimate of the 3p cross sections and secondly the value of the cascade factor is open to some discussions, see Tai et al. (1970). This latter point also applies to the other theoretical predictions considered.

The 2p excitation cross sections have been deduced from measurements of Long et al. (1968) and Ott et al. (1970). The data points agree well in both shape and magnitude with those of McGowan et al. (1969) when normalised to each other and to the Born approximation at 200 eV. The predictions of the Glauber approximation and of the pseudo state calculations agree well with these results. The one and four channel approximations give results that are too large. Even above 50 eV where exchange scattering is small the one and four channel results are still poor. If the 2p experimental results are normalised correctly, Damburg and Propin (1972) suggest they are not, then it would appear that our results are unsatisfactory for the 2p transition. This may well be due to the failure of the impact parameter method for electron scattering, as discussed in section 9, rather than a serious deficiency in our model.

In their experiment Ott et al. (1970) measured the polarization fraction of the Lyman-α radiation emitted in the decay of the 2p excited state. Since the magnetic sublevels of the 2p state are not equally populated the radiation emitted from the target will be polarized. The polarization fraction is defined as

$$P = \frac{I_{//} - I_{\perp}}{I_{//} + I_{\perp}} \qquad (12.1)$$

where $I_{//}$ and $I_{\perp}$ are the intensities, observed at 90° to the electron beam axis, of the respective Lyman-α components having electric vectors parallel and perpendicular to the beam axis. Percival and Seaton (1958) find that the polarization fraction may be expressed as

$$P = \frac{3(Q_0 - Q_1)}{7\,Q_0 + 1/2\,Q_1} \qquad (12.2)$$

where Q_m, m = 0 or 1 are the total cross sections for excitation to the $2p_m$ level. The application of equation (12.2) to the experimental situation is discussed by Gerjouy et al. (1972).

The experimental results are compared with our prediction for the polarization fraction in the four channel model and also with the predictions of Byron (1971) and of Gerjouy et al. (1972) in figure 15. It can be seen that our results are in poor agreement in comparison with the other two predictions. The discrepancy between the results of Byron and Gerjouy et al. is not understood since in both applications of Glauber theory the longitudinal momentum transfer is treated exactly, and all the other approximations made are the same. Our polarization results may be improved if we adopt the methods of Gerjouy et al. i.e. evaluate the scattering amplitudes with the $\hat{z}$ axis defined perpendicular to the momentum transfer, thereby removing the implicit approximation of neglecting the longitudinal momentum transfer, and then rotating to a system with $\hat{z}$ parallel to $\hat{K}_i$ to evaluate the usual polarization fraction.

(b) Differential Cross Sections

At higher energies where the total cross sections are similar for all considered approximations the relative merits of each may be distinguished by considering the differential cross sections. These were evaluated, for

electron scattering, using equation (10.21) in the one and four channel approximations for elastic and excitation to the n = 2 level scattering. Experimental data is available for both these processes. The elastic scattering results at 54, 100 and 200 eV are shown in figures 13a,b,c respectively, together with the experimental results of Teubner, Williams and Carver (unpublished, but see Tai et al. (1969)). Also shown is the first Born approximation. The data points are normalised to the one channel results at 60^{o}. The one and four channel approximation yield almost identical results which are in good agreement with experimental points. This indicates that the elastic channel dominates the elastic scattering process. This is also demonstrated very clearly by the results of the second Born approximation, shown in table 1, where the addition of explicit states fails to alter the real part of the forward elastic scattering amplitude to any great extent.

The differential cross sections for excitation of the n = 2 level are compared with the experimental points of Williams (1969) in figures 14 a,b,c again for energies 54, 100 and 200 eV. The experimental points are normalised to our one channel results at 20^{o}. For the smaller angles considered the shape of the data points and our one channel results agree quite well, this is probably the result of normalisation at small angles, but agreement at larger angles is poor. The addition of the 2s and 2p states in the four channel calculation has not improved the agreement. The Glauber approximation of Tai et al. (1970) appears to suffer from the same deficiencies. The requirement of comparatively large differential cross sections for wide angles appears to be somewhat inconsistent with the requirement for smaller total cross sections, though we have considered only part of the possible angular range.

13. Conclusion

A comparison of our results and experimental results has only been possible in the case of electron scattering. The uncertainty of the impact parameter approximation for electron collisions makes it difficult to draw definitive conclusions as to the utility of our approximation. However the results are sufficiently encouraging to suggest calculating our approximation using the wave formulation and possibly allowing for electron exchange. For proton impact it would appear that the charge transfer process is not allowed for and a great improvement may be made by including it explicitly. This would have the added benefit of allowing a comparison with experimental results for the charge transfer process. The problems associated with including charge exchange explicitly appear to be formidable from both a theoretical and computational point of view. In particular for any rearrangement collision the problem of 'double counting' must be resolved. The choice of effective energy, shown to be relatively unimportant in our present work may play a crucial part in determining the rearrangement boundary conditions.

Appendix I

To evaluate

$$I = \lim_{\varepsilon \to 0^+} \int \frac{e^{i\,\underset{\sim}{\eta}.(R-R')}}{c+2K.\hat{\underset{\sim}{\eta}}-i\varepsilon}\, d\underset{\sim}{\eta}$$

where c is real. Define $\hat{\eta}_z$ in the direction of $\hat{K}$, then

$$I = \int_{-\infty}^{\infty} e^{i\,\eta_x(R_x-R_x')}\, d\eta_x \int_{-\infty}^{\infty} e^{i\,\eta_y(R_y-R_y')}\, d\eta_y \int_{-\infty}^{\infty} \frac{e^{i\,\eta_z(R_z-R_z')}}{(c+2K\eta_z-i\varepsilon)}\, d\eta_z$$

$$= (2\pi)^2\, \delta(\underset{\sim}{b}-\underset{\sim}{b}')\int_{-\infty}^{\infty} \frac{e^{i\,\eta_z(R_z-R_z')}}{c+2K\eta_z-ic}\, d\eta_z$$

where $\underset{\sim}{b}$ and $\underset{\sim}{b}'$ are two dimensional vectors in a plane perpendicular to $\hat{\eta}_z$. Consider

$$\int_{-\infty}^{\infty} \frac{e^{i\,\eta_z(z-z')}}{c+2K\eta_z-ic}\, d\eta_z \qquad \text{where } |z'| < |z|$$

$$= \lim_{|R|\to\infty} \left[\oint_C \frac{e^{i\,\eta_z(z-z')}}{c+2K\eta_z-ic}\, d\eta_z - \int_\Gamma \frac{e^{i\,\eta_z(z-z')}}{c+2K\eta_z-ic}\, d\eta_z \right]$$

where the contours for these integrals are shown in figure (A1.1)

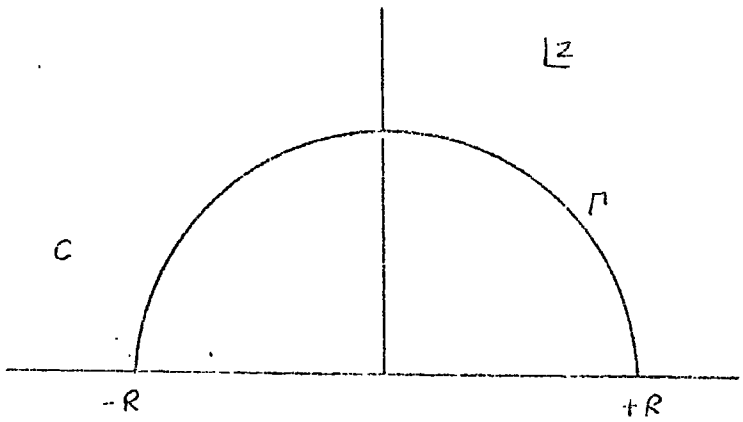


Figure (A1.1)

The integral about the semicircle Γ is of the form

$$\lim_{|R|\to\infty} \int e^{im\,\eta_z} f(\eta_z)\, d\eta_z$$

where $m > 0$ and $|f'(\eta_z)| \leq \frac{1}{R^K}$, $K > 0$. Thus,

$$\lim_{R\to\infty} \int_\Gamma \frac{e^{i\eta_z(z-z')}}{c+2K\eta_z-i\varepsilon}\, d\eta_z = 0$$

From Cauchy's Theorem

$$\oint_c \frac{e^{i\eta_z(z-z')}}{(2K\eta_z-ic+c)}\, d\eta_z = \frac{2\pi i}{2K} \exp\left[\frac{(ic-c)}{2K}(z-z')\right]$$

Now consider

$$\int_{-\infty}^{\infty} \frac{e^{i\eta_z(z-z')}}{c+2K\eta_z-i\varepsilon}\, d\eta_z \qquad \text{for } |z| < |z'|$$

$$= -\int_{-\infty}^{\infty} \frac{e^{i\eta_z(z'-z)}}{2K\eta_z-c+i\varepsilon}\, d\eta_z$$

$$= \lim_{R\to\infty} \left[\int_\Gamma \frac{e^{i\eta_z(z'-z)}}{2K\eta_z-c+i\varepsilon}\, d\eta_z - \oint_c \frac{e^{i\eta_z(z'-z)}}{2K\eta_z-c+i\varepsilon}\, d\eta_z\right]$$

$$= -\lim_{R\to\infty} \oint_c \frac{e^{i\eta_z(z'-z)}}{2K\eta_z-c+i\varepsilon}\, d\eta_z$$

This last integral has a pole at $\eta_z = \frac{c-i\varepsilon}{2K}$, this is outside the chosen contour, so that the integral is zero. Thus

$$\lim_{\varepsilon\to 0^+} \int_{-\infty}^{\infty} \frac{e^{i\eta_z(z-z')}}{(c+2K\eta_z-i\varepsilon)}\, d\eta_z = \frac{2\pi i}{2K}\, \theta(z-z')\, e^{-\frac{ic}{2K}(z-z')}$$

where $\theta(x) = 0 \qquad x < 0$

$\qquad\quad = 1 \qquad x > 0$

Therefore,

$$I = \lim_{\varepsilon\to 0^+} \int \frac{e^{\underline{\eta}.(R-R')}}{(c+2\underline{K}.\underline{\eta}-i\varepsilon)}\, d\underline{\eta}$$

$$= \frac{(2\pi)^3}{2K}\, i\, \delta(\underline{b}-\underline{b}')\, \theta(z-z')\, e^{-\frac{ic}{2K}(z-z')}$$

Appendix II

To evaluate

$$I = \int \frac{e^{-\alpha r}}{|\underset{\sim}{r}-\underset{\sim}{R}|^2} \, d\underset{\sim}{r}$$

in the limit of large R.

$$I = 2\pi \int_0^\infty e^{-\alpha r} r^2 \, dr \int_{-1}^{+1} \frac{dz}{(R^2+r^2-2Rrz)} = \frac{2\pi}{R} \int_0^\infty e^{-\alpha r} \ln \left|\frac{r+R}{r-R}\right| r \, dr$$

Consider $\int_0^\infty e^{-\alpha r} \ln(r+R)\, r\, dr$, integrating by parts we get

$$-\frac{1}{\alpha} \int_0^\infty e^{-\alpha r} \left[\ln(r+R) + 1 - \frac{R}{r+R} \right] dr$$

$$= \frac{1}{\alpha^2} (\ln R+1) + \left(\frac{1-\alpha R}{\alpha^2}\right) \int_0^\infty \frac{e^{-\alpha r}}{R+r} \, dr$$

$$= \frac{1}{\alpha^2} (\ln R+1) + \left(\frac{1-\alpha R}{\alpha^2}\right) e^{\alpha R} \int_R^\infty \frac{e^{-\alpha x}}{x} \, dx$$

$$= \frac{1}{\alpha^2} (\ln R+1) + \left(\frac{1-\alpha R}{\alpha^2}\right) \left[\sum_{n=0}^{N} \frac{(-1)^n \, n!}{(\alpha R)^{n+1}} \ldots + O\left(\frac{1}{\alpha R}\right)^{N+2} \right]$$

$$= \frac{1}{\alpha^2} \ln R - \frac{1}{\alpha^2} \sum_{n=1}^{N} (-1)^n \frac{(n+1)(n-1)!}{(\alpha R)^n}$$

$$= \frac{1}{\alpha^2} \ln R + \frac{2}{\alpha^3 R} - \frac{3}{\alpha^4 R^2} + \frac{8}{\alpha^5 R^3} - \frac{30}{\alpha^6 R^4} + \ldots$$

Also

$$\int_R^\infty r \, e^{-\alpha r} \ln(r-R) \, dr$$

$$= -\frac{\partial}{\partial \alpha} \int_R^\infty e^{-\alpha r} \ln(r-R) \, dr$$

$$= -\frac{\partial}{\partial \alpha} \int_0^\infty e^{-\alpha(z+R)} \ln(z) \, dz$$

$$= - \frac{\partial}{\partial \alpha} \left[\frac{e^{-\alpha R}}{\alpha} \int_0^\infty e^{-x} \left(\ell n(x) - \ell n(\alpha) \right) dx \right]$$

$$= - \frac{\partial}{\partial \alpha} \left[\frac{e^{-\alpha R}}{\alpha} \left(-\gamma - \ell n(\alpha) \right) \right]$$

where γ is Eulers constant. So

$$\int_R^\infty r\, e^{-\alpha r}\, \ell n(r-R)\, dr$$

$$= - \frac{R}{\alpha} \left(\gamma + \ell n(\alpha) \right) e^{-\alpha R} - e^{-\alpha R} \left(\frac{\gamma}{\alpha^2} + \frac{\ell n(\alpha)}{\alpha^2} - \frac{1}{\alpha^2} \right)$$

$$\sim 0 \quad \text{for large } R.$$

Then

$$\int_0^\infty r\, e^{-\alpha r}\, \ell n|r-R|\, dr \sim \int_0^R r\, e^{-\alpha r}\, \ell n(R-r)\, dr$$

Let

$$Y(R) = \int_0^R r\, e^{-\alpha r}\, \ell n(R-r)\, dr$$

$$= e^{-\alpha R} \int_0^R (R-z)\, e^{\alpha z}\, \ell n\, z\, dz$$

and $$Y'(R) = - \alpha\, Y(R) + e^{-\alpha R} \int_0^R e^{\alpha z}\, \ell n(z)\, dz$$

$$Y''(R) = - \alpha\, Y'(R) - \alpha(Y'(R) + \alpha\, Y(R)) + \ell n(R)$$

therefore

$$Y''(R) + 2\alpha\, Y'(R) + \alpha^2\, Y(R) = \ell n(R)$$

Let

$$Y(R) \underset{R \to \infty}{\to} \frac{1}{\alpha^2}\, \ell n(R) + a_0 + \frac{a_1}{R} + \frac{a_2}{R^2} + \ldots$$

and substituting this solution in the differential equation and equating coefficients we get

$$a_0 = 0 \quad , a_1 = -2/\alpha^3$$

$$a_2 = -3/\alpha_4, \; a_3 = -8/\alpha^5 \quad \text{and} \quad a_4 = -30/\alpha^6$$

So that

$$\int_0^R r\, e^{-\alpha r} \ln(R-r) \sim \frac{1}{\alpha^2} \ln(R) - \frac{2}{\alpha^3 R} - \frac{3}{\alpha^4 R^2} - \frac{8}{\alpha^5 R^3} - \frac{30}{\alpha^6 R^4} + \ldots$$

hence.

$$I \sim \frac{8\pi}{\alpha^5 R^2} + \frac{25\pi}{\alpha^5 R^4} + O\left(\frac{1}{R^6}\right)$$

So

$$\nu_{11}(t,t) = \frac{1}{\pi} \int \frac{e^{-2r}}{|\underset{\sim}{R}-\underset{\sim}{r}|^2}\, d\underset{\sim}{r}$$

$$\sim \frac{1}{R^2} + \frac{1}{R^4} + \ldots O\left(\frac{1}{R^6}\right)$$

for large R.

