Investigation of the impact parameter method for electron-atom collisions.

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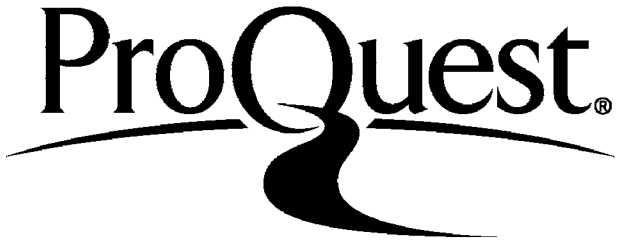

Abstract.

In this thesis we develop and investigate the use of a semi-classical impact parameter method for treating the excitation of atoms by electron impact. Our particular interest is forbidden, non-exchange transitions.

Chapter 1 contains a brief description of the method along with reasons for considering such a method. Previous work employing the same general ideas is reviewed, as are other theoretical calculations and experimental results of direct relevance to this thesis. The paper of Seaton (1962) which applies the impact parameter method to optically allowed transitions is reviewed in some detail as our treatment of the subject is based largely on this work.

In Chapter 2 we derive expressions for the transition probabilities and introduce the idea of the averaged probabilities. Cross section formulae are given which are applicable to dipole and quadrupole transitions and which include a strong coupling form. The formulae are generalized to apply to an incident point particle of arbitrary mass and charge.

Chapter 3 contains formulae for the averaged probabilities for arbitrary interaction potentials and these are applied to the case where the potential is a sum of spherical tensor operators. Expressions for cross sections, applicable to arbitrary transitions induced by electron or proton impact, are given and the explicit form evaluated for the case of hydrogen.

In Chapter 4 are presented results of calculations of cross sections for certain forbidden transitions in hydrogen and helium, both for electron and proton impact.

We examine the validity of the approximations made and discuss the choice of the cut-off.

Chapter 5 contains an evaluation of the method as well as suggestions for improving it and for further applications.

The derivation of certain results used in the thesis is presented in the appendices.

Acknowledgements.

I should like to express my gratitude to my supervisor, Dr. M.R.C.McDowell, for suggesting the problem upon which this thesis is based and for his continual interest and encouragement throughout, I should further like to thank him and Miss K.M.Pluta for permission to quote their results in advance of publication.

Note.

Since we have used a large number of results which appear in Edmonds, (1957) we refer to them by prefixing an E to the number of the particular equation to which we are referring. For example, (E4.6.6) designates the equation numbered (4.6.6) in Edmond's book.

Table of Contents.

Chapter 1

§1.1 Introduction

In this thesis we develop a semi-classical impact parameter method for calculating cross sections for excitation of atoms by impact of a charged point particle. This method is applicable to almost all transitions in an arbitrary atom and is based on earlier results of Seaton (1962) who treated optically allowed transitions by this method. In the course of this work we also derive some general results concerning transition probabilities calculated by means of first order time-dependent perturbation theory.

The basic model for this method is one in which the incident particle is a classical particle in a rectilinear orbit with a given impact parameter. This particle perturbs the atom and the probabilities for transitions between the various states of the atom are calculated by first order time-dependent perturbation theory. The contributions from all impact parameters are summed to give a cross section for a particular transition.

Since the incident particle is treated classically its spin is neglected. If the incident particle is an electron exchange of this electron for one of the atomic electrons is not considered. Exchange of the atomic nucleus with an incident nucleus is likewise not considered.

Certain other approximations are made during the course of the analysis and the range of validity of these approximations along with the range of validity of the method as a whole will be critically discussed at a later stage.

Because of the simplicity of the model we cannot expect it to produce the detailed structure that experiment and more elaborate calculations have shown to exist in the

shape of the cross section versus energy curve.(Among other things it is a two state approximation as is the first Born approximation.) Indeed, because of the presence of a parameter whose value we have not been able to determine exactly, the value of the cross section itself is not given absolutely by our formulae. However with the "correct" value of the parameter as we go to high impact energies our cross sections will approach those given by the first Born approximation and may in fact be superior to this approximation at lower energies.

On the other hand this simple model leads to relatively simple analytical formulae for the cross sections. Thus large numbers of them can be calculated in a fraction of the time it would take by using more exact methods. Even if our cross sections were only correct to within a factor of two they would provide valuable estimates in a number of areas. For instance the determination of the contribution of cascading from higher levels to experimentally measured cross sections, the calculations of processes taking place in laboratory plasmas and the investigation of astrophysical problems (e.g. studies of the upper atmosphere, the solar chromosphere and planetary nebulae) all require large numbers of these cross sections without requiring great accuracy. Further, naturally occuring phenomena involving the processes under investigation usually involve free electrons or other particles with a certain energy distribution (e.g. a Maxwellian distribution) with the result that the cross sections are effectively integrated over a certain energy range. This tends to obscure the detailed structure of the cross section so that the failure of our formulae to reproduce such structure does not necessarily preclude such phenomena being reasonably accurately predicted by them.

Finally we note that all calculations of these cross sections undertaken to date involve some approximations and that discrepancies still exist between theoretical and experimental values. While more and more accurate methods will undoubtedly be developed there is a need at the present time for the type of results to which our calculations are relevant. For these reasons we feel that the present investigation is valuable and necessary.

§1.2 Review of Previous Work.

In this section we shall consider in brief some of the work already carried out by semi-classical impact parameter methods and the justification for such methods. In semi-classical theories part of the system in question is treated classically and part quantum mechanically. One of the questions that naturally arises is how good is the classical approximation or under what conditions is the classical approximation valid. From this point of view it is instructive to mention recent theories that are completly classical.

The interest in completely classical theories of excitation and ionization of atoms by charged particles was revived largely by Gryzinski (1957, 1959, 1963a,b, 1965a,b) who obtained good agreement with experiment in various cases. Gryzinski's treatment has been improved by Stabler (1964) and a great many comparisons of this theory with experiment or with more exact quantum mechanical calculations have been carried out. (See for instance Kingston (1964)). Essentially exact numerical calculations for the case of hydrogen are being done by Abrines and Percival (1964a,b, 1965). All these calculations indicate that the classical theory is in reasonable agreement with experiment or other theoretical results for moderate energies. More particularly for

electron-atom collisions classical theory is correct to within a factor of two or three from just above threshold to about 1000 eV. Thus purely classical theories do seem to give a fairly reasonable description of atomic collision processes.

When the atomic system is treated quantum mechanically substantial theoretical improvements over purely classical treatments result. For instance questions such as what is meant by excitation to a discrete energy level have obvious answers. Also collision cross sections have the correct high energy behavior which does not seem to be the case with classical theories. (We disregard the results of Gryzinski (1963a) since they were obtained by using an incorrect momentum distribution. See Burgess (1964), Abrines and Percival (1965)). Hence we would expect semi-classical treatments of the collision problem to be able to give better results in general than classical theories.

Semi-classical impact parameter methods for atomic collisions have been in use for many years. Applications to heavy particle collisions were made in the early years of quantum mechanics by Gaunt (1927), Brinkman and Kramers (1930) and Mott (1931) and have been continued up to the present largely by Bates and his co-workers. (For a bibliography of this work see Bates (1962)). Coulombic excitation of nuclei has also been treated by this method. For a review of this work see Alder et al (1956). Williams (1933) and von Weizsacker (1934) have applied this method to problems involving high energy electrons. Seaton (1962) has treated optically allowed transitions caused by electron impact in this way and Burgess (1963) and (1964) has combined this method with classical theory to treat electronic excitation and ionization of both atoms and positive ions.

Since we base our treatment of the problem closely on the work of Seaton (1962) we shall review it in detail in §1.4. Here we will consider some of Bates's work on the more general problem. On the subject of the validity of the first order impact parameter approximation Bates (1962) states that the necessary conditions to be satisfied are that the charged particle moves with a constant velocity in a straight line and that if P_{ji} is the probability of the transition from state i to state j taking place then $\sum_{j \neq i} P_{ji} \ll 1$. This last condition is to ensure that the coefficients in the expansion of the total wave function in terms of the unperturbed wave functions can be written as a power series in the perturbation potential. Bates and Boyd (1962) have shown that the first condition is satisfied down to quite low velocities of the charged particle (even taking into account the smallness of the mass of the electron if this happens to be the incident particle). It is not easy to verify that the second condition is satisfied in any particular case since we calculate P_{ji} for only a few values of the final state j but it is obviously necessary to have $P_{ji} \ll 1$ since $0 \leqslant P_{ji} \leqslant 1$. If one knows the values of the largest P_{ji} in the sum (which will be the probabilities for the first few optical transitions in most cases) then one can at least estimate whether this condition is likely to be satisfied.

Bates (1961) shows that the principle of detailed balancing holds exactly for the probabilities as calculated by the impact parameter method. This is true only for the exact probabilities and not for the first order approximations. Hence the probabilities that we derive do not satisfy this principle automatically. However we ensure that our probabilities do satisfy this

principle by making suitable approximations.

Bates (1961)and (1962) has indicated that the impact parameter method (first order theory) and the first Born approximation are equivalent because the assumptions made are identical (provided the incident particle may be treated as classical). Arthurs (1961) has shown this equivalence mathematically for s-s transitions in the limit of weak interactions and high energies. (For a fuller discussion of this point see Bates (1957)). Since our cross sections have the correct high energy form (c.f. §3.7) our cross section will always be identical with the first Born (Bethe) approximation at high energies provided we choose our cut-off in the right way, (c.f. §1.4, Ch.2).Seaton (1962) has shown this equivalence for optically allowed transitions.

From the above discussion it is evident that the semi-classical impact parameter method ought to have a range of validity comparable to that of the first Born approximation and to approach the Born approximation at high energies. Since the first Born approximation seems to give fairly reasonable results in most cases where comparison with experiment is possible (except at very low energies) we conclude that the impact parameter method should provide a reasonable means of calculating atomic cross sections in a large number of cases.

In addition to the approximations outlined above certain others are made in the course of deriving our expressions for the cross sections for atomic transitions which are not specifically connected with the impact parameter method but which allow us to derive analytic expressions for the cross sections. These approximations are outlined in §§1.4, 2.1, 2.2 along with arguments for their validity. They will be more carefully analysed in Chs. 4 and 5 including some numerical examples.

Henceforth we will assume that the semi-classical impact parameter method is generally valid providing the conditions discussed above are satisfied. The validity of our further approximations will be judged by the error they introduce into the method as a whole.

§1.3 Other Theoretical Calculations and Experimental Results.

While the general arguments outlined in §1.2 give us some idea of the validity of the impact parameter method direct comparison of our results with other theoretical calculations and with experiment allows a more definite quantitative evaluation. For this reason we review here such other results as are available up to the present time.

Seaton (1962) has made these comparisons for optically allowed transitions so that we will restrict ourselves to forbidden quadrupole transitions for which we have done calculations. Theoretical calculations for these transitions are very few and have been done only for hydrogen and helium. For hydrogen Somerville (1963) has used a first Born approximation to the reactance matrix to obtain cross sections for all transitions induced by electron impact between levels up to and including n=3. Some transitions are also calculated in an improved Born approximation which satisfies the conservation condition. McCoyd et al (1960) and Scanlon and Milford (1961) have calculated by means of the first Born approximation certain forbidden transitions from the n=2 and 3 levels to the n=4 level as well as some transitions considered by Somerville. These two sets of calculations agree well with one another where comparison is possible. For helium calculations have been carried out for certain members of the $1^1S \rightarrow n^1D$

series of transitions induced by electron impact in the first Born approximation by Massey and Mohr (1933) and by Fox (see Seaton (1962a)). However these results lie a factor of three or four below the experimental results (see below) which agree among themselves reasonably well and we are led to conclude that the first Born approximation gives very poor results for these particular transitions except possibly at very high energies. In evaluating our results for these transitions we disregard the above theoretical calculations and assume that the experimental results give a reasonably true picture of the actual cross section.

No experimental results exist for forbidden transitions in hydrogen but for electron impact in helium various workers have examined the $1^1S \rightarrow n^1D$ series of transitions. Early work was carried out by Lees (1932) and Thieme (1932) who obtained both relative and absolute data. Other relative data are given by Yakhontova (1959), McFarland and Soltysik (1962a,b) Heddle and Lucas (1963) and St. John et al (1964). Absolute measurements were made by Yakhontova (1959), Gabriel and Heddle (1960) and St. John et al (1964). Percentage polarization of the emitted radiation has been measured by McFarland and Soltysik (1962a,b) and Heddle and Lucas (1963). A critical comparison of all these results is given by St. John et al (1964). Agreement between the various workers is reasonably good but variations do occur in both the relative and absolute data. These can be as much as 30% even when there is general overall agreement between various sets of results and in certain cases the data varies widely. The results of St. John et al (1964) are probably the best available for both relative and absolute values since they make allowances for both cascading and polarization and are in fairly good agreement with Yakhontova (1959) and somewhat less good agreement with

Heddle and Lucas (1963). As for the other data, Gabriel and Heddle (1960) do not allow for polarization (which means their measurements are in error by some 15%) and the remaining experiments were carried out at pressures which were too high to give reliable results.

For the case of forbidden transitions in atoms excited by proton impact Bates and Griffing (1953) have calculated the cross section for the 1s→3d transition in hydrogen in the first Born approximation. Carew and Milford (1963) have calculated cross sections for all the n=2 to n=3 and n=3 to n=4 transitions in hydrogen by means of an approximation which expresses the proton cross sections in terms of first Born electron cross sections.

Some experimental work has been done by Van Eck et al (1962) on the excitation of the 1'S→n'D series of transitions in He by proton impact but results are available only for relatively low values of the proton energy.

§1.4 The Impact Parameter Method Applied to Electron Excitation of Optically Allowed Atomic Transitions.

In this section we review the work of Seaton (1962) who has applied the impact parameter method to electron excitation of optically allowed atomic transitions. Since our formulation of the problem of excitation of forbidden transitions follows closely on Seaton's work we shall investigate in some detail the assumptions made in Seaton's paper and their justification.

The usual assumptions made in the impact parameter method are that the incident particle follows a rectilinear path and that first order perturbation theory may be used to calculate the transition probabilities. Exchange is neglected and the second assumption implies that the coupling between the initial and final states is weak and that coupling to intermediate states is

unimportant. These assumptions will be valid for all impact parameters when the incident energy is large but will be invalid for small impact parameters at smaller incident energies. These are essentially the same assumptions that are made in the first Born approximation.

In addition to these assumptions Seaton also introduces the following approximation: a) a cut-off in the integration over impact parameters, b) the use of the asymptotic form of the perturbation potential in place of its actual value, and c) the requirement that the transition probabilities satisfy the reciprocity condition.

Using approximation a) Seaton writes the cross section for transitions from state i to state j as

$$Q(i \to j) = \int_{R_o}^{\infty} P_{ji}(R_i)\, 2\pi R_i\, dR_i \qquad (1.4.1)$$

where $P_{ji}(R_i)$ is the transition probability at an impact parameter R_i and R_o is a cut-off which is independent of energy. R_o is to be chosen so that the cross section given by (1.4.1) agrees with the first Born cross section at high energies. One is able to introduce the cut-off in the case of optically allowed transitions because, as Seaton shows, a large contribution to the cross section comes from large impact parameters. By this means the region where the approximations are liable to be invalid, viz at small R_i, is eliminated. From a comparison of existing experimental and theoretical results it would seem that the Born approximation usually overestimates the value of the cross section at low energies. Hence one would hope that the above procedure would give better results than the Born approximation in this low energy region. In fact because of approximation b) the transition probabilities, $P_{ji}(R_i)$, tend to infinity as the impact parameter R_i tends to zero so that the introduction of the cut-off is necessary if nonsensical

answers are to be avoided.