Appendix III

The Evaluation of the Two Centre Matrix Elements $\mu_{nm}(t,t')$

$$\mu_{nm}(t,t') = \int \phi_n^*(\underset{\sim}{r}) \frac{1}{|\underset{\sim}{R}-\underset{\sim}{r}|} \frac{1}{|\underset{\sim}{R}'-\underset{\sim}{r}|} \phi_m(\underset{\sim}{r})\, d\underset{\sim}{r} \qquad (A3.1)$$

where

$$\underset{\sim}{R} = \underset{\sim}{\rho} + \underset{\sim}{v}\, t \quad \text{and} \quad \underset{\sim}{R}' = \underset{\sim}{\rho} + \underset{\sim}{v}\, t'$$

For all values of n and m μ_{nm} has the form

$$I(L_1,M_1;L_2,M_2) = \int \frac{f(r)\, Y_{L_1M_1}^*(\Omega)\, Y_{L_2M_2}(\Omega)}{|\underset{\sim}{R}-\underset{\sim}{r}|\, |\underset{\sim}{R}'-\underset{\sim}{r}|} d\underset{\sim}{r} \qquad (A3.2)$$

where $f(r) = \mu_{nL_1}(r)\, \mu_{mL_2}(r)$, $\mu_{n\ell}$ is a radial hydrogen eigenfunction, and Ω is the polar angle of $\underset{\sim}{r}$ with respect to the axes of quantization, shown in figure (A3.1)

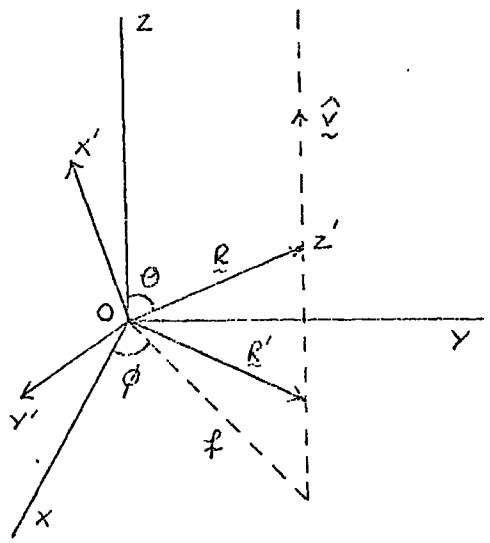


Figure (A3.1)

since $\underset{\sim}{R} = \underset{\sim}{\rho} + \underset{\sim}{v}\, t$ and $\underset{\sim}{R}' = \underset{\sim}{\rho} + \underset{\sim}{v}\, t'$, $\underset{\sim}{R}$ and $\underset{\sim}{R}'$ are in the same plane defined

by $\underset{\sim}{\rho}$ and $\underset{\sim}{v}$. If R' > R rotate to a new set of axes $[OX'Y'Z']$ with the Z' axis along $\underset{\sim}{R}$ and $\hat{\underset{\sim}{X}}'$ in the plane of $\hat{\underset{\sim}{Z}}$ and $\underset{\sim}{\rho}$. Then (α,β,γ) are the Euler angles taking $[OX'Y'Z']$ into $[OXYZ]$ such that

$$\alpha = 0, \quad \beta = \theta \quad \text{and} \quad \gamma = \pi - \phi \tag{A3.3}$$

thus $I(L_1,M_1;L_2,M_2)$

$$= \sum_{M_1'=-L_1}^{L_1} R^{L_1*}_{M_1'M_1}(\alpha,\beta,\gamma) \sum_{M_2'=-L_2}^{L_2} R^{L_2}_{M_2'M_2}(\alpha,\beta,\gamma)\, F(L_1,M_1';L_2,M_2') \tag{A3.4}$$

where $R^{L}_{M_1M_2}(\alpha,\beta,\gamma)$ are the rotation matrices defined in Messiah, Vol.II, Appendix C, and

$$F(L_1,M_1;L_2,M_2) = \int \frac{f(r)\, Y^*_{L_1M_1}(\omega)\, Y_{L_2M_2}(\omega)}{|\underset{\sim}{R}-\underset{\sim}{r}|\;|\underset{\sim}{R}'-\underset{\sim}{r}|}\, d\underset{\sim}{r} \tag{A3.5}$$

with ω the polar angle of $\underset{\sim}{r}$ with respect to the axes $[OX'Y'Z']$. Since

$$Y_{L_1M_1}(\omega)\, Y_{L_2M_2}(\omega) = \sum_{\ell=0}^{\infty} \left[\frac{(2L_1+1)(2L_2+1)(2\ell+1)}{4\pi}\right] \times \begin{pmatrix} L_1 & L_2 & \ell \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_1 & L_2 & \ell \\ M_1 & M_2 & m \end{pmatrix} Y^*_{\ell m}(\omega) \tag{A3.6}$$

where $\begin{pmatrix} L_1 & L_2 & L_3 \\ M_1 & M_2 & M_3 \end{pmatrix}$ are the Wigner-3-j symbols with the properties that if $M_3 = -(M_1+M_2)$, and when $M_1 = M_2 = M_3 = 0$ then $L_1 + L_2 + L_3 = 2p$ where p is integer, they are non-zero otherwise they are zero. Thus the allowed values of ℓ in equation (A3.6) are

$$|L_1-L_2|,\ |L_1-L_2|+2,\ \ldots\ L_1+L_2$$

and also $m = -(M_1+M_2)$.

Then equation (A3.5) becomes

$$F(L_1,M_1;L_2,M_2) = (-1)^{M_2}\left[\frac{(2L_1+1)(2L_2+1)}{4\pi}\right]$$

$$\times \sum_{\ell} (2\ell+1)^{1/2} \begin{pmatrix} L_1 & L_2 & \ell \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_1 & L_2 & \ell \\ -M_1 & M_2 & M_1-M_2 \end{pmatrix} I(\ell,M_2-M_1) \qquad (A3.7)$$

where

$$I(L,M) = \int \frac{f(r)\, Y_{LM}(\omega)}{|\underset{\sim}{R}-\underset{\sim}{r}|\,|\underset{\sim}{R}'-\underset{\sim}{r}|}\, d\underset{\sim}{r} \qquad (A3.8)$$

We require values of $\underset{\sim}{\mu}(t,t')$ for all combinations of states up to the $2p_{\pm1,0}$ level, so that $L_1 \leq 1$ and $L_2 \leq 1$ with the corresponding values of M_1 and M_2. Hence the values of ℓ in (A3.7) are restricted to $\ell = 0$ and $\ell = 0,1$ and 2. Since, from equation (A3.8)

$$I(L,M) = (-1)^{M} I^*(L,-M) \qquad (A3.9)$$

then we need only evaluate I(1,0), I(1,1), I(2,0), I(2,1) and I(2,2). I(0,0) is evaluted by the method of Coleman (1970).

The co-ordinate system used in the evaluation of equation (A3.8) is shown in figure (A3.2),

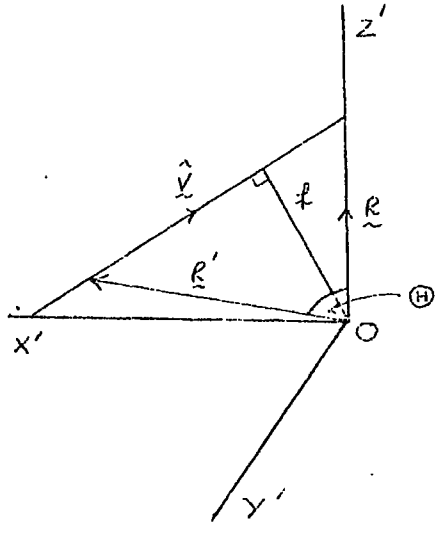


Figure (A3.2)

where R' > R.

If θ is the angle between $\underset{\sim}{R}$ and $\underset{\sim}{R}'$ then $|\underset{\sim}{R}-\underset{\sim}{r}|^{-1}$ and $|\underset{\sim}{R}'-\underset{\sim}{r}|^{-1}$ may be expanded in terms of spherical harmonics.

$$|\underset{\sim}{R}-\underset{\sim}{r}|^{-1} = \sum_{\lambda=0}^{\infty} \left[\frac{4\pi}{2\lambda+1}\right]^{1/2} \gamma_\lambda(r,R)\, Y_{\lambda,0}(\theta',\phi')$$

and

$$|\underset{\sim}{R}'-\underset{\sim}{r}|^{-1} = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{+\ell} \left(\frac{4\pi}{2\ell+1}\right) \gamma_\ell(r,R')\, Y^*_{\ell m}(\theta,0)\, Y_{\ell m}(\theta',\phi')$$

where

$$\gamma_\ell(r,R) = \frac{r^\ell}{R^{\ell+1}} \qquad r < R$$

$$= \frac{R^\ell}{r^{\ell+1}} \qquad r > R$$

and (θ',ϕ') are the polar angles of $\underset{\sim}{r}$ in the $[O\ X'Y'Z']$ axes.

Then the integral in equation (A3.8) becomes

$$I(L,M) = 4\pi \sum_{\ell=0}^{\infty} \sum_{\lambda=0}^{\infty} \sum_{m=-\ell}^{+\ell} \frac{1}{(2\ell+1)}\, Y^*_{\ell m}(\theta,0)\, \mathcal{G}_{\lambda\ell}(R,R')\, E(LM,\lambda O,\ell m) \tag{A3.10}$$

with

$$\mathcal{G}_{\lambda\ell}(R,R') = \int_0^\infty r^2\, f(r)\, \gamma_\lambda(r,R)\, \gamma_\ell(r,R')\, dr$$

and

$$E(L,M;\lambda O,\ell,m) = \left[\frac{4\pi}{2\ell+1}\right]^{1/2} \int Y_{LM}(\theta',\phi')\, Y_{\lambda O}(\theta',\phi')\, Y_{\ell m}(\theta',\phi')\, d\underset{\sim}{\omega}$$

$$= \left[(2\ell+1)(2L+1)\right]^{1/2} \begin{pmatrix} \lambda & \ell & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \lambda & \ell & L \\ 0 & m & M \end{pmatrix} \tag{A3.11}$$

The properties of the Wigner 3-j symbols imply that the right hand side of equation (A3.11) vanishes unless $m = -M$, $\ell + \lambda + L$ is even, and ℓ, λ and L satisfy the triangle inequalities. Thus, for given values of L and ℓ, the

possible values of λ are

$$|\ell-L|,\ |\ell-L|+2,\ \ldots\ \ell+L$$

also since

$$\frac{Y^*_{\ell m}(\Theta,O)}{(2\ell+1)^{\frac{1}{2}}} = \frac{(-1)^m}{\sqrt{4\pi}}\left[\frac{(\ell-m)!}{(\ell+m)!}\right]^{\frac{1}{2}} P_{\ell m}(z) \qquad (A3.12)$$

with $z = \cos\Theta$.

Equation (A3.10) becomes

$$I(L,M) = \left[4\pi(2L+1)\right]^{\frac{1}{2}} \sum_{\ell=m}^{\infty} P_{\ell m}(z) \sum_{\lambda} \mathcal{G}_{\lambda\ell}(R,R')\ \mathcal{J}(\ell,\lambda,L,M) \qquad (A3.13)$$

where

$$\mathcal{J}(\ell,\lambda,L,M) = \left[\frac{(\ell-M)!}{(\ell+M)!}\right]^{\frac{1}{2}} \begin{pmatrix}\lambda & \ell & L\\ O & O & O\end{pmatrix}\begin{pmatrix}\lambda & \ell & L\\ O & -M & M\end{pmatrix}$$

It is evident from equation (A3.13) that I(L,M) is real, then the relation (A3.9) becomes

$$I(L,-M) = (-1)^m\, I(L,M) \qquad (A3.14)$$

The radial functions $\mathcal{G}_{\lambda\ell}(R,R')$ may be simplified. In the case $R' > R$, $\mathcal{G}_{\lambda\ell}(R,R')$ becomes

$$\mathcal{G}_{\lambda\ell}(R,R') = \frac{1}{R^{\lambda+1}}\frac{}{R'^{\ell+1}} \int_o^R r^{\lambda+\ell+2} f(r)\,dr + \frac{R^\lambda}{(R')^{\ell+1}} \int_R^{R'} r^{\ell-\lambda+1} f(r)\,dr$$

$$+ R^\lambda\,(R')^\ell \int_{R'}^{\infty} r^{-\lambda-\ell} f(r)\,dr \qquad (A3.15)$$

Let $A_n(\alpha,\beta) = \int_\alpha^\beta r^{1-n} f(r)\,dr$.

Since in this case f(r) will be a product of bound state orbitals the integral $A_n(\alpha,\infty)$ exists for $\alpha > 0$ and also $A_n(0,\beta)$ exists for all $\beta \geq 0$ if

$n < \mu+2$ where

$$f(r) \underset{r\to 0}{\to} O(r^n)$$

Integration by parts gives

$$\int_0^R r^{\lambda+\ell+2} f(r)\, dr = \int_0^R r^{2\lambda+1} \frac{d}{dr}\left[A_{\lambda-\ell}(0,r)\right] dr$$

$$= R^{2\lambda+1} A_{\lambda-\ell}(0,R) - (2\lambda+1) \int_0^R r^{2\lambda} A_{\lambda-\ell}(0,r)\, dr$$

similarly

$$\int_{R'}^{\infty} r^{-\lambda-\ell} f(r)\, dr = - (R')^{-(2\ell+1)} A_{\lambda-\ell}(0,R') + (2\ell+1) \int_{R'}^{\infty} r^{-2(\ell+1)} A_{\lambda-\ell}(0,r)\, dr$$

then equation (A3.15) becomes

$$\mathcal{G}_{\lambda\ell}(R,R') = (2\ell+1) R^{\lambda} (R')^{\ell} \int_{R'}^{\infty} r^{-2(\ell+1)} A_{\lambda-\ell}(0,r)\, dr$$

$$- \frac{(2\lambda+1)}{R^{\lambda+1} (R')^{\ell+1}} \int_0^R r^{2\lambda} A_{\lambda-\ell}(0,r)\, dr \qquad \text{(A3.16)}$$

Making the transformations $r = R'/y$ and $r = Ry$ in the 1st and second integral respectively (A3.16) becomes

$$\mathcal{G}_{\lambda\ell}(R,R') = \frac{R^{\lambda}}{R'^{\ell+1}} \left[(2\ell+1) \int_0^1 A_{\lambda-\ell}(0,R'/y)\, y^{2\ell}\, dy - (2\lambda+1) \int_0^1 A_{\lambda-\ell}(0,Ry)\, y^{2\lambda}\, dy\right]$$

(A3.17)

Evaluation of I(1,M)

When L = 1 the possible values of λ are ℓ-1 and ℓ+1. Evaluation of the Wigner 3j symbols gives

$$\mathcal{J}(\ell,\ell-1,1,m) = \frac{(-1)^m\,(\ell-m)!}{(2\ell+1)(2\ell-1)(\ell-1)!\,\left[(1+m)!\,(1-m)!\right]^{1/2}} \qquad (A3.18)$$

and

$$\mathcal{J}(\ell,\ell+1,1,m) = \frac{(\ell+1)!}{(2\ell+3)(2\ell+1)(\ell+m)!\,\left[(1+m)!\,(1-m)!\right]^{1/2}} \qquad (A3.19)$$

and the required radial integrals are

$$\mathcal{G}_{\ell-1,\ell}(R,R') = \frac{X^\ell}{R\,R'}\left[(2\ell+1)\int_0^1 A_{-1}\left(0,\frac{R'}{y}\right) y^{2\ell}\,dy - (2\ell-1)\int_0^1 A_{-1}(0,Ry)\,y^{2\ell-2}\,dy\right]$$

where $X = R/R'$, and

$$\mathcal{G}_{\ell+1,\ell}(R,R') = X^{\ell+1}\left[(2\ell+1)\int_0^1 A_{+1}\left(0,\frac{R'}{y}\right) y^{2\ell}\,dy - (2\ell+3)\int_0^1 A_{+1}(0,Ry)\,y^{2\ell+2}\,dy\right]$$

Thus in the case $M = 0$ we have

$$I(1,0) = (12\pi)^{1/2}\sum_{\ell=1}^{\infty} P_\ell(z)\,\mathcal{G}_{\ell-1,\ell}(R,R')\,\frac{\ell}{(2\ell+1)(2\ell-1)} + (12\pi)^{1/2}\sum_{\ell=0}^{\infty} P_\ell(z)\,\mathcal{G}_{\ell+1,\ell}(R,R')\,\frac{\ell+1}{(2\ell+3)(2\ell+1)} \qquad (A3.20)$$

Since the integrals in $\mathcal{G}_{-1,1}(R,R')$ are finite then the $\ell = 0$ term in the first summation is zero and the summation may be extended to include $\ell = 0$ term. Thus

$$I(1,0) = \frac{(12\pi)^{1/2}}{R\,R'}\sum_{\ell=0}^{\infty} P_\ell(z)\,X^\ell\left[V_1 + V_2 + R^2(V_3+V_4)\right] \qquad (A3.21)$$

where

$$V_1 = \frac{\ell}{(2\ell-1)} \int_0^1 A_{-1}\left(0, \frac{R'}{y}\right) y^{2\ell}\, dy$$

$$V_2 = -\frac{\ell}{(2\ell+1)} \int_0^1 A_{-1}(0,Ry)\, y^{2\ell-2}\, dy$$

$$V_3 = \frac{\ell+1}{(2\ell+3)} \int_0^1 A_{+1}\left(0, \frac{R'}{y}\right) y^{2\ell}\, dy$$

and

$$V_4 = -\frac{\ell+1}{2\ell+1} \int_0^1 A_{+1}(0,Ry)\, y^{2\ell+2}\, dy$$

The expression for V_1 may be written

$$V_1 = \tfrac{1}{2} \int_0^1 A_{-1}\left(0, \frac{R'}{y}\right) y^{2\ell}\, dy + \tfrac{1}{2} H_1$$

where

$$H_1 = \frac{1}{(2\ell-1)} \int_0^1 A_{-1}\left(0, \frac{R'}{y}\right) y^{2\ell}\, dy$$

$$= \frac{1}{(2\ell-1)} \int_0^1 y^{2\ell-1} \frac{d}{dy} q_1(y)\, dy$$

where

$$\frac{dq_1}{dy} = y\, A_{-1}\left(0, \frac{R'}{y}\right)$$

$$= \tfrac{1}{2} \frac{d}{dy} y^2 A_{-1}\left(0, \frac{R'}{y}\right) - \tfrac{1}{2} y^2 \frac{d}{dy} A_{-1}\left(0, \frac{R'}{y}\right)$$

$$= \tfrac{1}{2}\left[\frac{d}{dy} y^2 A_{-1}\left(0, \frac{R'}{y}\right) + \tfrac{1}{2} y^2 \frac{R'^3}{y^4} f\left(\frac{R'}{y}\right)\right]$$

$$= \tfrac{1}{2} \frac{d}{dy}\left[y^2 A_{-1}\left(0, \frac{R'}{y}\right) - R'^2 A_{+1}\left(0, \frac{R'}{y}\right)\right]$$

thus a possible choice of $q_1(y)$ is

$$q_1(y) = \tfrac{1}{2}\left[y^2 A_{-1}\left(0, \frac{R'}{y}\right) - R'^2 A_{+1}\left(0, \frac{R'}{y}\right)\right]$$

but since we will require $\frac{q_1(y)}{y}$ to remain finite as $y \to 0$ then a better choice of q_2 is

$$q_1(y) = \tfrac{1}{2}\left[y^2 A_{-1}\left(0, \frac{R'}{y}\right) + R'^2 A_{+1}\left(\frac{R'}{y}, \infty\right)\right]$$