The perturbation potential is $V(t)=|\underline{r}-\underline{r}'|^{-1}$ where $\underline{r}$ is the coordinate of the atomic electron and $\underline{r}'$ is the coordinate of the incident particle. If we expand V(t) the dominant term for optically allowed transitions is $(\underline{r}_> \cdot \underline{r}_<)r^{-3}$ where $r_<$, $r_>$ are the lesser and greater of r, r' respectively. Approximation b) consists of replacing V(t) by $(\underline{r}.\underline{r}')r'^{-3}$. Seaton's justification for this is as follows: V(t) is multiplied by $\psi_j^* \psi_i$ where ψ_i, ψ_j are the initial and final state wave functions of the atomic system respectively. This product will be small whenever $r \gg \bar{r}_<$ where $\bar{r}_<$ is the lesser of the mean atomic radii of the initial and final states. Now $r' \geq \rho$ where ρ is the distance of closest approach of the incident particle (ρ is equal to the impact parameter for rectilinear orbits) so that if $\rho \gg \bar{r}_<$ the above replacement is justified. Since $\rho \geq R_o$ this implies that R_o must at least be greater than $\bar{r}_<$. Thus the range of validity of approximation b) coincides roughly with that of the impact parameter method as a whole. We will investigate numerically the validity of approximation b) in Chapter 4.

Approximation c) implies that $L_i \cong L_j$ and $W_i \cong W_j$ where L_i, L_j are the angular momenta and W_i, W_j the energy of the incident particle before and after the transition respectively. Since L_i and L_j differ by one quantum unit† for optically allowed transitions the first part of the approximation is good for high incident energies or large impact parameters. Also $|W_i - W_j| = \Delta E$ where ΔE is the difference in energy between the initial and final atomic states. Since ΔE is typically a few eV or less the second part of the approximation is valid except at low energies. Hence the range of validity of approximation c) corresponds to the range of validity of the impact parameter method as a whole.

For optically allowed transitions the cross section depends logarithmically on the cut-off parameter R_o, especially at high energies. Seaton gives a procedure for estimating R_o which produces reasonably accurate results.

Seaton also introduces a second method for calculating cross sections when the coupling is strong. In this case P_{ji} as calculated by the impact parameter method is liable to exceed unity even for moderate values of the incident energy or impact parameter. Assuming that the previous method is invalid when $P_{ji} \gtrsim 1/2$ Seaton defines a second cut-off parameter R_1 by the equation $P_{ji}(R_1)=1/2$. For $R_i \leq R_1$ the average value of P_{ji} is assumed to be 1/2 so that the formula for the cross section becomes

$$Q(i \to j) = \frac{\pi}{2} R_1^2 + \int_{R_1}^{\infty} P_{ji}(R_i)\, 2\pi R_i\, dR_i \qquad (1.4.2)$$

Approximations b) and c) are made as in the previous case. In this case, however, R_1 is energy dependent.

In practice both cross sections (1.4.1) and (1.4.2) are calculated and the smaller of the two results adopted.

+ Note: This argument as given by Seaton is fallacious. For a correct discussion of this point see §2.4.

Chapter 2

§2.1 Statement of the Problem.

In this chapter we extend the work of Seaton (1962) in a straightforward manner to include the contribution to the cross section from electric quadrupole transitions. In §1.4 we have discussed Seaton's formulation for the cross sections for optically allowed (electric dipole) transitions along with the approximations he makes and their justification. Here we shall assume that the same approximations are valid in the case under consideration and defer until Chapter 4 a critical examination of them.

We consider the effect of a charged point particle incident on an atomic system making the usual assumptions connected with the impact parameter method. This means that the cross sections for transitions in the atomic system are calculated in a non-relativistic, non-exchange approximation where the incident point particle is treated as a classical particle in a rectilinear orbit. If $\underline{r}'(t)$ is the position vector of the incident particle at time t this allows us to write

$$\underline{r}'(t) = \underline{R}_i + \underline{v}_i t \qquad (2.1.1)$$

where $\underline{R}_i$ and $\underline{v}_i$ are constant vectors, $\underline{v}_i$ being the velocity of the incident particle, and such that $\underline{R}_i \cdot \underline{v}_i = 0$. Thus R_i represents the impact parameter of the incident particle and also its distance of closest approach to the atom.

Let $P_{ji}(R_i)$ be the probability that the atomic system makes a transition from an initial state i to a final state j when the incident particle has impact parameter R_i. Within the context of the impact parameter approximation one usually assumes that these transition probabilities can be calculated sufficiently accurately

according to first order time-dependent perturbation theory (c.f.§1.2).

We can now write the cross section for a transition between states i and j as

$$Q(i \rightarrow j) = \int_0^\infty P_{ji}(R_i) 2\pi R_i dR_i \ . \qquad (2.1.1a)$$

In addition to the above approximations we make the following ones as did Seaton: a) introduction of a cut-off in the integration over impact parameters, b) the use of the asymptotic form of the perturbation potential in place of its actual value and c) the requirement that the transition probabilities satisfy the reciprocity condition (principle of detailed balancing) (Landau and Lifshitz, (1958), §116).

Approximation a) implies that we can write

$$Q(i \rightarrow j) = \int_{R_0}^\infty P_{ji}(R_i) 2\pi R_i dR_i \qquad (2.1.2)$$

in place of (2.1.1a) (c.f.(1.4.1)) while approximation c) requires that

$$\omega_i P_{ji}(R_i) = \omega_j P_{ij}(R_j) \qquad (2.1.3)$$

where ω_i and ω_j are the number of degenerate levels of the initial and final states, respectively, and R_i and R_j are the impact parameters of the incident particle in the original and time-reversed situation, respectively.

§2.2. Transition Probabilities.

For simplicity we assume that the incident particle is an electron. We will give the results for an arbitrary point particle in §2.10. The effect of the incident electron is the addition of a term V(t) to the potential of the atomic system. If the atomic system has N electrons and nuclear charge Z (for neutral atoms Z=N) and if the position of the k^{th} atomic electron is $\underline{r}_k$ then

$$V(t) = \frac{Ze^2}{|\underline{r}'(t)|} - \sum_{k=1}^{N} \frac{e^2}{|\underline{r}'(t) - \underline{r}_k|} \qquad (2.2.1)$$

where e is the magnitude of the charge on the electron. Then according to time-dependent perturbation theory the first order transition probabilities are given by (Landau and Lifshitz, (1958), §§40, 41)

$$P_{ji}(R_i) = \frac{1}{\hbar^2 \omega_i} \sum_s \left| \int_{-\infty}^{\infty} e^{ipt} V_{ji}(t)\, dt \right|^2 \qquad (2.2.2)$$

where $p = \Delta E/\hbar$ and $\Delta E = |E_i - E_j|$ is the magnitude of the difference in energy between the initial and final atomic states. The sum over "s" represents the sum over all degenerate levels of the initial and final states. If $\Psi_i(\underline{r}_1, \ldots, \underline{r}_N)$ and $\Psi_j(\underline{r}_1, \ldots, \underline{r}_N)$ are the fully anti-symmetrized wave functions for the initial and final states of the atomic system then the matrix element $V_{ji}(t)$ is given by

$$V_{ji}(t) = \int \Psi_j^*(\underline{r}_1, \ldots, \underline{r}_N) V(t)\, \Psi_i(\underline{r}_1, \ldots, \underline{r}_N) d\underline{r}_1 \ldots d\underline{r}_N \qquad (2.2.3)$$

where the asterisk denotes the complex conjugate of the function.

Expand

$$\frac{1}{|\underline{r}'(t) - \underline{r}_k|} = \sum_{\lambda=0}^{\infty} P_\lambda(\cos \gamma_k) \frac{r_<^\lambda}{r_>^{\lambda+1}} \qquad (2.2.4)$$

where γ_k is the angle between $\underline{r}'$ and $\underline{r}_k$ and $r_<$, $r_>$ are the lesser of r', r_k, respectively. Approximation b) implies that we put $r_< = r_k$, $r_> = r'$ and that we only retain the most important terms in (2.2.4). If we wish to consider quadrupole transitions we must retain the $\lambda = 2$ term which is the dominant one for these transitions. Thus we neglect all the terms for which $\lambda \geq 3$. Making these approximations in (2.2.4) and substituting in (2.2.1), (2.2.3) becomes

$$V_{ji}(t) = \sum_{k=1}^{N} \int \Psi_j^*(\underline{r}_1, \cdots, \underline{r}_N) \sum_{\lambda=0}^{2} \frac{e^2 P_\lambda(\cos \gamma_k)\, r_k^\lambda}{r'^{\lambda+1}} \cdot \Psi_i(\underline{r}_1, \cdots, \underline{r}_N)\, d\underline{r}_1 \cdots d\underline{r}_N \qquad (2.2.5)$$

where we have assumed that Ψ_i and Ψ_j are orthogonal functions normalized to unity. Thus there is no contribution from the term Ze^2/r' in (2.2.1). For the same reason the $\lambda = 0$ term in (2.2.5) always gives a zero contribution. If we had not made the assumption $r_> = r'$ this term would give a non-zero contribution in certain cases. (These cases arise when the angular parts of Ψ_i and Ψ_j are not orthogonal. On the basis of the independent particle model this situation occurs when $\Delta \ell = 0$ where $\Delta \ell$ is the change in the orbital angular momentum quantum number of the active atomic electron during the transition.) Hence we conclude that the assumption $r_> = r'$ is not good in this case since the $\lambda = 0$ term of (2.2.4) would be the dominant one. This is borne out by calculations (see Chapter 4). In other cases this assumption should be reasonable.

Since Ψ_i and Ψ_j are fully antisymmetrized we may replace the sum over k in (2.2.5) by a factor N. (Interchanging $\underline{r}_k$ and $\underline{r}_\ell$ in Ψ_i and Ψ_j merely introduces a factor (-1) into both of these functions and hence the contribution from each value of k in (2.2.5) is identical.) From (2.1.1) we note that r' depends only on t so that substituting (2.2.5) into (2.2.2) we obtain

$$P_{ji}(R_i) = \frac{e^4 N^2}{\hbar^2 \omega_i} \sum_s \left| \sum_{\lambda=1}^{2} \int_{-\infty}^{\infty} \frac{e^{i\omega t} R^{(\lambda)}(t)}{r'(t)^{\lambda+1}} dt \right|^2 \tag{2.2.6}$$

where

$$R^{(\lambda)}(t) = \langle j | r^\lambda P_\lambda(\cos\vartheta) | i \rangle \equiv \int \Psi_j^*(\underline{r}_1, \cdots, \underline{r}_N)\, r^\lambda P_\lambda(\cos\vartheta)\, \Psi_i(\underline{r}_1, \cdots, \underline{r}_N)\, d\underline{r}_1 \cdots d\underline{r}_N \tag{2.2.7}$$

and r and ϑ represent r_k and ϑ_k for any value of k from 1 to N since each value gives an identical contribution.

§2.3 The Averaged Probabilities.

We distinguish between two separate frames of reference. The first, which we denote by Σ is the external frame (often called the laboratory frame) with respect to which the spatial dependence of the perturbation V(t) is defined. The second frame, denoted by Σ', is an internal frame such that the wave functions which describe the atomic system when defined in this frame have associated with them a definite set of quantum numbers. In other words the atomic system is in a definite state when described in the frame Σ'. Σ' has some arbitrary orientation with respect to Σ and this allows us to describe the effect of the perturbation on an arbitrarily oriented atomic system.

An alternate way of looking at this is to consider the atom in a given state with respect to a fixed frame of reference and then apply the perturbation from some arbitrary orientation e.g. shoot an electron at the atom from any direction. These two descriptions are identical, the only difference being that the first description keeps Σ fixed and allows Σ' to have an arbitrary orientation while the second reverses the roles of Σ and Σ'. We will use the second description here and the first description in Chapter 3.

Most experimental data (e.g. cross sections, transition probabilities, polarization measurements) are the result of carrying out measurements on a large number of atoms with random orientations with respect to the laboratory frame. Hence in order to derive physically meaningful results we must average our transition probabilities over all possible orientations of the atomic system assuming all orientations are equally likely. We achieve this in practice by averaging over all possible orientations of Σ while keeping Σ' fixed.

We assume that the origins of both Σ and Σ' coincide with the nucleus of the atomic system. In the fixed frame Σ' the position vectors $\underline{r}_k$ of the atomic electrons have coordinates $(r_k, \theta_k, \varphi_k)$ and the vector $\underline{r}'$ has coordinates (r', θ', φ'). We define the frame Σ such that its z-axis is parallel to $\underline{v}_i$ and its x-axis parallel to $\underline{R}_i$ and in this frame $\underline{r}'$ has coordinates $(r', \Theta, 0)$ where

$$\cos\Theta = \frac{v_i t}{r'(t)} = \frac{v_i t}{\sqrt{R_i^2 + v_i^2 t^2}} \qquad (2.3.1)$$

(See Figure 2.1). Let the Euler angles specifying the rotations needed to bring the frame Σ into coincidence with Σ' be (α, β, γ). (We use the angles defined by Edmonds, (1957), §1.3).

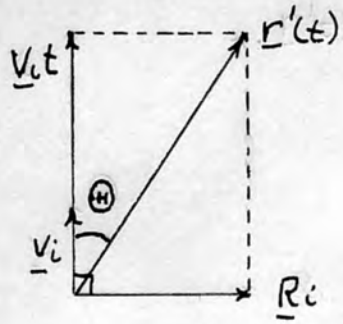

Fig. 2.1

The angle γ_k between $\underline{r}_k$ and $\underline{r}'$ can be expressed as (dropping the subscript k since it is unnecessary)

$$\cos\gamma = \cos\theta\cos\theta' + \sin\theta\sin\theta'\cos(\varphi - \varphi')$$

and hence by (E4.6.6)

$$P_\lambda(\cos\gamma) = \frac{4\pi}{2\lambda+1} \sum_{\mu=-\lambda}^{\lambda} Y_{\lambda\mu}(\theta,\varphi)\, Y^*_{\lambda\mu}(\theta',\varphi') . \qquad (2.3.2)$$

We may express the $Y_{\lambda\mu}(\theta',\varphi')$ in terms of the angles $(\Theta, 0)$ and (α, β, γ) as follows:

$$Y_{\lambda\mu}(\theta',\varphi') = \sum_{\mu'=-\lambda}^{\lambda} Y_{\lambda\mu'}(\Theta, 0)\, \mathcal{D}^{(\lambda)}_{\mu'\mu}(\alpha\beta\gamma) \qquad (2.3.3)$$

where the $\mathcal{D}^{(\lambda)}_{\mu'\mu}(\alpha\beta\gamma)$ are the matrix elements of the

rotation operator $\underline{\underline{D}}(\alpha\beta\gamma)$ which transforms Σ into Σ' (See Edmonds, (1957), §4.1).

From (2.2.7) using (2.3.2) and (2.3.3) we have

$$\mathcal{R}^{(\lambda)}(t) = \langle j | r^{\lambda} \frac{4\pi}{2\lambda+1} \sum_{\mu=-\lambda}^{\lambda} \sum_{\mu'=-\lambda}^{\lambda} Y_{\lambda\mu}(\Theta,\varphi)\, Y^{*}_{\lambda\mu'}(\Theta,0) \times \mathcal{D}^{(\lambda)*}_{\mu'\mu}(\alpha\beta\gamma) | i \rangle$$

$$= \frac{4\pi}{2\lambda+1} \sum_{\mu,\mu'=-\lambda}^{\lambda} \mathcal{D}^{(\lambda)*}_{\mu'\mu}(\alpha\beta\gamma)\, Y^{*}_{\lambda\mu'}(\Theta,0) \times \langle j | r^{\lambda} Y_{\lambda\mu}(\theta,\varphi) | i \rangle \qquad (2.3.4)$$

since Θ and $(\alpha\beta\gamma)$ are independent of the atomic coordinates (r,θ,φ). Note also that the time coordinate in $\mathcal{R}^{(\lambda)}(t)$ appears only via the angle Θ as given by (2.3.1). Hence (2.2.6) becomes

$$P_{ji}(R_i) = \frac{e^4 N^2}{\hbar^2 \omega_i} \sum_{S} \sum_{\lambda_1=1}^{2} \sum_{\lambda_2=1}^{2} \frac{(4\pi)^2}{(2\lambda_1+1)(2\lambda_2+1)} \times \sum_{\mu_1,\mu_1'=-\lambda_1}^{\lambda_1} \mathcal{D}^{(\lambda_1)*}_{\mu_1'\mu_1}(\alpha\beta\gamma)\, T^{\lambda_1\mu_1'}(R_i) \langle j | r^{\lambda_1} Y_{\lambda_1\mu_1}(\theta,\varphi) | i \rangle \times \sum_{\mu_2,\mu_2'=-\lambda_2}^{\lambda_2} \mathcal{D}^{(\lambda_2)}_{\mu_2'\mu_2}(\alpha\beta\gamma)\, T^{\lambda_2\mu_2'*}(R_i) \langle j | r^{\lambda_2} Y_{\lambda_2\mu_2}(\theta,\varphi) | i \rangle^{*} \qquad (2.3.5)$$

where

$$T^{\lambda\mu}(R_i) = \int_{-\infty}^{\infty} \frac{e^{ipt}}{r'(t)^{\lambda+1}} Y^{*}_{\lambda\mu}(\Theta,0)\, dt \,. \qquad (2.3.6)$$

Note that $Y_{\lambda\mu}(\Theta,0)$ is real so that we may neglect the asterisk in (2.3.6).

We have thus obtained the dependence of the $P_{ji}(R_i)$ on the relative orientation of Σ and Σ' (i.e. on the angles $\alpha\beta\gamma$) explicitly via the $\mathcal{D}^{(\lambda)}_{\mu'\mu}(\alpha\beta\gamma)$. Hence the averaged probabilities $\overline{P}_{ji}(R_i)$ are given by.

$$\overline{P}_{ji}(R_i) = \frac{1}{8\pi^2}\int_0^{2\pi}\int_0^{\pi}\int_0^{2\pi} P_{ji}(R_i)\, d\alpha \sin\beta\, d\beta\, d\gamma$$

$$= \frac{e^4 N^2}{\hbar^2 \omega_i} \sum_s \sum_{\lambda_1,\lambda_2=1}^{2} \frac{(4\pi)^2}{(2\lambda_1+1)(2\lambda_2+1)}$$

$$\times \sum_{\mu_1,\mu_1'=-\lambda_1}^{\lambda_1} \sum_{\mu_2,\mu_2'=-\lambda_2}^{\lambda_2} T^{\lambda_1\mu_1'}(R_i)\, T^{\lambda_2\mu_2'*}(R_i)$$

$$\times \langle j|r^{\lambda_1} Y_{\lambda_1\mu_1}(\theta,\varphi)|i\rangle \langle j|r^{\lambda_2} Y_{\lambda_2\mu_2}(\theta,\varphi)|i\rangle^*$$

$$\times \frac{1}{8\pi^2}\int_0^{2\pi}\int_0^{\pi}\int_0^{2\pi} \mathcal{D}^{(\lambda_1)*}_{\mu_1'\mu_1}(\alpha\beta\gamma)\, \mathcal{D}^{(\lambda_2)}_{\mu_2'\mu_2}(\alpha\beta\gamma)\, d\alpha \sin\beta\, d\beta\, d\gamma$$

$$= \frac{e^4 N^2}{\hbar^2 \omega_i} \sum_{\lambda=1}^{2} \frac{(4\pi)^2}{(2\lambda+1)^3} R^{(\lambda)}_{ji} \sum_{\mu'=-\lambda}^{\lambda} |T^{\lambda\mu'}(R_i)|^2 \qquad (2.3.7)$$

using (E 4.6.1) where

$$R^{(\lambda)}_{ji} = \sum_s \sum_{\mu=-\lambda}^{\lambda} |\langle j|r^{\lambda} Y_{\lambda\mu}(\theta,\varphi)|i\rangle|^2 \qquad (2.3.8)$$

and is a number depending on the initial and final states of the atom and on λ.

§2.4. Reciprocity.

In order that the reciprocity condition holds, (2.1.3) must be satisfied using the averages probabilities as given by (2.3.7). Now

$$|\langle j|r^{\lambda} Y_{\lambda\mu}|i\rangle|^2$$

$$= \int \Psi_j^* r^{\lambda} Y_{\lambda\mu} \Psi_i\, d\tau \int \Psi_j r^{\lambda} Y^*_{\lambda\mu} \Psi_i^*\, d\tau$$

$$= \int \Psi_j^* r^{\lambda} (-1)^{\mu} Y^*_{\lambda-\mu} \Psi_i\, d\tau \int \Psi_j r^{\lambda} (-1)^{\mu} Y_{\lambda-\mu} \Psi_i^*\, d\tau$$

$$= |\langle j|r^{\lambda} Y_{\lambda-\mu}|j\rangle|^2 \qquad (2.4.1)$$

using (E 2.5.6). Thus $R^{(\lambda)}_{ji}=R^{(\lambda)}_{ij}$ and the reciprocity condition is satisfied if

$$|T^{\lambda\mu}(R_i)|^2 = |T^{\lambda\mu}(R_j)|^2 . \qquad (2.4.2)$$

$T^{\lambda\mu}$ may be evaluated to give (Appendix A)

$$|T^{\lambda\mu}(R_i)|^2 = \frac{(2\lambda+1)\,K_\mu^2(\beta_i)}{\pi v_i^2(\lambda+\mu)!(\lambda-\mu)!}\left(\frac{p}{L_i}\right)^{2\lambda} \qquad (2.4.3)$$

where

$$\beta_i = \frac{R_i p}{v_i} = \frac{L_i p}{2W_i} \qquad (2.4.4)$$

and $L_i=mv_iR_i$ is the initial angular momentum of the incident particle of mass m relative to the atomic nucleus and $W_i=1/2mv_i^2$ is its initial energy. We have a similar expression for $|T^{\lambda\mu}(R_j)|^2$ with v_i replaced by v_j and β_i by $\beta_j=L_jp/2W_j$, $L_j=mv_jR_j$ being the final relative angular momentum of the incident particle and $W_j=1/2mv_j^2$ its final energy.

If $\mathcal{L}_i$ and $\mathcal{L}_j$ are respectively the magnitudes of the initial and final total orbital angular momentum of the atom (i.e. $\mathcal{L}_i^2$ and $\mathcal{L}_j^2$ are of the form $L(L+1)\hbar^2$ where L is an integer) then the initial total orbital angular momentum of the system atom plus incident particle can have magnitude in the range $(L_i+\mathcal{L}_i)$ to $|L_i-\mathcal{L}_i|$ and similarly for the final angular momentum. These limits are derived from a classical picture but are true quantum mechanically in the limit of large $\mathcal{L}_i$ and $\mathcal{L}_j$. If $\Delta L=L_i-L_j$ is the difference between tne initial and final angular momentum of the incident particle then from the conservation of angular momentum law we have that $|\Delta L| \leq \mathcal{L}_i+\mathcal{L}_j$. For all practical purposes $\mathcal{L}_i+\mathcal{L}_j \lesssim 10\hbar$. For comparison purposes we note that an electron with an energy of one Rydberg and an impact parameter of one Bohr radius has as angular momentum of $\hbar$. Thus we may assume that $L_i \cong L_j \cong L$ and this will be a good assumption

for all incident energies if $R_i >> \bar{r}_<$ and for high energies if $R_i > \bar{r}_<$. The situation is even somewhat better than the above discussion suggests since on averaging over all degenerate states ΔL will take on a range of values whose average will in general be considerably smaller in magnitude than the maximum possible value of ΔL.

Now $\Delta E = |W_i - W_j|$ is the difference in energy between the initial and final states of the atomic system. We define the average energy

$$W = (W_i + W_j)/2 \ . \qquad (2.4.5)$$

Then the reciprocity condition will be satisfied if we replace β_i and β_j by $\beta = Lp/2W$ and W_i and W_j by W in (2.4.2) so that

$$|T^{\lambda\mu}(R_i)|^2 = |T^{\lambda\mu}(R_j)|^2 = \frac{m(2\lambda+1)}{2\pi W(\lambda+\mu)!(\lambda-\mu)!} K_\mu^2(\beta_i) \left(\frac{mp^2}{2W}\right)^\lambda \ . \qquad (2.4.6)$$

If we restrict ourselves to the energy range $W_i \gtrsim 5\Delta E$ where our results seem reasonably reliable (c.f. Ch.4) then replacing W_i and W_j by W will introduce a maximum error of 10% and at high incident energies this error will be very small. At low energies ($W_i \cong 5\Delta E$) we expect that the errors introduced by this replacement will be more than offset by the fact that the reciprocity condition is satisfied.

§ 2.5. Expressions for the Cross Sections.

From the previous section we have that $P_{ji}(R_i)$ is a function of β where

$$\beta = \frac{Lp}{2W} = \frac{mv_i R_i \Delta E}{2\hbar W} = \frac{1}{2}\sqrt{\frac{W_i}{I_H}}\,\frac{\Delta E R_i}{W a_0} \qquad (2.5.1)$$

where $I_H = me^4/2\hbar^2$ is the ionization potential of hydrogen (13.60eV) i.e. it is the Rydberg unit of energy and

$a_0 = \hbar^2/me^2$ is the Bohr radius. Hence from (2.1.2) using (2.3.7)

$$Q(i \to j) = \frac{2\pi e^4 N^2}{\hbar^2 \omega_i} \sum_{\lambda=1}^{2} \frac{(4\pi)^2}{(2\lambda+1)^3} R_{ji}^{(\lambda)} \times \sum_{\mu=-\lambda}^{\lambda} \int_{R_0}^{\infty} |T^{\lambda\mu}(R_i)|^2 R_i \, dR_i. \quad (2.5.2)$$

From (2.4.6) and (2.5.1)

$$\int_{R_0}^{\infty} |T^{\lambda\mu}(R_i)|^2 R_i \, dR_i = \frac{(2\lambda+1) m^{\lambda+1} p^{2\lambda}}{\pi (\lambda+\mu)! (\lambda-\mu)! (2W)^{\lambda+1}} \times \left(2a_0 \sqrt{\frac{I_H}{W_i}} \frac{W}{\Delta E}\right)^2 \int_{\beta_0}^{\infty} K_\mu^2(\beta) \beta \, d\beta \quad (2.5.3)$$

where β_0 is β as given by (2.5.1) with R_i replaced by the cut-off R_0. Now

$$\int_{\beta_0}^{\infty} K_\mu^2(\beta) \beta \, d\beta = \frac{1}{2} \chi_\mu(\beta_0) \quad (2.5.4)$$

where

$$\chi_\mu(\beta_0) = \beta_0^2 \{ K_\mu'^2(\beta_0) - (1 + \mu^2/\beta_0^2) K_\mu^2(\beta_0) \} \quad (2.5.5)$$

(McLachlan, (1934) p.166). The prime denotes differentiation with respect to the argument of the function. Hence

$$Q(i \to j) = \frac{64\pi N^2 W}{\omega_i W_i} \left(\frac{I_H}{\Delta E}\right)^2 \sum_{\lambda=1}^{2} \frac{R_{ji}^{(\lambda)}}{(2\lambda+1)^2 a_0^{2\lambda}} \times \left(\frac{\Delta E^2}{4 I_H W}\right)^{\lambda} \sum_{\mu=-\lambda}^{\lambda} \frac{\chi_\mu(\beta_0)}{(\lambda-\mu)! (\lambda+\mu)!} (\pi a_0^2). \quad (2.5.6)$$

§ 2.6. Evaluation of χ_μ

Since (McLachlan, (1934))

$$\beta K_\mu'(\beta) = -\mu K_\mu(\beta) - \beta K_{\mu-1}(\beta) \quad (2.6.1)$$

(2.5.5) becomes

$$\chi_\mu(\beta_0) = 2\mu\beta_0 K_\mu(\beta_0) K_{\mu-1}(\beta_0) + \beta_0^2 (K_{\mu-1}^2(\beta_0) - K_\mu^2(\beta_0)). \quad (2.6.2)$$

Alternately using (McLachlan, (1934))

$$\beta K_\mu'(\beta) = \mu K_\mu(\beta) - \beta K_{\mu+1}(\beta) \quad (2.6.3)$$

(2.5.5) becomes

$$\chi_\mu(\beta_0) = -2\mu\beta_0 K_\mu(\beta_0) K_{\mu+1}(\beta_0) + \beta_0^2 (K_{\mu+1}^2(\beta_0) - K_\mu^2(\beta_0)). \quad (2.6.4)$$

Comparing (2.6.2) and (2.6.4) and noting that

$$K_\mu(\beta) = K_{-\mu}(\beta) \quad (2.6.5)$$

(McLachlan, (1934)) we see that

$$\chi_\mu(\beta_0) = \chi_{-\mu}(\beta_0). \quad (2.6.6)$$

Also since (McLachlan, (1934))

$$K_{\mu+1}(\beta) = \frac{2\mu}{\beta} K_\mu(\beta) + K_{\mu-1}(\beta) \quad (2.6.7)$$

we have using (2.6.2)

$$\begin{aligned}\chi_{\mu+1}(\beta_0) &= 2(\mu+1)\beta_0 K_{\mu+1}(\beta_0) K_\mu(\beta_0) + \beta_0^2 (K_\mu^2(\beta_0) - K_{\mu+1}^2(\beta_0)) \\ &= 4\mu K_\mu^2(\beta_0) - 2(\mu-1)\beta_0 K_\mu(\beta_0) K_{\mu-1}(\beta_0) + \beta_0^2 (K_\mu^2(\beta_0) - K_{\mu-1}^2(\beta_0)) \\ &= 4\mu K_\mu^2(\beta_0) + \chi_{\mu-1}(\beta_0) \quad (2.6.8)\end{aligned}$$

from (2.6.4).