Then integrating by parts H_3 becomes

$$H_3 = \frac{q_1(1)}{(2\ell-1)} - \int_0^1 y^{2\ell-2}\, q_1(y)\, dy$$

Similarly for V_2 we have

$$V_2 = -\tfrac{1}{2} \int_0^1 A_{-1}(0,Ry)\, y^{2\ell-2}\, dy + \tfrac{1}{2} H_2$$

where
$$H_2 = \frac{1}{(2\ell+1)} \int_0^1 A_{-1}(0,Ry)\, y^{2\ell-2}\, dy$$

$$= \frac{1}{(2\ell+1)} \int_0^1 y^{2\ell+1} \frac{d}{dy} q_2(y)\, dy$$

with

$$\frac{d\, q_2(y)}{dy} = y^{-3} A_{-1}(0,Ry) = -\tfrac{1}{2} \frac{d}{dy} \left[y^{-2} A_{-1}(0,Ry) - R^{+2} A_{+1}(0,Ry) \right]$$

and
$$q_2(y) = -\tfrac{1}{2} \left[y^{-2} A_{-1}(0,Ry) - R^{+2} A_{+1}(0,Ry) \right]$$

then
$$H_2 = \frac{q_2(1)}{(2\ell+1)} - \int_0^1 y^{2\ell}\, q_2(y)\, dy$$

and for V_3,

$$V_3 = \tfrac{1}{2} \int_0^1 A_{+1}\left(0, \frac{R'}{y}\right) y^{2\ell}\, dy - \tfrac{1}{2} H_3$$

where

$$H_3 = \frac{1}{(2\ell+3)} \int_0^1 y^{2\ell} A_{+1}\left(0, \frac{R'}{y}\right) dy = \frac{1}{(2\ell+3)} \int_0^1 y^{2\ell+3} \frac{d\, q_3(y)}{dy}$$

with

$$\frac{d\, q_3(y)}{dy} = y^{-3} A_{+1}\left(0, \frac{R'}{y}\right) = \tfrac{1}{2} \frac{d}{dy} \left[-y^{-2} A_{+1}\left(0, \frac{R'}{y}\right) + (R')^{-2} A_{-1}\left(0, \frac{R'}{y}\right) \right]$$

thus

$$q_3(y) = \tfrac{1}{2} \left[- y^{-2} A_{+1}\left(0, \frac{R'}{y}\right) + (R')^{-2} A_{-1}\left(0, \frac{R'}{y}\right) \right]$$

also $q_3(y) = (R')^{-2}\ q_1(1) - \tfrac{1}{2}\ A_{+1}(0,\infty)$,

and $$H_3 = \frac{q_3(1)}{(2\ell+3)} - \int_0^1 y^{2\ell+2}\ q_3(y)\ dy$$

and lastly

$$V_4 = -\tfrac{1}{2} \int_0^1 A_{+1}(0,Ry)\ y^{2\ell+2}\ dy - \tfrac{1}{2}\ H_4$$

where

$$H_4 = \frac{1}{(2\ell+1)} \int_0^1 A_{+1}(0,Ry)\ y^{2\ell+2}\ dy = \frac{1}{(2\ell+1)} \int_0^1 y^{2\ell+1} \frac{d}{dy}\ q_4(y)$$

where

$$\frac{d\ q_4(y)}{dy} = y\ A_{+1}(0,Ry) = \tfrac{1}{2} \frac{d}{dy} \left[y^2\ A_{+1}(0,Ry) - R^{-2}\ A_{-1}(0,Ry) \right]$$

with

$$q_4(y) = +\tfrac{1}{2} \left[y^2\ A_{+1}(0,Ry) - R^{-2}\ A_{-1}(0,Ry) \right] = y^2\ R^{-2}\ q_2(y)$$

thus

$$H_4 = \frac{q_4(1)}{(2\ell+1)} - \int_0^1 y^{2\ell}\ q_4(y)\ dy$$

Combining V_2 and V_4 we get

$$V_2 + R^2\ V_4 = \int_0^1 y^{2\ell}\ Q(y)\ dy$$

where

$$Q(y) = -\tfrac{1}{2} \left[y^{-2}\ A_{-1}(0,Ry) + (1-y^2)\ q_2(y) + R^2\ y^2\ A_{+1}(0,Ry) \right]$$

$$= -\tfrac{1}{4}\ (1+y^2) \left[y^{-2}\ A_{-1}(0,Ry) + R^2\ A_{+1}(0,Ry) \right]$$

Similarly

$$V_1 + R^2 V_3 = \tfrac{1}{2} q_1(1) \left[\frac{1}{(2\ell-1)} - \frac{x^2}{(2\ell+3)}\right] + \int_0^1 y^{2\ell} Q'(y)\, dy$$

with

$$Q'(y) = \tfrac{1}{4} (1+x^2y^2) \left[A_{-1}\left(0, \frac{R'}{y}\right) - (R')^2 y^{-2} A_{+1}\left(\frac{R'}{y}, \infty\right)\right]$$

$$+ \tfrac{1}{4} R^2(1+y^2) A_{+1}(0,\infty)$$

thus equation (A3.21) becomes

$$I(1,0) = \frac{(3\pi)^{1/2}}{(R R')} q_1(1) \sum_{\ell=0}^{\infty} P_\ell(z) x^\ell \left(\frac{1}{2\ell-1} - \frac{x^2}{2\ell+3}\right)$$

$$+ \frac{(12\pi)^{1/2}}{(R R')} \int_0^1 \left[Q(y) + Q'(y)\right] \sum_{\ell=0}^{\infty} (x y^2)^\ell P_\ell(z)\, dy \qquad (A3.22)$$

But

$$\sum_{\ell=0}^{\infty} (x y^2)^\ell P_\ell(z) = (1-2xzy^2+x^2y^4)^{1/2}$$

so that the second term of (A3.22) may be summed. The first summation may be done as follows.

$$\sum_{\ell=0}^{\infty} P_\ell(z) x^\ell \left(\frac{1}{(2\ell-1)} - \frac{x^2}{(2\ell+3)}\right)$$

$$= \sum_{n=1}^{\infty} \left(\frac{P_{n+1}(z)-P_{n-1}(z)}{2n+1}\right) x^{n+1} - 1 + x P_1(z)$$

But

$$P'_{n+1}(z) - P'_{n-1}(z) = (2n+1) P_n(z)$$

$$\therefore \qquad \frac{P_{n+1}(z)-P_{n-1}(z)}{(2n+1)} = - \int_z^1 P_n(t)\, dt \qquad n \geq 1$$

thus the sum becomes

$$-1 + x z - x \sum_{n=1}^{\infty} x^n \int_z^1 P_n(t)\, dt$$

$$= -1 + x - x \int_z^1 \frac{dt}{(1-2tx+x^2)^{1/2}}$$

$$= -(1-2xz+x^2)^{1/2} = -\frac{|R-R'|}{R'}$$

and therefore

$$I(1,0) = \frac{(3\pi)^{1/2}}{2R\,R'} \left[-2q_1(1) \frac{|R-R'|}{R'} + \int_0^1 \frac{T_1(y)\, dy}{(1-2xzy^2+x^2y^4)^{1/2}} \right] \qquad (A3.23)$$

with

$$T_1(y) = (1+x^2y^2) \left[A_{-1}\left(0, \frac{R'}{y}\right) - (R'^2)\, y^{-2}\, A_{+1}\left(\frac{R'}{y}, \infty\right) \right]$$

$$+ (1+y^2) \left[R^2\, A_{+1}(Ry, \infty) - y^{-2}\, A_{-1}(0, Ry) \right]$$

Now consider the M = +1 case.

$$I(1,1) = (6\pi)^{1/2} \sum_{\ell=1}^{\infty} P_{\ell 1}(z) \left[-\frac{\mathcal{G}_{\ell-1,\ell}(R,R')}{(2\ell+1)(2\ell-1)} + \frac{\mathcal{G}_{\ell+1,\ell}(R,R')}{(2\ell+3)(2\ell+1)} \right]$$

$$= \frac{(6\pi)^{1/2}}{R\,R'} \sum_{\ell=1}^{\infty} P_{\ell 1}(z) \left[-H_1 + H_2 + R^2(-H_4+H_3) \right] x^{\ell} \qquad (A3.24)$$

Using the forms of H_1, H_2, H_3 and H_4 derived previously we get

$$H_2 - R^2 H_4 = \int_0^1 y^{2\ell} (y^2-1)\, q_2(y)\, dy$$

and

$$R^2 H_3 - H_1 = (R')^2\, q_3(1) \left(\frac{x^2}{2\ell+3} - \frac{1}{2\ell-1} \right) +$$

$$+ (R')^2 \int_0^1 y^{2\ell} (1-x^2y^2)\, q_3(y)\, dy$$

The Legendre series of equation (A3.24) is summed using the relation

$$\sum_{\ell=m}^{\infty} t^{\ell} P_{\ell m}(z) = \frac{(1-z^2)^{m/2}\, (2m-1)!!\, t^m}{(1-2tz+t^2)^{m+1/2}} \qquad (A3.25)$$

In particular

$$\sum_{\ell=1}^{\infty} P_{\ell 1}(z)\, x^{\ell} \left(\frac{x^2}{2\ell+3} - \frac{1}{2\ell-1}\right)$$

$$= \sum_{\ell=1}^{\infty} P_{\ell 1}(z)\, x^{\ell} \int_0^1 (x^2 y^{2\ell+2} - y^{2\ell-2})\, dy$$

$$= - x \sin\theta \int_0^1 \frac{(1-x^2y^4)}{(1-2xzy^2+x^2y^4)^{3/2}}\, dy$$

and

$$\sum_{\ell=1}^{\infty} P_{\ell 1}(z)\, x^{\ell} \int_0^1 y^{2\ell} \left[(y^2-1)\, q_2(y) + (R')^2\, (1-x^2y^2)\, q_3(y)\right] dy$$

$$= x \sin\theta \int_0^1 \frac{T'(y)}{(1-2xzy^2+x^2y^4)^{3/2}}\, dy$$

where

$$T'(y) = \tfrac{1}{2}(1-y^2) \left[A_{-1}(0,Ry) - R^2\, y^2\, A_{+1}(0,Ry)\right]$$

$$+ \tfrac{1}{2}(1-x^2y^2) \left[y^2\, A_{-1}\left(0, \frac{R'}{y}\right) - (R')^2\, A_{+1}\left(0, \frac{R'}{y}\right)\right]$$

Thus combining these results we get

$$I(1,1) = \frac{(6\pi)^{1/2}}{2} \frac{\sin\theta}{(R')^2} \int_0^1 \frac{T_2(y)\, dy}{(1-2xzy^2+x^2y^4)^{3/2}} \qquad (A3.26)$$

where

$$T_2(y) = (1-y^2) \left[A_{-1}(0,Ry) - R^2\, y^2\, A_{+1}(0,Ry)\right]$$

$$+ (1-x^2y^2) \left[y^2\, A_{-1}\left(0, \frac{R'}{y}\right) - (R')^2\, A_{+1}\left(0, \frac{R'}{y}\right)\right]$$

$$- (1-x^2y^4) \left[A_{-1}(0,R') - (R')^2\, A_{+1}(0,R')\right] \qquad (A3.27)$$

Evaluation of I(2,M)

In this case equation (A3.13) becomes

$$I(2,M) = (20\pi)^{1/2} \sum_{\ell=M}^{\infty} P_{\ell m}(z) \sum_{\lambda} \mathcal{G}_{\lambda\ell}(R,R') \; \mathcal{J}(\ell,\lambda,2,M)$$

and the form of $\mathcal{J}(\ell,\lambda,2,M)$ restricts λ to be $\ell-2,\ell$ or $\ell+2$. Evaluating $\mathcal{J}(\ell,\lambda,2,M)$ in the case M = 0 we get

$$I(2,0) = (5\pi)^{1/2} \sum_{\ell=0}^{\infty} P_{\ell}(z) \left[-\frac{3\ell(\ell-1)\,\mathcal{G}_{\ell-2,\ell}(R,R')}{(2\ell-3)(2\ell-1)(2\ell+1)} + \frac{2\ell(\ell+1)\,\mathcal{G}_{\ell\ell}(R,R')}{(2\ell-1)(2\ell+1)(2\ell+3)} + \frac{3(\ell+1)(\ell+2)\,\mathcal{G}_{\ell+2,\ell}(R,R')}{(2\ell+1)(2\ell+3)(2\ell+5)} \right] \tag{A3.28}$$

Using the explicit forms of $\mathcal{G}_{\ell\ell'}$ we get

$$I(r,0) = \frac{(5\pi)^{1/2}}{R'} \sum_{\ell=0}^{\infty} P_{\ell}(z)\, x^{\ell} \left[R^{-2}(V_1+V_2) + V_3 + V_4 + R^2(V_5+V_6) \right] \tag{A3.29}$$

where

$$V_1 = \frac{3\ell(\ell-1)}{(2\ell-3)(2\ell-1)} \int_0^1 A_{-2}\left(0, \frac{R'}{y}\right) y^{2\ell}\, dy$$

$$V_2 = \frac{-3\ell(\ell-1)}{(2\ell-1)(2\ell+1)} \int_0^1 A_{-2}(0,Ry)\, y^{2\ell-4}\, dy$$

$$V_3 = \frac{2\ell(\ell+1)}{(2\ell-1)(2\ell+3)} \int_0^1 A_0\left(0, \frac{R'}{y}\right) y^{2\ell}\, dy$$

$$V_4 = \frac{-2\ell(\ell+1)}{(2\ell-1)(2\ell+3)} \int_0^1 A_0(0,Ry)\, y^{2\ell}\, dy$$

$$V_5 = \frac{3(\ell+1)(\ell+2)}{(2\ell+3)(2\ell+5)} \int_0^1 A_{+2}\left(0, \frac{R'}{y}\right) y^{2\ell}\, dy$$

$$V_6 = -\frac{3(\ell+1)(\ell+2)}{(2\ell+1)(2\ell+3)} \int_0^1 A_{+2}(0,Ry)\, y^{2\ell+4}\, dy$$

The ℓ factors preceding these terms may be simplified by use of partial fractions so that

$$V_1 = \tfrac{3}{8}\left[J_8 + 3J_7 + 2\int_0^1 A_{-2}\left(0, \frac{R'}{y}\right) y^{2\ell}\, dy\right]$$

$$V_2 = \tfrac{3}{8}\left[3J_1 + J_2 - 2\int_0^1 A_{-2}(0,Ry)\, y^{2\ell-4}\, dy\right]$$

$$V_3 = \tfrac{1}{8}\left[3J_9 - 3J_{10} + 4\int_0^1 A_0\left(0, \frac{R'}{y}\right) y^{2\ell}\, dy\right]$$

$$V_4 = -\tfrac{1}{8}\left[3J_3 - 3J_4 + 4\int_0^1 A_0(0,Ry)\, y^{2\ell}\, dy\right]$$

$$V_5 = -\tfrac{3}{8}\left[J_{11} + 3J_{12} - 2\int_0^1 A_{+2}\left(0, \frac{R'}{y}\right) y^{2\ell}\, dy\right]$$

$$V_6 = -\tfrac{3}{8}\left[J_5 + 3J_6 + 2\int_0^1 A_{+2}(0,Ry)\, y^{2\ell+4}\, dy\right]$$

Using the procedures utilized in evaluating $H_{1\to4}$ we have

$$J_1 = \frac{1}{(2\ell+1)}\int_0^1 A_{-2}(0,Ry)\, y^{2\ell-4}\, dy$$

$$= \frac{r_1(1)}{(2\ell+1)} - \int_0^1 y^{2\ell}\, r_1(y)\, dy$$

$$r_1(y) = \tfrac{1}{4}\left[R^4 A_{+2}(0,Ry) - y^{-4} A_{-2}(0,Ry)\right]$$

$$J_2 = \frac{1}{(2\ell-1)}\int_0^1 A_{-2}(0,Ry)\, y^{2\ell-4}\, dy$$

$$= \frac{p_1(1)}{(2\ell-1)} - \int_0^1 y^{2\ell-2}\, p_1(y)\, dy$$

$$p_1(y) = \tfrac{1}{2}\left[R^2 A_0(0,Ry) - y^{-2} A_{-2}(0,Ry)\right]$$

$$J_3 = \frac{1}{(2\ell-1)}\int_0^1 A_0(0,Ry)\, y^{2\ell}\, dy$$

$$= \frac{p_1(1)}{(2\ell-1)\,R^2} - \frac{1}{R^2}\int_0^1 y^{2\ell}\, p_1(y)\, dy$$

$$J_4 = \frac{1}{(2\ell+3)} \int_0^1 A_0(0,Ry)\, y^{2\ell}\, dy$$

$$= \frac{p_3(1)}{(2\ell+3)} - \int_0^1 y^{2\ell+2}\, p_3(y)\, dy$$

$$p_3(y) = \tfrac{1}{2}\left[R^2\, A_{+2}(0,Ry) - y^{-2}\, A_0(0,Ry)\right]$$

$$J_5 = \frac{1}{(2\ell+3)} \int_0^1 A_{+2}(0,Ry)\, y^{2\ell+4}\, dy$$

$$= \frac{p_3(1)}{R^2(2\ell+3)} - \frac{1}{R^2} \int_0^1 y^{2\ell+4}\, p_3(y)\, dy$$

$$J_6 = \frac{1}{(2\ell+1)} \int_0^1 A_{+2}(0,Ry)\, y^{2\ell+4}\, dy$$

$$= \frac{r_1(1)}{(2\ell+1)\, R^4} - \frac{1}{R^4} \int_0^1 y^{2\ell+4}\, r_1(y)\, dy$$

In the remaining integrals it is necessary to allow for the possibility that $\ell = 0$ or 1 in the definitions of the r(y) and p(y) functions. We consider $\ell \geq 0$ initially and indicate the differences for $\ell \geq 1$ and $\ell \geq 2$ later.

$$J_7 = \frac{1}{(2\ell-3)} \int_0^1 A_{-2}\left(0, \frac{R'}{y}\right) y^{2\ell}\, dy$$

$$= \frac{r_2(1)}{(2\ell-3)} - \int_0^1 y^{2\ell-4}\, r_2(y)\, dy$$

$$r_2(y) = \tfrac{1}{4}\left[y^4\, A_{-2}\left(0, \frac{R'}{y}\right) + R'^4\, A_{+2}\left(\frac{R'}{y}, \infty\right)\right]$$

$$J_8 = \frac{1}{(2\ell-1)} \int_0^1 A_{-2}\left(0, \frac{R'}{y}\right) y^{2\ell}\, dy$$

$$= \frac{p_4(1)}{(2\ell-1)} - \int_0^1 y^{2\ell-2}\, p_4(y)\, dy$$

$$p_4(y) = \tfrac{1}{2}\left[y^2\, A_{-2}\left(0, \frac{R'}{y}\right) + (R')^2\, A_0\left(\frac{R'}{y}, \infty\right)\right]$$

$$J_9 = \frac{1}{(2\ell-1)} \int_0^1 A_0\left(0, \frac{R'}{y}\right) y^{2\ell}\, dy$$

$$= \frac{p_5(1)}{(2\ell-1)} - \int_0^1 y^{2\ell-2}\, p_5(y)\, dy$$

$$p_5(y) = \tfrac{1}{2}\left[y^2 A_0\left(0, \frac{R'}{y}\right) + (R')^2 A_{+2}\left(\frac{R'}{y}, \infty\right)\right]$$

$$J_{10} = \frac{1}{(2\ell+3)} \int_0^1 A_0\left(0, \frac{R'}{y}\right) y^{2\ell}\, dy$$

$$= \frac{p_6(1)}{(2\ell+3)} - \int_0^1 y^{2\ell+2}\, p_6(y)\, dy$$

$$p_6(y) = \tfrac{1}{2}\left[(R')^{-2} A_{-2}\left(0, \frac{R'}{y}\right) - y^{-2} A_0\left(0, \frac{R'}{y}\right)\right]$$

$$J_{11} = \frac{1}{(2\ell+3)} \int_0^1 A_{+2}\left(0, \frac{R'}{y}\right) y^{2\ell}\, dy$$

$$= \frac{p_7(1)}{(2\ell+3)} - \int_0^1 y^{2\ell+2}\, p_7(y)\, dy$$

$$p_7(y) = \tfrac{1}{2}\left[(R')^{-2} A_0\left(0, \frac{R'}{y}\right) - y^{-2} A_{+2}\left(0, \frac{R'}{y}\right)\right]$$

$$J_{12} = \frac{1}{2\ell+5} \int_0^1 A_{+2}\left(0, \frac{R'}{y}\right) y^{2\ell}\, dy$$

$$= \frac{r_3(1)}{(2\ell+5)} - \int_0^1 y^{2\ell+4}\, r_3(y)\, dy$$

$$r_3(y) = \tfrac{1}{4}\left[(R')^{-4} A_{-2}\left(0, \frac{R'}{y}\right) - y^{-4} A_{+2}\left(0, \frac{R'}{y}\right)\right]$$

If $\ell \geq 1$ J_8 and J_9 may be replaced by

$$J_8 = \frac{(R')^2\, p_6(1)}{(2\ell-1)} - (R')^2 \int_0^1 y^{2\ell}\, p_6(y)\, dy$$

and

$$J_9 = \frac{(R')^2\, p_7(1)}{(2\ell-1)} - (R')^2 \int_0^1 y^{2\ell}\, p_7(y)\, dy$$

and if $\ell \geq 2$ J_7 becomes

$$J_7 = \frac{(R')^4\, r_3(1)}{(2\ell-3)} - (R')^4 \int_0^1 y^{2\ell}\, r_3(y)\, dy$$

Combining these results, we have

$$R^{-2}\, V_2 + V_4 + R^2\, V_6 = \int_0^1 y^{2\ell}\, Q(y)\, dy \qquad (A3.30)$$

with

$$Q(y) = -\frac{(3+2y^2+3y^4)}{32\, R^2 y^4}\left[3\, A_{-2}(0,Ry) + 2\, R^2y^2\, A_0(0,Ry) + 3\, R^4y^4\, A_{+2}(0,Ry)\right]$$

and

$$R^{-2}\, V_1 + V_3 + R^2\, V_5 = \frac{9\, r_2(1)}{8\, R^2}\left[\frac{1}{2\ell-3} - \frac{x^4}{2\ell+5}\right]$$

$$+ \tfrac{3}{8}\left[R^{-2}\, p_4(1) + p_5(1)\right]\left[\frac{1}{(2\ell-1)} - \frac{x^2}{2\ell+3}\right] + \int_0^1 y^{2\ell}\, Q'(y)\, dy \qquad (A3.31)$$

with

$$Q'(y) = \frac{1}{32\, R^2}\left[3\, R^4(3+2y^2+3y^4)\, A_{+2}(0,\infty)\right.$$

$$+ (3+2x^2y^2+3x^4y^4)\left\{3\, A_{-2}\left(0, \frac{R'}{y}\right) - 2(R')^2\, y^{-2}\, A_0\left(\frac{R'}{y}, \infty\right) - (R')^4\, y^{-4}\, A_{+2}\left(\frac{R'}{y}, \infty\right)\right\}$$

$$\left. + 2R^2(3y^2+2+3x^2y^2)\, A_0(0,\infty)\right]$$

The series

$$\sum_{\ell=0}^{\infty} P_\ell(z)\, x^\ell \left(\frac{1}{2\ell-3} - \frac{x^4}{2\ell+5}\right)$$

may be written as

$$\sum_{\lambda=2}^{\infty}\left(\frac{P_{\lambda+2}(z) - P_{\lambda-2}(z)}{(2\lambda+1)}\right) x^{\lambda+2} + \sum_{\ell=0}^{3} \frac{1}{2\ell-3}\, P_\ell(z)\, x^\ell \qquad (A3.32)$$

but for $\lambda \geq 2$

$$\frac{P_{\lambda+2}(z)-P_{\lambda-2}(z)}{2\lambda+1} = -\int_z^1 \left[P_{\lambda+1}(t) + P_{\lambda-1}(t)\right] dt$$

$$+ 2\int_z^1 dt \int_t^1 P_\lambda(\mu)\, d\mu$$

and $$\int_z^1 dt \int_t^1 P_\lambda(\mu)\, d\mu = \int_z^1 (t-z)\, P_\lambda(t)\, dt$$

thus for $\lambda \geq 2$

$$\frac{P_{\lambda+2}(z)-P_{\lambda-2}(z)}{(2\lambda+1)} = \int_z^1 \left[2(t-z)\, P_\lambda(t) - P_{\lambda+1}(t) - P_{\lambda-1}(t)\right] dt$$

With the convention $P_n^m(z) = 0 \quad n < m$ the summation of (A3.32) may be extended to include $\lambda = 0,1$.

Therefore

$$\sum_{\ell=0}^{\infty} x^\ell \frac{P_{\ell+2}(z)-P_{\ell-2}(z)}{(2\ell+1)} = \sum_{\ell=0}^{\infty} x^\ell \int_z^1 \left[2(t-z)\, P_\ell(t) - P_{\ell+1}(t) - P_{\ell-1}(t)\right] dt$$

$$+ x/3 + 2z - 1$$

The summation is done by using the generating function for the Legendre polynomials, and doing the integration with respect to t we get

$$\sum_{\ell=0}^{\infty} x^\ell \frac{P_{\ell+2}(z)-P_{\ell-2}(z)}{(2\ell+1)} = -\tfrac{1}{3} \frac{|R-R'|^3}{R'^3} - \frac{2xz|R-R'|}{R'}$$

$$= -\frac{(1+4xz+x^2)}{3R'} |R-R'| \qquad \text{(A3.33)}$$

The second series $\sum_{\ell=0}^{\infty} x^\ell P_\ell(z) \left[\frac{1}{2\ell-1} - \frac{x^2}{2\ell+3}\right]$ has been done previously and is equal to

$$-\frac{|R-R'|}{R'}$$

The final expression for $I(2,0)$ is

$$I(2,0) = -\frac{3(5\pi)^{\frac{1}{2}}}{8R^2(R')^2}\,|\underset{\sim}{R}-\underset{\sim}{R}'|\,\left[p_4(1) + R^2\,p_5(1) + r'_2(1)\,(1+4xz+x^2)\right]$$

$$+\frac{(5\pi)^{\frac{1}{2}}}{R'}\int_0^1 \frac{(Q(y)+Q'(y))}{(1-2xzy^2+x^2y^4)^{\frac{1}{2}}}\,dy \qquad (A3.34)$$

For $M = 1$, equation (A3.13) becomes

$$I(2,1) = (30\pi)^{\frac{1}{2}} \sum_{\ell=1}^{\infty} P_{\ell 1}(z)\left[-\frac{(\ell-1)\,\mathcal{G}_{\ell-2,\ell}(R,R')}{(2\ell-3)(2\ell-1)(2\ell+1)}\right.$$

$$\left.-\frac{\mathcal{G}_{\ell\ell}(R,R')}{(2\ell-1)(2\ell+1)(2\ell+3)} + \frac{(\ell+2)\,\mathcal{G}_{\ell+2,\ell}(R,R')}{(2\ell+1)(2\ell+3)(2\ell+5)}\right] \qquad (A3.35)$$

$$= \frac{(30\pi)^{\frac{1}{2}}}{R'} \sum_{\ell=1}^{\infty} P_{\ell 1}(z)\,x^{\ell}\left[R^{-2}(V_1+V_2) + V_3 + V_4 + R^2(V_5+V_6)\right]$$

with

$$V_1 = -\tfrac{1}{4}\,(J_7+J_8)$$

$$V_2 = \tfrac{1}{4}\,(3J_1-J_2)$$

$$V_3 = \tfrac{1}{4}\,(J_{10}-J_9)$$

$$V_4 = \tfrac{1}{4}\,(J_3-J_4)$$

$$V_5 = \tfrac{1}{4}\,(J_{11}+J_{12})$$

$$V_6 = \tfrac{1}{4}\,(J_5-3J_6)$$

using the results obtained in the $I(2,0)$ case. Then

$$R^{-2}\,V_2 + V_4 + R^2\,V_6 = \int_0^1 y^{2\ell}\,Q(y)\,dy$$

where

$$Q(y) = \frac{1}{16}(1-y^2)\,R^{-2}\left[2R^2 y^{-2}(1-y^2)\,A_0(0,Ry) + (1+3y^2)\{y^{-4}A_{-2}(0,Ry) - R^4 A_{+2}(0,Ry)\}\right]$$

and

$$R^{-2}V_1 + V_3 + R^2 V_5 = \frac{r_2(1)}{4R^2}\left(-\frac{1}{2\ell-3} + \frac{x^4}{2\ell+5}\right) + \frac{1}{4x^2}\left(-\frac{1}{2\ell-1} + \frac{x^2}{2\ell+3}\right)\{p_6(1) + R^2 p_7(1)\} + \int_0^1 Q'(y)\,y^{2\ell}\,dy$$

with

$$Q'(y) = \frac{(1-x^2y^2)}{16R^2}\left[(x^2y^2+3)\,A_{-2}\left(0, \frac{R'}{y}\right) + (1+3x^2y^2)(R')^4 y^{-1} A_{+2}\left(\frac{R'}{y}, \infty\right) - 2(R')^2 y^{-2}(1-x^2y^2)\,A_0\left(0, \frac{R'}{y}\right)\right] - (2-3x^2y^2+x^2y^6)\frac{(R')^2}{16y^2}A_{+2}(0,\infty)$$

The series

$$\sum_{\ell=1}^{\infty} P_{\ell 1}(z)\,x^{\ell}\left(\frac{x^2}{2\ell+3} - \frac{1}{2\ell-1}\right)$$

has been evaluated previously and is equal to

$$-x\sin\theta\int_0^1 \frac{(1-x^2y^4)}{(1-2xzy^2+x^2y^4)^{3/2}}\,dy$$

The techniques used to evaluate this result cannot be used for the series

$$\sum_{\ell=1}^{\infty} P_{\ell 1}(z)\,x^{\ell}\left(\frac{x^4}{2\ell+5} - \frac{1}{2\ell-3}\right)$$

But

$$\sum_{\ell=1}^{\infty} P_{\ell 1}(z)\, x^{\ell} \left[\frac{x^4}{2\ell+5} - \frac{1}{2\ell-3}\right]$$

$$= \sum_{n=1}^{\infty} \left[\frac{P^{1}_{n+2}(z) - P^{1}_{n-2}(z)}{2n+1}\right] x^{n+2}$$

$$= \sin\theta\, x^2 \left[\frac{1}{x} \sum_{\ell=0}^{\infty} P_{\ell}(z)\, x^{\ell} + x \sum_{\ell=0}^{\infty} P_{\ell}(z)\, x^{\ell} - 2\left[\int_z^1 \sum_{\ell=0}^{\infty} P_{\ell}(t)\, x^{\ell}\, dt - 1 + \frac{1}{x}\right]\right]$$

$$= \frac{R \sin\theta\, (1-4xz+x^2)}{|\underset{\sim}{R}-\underset{\sim}{R}'|}$$

When these results are combined we get

$$I(2,1) = (30\pi)^{1/2} \frac{\sin\theta}{R'} \left[\frac{r_2(1)(1-4xz+x^2)}{4R\,|\underset{\sim}{R}-\underset{\sim}{R}'|} + \int_0^1 \frac{T_4'(y)}{(1-2xzy^2+x^2y^4)^{3/2}}\right] \quad (A3.36)$$

Where

$$T_4(y) = x\, y^2(Q(y)+Q'(y)) - \frac{1}{4x}(1-x^2y^4)(p_6(1)+R^2\, p_7(1))$$

Since $|\underset{\sim}{R}-\underset{\sim}{R}'|^{-1}$ is singular when $\underset{\sim}{R} = \underset{\sim}{R}'$, as is the integrand of equation (A3.36), the two terms are combined to remove any singularities. Since

$$\frac{R'}{|\underset{\sim}{R}-\underset{\sim}{R}'|} = 1 + \int_0^1 \frac{2xy(z-xy^2)}{(1-2xy^2+x^2y^4)^{3/2}}\, dy$$