We list below the expressions for $\chi_\mu(\beta_0)$ for $\mu=0,1,2$ in terms of the functions $K_0(\beta_0)$ and $K_1(\beta_0)$ which are well tabulated (British Association Mathematical Tables, (1958), (1952)). To evaluate χ_0 we have used (2.6.4), for χ_1 (2.6.2) and for χ_2 (2.6.8) and the expression for χ_0.

$$\chi_0(\beta_0) = \beta_0^2 (K_1^2(\beta_0) - K_0^2(\beta_0)), \quad (2.6.9)$$

$$\chi_1(\beta_0) = 2\beta_0 K_0(\beta_0) K_1(\beta_0) + \beta_0^2 (K_0^2(\beta_0) - K_1^2(\beta_0)), \quad (2.6.10)$$

$$\chi_2(\beta_0) = (4+\beta_0^2) K_1^2(\beta_0) - \beta_0^2 K_0^2(\beta_0). \quad (2.6.11)$$

To express χ_μ in terms of K_0 and K_1 for other values of μ we can use (2.6.2) and (D.1 a,b) for K_μ in terms of K_0 and K_1. Alternately (2.6.8) may be used if $\chi_{\mu-2}$ is known.

We define

$$\Omega_\lambda(\beta_0) = \sum_{\mu=-\lambda}^{\lambda} \frac{\chi_\mu(\beta_0)}{(\lambda-\mu)!\,(\lambda+\mu)!} \tag{2.6.12}$$

which is the expression involving β_0 appearing in the formula for the cross section (2.5.6). Using (2.6.6), (2.6.9), (2.6.10) and (2.6.11) we obtain

$$\Omega_1(\beta_0) = \chi_0(\beta_0) + \chi_1(\beta_0) = 2\beta_0 K_0(\beta_0) K_1(\beta_0), \tag{2.6.13}$$

$$\Omega_2(\beta_0) = \frac{\chi_0(\beta_0)}{4} + \frac{\chi_1(\beta_0)}{3} + \frac{\chi_2(\beta_0)}{12}$$

$$= \frac{2}{3}\beta_0 K_0(\beta_0) K_1(\beta_0) + \frac{1}{3} K_1^2(\beta_0). \tag{2.6.14}$$

Apart from a factor of two $\Omega_1(\beta_0)$ is identical with the function $\varphi(\beta_0)$ defined by Seaton, (1962). In his paper Seaton gives a table of values of $\varphi(\beta_0)$ as well as expansion formulae for small and large values of β_0. To examine the high energy behaviour of the cross section we shall need the form of $\Omega_2(\beta_0)$ when $\beta_0 \ll 1$. From the power series expansion of K_0 and K_1 (McLachlan, (1934)) we see that

$$\Omega_2(\beta_0) = \frac{1}{2\beta^2} - \frac{1}{2}\ln\left(\frac{\beta}{2}\right) - \left(\frac{1}{4} + \frac{\gamma}{2}\right) + O[\beta^2(\ln\beta)^2] \tag{2.6.15}$$

where $\gamma = 0.57722\ldots$ is Euler's constant.

§2.7. High Energy Behaviour of the Cross Section.

We assume that the wave functions describing the initial and final atomic states have a definite parity and since the rotation operator commutes with the parity

operator the parity of a given state is independent of its magnetic quantum number. The parity of $r^\lambda Y_{1\mu}(\theta,\varphi)$ is $(-1)^\lambda$ (Brink and Satchler, (1962)). Hence if the initial and final states have opposite parity $R_{ji}^{(\lambda)}$ as defined by (2.3.8) is non-zero only if λ is odd. This does not imply, however, that $R_{ji}^{(\lambda)}$ is non-zero for all odd values of λ. Similarly if the initial and final states have the same parity $R_{ji}^{(\lambda)}$ is non-zero only if λ is even. Hence in the formula for the cross section (2.5.6) only the λ =1 term contributes when the transition is optically allowed ($\Delta\ell$=1) and only the λ =2 term contributes when it is a forbidden (electric quadrupole) transition ($\Delta\ell$=2) where $\Delta\ell$ is the magnitude of the difference in the orbital angular momentum quantum number of the initial and final atomic states.

We next compare our expression for the cross section for optically allowed transitions to that obtained by Seaton, (1962). We note that

$$r Y_{10}(\theta,\varphi) = \sqrt{\frac{3}{4\pi}}\, z, \qquad r Y_{1\pm1}(\theta,\varphi) = \sqrt{\frac{3}{8\pi}}\,(x \pm iy) \tag{2.7.1}$$

so that

$$R_{ji}^{(1)} = \frac{3}{4\pi} R_{ji} \tag{2.7.2}$$

where R_{ji} is defined by Seaton as

$$R_{ji} = \sum_s |\langle j|\underline{r}|i\rangle|^2 \tag{2.7.3}$$

Seaton's expression for the cross section is

$$Q(i\to j) = \frac{8 I_H R_{ji}}{3 \omega_i W_i a_0^2} \beta_0 K_0(\beta_0) K_1(\beta_0) (\pi a_0^2). \tag{2.7.4}$$

Retaining only the λ =1 term of (2.5.6) and using (2.6.13) and (2.7.3) we see that our formula for the cross section is the same as (2.7.4) except for a factor N^2. This difference arises because in the derivation of (2.7.4) Seaton apparently considers only one electron atoms. However he later expresses R_{ji} in terms of the oscillator strength for the transition and since the usual definition

of the oscillator strength contains a summation over the atomic electrons (Condon and Shortley, (1963), Landau and Lifshitz, (1958)) we may assume that the factor N^2 is implicit in (2.7.4)

Seaton has shown that his expression for the cross section has the correct asymptotic form at high impact energies, viz. $\ln W_i/W_i$. Since our expression for the cross section for optically allowed transitions is equivalent to (2.7.4) it is obvious that it also will have the correct asymptotic form at high energies.

For electric quadrupole transitions we retain only the $\lambda = 2$ term of (2.5.6). Using (2.6.14) we find that in this case the expression for the cross section is given by

$$Q(i \to j) = \frac{8\pi N^2 \Delta E^2 R_{ji}^{(2)}}{75\, w_i\, WW_i\, a_0^4}\, 4(\beta_0)\, (\pi a_0^2) \tag{2.7.5}$$

where

$$4(\beta) = \beta K_0(\beta) K_1(\beta) + \frac{1}{2} K_1^2(\beta). \tag{2.7.6}$$

From (2.5.1) $\beta_0 \sim W_i^{-1/2}$ for large W_i. Also (McLachlan, (1934))

$$K_n(\beta) \sim \beta^{-n}, \quad n \neq 0,$$
$$K_0(\beta) \sim \ln \beta \tag{2.7.7}$$

for small β. Hence from (2.7.5)

$$Q(i \to j) \sim W_i^{-2}(\ln W_i + W_i^2) \sim W_i^{-1} \tag{2.7.8}$$

for large W_i for forbidden transitions i.e. it has the correct asymptotic form.

§2.8. Strong Coupling Case.

In §1.4 we have discussed the method which Seaton suggests for calculating the cross section for transitions in which the coupling between initial and final states is strong. The formula for the cross section is given by

(1.4.2). In this case we obtain the cut-off R_1 by the condition

$$P_{ji}(R_1) = 1/2 \tag{2.8.1}$$

For electric quadrupole transitions (2.8.1) becomes using (2.3.7) and (2.4.6)

$$\frac{1}{2} = \frac{\pi N^2 \Delta E^4 R_{ji}^{(2)}}{225 \omega_i I_H W^3 a_0^4} \eta(\beta_1) \tag{2.8.2}$$

where β_1 is given by (2.5.1) with $R_i = R_1$, the new cut-off and

$$\eta(\beta) = 9 \sum_{\mu=-2}^{2} \frac{K_\mu^2(\beta)}{(2+\mu)!\,(2-\mu)!}$$

$$= 3\left\{\left(1 + \frac{1}{\beta^2}\right) K_1^2(\beta) + \frac{K_1(\beta) K_0(\beta)}{\beta} + K_0^2(\beta)\right\} \tag{2.8.3}$$

Hence (1.4.2) becomes using (2.7.5) and (2.8.2)

$$Q(i \to j) = \frac{4\pi N^2 \Delta E^2 R_{ji}^{(2)}}{225 \omega_i W W_i a_0^4} \left\{\beta_1^2 \eta(\beta_1) + 6 \psi(\beta_1)\right\} \tag{2.8.4}$$

which is the formula for the cross section for electric quadrupole transitions when the coupling is strong.

To investigate the high energy form of (2.8.4) we note that (2.8.2) implies that $\eta(\beta_1) \to \infty$ as $W_i \cong W \to \infty$. This in turn implies that $\beta_1 \to 0$ as $W_i \to \infty$. For β_1 small we find from (2.8.3) using (2.7.7) that $\eta(\beta_1) \sim \beta_1^{-4}$. Hence from (2.8.2) $\beta_1 \sim W_i^{-3/4}$ for large W_i and we conclude from (2.8.4) that $Q(i \to j) \sim W_i^{-1/2}$ (since $\psi(\beta_1) \sim \beta_i^{-2}$) i.e. the cross section as given by (2.8.4) has the wrong asymptotic form at high impact energies. (This is not true of Seaton's strong coupling formula for optically allowed transitions which does have the correct high energy form). Therefore we would expect (2.8.4) to be valid only at moderate impact energies if it is valid at all.

§ 2.9. Maximum of the Cross Section.

In this section we derive an expression for the value of the energy at which the cross section given by (2.7.5) has a maximum value.

We note first of all from (2.5.4), (2.6.12), (2.6.14), (2.7.6) and (2.8.3) that

$$\frac{d\,\mathcal{Y}(\beta_0)}{d\beta_0} = -\frac{1}{3}\,\beta_0\,\eta(\beta_0). \tag{2.9.1}$$

Since $W_i = W + \Delta E/2$, we have $\frac{\partial}{\partial W_i} = \frac{\partial}{\partial W}$. Hence from (2.5.1)

$$\frac{\partial \beta_0}{\partial W_i} = \left(\frac{1}{2W_i} - \frac{1}{W}\right)\beta_0 \,. \tag{2.9.2}$$

The necessary condition for $Q(W_i)$ to have an extremum is

$$\frac{\partial Q(W_i)}{\partial W_i} = 0 \,. \tag{2.9.2a}$$

Using (2.7.5) and (2.9.2), (2.9.2a) becomes

$$\left(\frac{1}{2W_i} - \frac{1}{W}\right)\frac{\beta_0^2\,\eta(\beta_0)}{3\,W\,W_i} + \frac{\mathcal{Y}(\beta_0)}{(W W_i)^2}\left(2W_i - \frac{\Delta E}{2}\right) = 0. \tag{2.9.3}$$

Solving (2.9.3) for W_i yields the value of the energy at which Q attains its maximum. (We assume here that Q has only one extremum for finite values of $W_i \geq \Delta E$ and that this is a maximum. We will show in Ch.4 that calculations bear out this assumption). Let this energy be denoted by $(W_i)_{max} = (1+\varepsilon)\,\Delta E$ where ε is a pure number. Hence $W = (1/2+\varepsilon)\,\Delta E$ and from (2.9.3) we obtain the following equation for ε:

$$\varepsilon = \frac{3}{2}\,\frac{\beta_0^2\,\eta(\beta_0) - 6\,\mathcal{Y}(\beta_0)}{12\,\mathcal{Y}(\beta_0) - \beta_0^2\,\eta(\beta_0)} \,. \tag{2.9.4}$$

Note that the β_0 in (2.9.4) is given by (2.5.1) with $W_i = (W_i)_{max}$ i.e. β_0 depends on ε. Thus (2.9.4) does not

give an explicit expression for ε. However we can express ε as a function of β_0 via (2.5.1) allowing us to solve (2.9.4) graphically. Doing this we obtain

$$\varepsilon = (1-4x^2+\sqrt{8x^2+1})/8x^2 \qquad (2.9.5)$$

where $x = \beta_0\sqrt{\frac{I_H}{E}}\frac{a_0}{R_0}$ and we have made use of the fact that $\varepsilon > 0$. Note that x depends on the particular transition in question via R_0 and ΔE. We must have $x > 0$ and from (2.9.5) we find $0 < x < 1$ since $\varepsilon > 0$. The behaviour of (2.9.5) is shown in Fig. 2.2. We shall show graphically in Ch.4 that (2.9.4) yields a unique value for $(W_i)_{max}$ for a given transition.

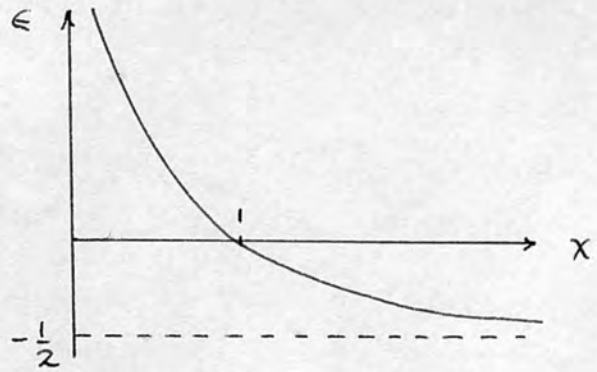

Fig. 2.2

Alternately if we know the value of $(W_i)_{max}$ and hence ε we can use (2.9.4) to find β_0 and this then yields a value for the cut-off R_0 for the particular transition.

§ 2.10. Cross Sections for Transitions Induced by Point Particles of Arbitrary Charge.

Until now we have assumed that the incident particle was an electron. However the method is valid when the incident particle is any point particle with an arbitrary charge e.g. a proton, positron, alpha particle, etc. (We

mean by a point particle any system whose charge is effectively contained in a volume whose dimensions are small compared with atomic dimensions). We consider the result when a particle of mass Mm and charge $Z'e$ is incident on an atomic system. Here m is the electronic mass and e the magnitude of the electronic charge so that M and Z' are dimensionless numbers. In this case the perturbation potential given by (2.2.1) is replaced by

$$V(t) = \frac{ZZ'e^2}{|\underline{r}'(t)|} - \sum_{k=1}^{N} \frac{Z'e^2}{|\underline{r}'(t)-\underline{r}_k|} \,. \qquad (2.10.1)$$

The rest of the analysis of §2.2 goes through as before except that e^2 is everywhere replaced by $Z'e^2$. For instance (2.2.6) becomes

$$P_{ji}(R_i) = \frac{Z'^2 e^4}{\hbar^2 \omega_i} \sum_s \left| \sum_{\lambda=1}^{2} \int_{-\infty}^{\infty} \frac{e^{ipt}\, \mathcal{R}^{(\lambda)}(t)}{r'(t)^{\lambda+1}}\, dt \right|^2 . \qquad (2.10.2)$$

The same holds true for the averaging procedure of §2.3. The reciprocity analysis of §2.4 is unchanged except that m is replaced by Mm. For example the initial angular momentum of the incident particle is $L_i = Mmv_iR_i$ and its energy is $W_i = \frac{1}{2}Mmv_i^2$. Also (2.4.6) becomes

$$|T^{\lambda\mu}(R_i)|^2 = \frac{Mm(2\lambda+1)\, K_\mu^2(\beta_i)}{2\pi W (\lambda+\mu)!\,(\lambda-\mu)!} \left(\frac{Mmp^2}{2W}\right)^{\lambda} \qquad (2.10.3)$$

where W now also contains the factor M.