Equation (A3.36) becomes

$$I(2,1) = (30\pi)^{1/2} \frac{\sin\theta}{R'} \left[\int_0^1 \frac{T_4(y)}{(1-2xzy^2+x^2y^4)^{3/2}}\, dy + \frac{r_2(1)(1-4xz+x^2)}{4x}\right] \quad (A3.37)$$

where $$T_4(y) = T_4'(y) + \frac{2y(z-xy^2)}{4}\, r_2(1)$$

For M = 2, equation (A3.13) becomes

$$I(2,2) = \left(\frac{15\pi}{2}\right)^{1/2} \sum_{\ell=2}^{\infty} P_{\ell 2}(z) \left[\frac{\mathcal{G}_{\ell-2,\ell}(R,R')}{(2\ell-3)(2\ell-1)(2\ell+1)} - \frac{2\,\mathcal{G}_{\ell\ell}(R,R')}{(2\ell-1)(2\ell+1)(2\ell+3)} + \frac{\mathcal{G}_{\ell+2,\ell}(R,R')}{(2\ell+1)(2\ell+3)(2\ell+5)} \right] \quad (A3.38)$$

$$= \left(\frac{15\pi}{2}\right)^{1/2} \frac{1}{R'} \sum_{\ell=2}^{\infty} P_{\ell 2}(z) \left[R^{-2}(V_1+V_2) + V_3 + V_4 + R^2(V_5+V_6) \right] \quad (A3.39)$$

where

$$V_1 = \tfrac{1}{2}\,(J_7-J_8) \qquad V_2 = \tfrac{1}{2}\,(J_1-J_2)$$

$$V_3 = \tfrac{1}{2}\,(J_{10}-J_9) \qquad V_4 = \tfrac{1}{2}\,(J_3-J_4)$$

$$V_5 = \tfrac{1}{2}\,(J_{11}-J_{12}) \qquad V_6 = \tfrac{1}{2}\,(J_5-J_6)$$

J_{1-12} are as defined previously allowing for the fact that $\ell \geqslant 2$. Then

$$R^{-2} V_2 + V_4 + R^2 V_6 = \int_0^1 y^{2\ell} Q(y)\, dy$$

where

$$Q(y) = -\tfrac{1}{8}\,(1-y^2)^2 \left[R^2 A_{+2}(0,Ry) - 2y^{-2} A_0(0,Ry) + R^{-2} y^{-4} A_{-2}(0,Ry) \right]$$

and

$$R^{-2} V_1 + V_3 + R^2 V_5 = \frac{(R')^2 r_3(1)}{2x^2} \left(\frac{1}{2\ell-3} - \frac{x^4}{2\ell+5} \right)$$

$$- \tfrac{1}{2}\,(R')^2 \left(\frac{1}{2\ell-1} - \frac{x^2}{2\ell+3} \right) (R^{-2} p_6(1) + p_7(1)) + \int_0^1 y^{2\ell} Q'(y)\, dy$$

with

$$Q'(y) = \tfrac{1}{8}\, x^{-2}(1-x^2y^2)^2 \left[(R')^2 y^{-2} A_{+2}\left(0, \frac{R'}{y}\right) - 2y^{-2} A_0\left(0, \frac{R'}{y}\right) + R'^2 A_{-2}\left(0, \frac{R'}{y}\right) \right]$$

The series of equation (A3.39) can now be summed using the generating function for $P_{\ell 2}(z)$. Thus

$$\sum_{\ell=2}^{\infty} P_{\ell 2}(z)\, x^{\ell} \left(\frac{1}{2\ell-1} - \frac{x^2}{2\ell+3}\right) = 3y^2 \sin^2\theta \int_0^1 \frac{y^2(1-x^2y^4)}{(1-2xzy^2+x^2y^4)^{5/2}}$$

and

$$\sum_{\ell=2}^{\infty} P_{\ell 2}(z)\, x^{\ell} \left(\frac{1}{2\ell-3} - \frac{y^4}{2\ell+5}\right) = 3x^2 \sin^2\theta \int_0^1 \frac{(1-x^4y^8)}{(1-2xzy^2+x^2y^4)^{5/2}}\, dy$$

and the final result is

$$I(2,2) = \left(\frac{15\pi}{2}\right)^{1/2} \frac{3 \sin^2\theta}{R'} \int_0^1 \frac{T_5(y)}{(1-2xzy^2+x^2y^4)^{5/2}} \qquad \text{(A3.40)}$$

with

$$T_5(y) = x^2y^4(Q(y)+Q'(y)) + \tfrac{1}{2}\,(R')^2\,(1-x^4y^8)\, r_3(1)$$

$$- \tfrac{1}{2}\, y^2(1-x^2y^4)\,(p_6(1)+R^2\, p_7(1))$$

The above analysis gives a method of reducing the matrix elements to single dimension integrals on the interval $[0,1]$, which are calculated numerically.

The matrix elements $F(L_1\ M_1, L_2\ M_2)$ evaluated with respect to the axes in the $\hat{R}$ direction for $R < R'$ can now be obtained. Using equation (A3.7) we have

$$F(0,0;1,0) = I(1,0)$$

$$F(0,0;1,1) = I(1,1)$$

$$F(1,0;1,0) = (4\pi)^{-1/2}\, I(0,0) + (5\pi)^{1/2}\, I(2,0)$$

$$F(1,0;1,1) = \left(\frac{3}{20\pi}\right)^{1/2} I(2,1)$$

$$F(1,1;1,1) = (4\pi)^{-1/2}\, I(0,0) - (20\pi)^{1/2}\, I(2,0)$$

$$F(1,1;1,-1) = -\left(\frac{3}{10\pi}\right)^{1/2} I(2,2)$$

The remaining expressions for $F(L_1,M_1;L_2,M_2)$; $L_1,L_2 \leq 1$ and $M_1,M_2 < 1$, are obtained using the symmetry relations

$$F(L_1,M_1;L_2,M_2) = F(L_2\ M_2;\ L_1\ M_1)$$

$$= (-1)^{M_1+M_2}\ F(L_1-M_1,L_2-M_2)$$

To evaluate the two centred matrix elements in the chosen direction of quantisation we use equation (A3.4)

with $$R^{L}_{m'm}(\alpha,\beta,\gamma) = (-1)^{m}\ e^{im\phi}\ r^{L}_{m'm}(\theta)$$

where (θ,ϕ) are the polar angles of $\hat{\underset{\sim}{R}}$ and $r^{L}_{m'm}(\theta)$ are the rotation matrix elements defined in Messiah Vol.II, then

$$I(0,0;1,0) = \cos\theta\ F(0,0;1,0) - \sqrt{2}\ \sin\theta\ F(0,0;1,1)$$

$$I(0,0;1,1) = -\ e^{i\phi}\left[\frac{1}{\sqrt{2}}\ \sin\theta\ F(0,0;1,0) + \cos\theta\ F(0,0;1,1)\right]$$

$$I(1,0;1,0) = \cos^2\theta\ F(1,0;1,0) + \sin^2\theta\ F(1,1;1,1)$$

$$- \sin^2\theta\ F(1,1;1,-1) - 2\sqrt{2}\ \sin\theta\ \cos\theta\ F(1,0;1,1)$$

$$I(1,0;1,1) = e^{-i\phi}\left[\frac{1}{\sqrt{2}}\ \sin\theta\ \cos\theta\ F(1,0;1,0)\right.$$

$$- \frac{1}{\sqrt{2}}\ \sin\theta\ \cos\theta\ F(1,1;1,1) + \frac{1}{\sqrt{2}}\ \sin\theta\ \cos\theta\ F(1,1;1,-1)$$

$$\left. + (\cos^2\theta-\sin^2\theta)\ F(1,0;1,1)\right]$$

$$I(1,1;1,1) = \tfrac{1}{2}\ \sin^2\theta\ F(1,0;1,0) + \tfrac{1}{2}\ (1+\cos^2\theta)\ F(1,1;1,1)$$

$$+ \tfrac{1}{2}\ (1-\cos^2\theta)\ F(1,1;1,-1) + \sqrt{2}\ \sin\theta\ \cos\theta\ F(1,0;1,1)$$

and

$$I(1,1;1,-1) = e^{2i\phi}\left[\tfrac{}{}\right.- \tfrac{1}{2}\sin^2\theta\, F(1,0;1,0)$$

$$+ \tfrac{1}{2}(1-\cos^2\theta)\, F(1,1;1,1) + \tfrac{1}{2}(1+\cos^2\theta)\, F(1,1;1,-1)$$

$$\left. - \sqrt{2}\sin\theta\cos\theta\, F(1,0;1,1)\right]$$

The remaining expressions for $I(L_1,M_1;L_2,M_2)$; $L_1,L_2 \leq 1$ are obtained using the relation

$$I(L_1,M_1;L_2,M_2) = (-1)^{M_1+M_2}\, I^*(L_1,-M_1;L_2,-M_2)$$

$$= I^*(L_2,M_2;L_1,M_1)$$

In the notation of section (10) the non-spherical matrix elements are

$$\left.\begin{aligned}
\mu_{13}(t,t') &= I(0,0;1,0)\\
\mu_{14}(t,t') &= I(0,0;1,1)\\
\mu_{15}(t,t') &= (-1)\, I^*(0,0;1,1)
\end{aligned}\right\} \text{ with } f(r) = \frac{r}{\sqrt{6}}\, e^{-\frac{3}{2}r}$$

$$\left.\begin{aligned}
\mu_{23}(t,t') &= I(0,0;1,0)\\
\mu_{24}(t,t') &= I(0,0;1,1)\\
\mu_{25}(t,t') &= (-1)\, I^*(0,0;1,1)
\end{aligned}\right\} \text{ with } f(r) = \frac{1}{8\sqrt{3}}(2-r)r\, e^{-r}$$

$$\left.\begin{aligned}
\mu_{33}(t,t') &= I(1,0;1,0)\\
\mu_{34}(t,t') &= I(1,0;1,1)\\
\mu_{35}(t,t') &= (-1)\, I^*(1,0;1,1)
\end{aligned}\right\} \text{ with } f(r) = \frac{r^2}{24}\, e^{-r}$$

$$\left.\begin{aligned}
\mu_{44}(t,t') &= I(1,1;1,1)\\
\mu_{45}(t,t') &= I(1,1;1,-1)\\
\mu_{55}(t,t') &= I^*(1,1;1,1)
\end{aligned}\right\} \text{ with } f(r) = \frac{r^2}{24}\, e^{-r}$$

The ϕ dependence of the $\underset{\sim}{\mu}$ matrix elements required in section (11) is now apparent.

Throughout this derivation we have assumed that R' > R. However the results obtained are easily converted to the case R > R'. In this latter case the initial rotation of axes is made to the $\underset{\sim}{R}'$ axis, then with the interchange of R and R' all the following analysis holds. The final rotation to the quantization axes is now defined by the polar angles of $\underset{\sim}{R}'$.

Appendix IV

The expressions obtained for the single centred matrix elements, $V_{n_1 n_2}(t)$ are given explicitly for a combination of $(n_1 \ell_1 m_1)$ and $(n_2 \ell_2 m_2)$ up to the 2p-level.

$$V_{n_1 n_2}(t) = \eta \int \phi_{n_1}^*(\underset{\sim}{r}) \left[\frac{1}{R} - \frac{1}{|\underset{\sim}{R}-\underset{\sim}{r}|} \right] \phi_{n_2}^*(\underset{\sim}{r}) \, d\underset{\sim}{r}$$

where η is the charge of the incoming particle, and

$$V_{n_1 n_2}(t) = \eta \left[\frac{\delta_{12}}{R} - \bar{V}_{n_1 n_2}(t) \right]$$

where $$\bar{V}_{n_1 n_2}(t) = \int \phi_{n_1}^*(\underset{\sim}{r}) \frac{1}{|\underset{\sim}{R}-\underset{\sim}{r}|} \phi_{n_2}(\underset{\sim}{r}) \, d\underset{\sim}{r}$$

We use the notation already established in Section (10), and since

$$V_{n_1 n_2}(t) = V^*_{n_2 n_1}(t)$$

not all possible combinations are given. Let

$$c_1 = 1 - e^{-2R}(R+1)$$

$$c_2 = e^{-1.5R}(3R+2)$$

$$c_3 = 8 - e^{-\alpha R}((\alpha R)^3+4(\alpha R)^2+8\alpha R+8)), \qquad \alpha = 1.5$$

$$c_4 = 8 - e^{-R}(R^3+2R^2+6R+8)$$

$$c_5 = 24 - e^{-R}(R^4+4R^3+12R^2+24R+24)$$

$$c_6 = 24 - e^{-R}(R^3+6R^2+18R+24)$$

and $$c_7 = 144 - e^{-R}(R^5+6R^4+24R^3+72R^2+144R+144)$$

then

$$\bar{V}_{11}(t) = R^{-1}\, c_1$$

$$\bar{V}_{12}(t) = \frac{4}{27\sqrt{2}}\, c_2$$

$$\bar{V}_{13}(t) = \frac{1}{\sqrt{2}}\,(2/3)^5\,\frac{\cos\theta}{R^2}\, c_3$$

$$\bar{V}_{14}(t) = -\,1/2\,(2/3)^5\,\frac{\sin\theta}{R^2}\, e^{i\phi}\, c_3$$

$$\bar{V}_{15}(t) = -\,\bar{V}^{*}_{14}(t)$$

$$\bar{V}_{22}(t) = \frac{1}{8R}\, c_4$$

$$\bar{V}_{23}(t) = -\,\frac{\cos\theta}{8R^2}\, c_5$$

$$\bar{V}_{24}(t) = \frac{1}{8\sqrt{2}}\,\frac{\sin\theta}{R^2}\, e^{i\phi}\, c_5$$

$$\bar{V}_{25}(t) = -\,\bar{V}^{*}_{24}(t)$$

$$\bar{V}_{33}(t) = \frac{1}{24R}\, c_6 + \frac{(3\cos^2\theta - 1)}{24R^3}\, c_7$$

$$\bar{V}_{34}(t) = -\,\frac{3}{24\sqrt{2}}\,\frac{\sin\theta\cos\theta}{R^3}\, e^{i\phi}\, c_7$$

$$\bar{V}_{35}(t) = -\,\bar{V}^{*}_{34}(t)$$

$$\bar{V}_{44}(t) = \frac{1}{24R}\, c_6 - \frac{(3\cos^2\theta - 1)}{48\,R^3}\, c_7$$

$$\bar{V}_{45}(t) = -\,\frac{\sin^2\theta}{16\,R^3}\, e^{-2i\phi}\, c_7$$

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Figure Captions

Figure 4 1s-2s excitation by protons

Curve 1. First Born approximation
2. One channel approximation
3. Two state approximation
4. Two channel approximation
5. Four state approximation (Flannery 1969)
6. Four channel approximation
Δ Two channel approximation, $\varepsilon' = 0.0$ a.u.

Figure 5 1s-2s excitation by protons

Curve 1. Glauber approximation (Franco and Thomas 1971)
2. One channel approximation
3. Four channel approximation
o Pseudo state approximation (Cheshire et al. 1970)

Figure 6 1s-2p excitation by protons

Curve 1. First Born approximation
2. One channel approximation
3. Four state approximation (Flannery 1969)
4. Four channel approximation

Figure 7 1s-2p excitation by protons

Curve 1. Glauber approximation (Franco and Thomas 1971)
2. One channel approximation
3. Four channel approximation
o Pseudo state approximation (Cheshire et al. 1970)

Figure 8 1s-2s excitation by electrons

Curve 1. First Born approximation
2. One channel approximation
3. Two channel approximation
4. Four channel approximation
5. 1s-2s-2p close coupling (Burke et al. 1963)

Figure 9 1s-2s excitation by electrons

Curve 1. One channel approximation
2. Glauber approximation (Tai et al. 1970)
3. Four channel approximation
4. Two channel approximation
⊗ Pseudo state approximation (Burke and Webb 1970)

Figure 10 1s-2p excitation by electrons

Curve 1. First Born approximation
2. One channel approximation
3. Four channel approximation
4. 1s-2s-2p close coupling approximation (Burke et al. 1963)

Figure 11 1s-2p excitation by electrons

Curve 1. One channel approximation
2. Glauber approximation (Tai et al. 1970)
3. Four channel approximation
○ Pseudo state approximation (Burke and Webb 1970)
△ Experimental points of Long et al. (1968)

Figure 12 Q(1s-2s) + 0.23 Q(1s-2p) for electron impact

Curve 1. Four channel approximation
2. Glauber approximation (Tai et al. 1970)
○ Pseudo state approximation (Burke and Webb 1970)
△ Experimental points of Kauppilla et al. (1970)

Figure 13 Differential cross sections for elastic scattering of electrons at (a) 54 eV, (b) 100 eV, (c) 200 eV.

Curve 1. One and Four channel approximations
2. First Born approximation
I Experimental points quoted in Tai et al. (1969)

Figure 14 Differential cross sections for excitation of n = 2 level by electron impact at (a) 54 eV, (b) 100 eV, (c) 200 eV.

Curve 1. One channel approximation
2. Four channel approximation
I Experimental points of Williams (1969)

Figure 15 Lyman-α radiation polarization fraction

Curve 1. Glauber approximation (Gerjouy et al. 1972)
2. Four channel approximation
● Experimental points of Ott et al. (1970)
▲ Glauber approximation (Byron 1971)

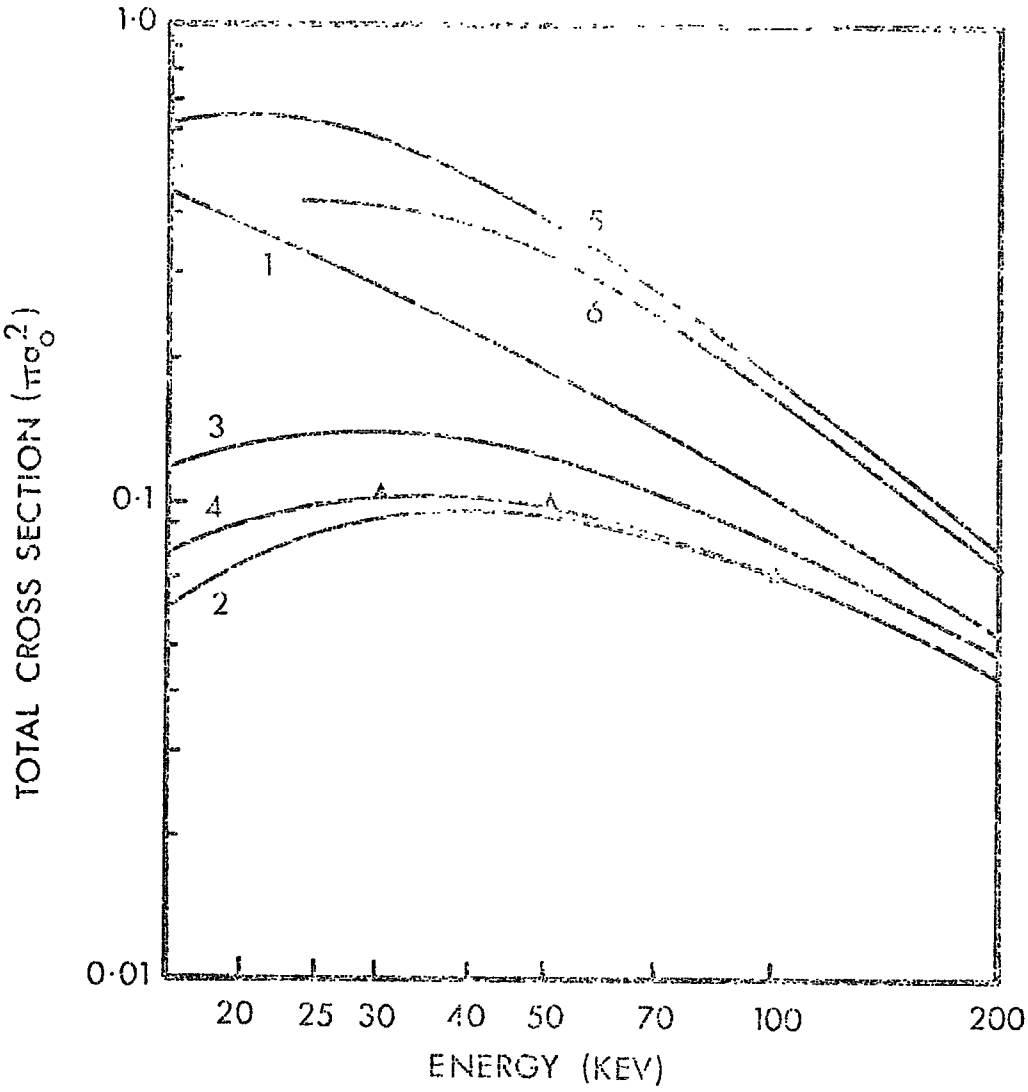

1·0
0·1
0·01
TOTAL CROSS SECTION (πr_0^2)
1
2
3
4
5
6
20
25
30
40
50
70
100
200
ENERGY (KEV)

Fig. 4.

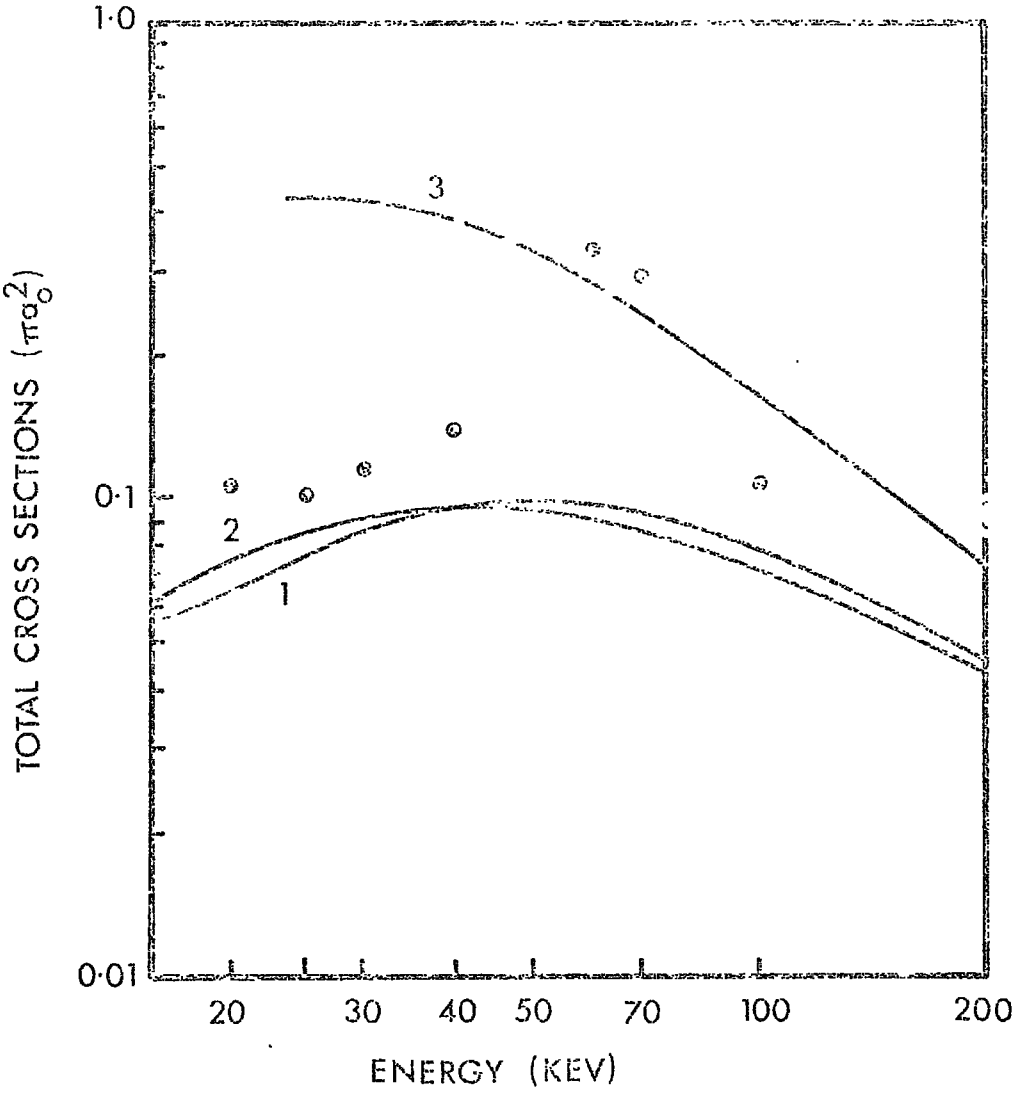

1·0
0·1
0·01
TOTAL CROSS SECTIONS (πa_0^2)
3
2
1
20
30
40
50
70
100
200
ENERGY (KEV)

Fig.5.

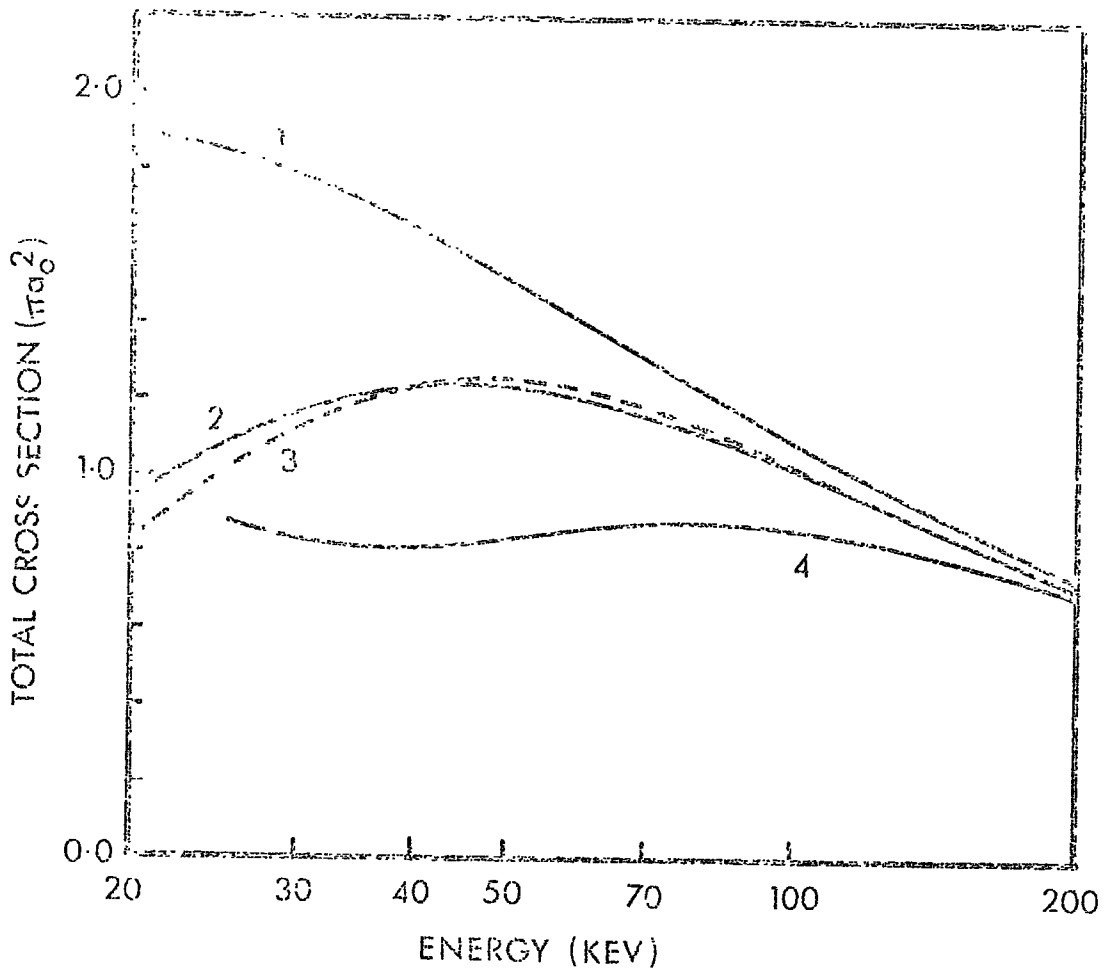

2·0
1·0
0·0
TOTAL CROSS SECTION (πa_0^2)
1
2
3
4
20
30
40
50
70
100
200
ENERGY (KEV)

Fig. 6.

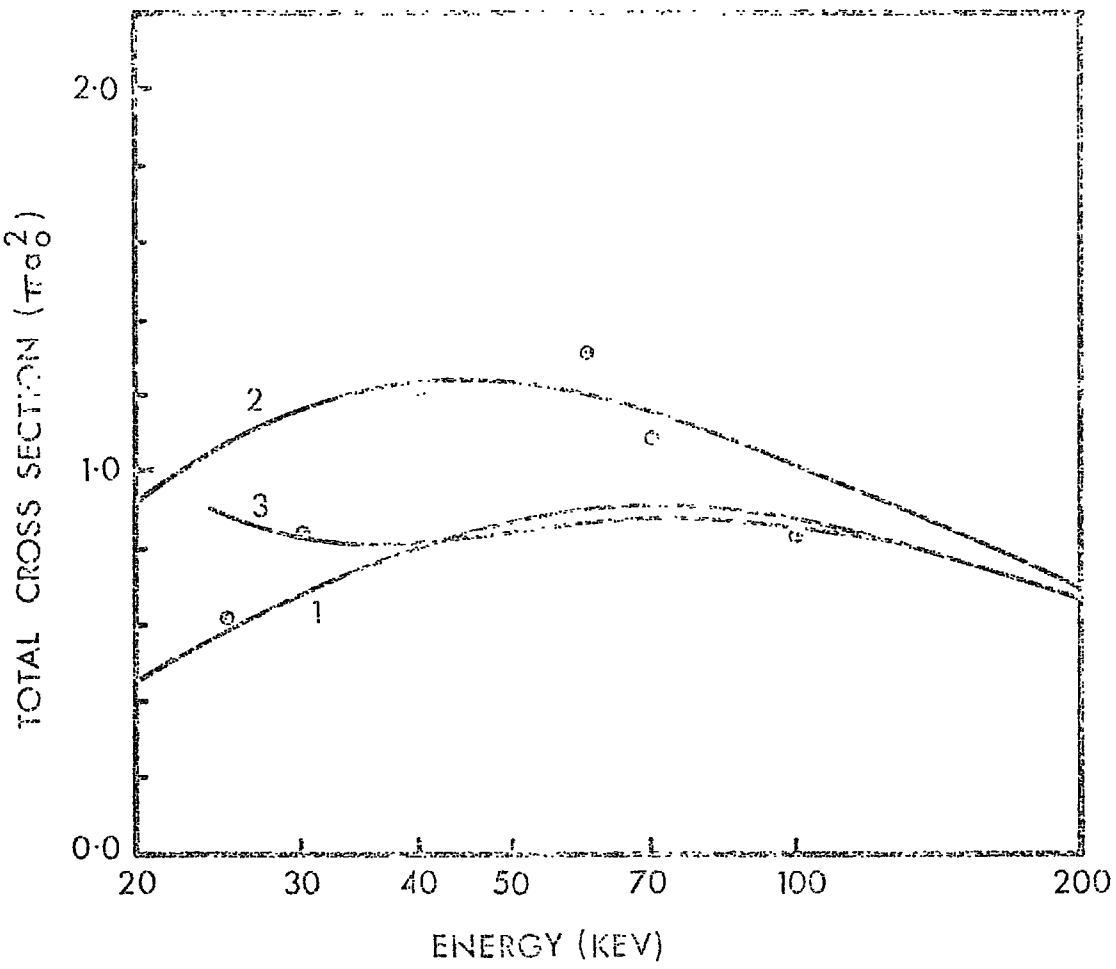

TOTAL CROSS SECTION (πa_0^2)
2·0
1·0
0·0
20
30
40
50
70
100
200
ENERGY (KEV)
1
2
3

Fig. 7.

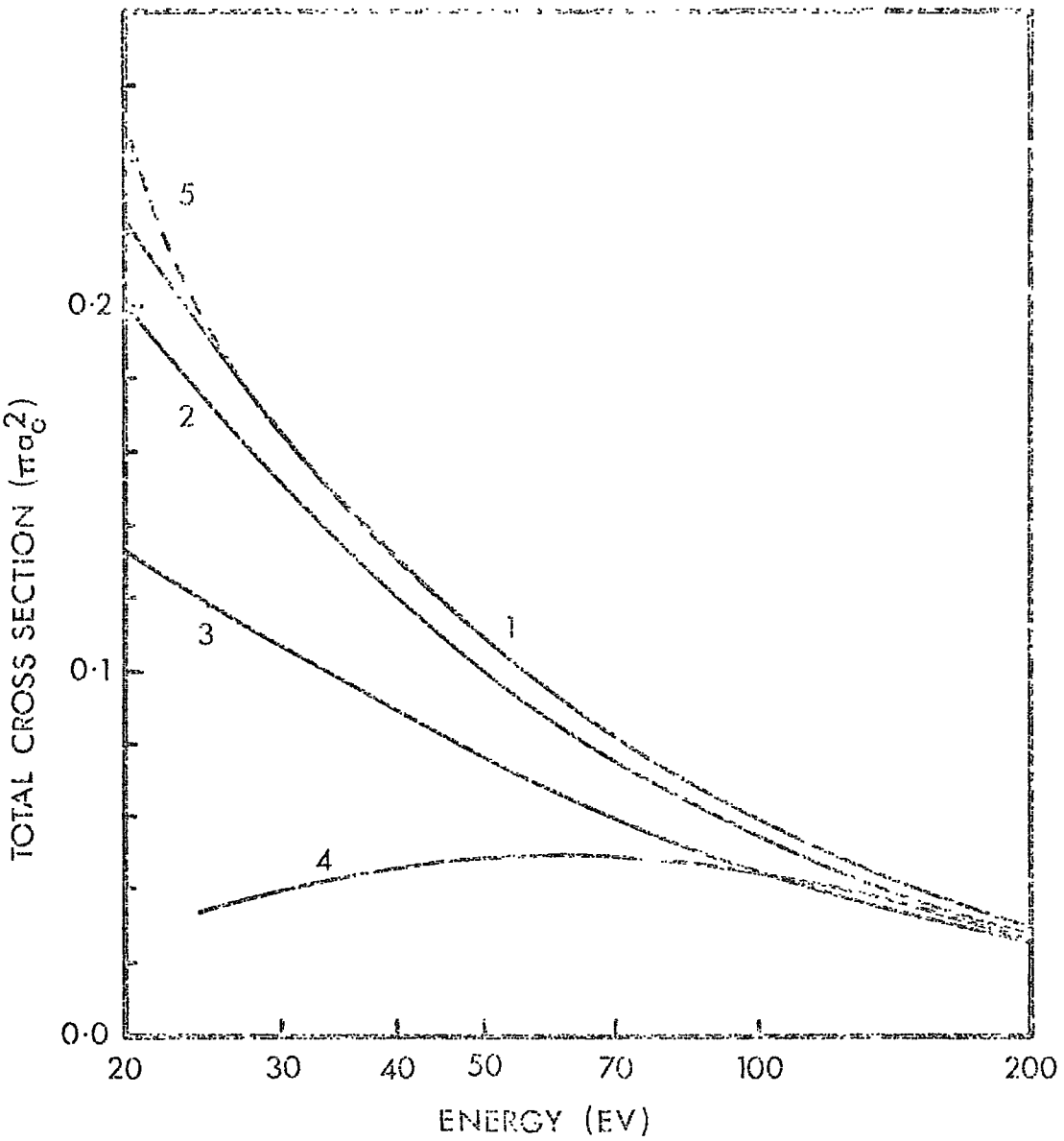

TOTAL CROSS SECTION (πa_0^2)
0·2
0·1
0·0
20
30
40
50
70
100
200
ENERGY (EV)
1
2
3
4
5

Fig.8.