Equation (2.5.1) becomes

$$\beta = \frac{\sqrt{M}}{2} \sqrt{\frac{W_i}{I_H}}\, \frac{\Delta E}{W}\, \frac{R_i}{a_0} \qquad (2.10.4)$$

and (2.5.6) is now

$$Q(i \to j) = \frac{64\pi Z'^2 N^2 W}{\omega_i W_i} \left(\frac{I_H}{\Delta E}\right)^2 \times \sum_{\lambda=1}^{2} \frac{R_{ji}^{(\lambda)}}{(2\lambda+1)^2 a_0^{2\lambda}} \left(\frac{M\Delta E^2}{4 I_H W}\right)^{\lambda} \Omega^{\lambda}(\beta_0)\, (\pi a_0^2). \qquad (2.10.5)$$

§ 2.6 is unaffected by this change as is §2.7 except that (2.10.5) is used as the formula for the cross section so that factors of M and Z' are introduced into the formulae.

In the strong coupling case (2.8.2) now reads

$$\frac{1}{2} = \frac{\pi Z'^2 N^2 M^3 \Delta E^4 R_{ji}^{(2)}}{225 \omega_i I_H W^3 a_0^4} \eta(\beta_1) \qquad (2.10.6)$$

and the cross section becomes

$$Q(i \to j) = \frac{4\pi Z'^2 N^2 M^2 \Delta E^2 R_{ji}^{(2)}}{225 \omega_i W W_i a_0^4} \{\beta_1^2 \eta(\beta_1) + 6 \chi(\beta_1)\}. \qquad (2.10.7)$$

Finally the formulae for finding the position of the maximum of the cross section is not changed.

Chapter 3

§ 3.1. Introduction.

In this chapter we derive some general formulae for transition probabilities for atomic systems which are calculated by means of first order time-dependent perturbation theory. The potential operator produced by some external perturbation is assumed to have a spatial dependence which can be expressed in terms of spherical tensor operators.

These results are applied to the problem considered in Chapter 2 i.e. where the perturbation is due to a charged point particle in a classical rectilinear orbit. By these means we are able to include the contributions from all the multipoles in the expansion of the potential $|\underline{r}'-\underline{r}|^{-1}$ whereas before we only took into account the dipole and quadrupole contributions.

§ 3.2. Transition Probabilities. General Formulae.

Consider an atomic system which has an unperturbed Hamiltonian H to which a time dependent perturbation V(t) is added. Then to the first order in the perturbation the probability that the system makes a transition from an initial state a to a final state b is

$$P_{ba} = \frac{1}{\hbar^2}\left|\int_{-\infty}^{\infty} V_{ba}(t)\, e^{ipt}\, dt\right|^2 \qquad (3.2.1)$$

(Landau and Lifshitz, (1958), §§40, 41) where

$$V_{ba}(t) = \langle \Psi_b | V(t) | \Psi_a \rangle$$

and the wave functions Ψ_a, Ψ_b are time-independent eigenfunctions of the unperturbed Hamiltonian i.e.

$$H\Psi_n = E_n \Psi_n.$$

Also $$p = \frac{\Delta E}{\hbar} = \frac{|E_a - E_b|}{\hbar} .$$

We specify the different states of the system by the quantum numbers $(\Gamma LSJM_J)$ or $(\Gamma LM_L SM_S)$ where L, S and J are respectively the total orbital, the spin and the total angular momentum quantum numbers of the atomic system ($\underline{J}=\underline{L}+\underline{S}$) and M_L, M_S and M_J are the values of the z-components of the angular momentum vectors specified by the subscript in each case. Γ denotes the remaining quantum numbers of the system (e.g. energy, parity, principal quantum number, etc.)

If we consider transitions between two energy levels of the system we must average over all degenerate levels of the initial state and sum over all degenerate levels of the final state. Thus in the $(\Gamma LSJM_J)$ scheme (3.2.1) is replaced by

$$P_{ba} = \frac{1}{\hbar^2(2J_a+1)} \sum_{M_{J_a} M_{J_b}} \left| \int_{-\infty}^{\infty} \langle \Psi_b(\Gamma_b L_b S_b J_b M_{J_b}) | V(t) | \Psi_a(\Gamma_a L_a S_a J_a M_{J_a}) \rangle e^{ipt}\, dt \right|^2 \qquad (3.2.2)$$

In order to obtain the averaged probabilities we use the opposite procedure to that used in §2.3. If Σ denotes the laboratory frame and Σ' the internal frame then we average over all possible orientations of Σ' keeping Σ fixed. Suppose the orientation of Σ' with respect to Σ is described by the Euler angles α,β,γ. In the frame Σ' the atomic system is described by wave functions $\Psi'(\Gamma LSJM'_J)$. The prime denotes that the spatial coordinates upon which Ψ' depends are defined with respect to Σ'. Then if $P_{ba}(\alpha\beta\gamma)$ denotes the transition probability for the atomic system calculated via the wave functions Ψ' we define the averaged probability as

$$\overline{P}_{ba} = \frac{1}{8\pi^2} \int_0^{2\pi}\int_0^{\pi}\int_0^{2\pi} P_{ba}(\alpha\beta\gamma)\, d\alpha \sin\beta\, d\beta\, d\gamma . \qquad (3.2.3)$$

We can express the wave functions $\bar{\Psi}'$ in terms of the unprimed wave functions $\bar{\Psi}$ whose spatial coordinates are defined with respect to Σ by

$$\Psi'(\Gamma LSJM_J') = D(\alpha\beta\gamma)\Psi(\Gamma LSJM_J')$$
$$= \sum_{M_J=-J}^{J} \mathcal{D}^{(J)}_{M_J M_J'}(\alpha\beta\gamma)\Psi(\Gamma LSJM_J) \qquad (3.2.4)$$

(E 4.1.5). $D(\alpha\beta\gamma)$ is the rotation operator which rotates Σ into Σ' and the $\mathcal{D}^{(J)}_{M_J M_J'}$ are the matrix elements of this operator in an angular momentum representation i.e.

$$\mathcal{D}^{(J)}_{M_J M_J'}(\alpha\beta\gamma) = \langle \Psi(JM_J)|D(\alpha\beta\gamma)|\Psi(JM_J')\rangle$$

(E4.1.10). Hence from (3.2.2) we have

$$P_{ba}(\alpha\beta\gamma) = \frac{1}{\hbar^2(2J_a+1)} \sum_{M_{J_a}' M_{J_b}'} \left| \int_{-\infty}^{\infty} \langle \Psi_b'(\Gamma_b L_b S_b J_b M_{J_b}')| V(t)| \Psi_a'(\Gamma_a L_a S_a J_a M_{J_a}')\rangle e^{ipt}\, dt \right|^2$$

which becomes using (3.2.4)

$$P_{ba}(\alpha\beta\gamma) = \frac{1}{\hbar^2(2J_a+1)} \sum_{M_{J_a}' M_{J_b}'} \sum_{\substack{M_{J_a} M_{J_b} \\ M_{J_a}'' M_{J_b}''}} \mathcal{D}^{(J_b)*}_{M_{J_b} M_{J_b}'}(\alpha\beta\gamma)\mathcal{D}^{(J_a)}_{M_{J_a} M_{J_a}'}(\alpha\beta\gamma)$$

$$\times \mathcal{D}^{(J_b)}_{M_{J_b}'' M_{J_b}'}(\alpha\beta\gamma)\mathcal{D}^{(J_a)*}_{M_{J_a}'' M_{J_a}'}(\alpha\beta\gamma)\left(\mathcal{M}^{J_a J_b}_{M_{J_a} M_{J_b}}\right)\left(\mathcal{M}^{J_a J_b}_{M_{J_a}'' M_{J_b}''}\right)^* \qquad (3.2.5)$$

where

$$\mathcal{M}^{J_a J_b}_{M_{J_a} M_{J_b}} = \int_{-\infty}^{\infty} \langle \Psi_b(\Gamma_b L_b S_b J_b M_{J_b})| V(t)| \Psi_a(\Gamma_a L_a S_a J_a M_{J_a})\rangle e^{ipt}\, dt \qquad (3.2.6)$$

and we have used the fact that the $\mathcal{D}^{(J)}_{MM'}$ are independent of space, spin and time coordinates i.e. they depend only on $(\alpha\beta\gamma)$. Hence from (3.2.3) the averaged probabilities are given by

$$\bar{P}_{ba} = \frac{1}{\hbar^2(2J_a+1)} \sum_{\substack{M_{J_a} M_{J_a}' M_{J_a}'' \\ M_{J_b} M_{J_b}' M_{J_b}''}} \sum_{J_c M_{J_c} M_{J_c}'} (2J_c+1) \begin{pmatrix} J_a & J_b & J_c \\ M_{J_a} & M_{J_b}'' & M_{J_c} \end{pmatrix}$$

$$\times \begin{pmatrix} J_a & J_b & J_c \\ M_{J_a}'' & M_{J_b} & M_{J_c} \end{pmatrix} \begin{pmatrix} J_a & J_b & J_c \\ M_{J_a}' & M_{J_b}' & M_{J_c}' \end{pmatrix}^2 \left(\mathcal{M}^{J_a J_b}_{M_{J_a} M_{J_b}}\right)\left(\mathcal{M}^{J_a J_b}_{M_{J_a}'' M_{J_b}''}\right)^*$$

where we have used the results of Appendix B. Summing firstly over M'_{J_a} and M'_{J_b} noting (E 3.7.8), secondly over M'_{J_c} which merely reintroduces the factor $(2J_c+1)$, thirdly over J_c and M_{J_c} noting (E 3.7.7) and finally over M''_{J_a} and M''_{J_b} we obtain

$$\bar{P}_{ba} = \frac{1}{\hbar^2(2J_a+1)} \sum_{M_{Ja} M_{Jb}} \left| \mathcal{M}^{J_a J_b}_{M_{Ja} M_{Jb}} \right|^2 . \qquad (3.2.7)$$

We make two points before proceeding further. Firstly (3.2.7) is valid for a wider class of expressions than first order transition probabilities. Thus if

$$A(\alpha\beta\gamma) = \sum_{M'_{J_a} M'_{J_b}} | \langle \Psi'_b(\Gamma_b L_b S_b J_b M'_{J_b}) | O | \Psi'_a(\Gamma_a L_a S_a J_a M'_{J_a}) \rangle |^2$$

where O is any operator defined in Σ, the averaged quantity $\bar{A}$ is given by

$$\bar{A} = \frac{1}{8\pi^2} \int_0^{2\pi} \int_0^{\pi} \int_0^{2\pi} A(\alpha\beta\gamma)\, d\alpha \sin\beta\, d\beta\, d\gamma$$

$$= \sum_{M_{Ja} M_{Jb}} | \langle \Psi_b(\Gamma_b L_b S_b J_b M_{Jb}) | O | \Psi_a(\Gamma_a L_a S_a J_a M_{Ja}) \rangle |^2 . \qquad (3.2.8)$$

Such quantities appear for example in radiative transition probabilities (Condon and Shortley, (1963), Ch.4.)

Secondly we may interpret the result (3.2.7) from another point of view. Defining all quantities in the frame Σ we may write the wave function for any state with quantum numbers (ΓLSJ) but unspecified M_J as

$$\bar{\Psi} = \sum_{M_J=-J}^{J} C_{M_J} \bar{\Psi}(\Gamma LSJ M_J) \qquad (3.2.9)$$

where the C_{M_J} are constants such that $|C_{M_J}|^2$ represents the probability that a measurement of the z-component of $\underline{J}$ yields a result M_J provided that the condition $\sum_{M_J} |C_{M_J}|^2 = 1$ holds. Thus these coefficients can take any (complex)

value allowed by the condition $0 \leq |C_{M_J}|^2 \leq 1$ plus the above condition on their sum. Averaging over all possible values of the C_{M_J} in an expression like (3.2.2) then gives a quantity corresponding to experimental measurements. In this context (3.2.4) gives the probability distribution of the C_{M_J} corresponding to a spherically symmetric distribution of the direction of the vector $\underline{J}$ by expressing the C_{M_J} in terms of the $\mathcal{D}^{(J)}_{MM'}(\alpha\beta\gamma)$.

Alternately measurements of the z-component of $\underline{J}$ for a large number of randomly oriented atoms will yield an average value for $|C_{M_J}|^2$ of $(2J+1)^{-1}$. Using these values for C_{M_J} in(3.2.9) to represent an "average" atom and allowing for the fact that there are $2J_b+1$ final states for every initial state will yield the result (3.2.7) (or (3.2.8)). This line of argument, while intuitively simple, lacks the rigour of our derivation of (3.2.7).

We can express the transition probabilities in the (LM_LSM_S) scheme as follws. From (E 3.5.1)

$$\Psi(\Gamma LSJM_J) = \sum_{M_L M_S} \Psi(\Gamma LM_L SM_S)(LM_L SM_S | LSJM_J) \qquad (3.2.10)$$

where $(LM_L SM_S | LSJM_J)$ are the vector-coupling coefficients and are real i.e. $(LM_L SM_S | LSJM_J) = (LSJM_J | LM_L SM_S)$. Thus from (3.2.6)

$$\mathcal{M}^{J_a J_b}_{M_{J_a} M_{J_b}} = \sum_{\substack{M_{La} M_{Sa} \\ M_{Lb} M_{Sb}}} (L_b S_b J_b M_{J_b} | L_b M_{Lb} S_b M_{Sb}) \times (L_a M_{La} S_a M_{Sa} | L_a S_a J_a M_{Ja}) \mathcal{M}^{L_a S_a, L_b S_b}_{M_{La} M_{Sa}, M_{Lb} M_{Sb}} \qquad (3.2.11)$$

where

$$\mathcal{M}^{L_a S_a, L_b S_b}_{M_{La} M_{Sa}, M_{Lb} M_{Sb}} = \int_{-\infty}^{\infty} \langle \Psi_b(\Gamma_b L_b M_{Lb} S_b M_{Sb} | V(t)) | \Psi_a(\Gamma_a L_a M_{La} S_a M_{Sa}) \rangle e^{ipt} dt. \qquad (3.2.12)$$

If we assume there is no spin-orbit ($\underline{L}.\underline{S}$) coupling then the degenerate states of a given energy level consist of those with all possible quantum numbers (JM_J) consistent with given values of L and S. Hence when we average over all degenerate initial levels and sum over all degenerate final levels (3.2.2) will have the factor $(2J_a+1)^{-1}$ replaced by $(2L_a+1)^{-1}(2S_a+1)^{-1}$ and will include summation over J_a and J_b. Hence (3.2.7) becomes

$$\bar{P}^{RS}_{ba} = \frac{1}{\hbar^2(2L_a+1)(2S_a+1)} \sum_{\substack{J_a J_b \\ M_{J_a} M_{J_b}}} \left| \mathcal{M}^{J_a J_b}_{M_J M_{J_a} M_{J_b}} \right|^2$$

$$= \frac{1}{\hbar^2(2L_a+1)(2S_a+1)} \sum_{\substack{J_a J_b \\ M_{J_a} M_{J_b}}} \sum_{\substack{M_{L_a} M_{S_a} \\ M_{L_b} M_{S_b}}} \sum_{\substack{M'_{L_a} M'_{S_a} \\ M'_{L_b} M'_{S_b}}}$$

$$\times (L_b S_b J_b M_{J_b} | L_b M_{L_b} S_b M_{S_b})(L_a M_{L_a} S_a M_{S_a} | L_a S_a J_a M_{J_a})$$

$$\times (L_b M'_{L_b} S_b M'_{S_b} | L_b S_b J_b M_{J_b})(L_a S_a J_a M_{J_a} | L_a M'_{L_a} S_a M'_{S_a})$$

$$\times \left(\mathcal{M}^{L_a S_a, L_b S_b}_{M_{L_a} M_{S_a}, M_{L_b} M_{S_b}} \right) \left(\mathcal{M}^{L_a S_a, L_b S_b}_{M'_{L_a} M'_{S_a}, M'_{L_b} M'_{S_b}} \right)^* \qquad (3.2.13)$$

where the superscript RS indicates the Russel-Saunders approximation of neglecting ($\underline{L}.\underline{S}$) coupling (Condon and Shortley, (1963), Ch.7). Summing over $J_a M_{J_a}$ and $J_b M_{J_b}$ using (E 3.5.3), (3.2.13) becomes

$$\bar{P}^{RS}_{ba} = \frac{1}{\hbar^2(2L_a+1)(2S_a+1)} \sum_{\substack{M_{L_a} M_{S_a} \\ M_{L_b} M_{S_b}}} \left| \mathcal{M}^{L_a S_a, L_b S_b}_{M_{L_a} M_{S_a}, M_{L_b} M_{S_b}} \right|^2 . \qquad (3.2.14)$$

§ 3.3. Perturbation Operators in Terms of Spherical Tensor Operators.