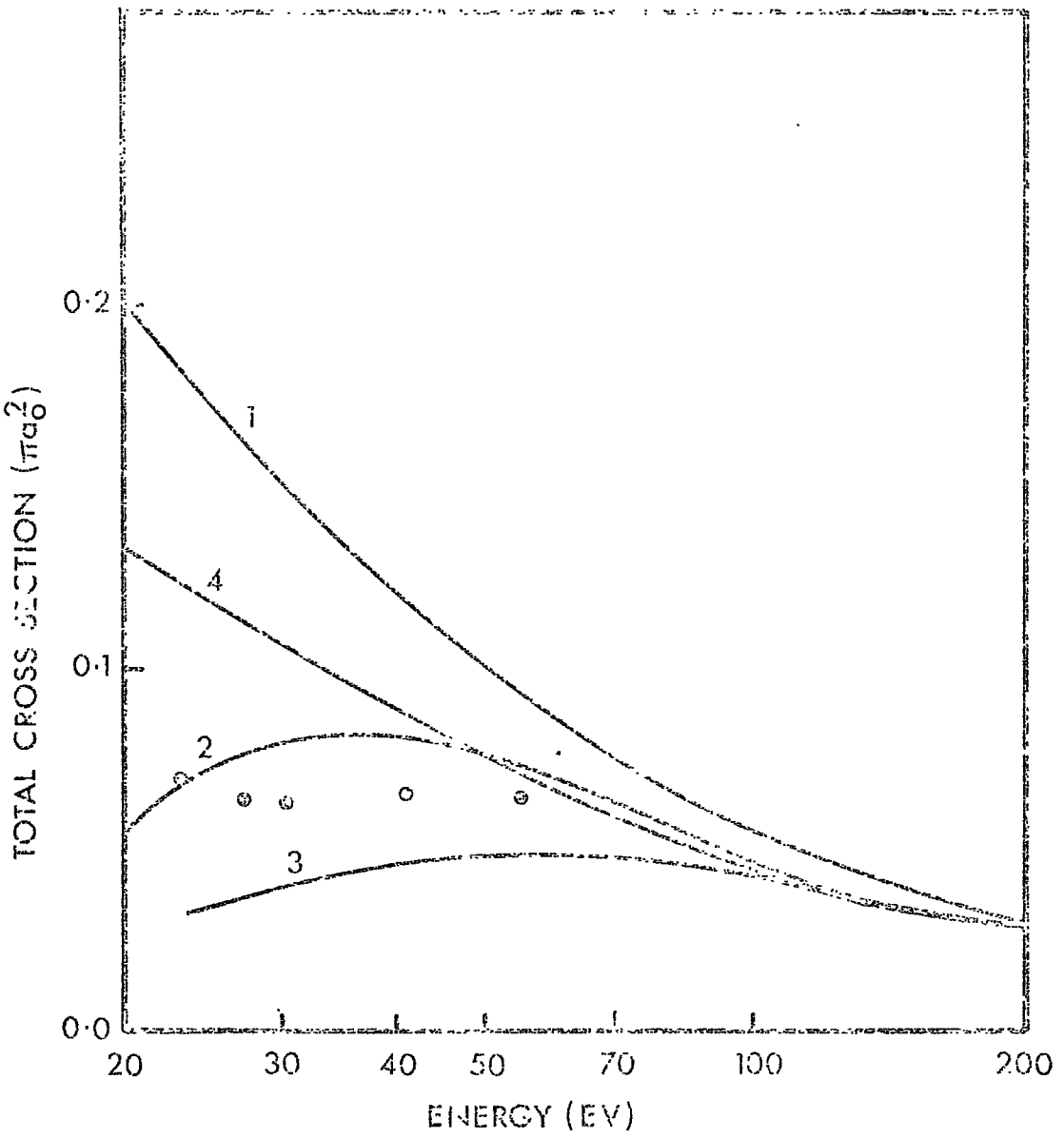

TOTAL CROSS SECTION (πa_0^2)
0·2
0·1
0·0
1
2
3
4
20
30
40
50
70
100
200
ENERGY (EV)

Fig. 9.

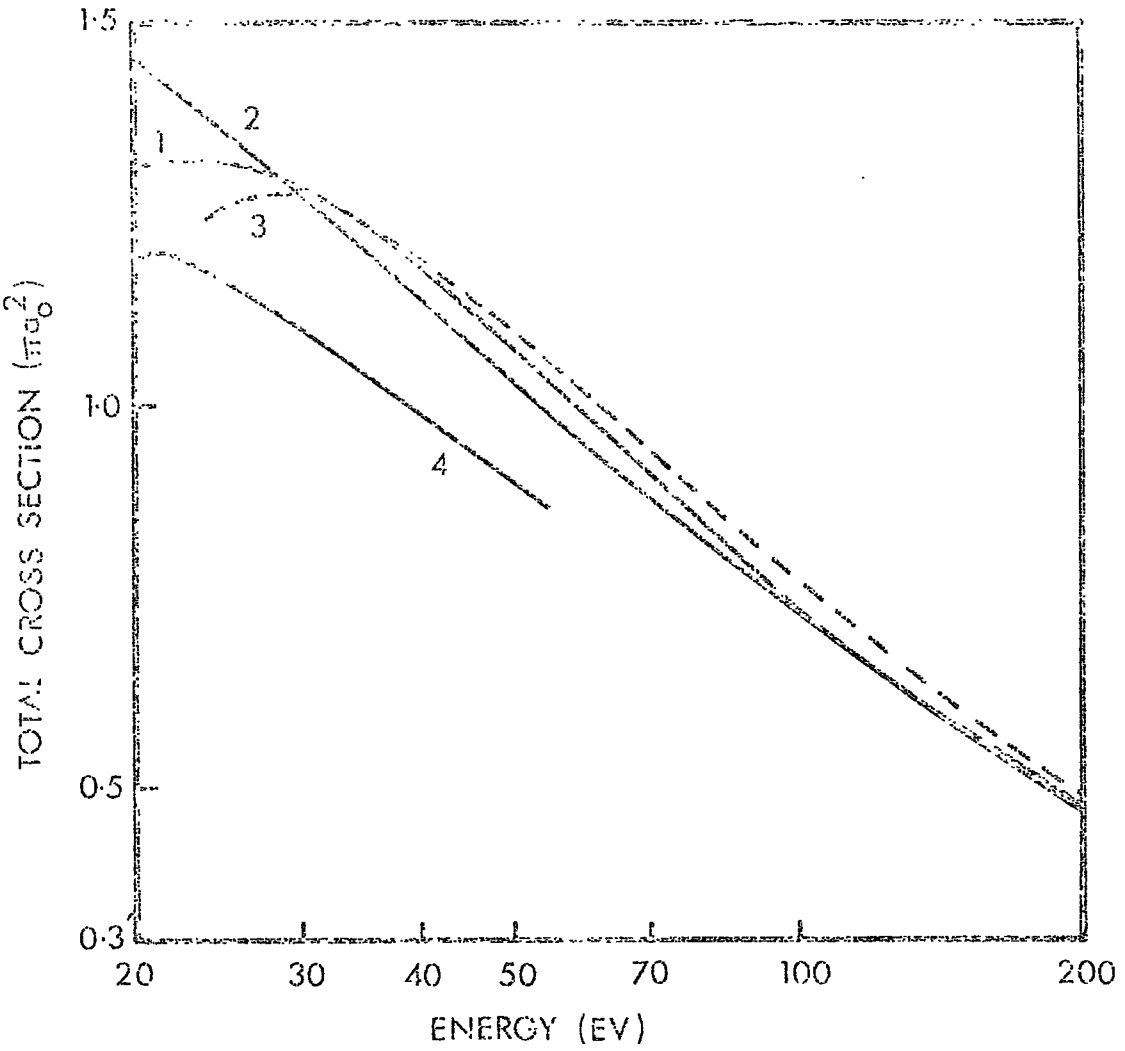

1·5
1·0
0·5
0·3
TOTAL CROSS SECTION (πa_0^2)
1
2
3
4
20
30
40
50
70
100
200
ENERGY (EV)

Fig.10.

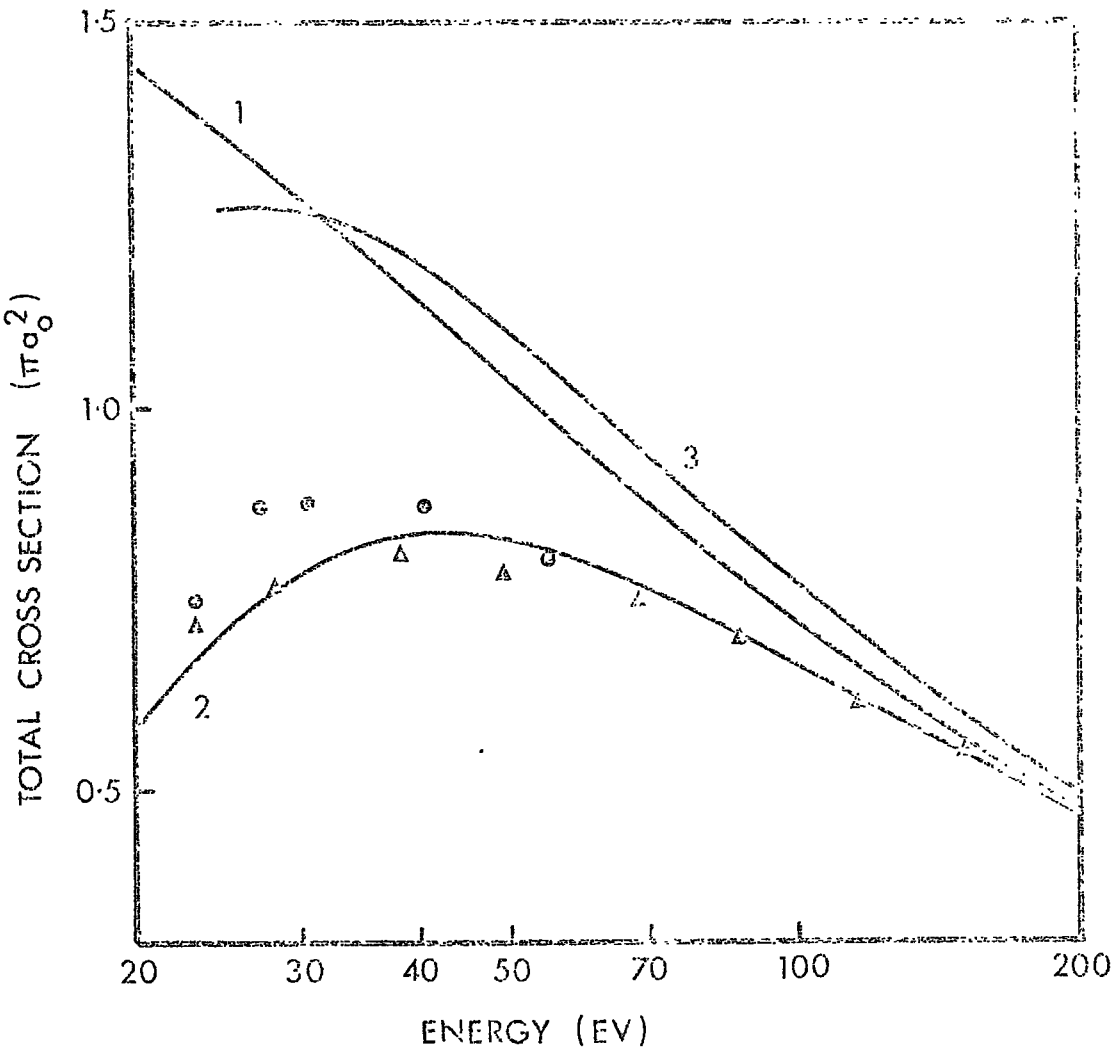

1·5
1·0
0·5
TOTAL CROSS SECTION (πa_0^2)
1
2
3
20
30
40
50
70
100
200
ENERGY (EV)

Fig. 11.

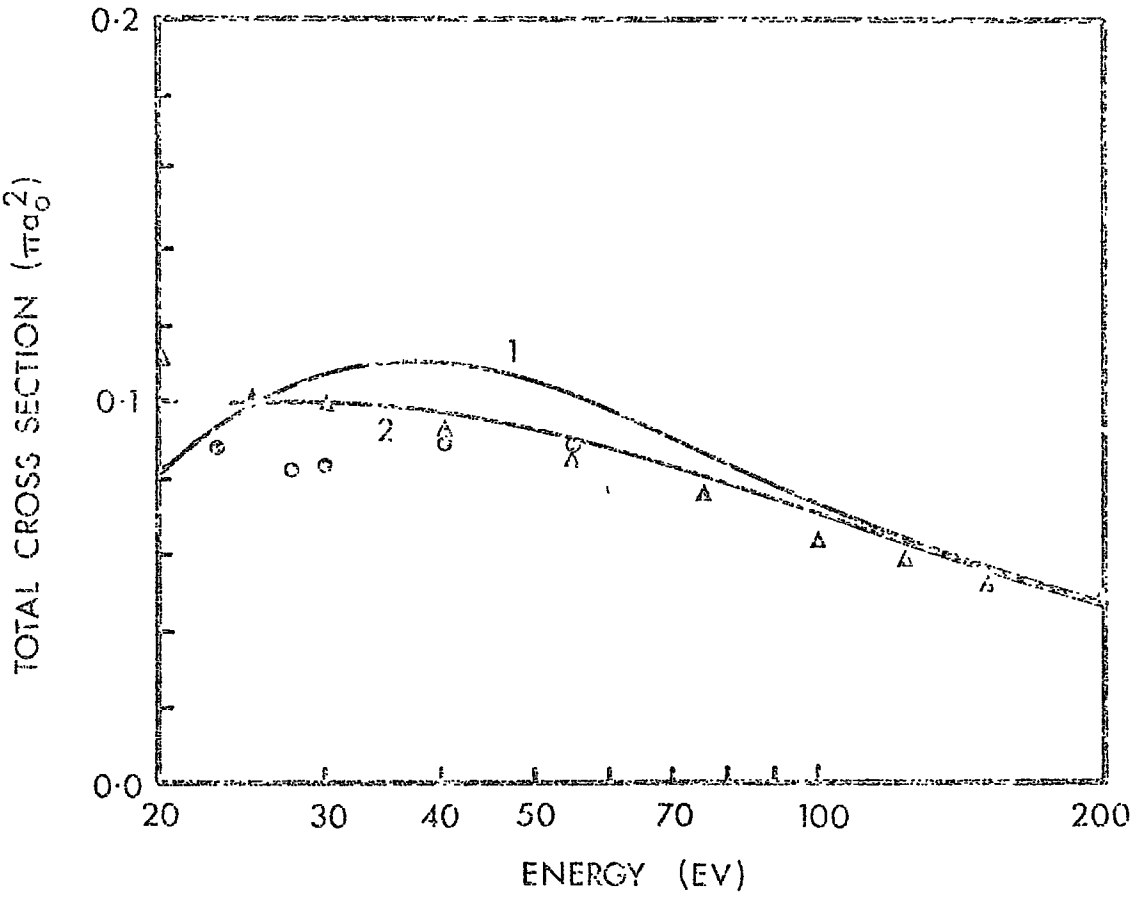
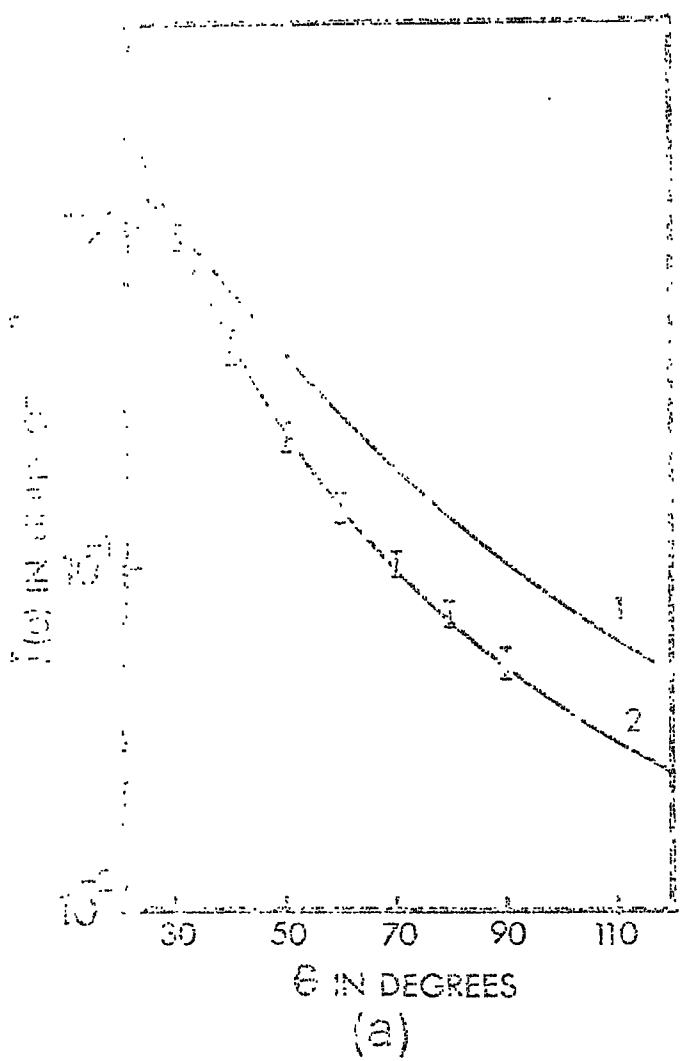
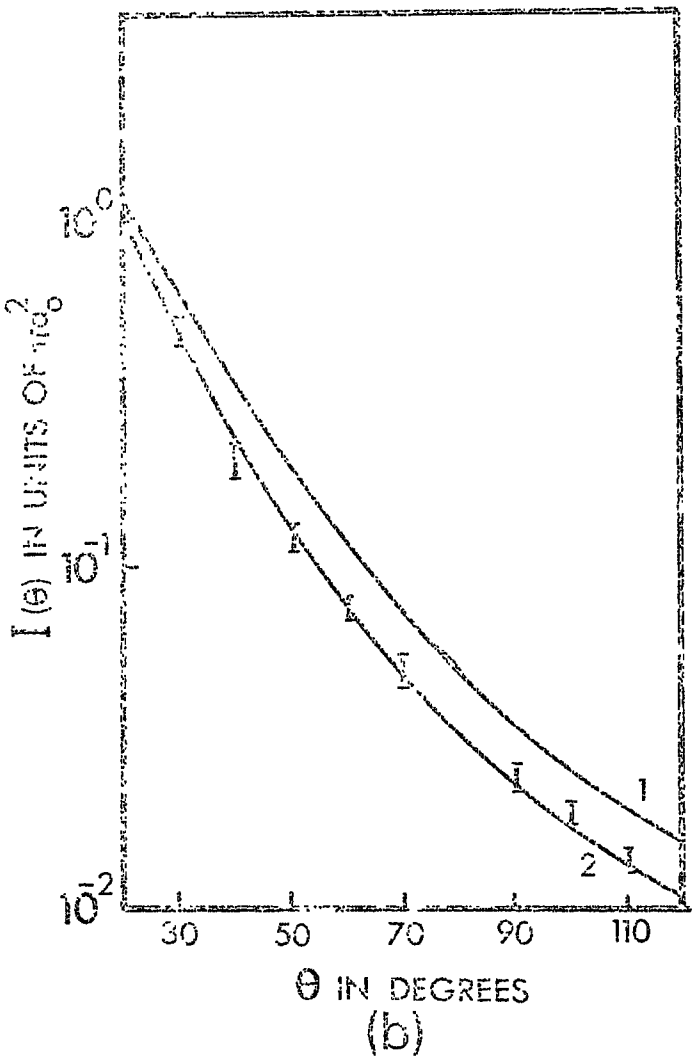