In the following investigation we shall restrict ourselves to the case where the perturbing potential operator V(t) is expressible in terms of a sum of spherical tensor operators. Examples of this type of operator are the

position vector $\underline{r}$ and linear momentum $\underline{p}$ of a particle, the angular momentum $\underline{J}$ of a system, multipole moments of a system and any operator which may be expressed in terms of the spherical harmonics $Y_{\ell m}(\theta,\varphi)$. Thus the restriction to these operators is by no means a severe one.

Under a rotation of the frame of reference given by the operator $D(\alpha\beta\gamma)$ any operator O will be transformed into an operator O' where

$$O' = D(\alpha\beta\gamma)OD^{-1}(\alpha\beta\gamma) .$$

A spherical tensor operator of rank λ, $\underline{T}(\lambda)$ is a set of $2\lambda+1$ operators $T(\lambda\mu)$, $(\mu=-\lambda, -\lambda+1, \ldots, \lambda-1, \lambda)$, which transform under rotations of the frame of reference as follows:

$$D(\alpha\beta\gamma)T(\lambda\mu)D^{-1}(\alpha\beta\gamma) = \sum_{\mu'=-\lambda}^{\lambda} T(\lambda\mu')\,\mathcal{D}^{(\lambda)}_{\mu'\mu}(\alpha\beta\gamma) \qquad (3.3.1)$$

(see Edmonds, (1957), §5.2). We therefore assume that

$$V(t) = \sum_{k\lambda\mu} C_{k\lambda\mu} T_k(\lambda\mu) \qquad (3.3.2)$$

where the $T_k(\lambda\mu)$ are spherical tensor operators of rank λ which act on the atomic system. The subscript k distinguishes between different operators with the same rank. The quantities $C_{k\lambda\mu}$ represent those parts of V(t) which do not operate on the atomic system i.e. they depend only on the time and on those variables upon which the atomic wave functions do not depend. In other words we may take the $C_{k\lambda\mu}$ outside any matrix element based on the atomic wave functions.

In this case our averaged transition probabilities become

$$\bar{P}_{ba} = \frac{1}{\hbar^2(2J_a+1)} \sum_{M_{J_a}M_{J_b}} \sum_{\substack{k\lambda\mu \\ k'\lambda'\mu'}} \left(\eta^{J_a J_b}_{M_{J_a}M_{J_b}}(k\lambda\mu)\right)\left(\eta^{J_a J_b}_{M_{J_a}M_{J_b}}(k'\lambda'\mu')\right)^{*} \qquad (3.3.3)$$

using (3.3.2) and (3.2.7) where

$$\eta^{J_a J_b}_{M_{J_a}M_{J_b}}(k\lambda\mu) = \int_{-\infty}^{\infty} e^{ipt} C_{k\lambda\mu} \langle \Psi_b(\Gamma_b L_b S_b J_b M_{J_b}) | T_k(\lambda\mu) | \Psi_a(\Gamma_a L_a S_a J_a M_{J_a}) \rangle dt . \qquad (3.3.4)$$

Making use of the Wigner-Eckart factorization theorem we may write

$$\langle \Psi_b(\Gamma_b L_b S_b J_b M_{J_b}) | T_k(\lambda\mu) | \Psi_a(\Gamma_a L_a S_a J_a M_{J_a}) \rangle$$

$$= (-1)^{J_b - M_{J_b}} \begin{pmatrix} J_b & \lambda & J_a \\ -M_{J_b} & \mu & M_{J_a} \end{pmatrix} (\Gamma_b L_b S_b J_b \| \underline{\underline{T}}_k(\lambda) \| \Gamma_a L_a S_a J_a) \tag{3.3.5}$$

(E 5.4.1) where the reduced matrix elements $(\Gamma_b L_b S_b J_b \| \| \underline{\underline{T}}_k(\lambda) \| \Gamma_a L_a S_a J_a)$ are independent of M_{J_a}, M_{J_b} and μ and are defined by (3.3.5).

By substituting (3.3.5) into (3.3.3) and summing over $M_{J_a} M_{J_b}$ noting (E 3.7.8) we obtain

$$\bar{P}_{ba} = \frac{1}{\hbar^2 (2J_a + 1)} \sum_{\lambda\mu} \frac{1}{2\lambda + 1} |N_{J_a J_b}(\lambda\mu)|^2 \tag{3.3.6}$$

where

$$N_{J_a J_b}(\lambda\mu) = \sum_k \int_{-\infty}^{\infty} e^{ipt} C_{k\lambda\mu} \times (\Gamma_b L_b S_b J_b \| \underline{\underline{T}}_k(\lambda) \| \Gamma_a L_a S_a J_a) dt \,. \tag{3.3.7}$$

If the operators $T_k(\lambda\mu)$ operate only on the space part of the coupled system $(LSJM_J)$ i.e. if they are independent of the spin then by (E 7.1.7) we can write

$$(\Gamma_b L_b S_b J_b \| \underline{\underline{T}}_k(\lambda) \| \Gamma_a L_a S_a J_a)$$

$$= (-1)^{L_b + S_a + J_a + \lambda} \delta_{S_a S_b} \sqrt{(2J_a + 1)(2J_b + 1)}$$

$$\times \begin{Bmatrix} L_b & J_b & S_a \\ J_a & L_a & \lambda \end{Bmatrix} (\Gamma_b L_b \| \underline{\underline{T}}_k(\lambda) \| \Gamma_a L_a) \tag{3.3.8}$$

where $\begin{Bmatrix} L_b & J_b & S_a \\ J_a & L_a & \lambda \end{Bmatrix}$ are the Wigner 6-j symbols and the reduced matrix element on the r.h.s. of (3.3.8) is defined in the $(\Gamma L M_L S M_S)$ scheme analogously to (3.3.5) i.e. by

$$\langle \Psi_b(\Gamma_b L_b M_{L_b} S_b M_{S_b} | T_k(\lambda\mu) | \Psi_a(\Gamma_a L_a M_{L_a} S_a M_{S_a}) \rangle =$$

$$= \delta_{S_a S_b} \delta_{M_{S_a} M_{S_b}} (-1)$$

$$= \delta_{S_a S_b}\,\delta_{M_{S_a} M_{S_b}}\,(-1)^{L_b - M_{L_b}} \begin{pmatrix} L_b & \lambda & L_a \\ -M_{L_b} & \mu & M_{L_a} \end{pmatrix}$$

$$\times (\Gamma_b L_b \| \underline{\underline{T}}_k(\lambda) \| \Gamma_a L_a) . \qquad (3.3.9)$$

Thus (3.3.6) becomes

$$\bar{P}_{ba} = \frac{1}{\hbar^2 (2J_a+1)} \sum_{\lambda\mu} \frac{1}{2\lambda+1} \Big| \sum_k \int_{-\infty}^{\infty} e^{ipt} C_{k\lambda\mu}$$

$$\times (\Gamma_b L_b \| \underline{\underline{T}}_k(\lambda) \| \Gamma_a L_a) dt \Big|^2 \delta_{S_a S_b} (2J_a+1)$$

$$\times (2J_b+1) \begin{Bmatrix} L_b & J_b & S_a \\ J_a & L_a & \lambda \end{Bmatrix}^2 . \qquad (3.3.10)$$

Assuming no spin-orbit coupling we replace $(2J_a+1)^{-1}$ by $(2L_a+1)^{-1}(2S_a+1)^{-1}$ and sum over $J_a J_b$ in (3.3.10) (see §3.2). Using (E 6.2.9) noting (E 6.2.4) and (E 6.2.5) we obtain

$$\bar{P}^{RS}_{ba} = \frac{1}{\hbar^2 (2L_a+1)(2S_a+1)} \sum_{\lambda\mu} \frac{1}{2\lambda+1} \Big| \sum_k \int_{-\infty}^{\infty} e^{ipt} C_{k\lambda\mu}$$

$$\times (\Gamma_b L_b \| \underline{\underline{T}}_k(\lambda) \| \Gamma_a L_a) dt \Big|^2 \sum_{J_a} \frac{2J_a+1}{2L_a+1}$$

$$= \frac{1}{\hbar^2 (2L_a+1)} \sum_{\lambda\mu} \frac{1}{(2\lambda+1)} \Big| \sum_k \int_{-\infty}^{\infty} e^{ipt} C_{k\lambda\mu}$$

$$\times (\Gamma_b L_b \| \underline{\underline{T}}_k(\lambda) \| \Gamma_a L_a) dt \Big|^2 \qquad (3.3.11)$$

since

$$\sum_{J_a = |L_a - S_a|}^{L_a + S_a} (2J_a+1) = (2L_a+1)(2S_a+1).$$

We stress the fact that (3.3.11) is only valid if the $T_k(\lambda\mu)$ are spin independent.

Note that (3.3.11) could have been obtained directly from (3.2.14). Substituting (3.3.2) into (3.2.14) we have

$$\bar{P}^{RS}_{ba} = \frac{1}{\hbar^2 (2L_a+1)(2S_a+1)} \sum_{\substack{M_{L_a} M_{S_a} \\ M_{L_b} M_{S_b}}} \sum_{\substack{k\lambda\mu \\ k'\lambda'\mu'}} \left(\eta^{L_a S_a, L_b S_b}_{M_{L_a} M_{S_a}, M_{L_b} M_{S_b}} (k\lambda\mu) \right)$$

$$\left(\eta^{L_a S_a, L_b S_b}_{M_{L_a} M_{S_a}, M_{L_b} M_{S_b}} (k'\lambda'\mu') \right)^* \qquad (3.3.12)$$

where

$$\eta^{L_a S_a, L_b S_b}_{M_{L_a} M_{S_a}, M_{L_b} M_{S_b}}(k\lambda\mu) = \int_{-\infty}^{\infty} e^{ipt} C_{k\lambda\mu} \times \langle \Psi_b(\Gamma_b L_b M_{L_b} S_b M_{S_b}) | T_k(\lambda\mu) | \Psi_a(\Gamma_a L_a M_{L_a} S_a M_{S_a}) \rangle dt \quad . \quad (3.3.13)$$

If we again assume that $T_k(\lambda\mu)$ is spin independent then using (3.3.9), (3.3.13) becomes identical with (3.3.11) when (3.3.13) is summed over $M_{S_a} M_{S_b}$ and $M_{L_a} M_{L_b}$ noting (E 3.7.8).

§3.4. Transition Probabilities for Atomic Systems due to Electron Impact (Semi-Classical).

We apply our formulae (3.3.6) and (3.3.11) to the problem treated in Ch.2, i.e. where the perturbation of the atomic system is due to a classical electron in a rectilinear orbit. Hence from (2.2.1) using (2.2.4) and (2.3.2)

$$V(t) = \frac{Ze^2}{|\underline{r}'(t)|} - \sum_{n=1}^{N} \frac{e^2}{|\underline{r}'(t) - \underline{r}_n|}$$

$$= \frac{Ze^2}{|\underline{r}'(t)|} - e^2 \sum_{n=1}^{N} \sum_{\lambda=0}^{\infty} \sum_{\mu=-\lambda}^{\lambda} \frac{4\pi}{2\lambda+1} \gamma_\lambda(r; r_n) \times Y_{\lambda\mu}(\theta_n, \varphi_n) Y^*_{\lambda\mu}(\Theta, 0) \quad (3.4.1)$$

where the coordinates of the nth atomic electron are $(r_n, \theta_n, \varphi_n)$ and of the incident electron are $(r; \Theta, 0)$ since we are in the laboratory frame of reference, (see §2.3). Also

$$\gamma_\lambda(r; r_n) = H(r' - r_n) \frac{r_n^\lambda}{r'^{\lambda+1}} + H(r_n - r') \frac{r'^\lambda}{r_n^{\lambda+1}} \quad (3.4.2)$$

where $H(x)$ is the Heaviside step function defined so that

$$H(x) = \begin{cases} 0 \text{ for } x < 0 \\ 1 \text{ for } x \geq 0 \end{cases}$$

i.e. it is the integral of the Dirac delta function

$$H(x) = \int_{-\infty}^{x} \delta(x') dx'.$$

Now $r_n^{\lambda} Y_{\lambda\mu}(\theta_n,\varphi_n)$ and $r_n^{-(\lambda+1)} Y_{\lambda\mu}(\theta_n,\varphi_n)$ are spherical tensor operators of rank λ since they satisfy (3.3.1) (see (E 4.1.4)) so we put

$$T_{2n-1}(\lambda\mu) = -H(r'-r_n) r_n^{\lambda} Y_{\lambda\mu}(\theta_n,\varphi_n) + \frac{\delta_{o\lambda} Z}{4\pi},$$

$$T_{2n}(\lambda\mu) = -H(r_n-r') \frac{Y_{\lambda\mu}(\theta_n,\varphi_n)}{r_n^{\lambda+1}} \qquad (3.4.3)$$

and

$$C_{2n-1,\lambda\mu} = \frac{4\pi e^2}{(2\lambda+1)} \frac{Y^*_{\lambda\mu}(\Theta,0)}{r'^{\lambda+1}},$$

$$C_{2n,\lambda\mu} = \frac{4\pi e^2}{2\lambda+1} r'^{\lambda} Y^*_{\lambda\mu}(\Theta,0). \qquad (3.4.4)$$

Thus (3.4.1) becomes

$$V(t) = \sum_{k=1}^{2N} \sum_{\lambda=0}^{\infty} \sum_{\mu=-\lambda}^{\lambda} C_{k\lambda\mu} T_k(\lambda\mu) \qquad (3.4.5)$$

which is of the form (3.3.2). Hence we can use (3.3.6) or (3.3.11) to evaluate transition probabilities for a given impact parameter R_i.

To evaluate $(\Gamma_b L_b S_b J_b \| \underline{\underline{T}}_k(\lambda) \| \Gamma_a L_a S_a J_a)$ and $(\Gamma_b L_b \| \underline{\underline{T}}_k(\lambda) \| \Gamma_a L_a)$ we use (3.3.5) and (3.3.9). Since we assume Ψ_a and Ψ_b are completely antisymmetrized the reduced matrix elements of $\underline{\underline{T}}_{2n-1}(\lambda)$ and $\underline{\underline{T}}_{2n}(\lambda)$ are independent of n as are the coefficients $C_{2n-1,\lambda\mu}$ and $C_{2n,\lambda\mu}$.

We now assume that we can put $H(r'-r_n)=1$ and $H(r_n-r')=0$ in (3.4.3). This is identical to the approximation $r_<=r_n$, $r_>=r'$ made in §2.2. The effect of this approximation will be discussed in Ch.4. Thus

$$(\Gamma_b L_b S_b J_b \| \underline{\underline{T}}_{2n-1}(\lambda) \| \Gamma_a L_a S_a J_a) = (\Gamma_b L_b S_b J_b \| \underline{\underline{T}}(\lambda) \| \Gamma_a L_a S_a J_a)$$

$$(\Gamma_b L_b \| \underline{\underline{T}}_{2n-1}(\lambda) \| \Gamma_a L_a) = (\Gamma_b L_b \| \underline{\underline{T}}(\lambda) \| \Gamma_a L_a)$$

$$(\Gamma_b L_b S_b J_b \| \underline{\underline{T}}_{2n}(\lambda) \| \Gamma_a L_a S_a J_a) = 0$$

$$(\Gamma_b L_b \| \underline{\underline{T}}_{2n}(\lambda) \| \Gamma_a L_a) = 0$$

where the tensor operator $\underline{\underline{T}}(\lambda)$ has components

$$T(\lambda\mu) = -r^{\lambda} Y_{\lambda\mu}(\theta,\varphi) + \frac{Z\delta_{o\lambda}}{4\pi}$$

where (r,θ,φ) are the coordinates of any atomic electron. Note that the reduced matrix elements of $\underline{\underline{T}}(0)$ are zero since we assume that Ψ_a and Ψ_b are orthogonal and $\underline{\underline{T}}(0)$ is independent of the coordinates of the atomic electrons. Hence we find that (3.3.6) becomes

$$\bar{P}_{ba}(R_i) = \frac{(4\pi)^2 e^4 N^2}{\hbar^2 (2J_a+1)} \sum_{\lambda=1}^{\infty} \frac{1}{(2\lambda+1)^3} \times |(\Gamma_b L_b S_b J_b \| \underline{\underline{T}}(\lambda) \| \Gamma_a L_a S_a J_a)|^2 \sum_{\mu=-\lambda}^{\lambda} |T^{\lambda\mu}(R_i)|^2 \quad (3.4.6a)$$

and (3.3.11) becomes

$$\bar{\bar{P}}^{RS}_{ba}(R_i) = \frac{(4\pi)^2 e^4 N^2}{\hbar^2 (2L_a+1)} \sum_{\lambda=1}^{\infty} \frac{1}{(2\lambda+1)^3} |(\Gamma_b L_b \| \underline{\underline{T}}(\lambda) \| \Gamma_a L_a)|^2 \times \sum_{\mu=-\lambda}^{\lambda} |T^{\lambda\mu}(R_i)|^2 \quad (3.4.6b)$$

where we have replaced the sum over k by N and defined $T^{\lambda\mu}(R_i)$ as in (2.3.6). This latter expression is evaluated in Appendix A.

If we give to those states of the atomic system which in Ch.2 we have labelled i and j the quantum numbers $(\Gamma_a L_a M_{L_a})$ and $(\Gamma_b L_b M_{L_b})$ respectively then $\omega_i = (2L_a+1)$ and (2.3.8) becomes

$$R^{(\lambda)}_{ji} = \sum_{M_{La} M_{Lb}} \sum_{\mu} |(\Gamma_b L_b \| \underline{\underline{T}}(\lambda) \| \Gamma_a L_a)|^2 \begin{pmatrix} L_b & \lambda & L_a \\ -M_{L_b} & \mu & M_{La} \end{pmatrix}^2$$
$$= |(\Gamma_b L_b \| \underline{\underline{T}}(\lambda) \| \Gamma_a L_a)|^2$$

using (E 5.4.1) and (E 3.7.8). Hence (2.3.7) and (3.4.6b) are identical except that the sum over λ extends from 1 to ∞ in the latter case instead of only from 1 to 2 as in the former. In other words we have extended the work of Ch.2 to include contributions from all the multipoles of the perturbing potential (except possibly the monopole).

The analysis of §§2.4 and 2.5 is valid for all values of λ and μ and hence we can immediately write down the cross section derived from (3.4.6b) by replacing in (2.5.6) $R_{ji}^{(\lambda)}$ by $|(\Gamma_b L_b \| \underline{\underline{T}}(\lambda) \| \Gamma_a L_a)|^2$, ω_i by $2L_a+1$ and by extending the sum over λ to ∞. That is, the formula for the cross section now reads

$$Q^{RS}(a\to b)=\frac{64\pi N^2}{(2L_a+1)}\frac{W}{W_i}\left(\frac{I_H}{\Delta E}\right)^2\sum_{\lambda=1}^{\infty}\frac{1}{(2\lambda+1)^2}$$
$$\times\frac{|(\Gamma_b L_b \| \underline{\underline{T}}(\lambda) \| \Gamma_a L_a)|^2}{a_0^{2\lambda}}\left(\frac{\Delta E^2}{4I_H W}\right)^{\lambda}\sum_{\mu=-\lambda}^{\lambda}\frac{\chi_\mu(\beta_0)}{(\lambda-\mu)!(\lambda+\mu)!}(\pi a_0^2). \tag{3.4.7}$$

In using (2.5.6) in this manner we have required that $\bar{P}_{ba}^{RS}(R_i)$ satisfy the reciprocity condition (§2.4).

§ 3.5. Evaluation of the Reduced Matrix Elements for Hydrogen.

In order to use (3.4.7) to calculate cross sections a knowledge of the values of the reduced matrix elements is needed. Since exact wave functions are only available for hydrogenic systems it is not possible to calculate these matrix elements exactly in the great majority of cases. (There is a possibility of obtaining values for some of these matrix elements from experimental data. For instance the matrix element for $\lambda=1$ is related to the oscillator strength for the particular transition in question. Cf. Seaton, (1962)). However values of these matrix elements sufficiently accurate for our purposes should be obtainable by the use of good approximate wave functions.

The case of hydrogenic systems is particularly important though since we can calculate cross sections via (3.4.7) without making additional approximations. Thus comparison with experiment and with other theoretical calculations

will give us some idea of the validity and usefulness of our results. There is the additional advantage that a great many theoretical calculations already exist for this particular system making comparisons easy. For these reasons we derive explicit formulae for the matrix elements which we require using hydrogenic wave functions.

The formulae of this section can be extended in a straightforward manner to arbitrary atomic systems if separable wave functions with central-field type one-electron functions are used to represent the system (e.g. Roothaan Hartree-Fock functions). In this case the one-electron functions are of the same form as for the hydrogenic case and the hydrogenic formula will be applicable in a somewhat modified form. Note that since the tensor operators $T(\lambda\mu)$ are one-electron operators only one electron can have a different set of quantum numbers in the initial and final states.

We write the (spin-independent) hydrogenic wave functions as

$$\psi_{n\ell m}(\underline{r}) = R_{n\ell}(r)Y_{\ell m}(\theta,\varphi) \qquad (3.5.1)$$

where n is the principal, ℓ the orbital angular momentum and m the magnetic quantum numbers. Using (3.3.9) with $T_k(\lambda\mu) = -r^\lambda Y_{\lambda\mu}(\theta,\varphi)$ we have

$$\begin{aligned}
&(-1)^{\ell_b - m_b}\begin{pmatrix} \ell_b & \lambda & \ell_a \\ -m_b & \mu & m_a \end{pmatrix}(n_b\ell_b \| \underline{\underline{T}}(\lambda) \| n_a\ell_a) \\
&= \int R^*_{n_b\ell_b}(r)\, Y^*_{\ell_b m_b}(\theta,\varphi)\left(-r^\lambda Y_{\lambda\mu}(\theta,\varphi)\right) \\
&\quad \times R_{n_a\ell_a}(r)\, Y_{\ell_a m_a}(\theta,\varphi)\, \underline{dr} \\
&= -\langle n_b\ell_b | r^\lambda | n_a\ell_a\rangle \int_0^{2\pi}\int_0^{\pi} Y^*_{\ell_b m_b}(\theta,\varphi) \\
&\quad \times Y_{\lambda\mu}(\theta,\varphi)\, Y_{\ell_a m_a}(\theta,\varphi)\, \sin\theta\, d\theta\, d\varphi
\end{aligned} \qquad (3.5.2)$$

where

$$\langle n_b l_b | r^\lambda | n_a l_a \rangle = \int_0^\infty R^*_{n_b l_b}(r)\, R_{n_a l_a}(r)\, r^{\lambda+2}\, dr. \tag{3.5.3}$$

Using (E 2.5.6) we have by (E 4.6.3)

$$\int_0^{2\pi}\int_0^{\pi} Y^*_{l_b m_b}(\theta,\varphi)\, Y_{\lambda\mu}(\theta,\varphi)\, Y_{l_a m_a}(\theta,\varphi) \sin\theta\, d\theta\, d\varphi$$

$$= (-1)^{m_b} \sqrt{\frac{(2l_b+1)(2\lambda+1)(2l_a+1)}{4\pi}} \begin{pmatrix} l_b & \lambda & l_a \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_b & \lambda & l_a \\ -m_b & \mu & m_a \end{pmatrix}. \tag{3.5.4}$$

Thus from (3.5.2) and (3.5.4)

$$|(n_b l_b || \underline{\underline{T}}(\lambda) || n_a l_a)|^2 = \frac{(2l_a+1)(2l_b+1)(2\lambda+1)}{4\pi} \begin{pmatrix} l_b & \lambda & l_a \\ 0 & 0 & 0 \end{pmatrix}^2 |\langle n_b l_b | r^\lambda | n_a l_a \rangle|^2 . \tag{3.5.5}$$

(We are assuming throughout that m can take only integral values as must be the case for hydrogenic systems. But our formulae in this section do not necessarily hold if one extended the analysis to operators which involve the spin of the system). Hence (3.4.7) becomes

$$Q^{RS}(a\to b) = 16\pi^2 (2l_a+1) \frac{W}{W_i} \left(\frac{I_H}{\Delta E}\right)^2 \cdot \sum_{\lambda=1}^{\infty} \frac{1}{2\lambda+1} \left(\frac{\Delta E^2}{4 I_H W}\right)^\lambda \begin{pmatrix} l_b & \lambda & l_a \\ 0 & 0 & 0 \end{pmatrix}^2 \frac{|\langle n_b l_b | r^\lambda | n_a l_a \rangle|^2}{a_0^{2\lambda}} \cdot \sum_{\mu=-\lambda}^{\lambda} \frac{\chi_\mu(\beta_0)}{(\lambda-\mu)!\,(\lambda+\mu)!} \quad (\pi a_0^2). \tag{3.5.6}$$

§ 3.6. An Alternate Derivation.

The results of the last section can be derived by a somewhat different method. This consists of interchanging the order of space and time integration in (3.2.12) i.e. of assuming

$$M^{L_a S_a, L_b S_b}_{M_{L_a} M_{S_a}, M_{L_b} M_{S_b}} = \langle \Psi_b(\Gamma_b L_b M_{L_b} S_b M_{S_b}) | \left| \int_{-\infty}^{\infty} e^{ipt} V(t) dt \right| \Psi_a(\Gamma_a L_a M_{L_a} S_a M_{S_a}) \rangle \qquad (3.6.1)$$

when V(t) is given by (2.2.1) and also of making the same approximations as before in order to carry out the space integration. While this change of order of integration is not necessarily justified we shall show that it does in fact give the same results as in §3.5.

The reasons for considering this method which we do not explicitly justify when we do in fact have a rigorous method for dealing with this particular problem is that we hope it might equally well be valid for potentials other than (2.2.1). The possible advantages of this method are that we do not make use of the fact that V(t) is a sum of spherical tensor operators (hence widening the field of possible potentials) and that the actual integrations involved in evaluating the expression for the cross section may be more easily carried out in this order.

As before in evaluating (3.6.1) using (2.2.1) for V(t) we can neglect the first term of (2.2.1) and replace the sum over k by N. We are left with the integral

$$I(\underline{r}) = \int_{-\infty}^{\infty} \left| \frac{e^{ipt}}{\underline{r}'(t)-\underline{r}} \right| dt \qquad (3.6.2)$$

to evaluate where $\underline{r}=(x,y,z)=(r,\theta,\varphi)$ is the coordinates of any one of the atomic electrons and $\underline{r}'(t)$ is given by

$$\underline{r}'(t) = \underline{R}_i + \underline{v}_i t \qquad (3.6.3)$$

with $\underline{R}_i \cdot \underline{v}_i = 0$.

The laboratory frame Σ is taken with its z-axis parallel to $\underline{v}_i$ and its x-axis parallel to $\underline{R}_i$ so that from (3.6.3)

$$|\underline{r}'(t)-\underline{r}| = \sqrt{(R_i-x)^2+y^2+(v_i t-z)^2} \qquad (3.6.4)$$

and (3.6.2) becomes

$$I(\underline{r}) = \int_{-\infty}^{\infty} \frac{\exp(\frac{ipu}{v_i} + \frac{ipz}{v_i})}{\sqrt{(a^2 + u^2)}} \frac{du}{v_i} \qquad (3.6.5)$$

where we have put

$$u = v_i t - z$$

and

$$a^2 = (R_i - x)^2 + y^2.$$

Since the denominator of the integrand is an even function of u, (3.6.5) becomes

$$I(\underline{r}) = \frac{2\exp(\frac{ipz}{v_i})}{v_i} \int_0^{\infty} \frac{\cos(\frac{pu}{v_i})}{\sqrt{(a^2+u^2)}} \, du$$

$$= \frac{2\exp(\frac{ipz}{v_i})}{v_i} K_o(\frac{ap}{v_i}) \qquad (3.6.6)$$

by Erdelyi et al, (1954), p.11. Now

$$K_o(\frac{ap}{v_i}) = K_o(\frac{p}{v_i}\sqrt{R_i^2 - 2R_i r\sin\theta\cos\varphi + r^2\sin^2\theta})$$

$$= K_o(\sqrt{\beta_i^2 - 2\beta_i\alpha_i\cos\varphi + \alpha_i^2})$$

where $\beta_i = \frac{pR_i}{v_i}$, $\alpha_i = \frac{pr}{v_i}\sin\theta$. If we make the assumption as before that $r' \geqslant r$ for all time t then $r^2 \leqslant R_i^2 + v_i^2 t^2$ for all t which implies that $\beta_i \geqslant \alpha_i$. Hence by Erdelyi et al, (1953), p.102

$$K_o(\frac{ap}{v_i}) = \sum_{\nu=-\infty}^{\infty} K_\nu(\beta_i) I_\nu(\alpha_i) e^{i\nu\varphi} \qquad (3.6.7)$$

where $I_\nu(\alpha_i)$ is the modified Bessel function of the first kind. We now assume that the wave functions in (3.6.1) are hydrogenic i.e. of the form (3.5.1). (We could also extend the analysis to other systems using separable wave functions). Thus (3.6.1) becomes putting $L_a = \ell_a$, $M_{L_a} = m_a$, etc.