0·2
0·1
0·0
TOTAL CROSS SECTION (πa_0^2)
1
2
20
30
40
50
70
100
200
ENERGY (EV)

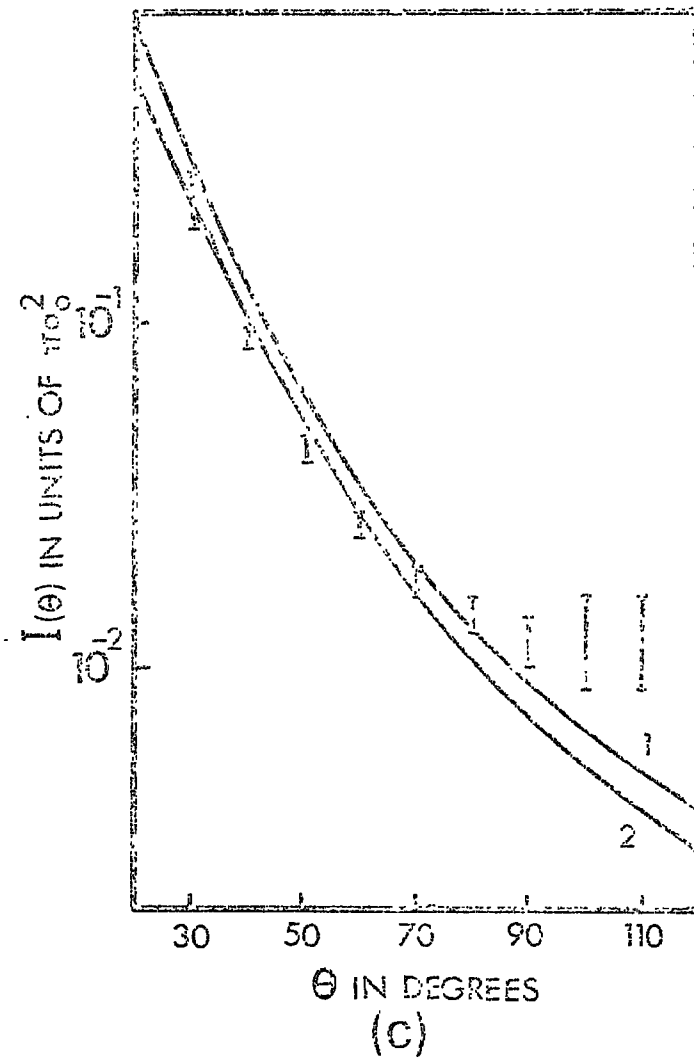
Fig. 12.


30
50
70
90
110
θ IN DEGREES
1
2

(a)

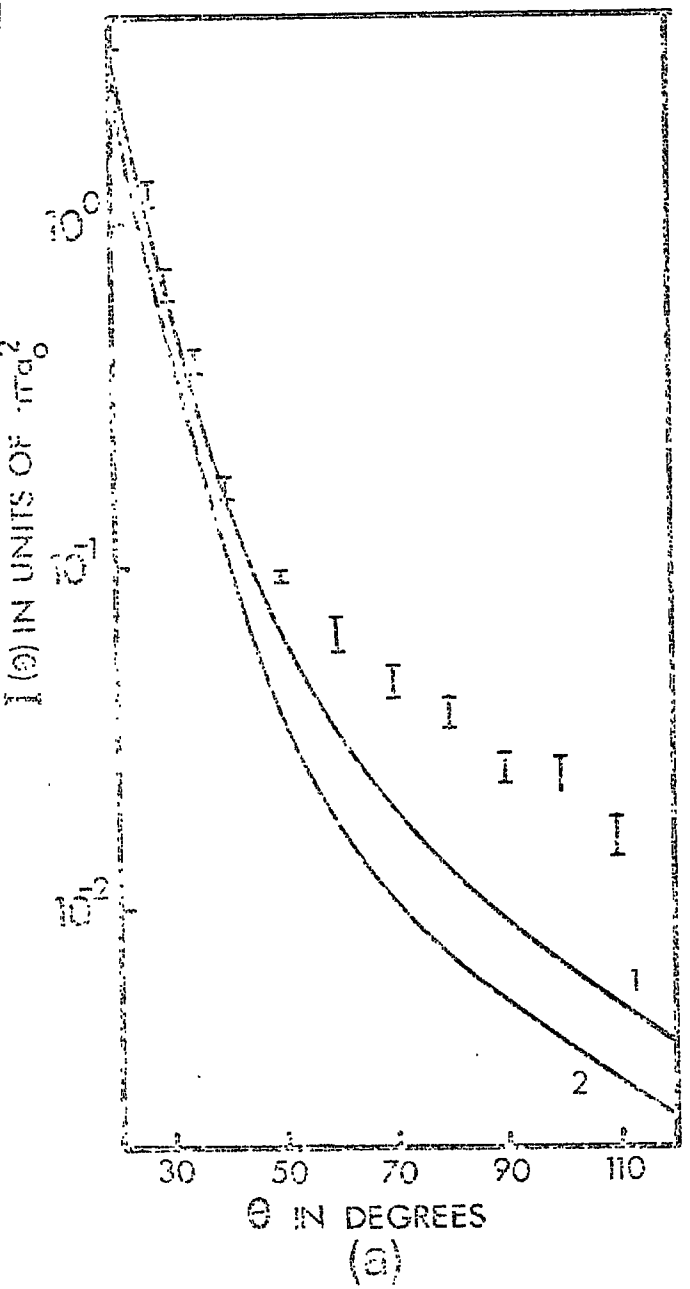

I (θ) IN UNITS OF πa₀²
10⁰
10⁻¹
10⁻²
30
50
70
90
110
θ IN DEGREES
1
2

(b)

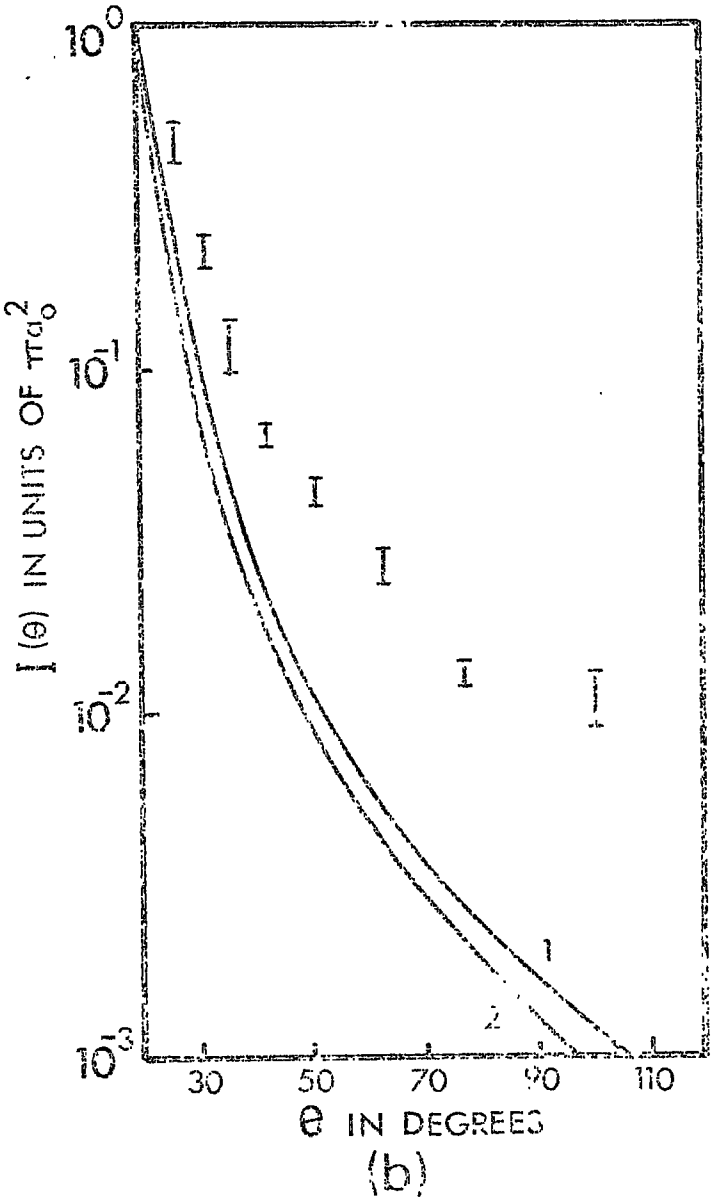

I(θ) IN UNITS OF πa₀²
10⁻¹
10⁻²
30
50
70
90
110
θ IN DEGREES
1
2

(c)

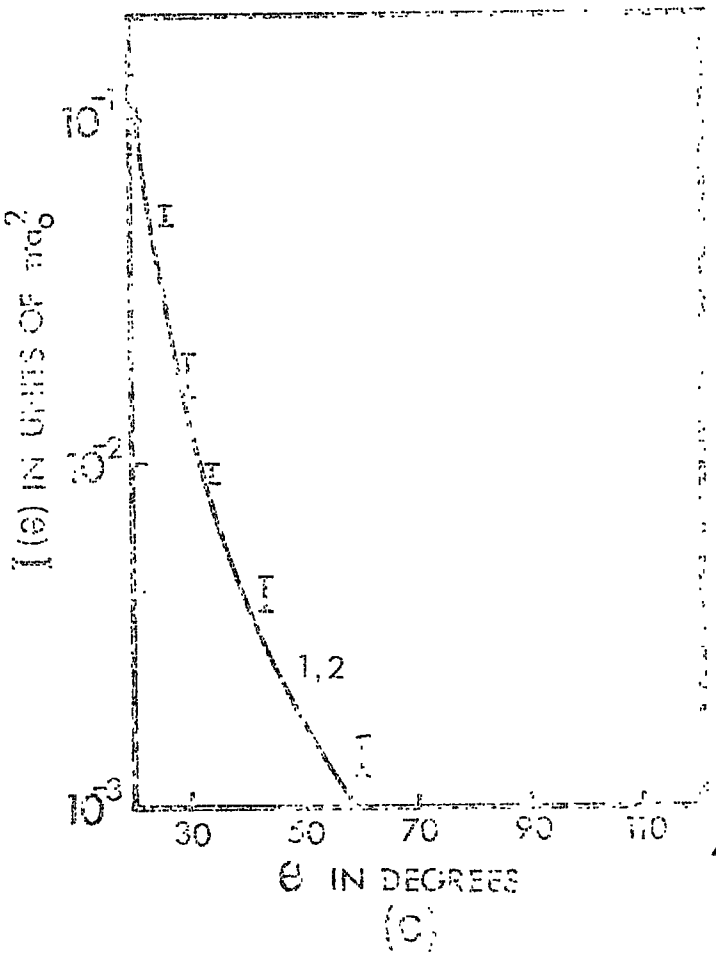
Fig. 13.


I (θ) IN UNITS OF πa$_o^2$
10^0
10^{-1}
10^{-2}
30
50
70
90
110
θ IN DEGREES
1
2

(a)


I (θ) IN UNITS OF πa$_o^2$
10^0
10^{-1}
10^{-2}
10^{-3}
30
50
70
90
110
θ IN DEGREES
1
2

(b)


I (θ) IN UNITS OF πa$_o^2$
10^{-1}
10^{-2}
10^{-3}
30
50
70
90
110
θ IN DEGREES
1, 2

(c)

Fig. 14.

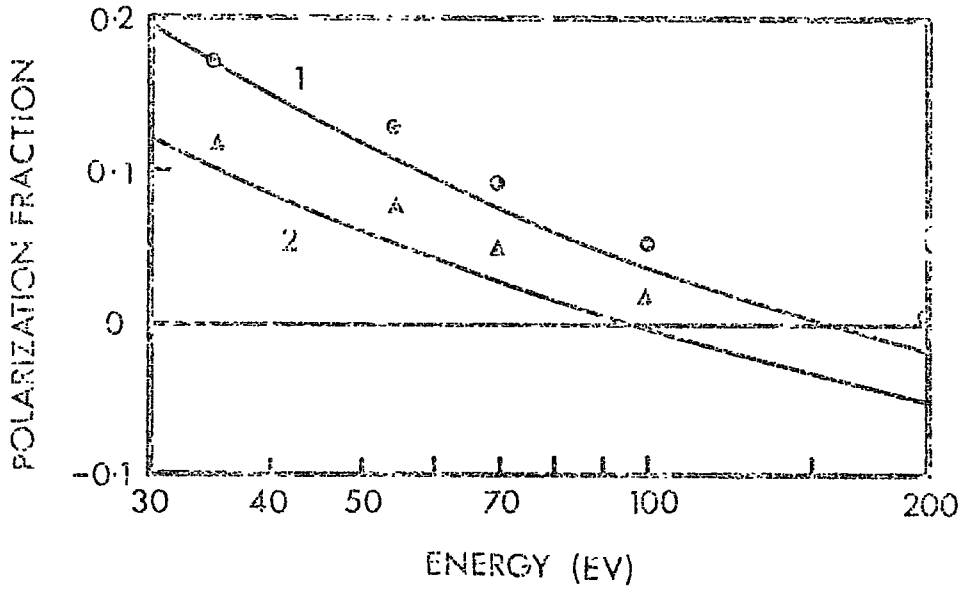


Fig.15.