$$\mathcal{M}^{L_a S_a, L_b S_b}_{M_{L_a} M_{S_a}, M_{L_b} M_{S_b}} = \delta_{S_a S_b} \delta_{M_{S_a} M_{S_b}} \frac{2Ne^2}{v_i} \sum_{\nu=-\infty}^{\infty} K_\nu(\beta_i)$$

$$\times \int R^*_{n_b l_b}(r) Y^*_{l_b m_b}(\theta,\varphi) \exp\left(\frac{ipr}{v_i}\cos\theta\right) I_\nu(\alpha_i) e^{i\nu\varphi}$$

$$\times R_{n_a l_a}(r) Y_{l_a m_a}(\theta,\varphi) \underline{dr} \,. \qquad (3.6.8)$$

Now by (E 2.5.6), (E 2.5.29) and (E 4.6.5)

$$Y^*_{l_b m_b}(\theta,\varphi) Y_{l_a m_a}(\theta,\varphi) = \sum_{\lambda\mu} (-1)^{m_b+\mu}$$

$$\times \sqrt{(2l_a+1)(2l_b+1)\frac{(\lambda-\mu)!}{(\lambda+\mu)!}} \frac{2\lambda+1}{4\pi} \begin{pmatrix} l_b & l_a & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_b & l_a & \lambda \\ -m_b & m_a & \mu \end{pmatrix}$$

$$\times P^\mu_\lambda(\cos\theta) e^{-i\mu\varphi} \qquad (3.6.9)$$

so that substituting (3.6.9) in (3.6.8) and integrating over φ we get

$$\mathcal{M}^{l_a S_a, l_b S_b}_{m_a M_{S_a}, m_b M_{S_b}} = \delta_{S_a S_b} \delta_{M_{S_a} M_{S_b}} \frac{e^2}{v_i} \sum_{\lambda\mu} (-1)^{m_b+\mu}$$

$$\times \sqrt{(2l_a+1)(2l_b+1)\frac{(\lambda-\mu)!}{(\lambda+\mu)!}} (2\lambda+1) \begin{pmatrix} l_b & l_a & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_b & l_a & \lambda \\ -m_b & m_a & \mu \end{pmatrix}$$

$$\times K_\mu(\beta_i) \int_0^\infty R^*_{n_b l_b}(r) R_{n_a l_a}(r) \mathcal{J}_{\lambda\mu}(r) r^2 dr \qquad (3.6.10)$$

where

$$\mathcal{J}_{\lambda\mu}(r) = \int_0^\pi P^\mu_\lambda(\cos\theta) e^{i\gamma_i\cos\theta} I_\mu(\alpha_i) \sin\theta \, d\theta \qquad (3.6.11)$$

and

$$\gamma_i = \frac{pr}{v_i}. \qquad (3.6.12)$$

$\mathcal{J}_{\lambda\mu}(r)$ is evaluated in Appendix C. Hence (3.2.14) becomes on summing over spin states and noticing that $S_a = S_b$ for hydrogenic systems

$$\bar{P}^{RS}_{ba} = \frac{e^4(2l_b+1)}{\hbar^2 v_i^2} \sum_{m_a m_b} \sum_{\substack{\lambda\mu \\ \lambda'\mu'}} (-1)^{\mu'+\mu} (2\lambda+1)(2\lambda'+1)$$

$$\times\sqrt{\frac{(\lambda-\mu)!\,(\lambda'-\mu')!}{(\lambda+\mu)!\,(\lambda'+\mu')!}}\begin{pmatrix} l_b & l_a & \lambda \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l_b & l_a & \lambda \\ -m_b & m_a & \mu \end{pmatrix}\begin{pmatrix} l_b & l_a & \lambda' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l_b & l_a & \lambda' \\ -m_b & m_a & \mu' \end{pmatrix}$$

$$\times K_\mu(\beta_i)\,K_{\mu'}(\beta_i)\int_0^\infty R^*_{n_b l_b}(r)\,R_{n_a l_a}(r)\,J_{\lambda\mu}(r)\,r^2\,dr$$

$$\times\int_0^\infty R_{n_b l_b}(r)\,R^*_{n_a l_a}(r)\,J^*_{\lambda'\mu'}(r)\,r^2\,dr$$

$$=\frac{4e^4(2l_b+1)}{\hbar^2 v_i^2}\sum_{\lambda\mu}\frac{1}{(2\lambda+1)}\left(\frac{\rho}{v_i}\right)^{2\lambda}\begin{pmatrix} l_a & l_b & \lambda \\ 0 & 0 & 0 \end{pmatrix}^2$$

$$\times\frac{K_\mu^2(\beta_i)}{(\lambda-\mu)!\,(\lambda+\mu)!}\,|\langle n_b l_b|\,r^\lambda\,|n_a l_a\rangle|^2 \qquad (3.6.13)$$

where we have summed over $m_a m_b$ using (E 3.7.8) and then over $\lambda'\mu'$.

On the question of reciprocity we observe that the analysis of §2.4 is valid here since the dependence of (3.6.13) on β_i and v_i is the same as (2.3.7) noting (2.4.3). Hence to satisfy reciprocity we replace β_i and β_j by β and W_i and W_j by W as in §2.4.

The integration over impact parameters in order to obtain an expression for the cross section is carried out as in §2.5 to yield

$$Q(a\to b)=16(2l_b+1)\,\frac{W}{W_i}\left(\frac{I_H}{\Delta E}\right)^2\sum_{\lambda=1}^{\infty}\frac{1}{2\lambda+1}$$

$$\times\left(\frac{\Delta E^2}{4I_H W}\right)^\lambda\begin{pmatrix} l_a & l_b & \lambda \\ 0 & 0 & 0 \end{pmatrix}^2\frac{|\langle n_b l_b|r^\lambda|n_a l_a\rangle|^2}{a_0^{2\lambda}}\sum_{\mu=-\lambda}^{\lambda}\frac{\chi_\mu(\beta_0)}{(\lambda-\mu)!\,(\lambda+\mu)!}\,(\pi a_0^2)$$

(3.6.14)

which is identical to (3.5.6).

§ 3.7. High Energy Form of the Cross Section and Multiply Charged Incident Particles.

We wish to study the behaviour of the cross section given by (3.4.7) when the energy of the incident electron is large. We have already discussed this problem in §2.7 for the cross section given by (2.7.5).

As $W_i \to \infty$ $\beta \to 0$ and the dominant term in $K_\mu(\beta)$ is (McLachlan,(1934))

$$K_\mu(\beta) \sim \frac{(\mu-1)!}{2}\left(\frac{2}{\beta}\right)^\mu, \quad \mu \neq 0 \tag{3.7.1}$$

$$K_0(\beta) \sim -\ln\beta .$$

Then from (2.6.2) the dominant term in $\chi_\mu(\beta)$ as $\beta \to 0$ is

$$\chi_\mu(\beta) \sim 2\mu\beta\,\frac{(\mu-1)!}{2}\left(\frac{2}{\beta}\right)^\mu \frac{(\mu-2)!}{2}\left(\frac{2}{\beta}\right)^{\mu-1} - \beta^2\left(\frac{(\mu-1)!}{2}\right)^2\left(\frac{2}{\beta}\right)^{2\mu}$$

$$= (\mu-1)!\,(\mu-2)!\left(\frac{2}{\beta}\right)^{2\mu-2} \quad \text{for } \mu \geq 2 . \tag{3.7.2}$$

Hence (2.6.12) becomes as $\beta \to 0$

$$\Omega_\lambda(\beta) \sim 2(\lambda-1)!\,(\lambda-2)!\left(\frac{2}{\beta}\right)^{2\lambda-2} \tag{3.7.3}$$

for $\lambda \geq 2$ since $\chi_{-\mu}(\beta) = \chi_\mu(\beta)$ (2.6.6). For $\lambda = 1$ $\Omega_\lambda(\beta)$ is given by (2.6.13). From this equation

$$\Omega_1 \sim -2\ln\beta . \tag{3.7.4}$$

For large W_i, $W_i \tilde{=} W$ and $\beta \sim W_i^{-1/2}$ from (2.5.1). Hence

$$Q^{RS}(a \to b) \sim \frac{W}{W_i}\left\{ -\frac{2C_1}{W}\ln\beta + \sum_{\lambda=2}^{\infty}\frac{C_\lambda}{W^\lambda}\left(\frac{1}{\beta}\right)^{2\lambda-2}\right\}$$

$$\sim \left\{C_1\,\frac{\ln W_i}{W_i} + \sum_{\lambda=2}^{\infty}\frac{C_\lambda}{W_i}\right\} \tag{3.7.5}$$

where the C_λ are non-negative constants involving $|(\Gamma_b L_b \| \underline{\underline{T}}(\lambda) \| \Gamma_a L_a)|^2$. If the transition is optically allowed then $|(\Gamma_b L_b \| T(1) \| \Gamma_a L_a)|^2$ is non-zero in general. For forbidden transitions it is identically zero (c.f.§2.7). Hence for optically allowed transitions $Q^{RS}(a \to b) \sim \ln W_i / W_i$

while for forbidden transitions $Q^{RS}(a\rightarrow b)\sim 1/W_i$.

We may also generalize (3.4.7) to the case where the incident particle has mass Mm and charge $Z'e$ as was considered in §2.10. In this case (3.4.7) becomes by a straightforward extension of (2.10.5)

$$Q^{RS}(a\rightarrow b) = \frac{64\pi Z'^2 N^2}{2L_a+1}\ \frac{W}{W_i}\ \left(\frac{I_H}{\Delta E}\right)^2 \sum_{\lambda=1}^{\infty} \frac{1}{(2\lambda+1)^2}$$

$$\left(\frac{M\Delta E^2}{4I_H W}\right)^{\lambda} \frac{|(\Gamma_b L_b \| \underline{\underline{T}}(\lambda) \| \Gamma_a L_a)|^2}{a_o^{2\lambda}}\ \Omega_\lambda(\beta_o)(\pi a_o^2). \quad (3.7.6)$$

Chapter 4

§4.1. Calculations Performed.

A number of cross sections for forbidden quadrupole transitions in hydrogen and helium have been calculated using (2.7.5) and the strong coupling formula (2.8.4) for electron impact and (2.10.5) for proton impact. These transitions are listed in Table 4.1. We have also investigated the effect of including the higher order multipoles via (3.4.7) in several representative cases. In addition we report on calculations carried out by other persons using the formulae mentioned above.

Table 4.1.

Transitions investigated

Hydrogen		Helium
$\Delta\ell = 2$	$\Delta\ell = 0$	$\Delta\ell = 2$
1s - 3d	2p - 3p	$1'S(1s)^2$ - $3'D(1s)(3d)$
2s - 3d	3p - 4p	$1'S(1s)^2$ - $4'D(1s)(4d)$
2p - 4f	3d - 4d	
3s - 4d		
3p - 4f		
3d - 4s		

$\Delta\ell$ is the change in orbital angular momentum undergone by the active atomic electron during the transition.

For the transitions we have investigated there exists either other theoretical calculations or else experimental results for the cross section. Thus we are able to normalize our cross sections to these results at high energies. This procedure yields a value for the cut-off parameter R_o which appears in (2.7.5). By this means we are led to two formulae for predicting R_o for transitions for which there are no theoretical or experimental data available. The reliability of these formulae are critically evaluated.

In order to evaluate the various cross sections we must have a knowledge of the functions $\eta(\beta)$ and $\psi(\beta)$. An illustrative table of these functions is given in Table 4.2.

§ 4.2. Results for Hydrogen.

The method of evaluating the reduced matrix elements $R^{(2)}_{ji} = |(n_b \ell_b || T(2) || n_a \ell_a)|^2$ (c.f.§3.4) in the case of hydrogen has been given in §3.5. In particular we must evaluate (3.5.5) for $\lambda = 2$. The numerical values for the Wigner 3-j coefficients $\begin{pmatrix} \ell_b & \lambda & \ell_a \\ 0 & 0 & 0 \end{pmatrix}$ are given by Rotenberg et al, (1959), p.41. (For an analytic expression for these symbols see, for example, Edmonds, (1957), Table 2). The radial integrals $\langle n_b \ell_b | r^2 | n_a \ell_a \rangle$ (3.5.3) can be evaluated analytically using the explict form for the radial parts $R_{n\ell}(r)$ of the hydrogen wave function. (See, for instance, Pauling and Wilson, (1935), §21).

For example

$$R_{1s}(r) = 2a_o^{-3/2} e^{-r/a_o}$$

$$R_{3d}(r) = \frac{4}{81\sqrt{30}} a_o^{-3/2} \left(\frac{r}{a_o}\right)^2 e^{-r/3a_o}.$$

Table 4.2

The functions $\eta(\beta)$ and $\psi(\beta)$ defined by equations (2.8.3) and (2.7.6) as functions of β.

β	$\eta(\beta)$	$\psi(\beta)$	β	$\eta(\beta)$	$\psi(\beta)$
0.00	∞	∞	0.90	5.3151, 0	5.706,-1
0.05	4.8063, 5	2.0130, 2	1.00	3.4658, 0	4.346,-1
0.10	3.0156, 4	5.0943, 1	1.10	2.3339, 0	3.348,-1
0.15	5.9955, 3	2.2948, 1	1.20	1.6105, 0	2.605,-1
0.20	1.9139, 3	1.3079, 1	1.30	1.1342, 0	2.041,-1
0.25	7.8846, 2	8.464, 0	1.40	8.1201,-1	1.610,-1
0.30	3.8691, 2	5.929, 0	1.50	5.8917,-1	1.274,-1
0.40	1.2577, 2	3.359, 0	1.60	4.3233,-1	1.013,-1
0.50	5.2905, 1	2.137, 0	1.70	3.2031,-1	8.082,-2
0.60	2.6115, 1	1.457, 0	1.80	2.3923,-1	6.464,-2
0.70	1.4345, 1	1.037, 0	1.90	1.8018,-1	5.183,-2
0.80	8.4951, 0	7.611, -1	2.00	1.3617,-1	4.164,-2

The figure after the comma in each entry indicates the power of ten by which the entry is to be multiplied.

Using the fact that

$$\int_0^\infty e^{-\alpha r}\, r^s dr = s!/\alpha^{s+1}$$

we find that

$$\langle 3d|r^2|1s\rangle = \frac{8a_o^2}{81\sqrt{30}} \int_0^\infty \rho^6 e^{-4\rho/6}\, d\rho$$

$$= \frac{8}{81\sqrt{30}}\, 6!\left(\frac{3}{4}\right)^7 a_o^2$$

or

$$|(3d||T(2)||1s)|^2 = \frac{5^2 \cdot 2^9}{2^{17}\pi}\, a_o^4.$$

Results for other transitions are given in Table 4.3

Table 4.3

Reduced matrix elements for hydrogen

$n_a \ell_a$	$n_b \ell_b$	$4\pi\|(n_b \ell_b \|\|T(2)\|\| n_a \ell_a)\|^2/a_o^4$
1s	3d	1.502,1
2s	3d	1.385,4
2p	4f	5.238,3
3s	4d	1.944,5
3p	4f	4.187,5
3d	4s	1.063,4
2p	3p	3.896,3
3p	4p	7.910,4
3d	4d	6.150,4

The figure after the comma in each entry of the last column indicates the power of ten by which the entry is to be multiplied.

We also note that for hydrogen

$$\Delta E = \left(\frac{1}{n_a^2} - \frac{1}{n_b^2}\right) I_H \qquad (4.2.1)$$

so that for quadrupole transitions, (2.7.5) becomes (putting $N=1$, $\omega_i = 2\ell_a + 1$)

$$Q(n_a \ell_a \rightarrow n_b \ell_b) = \frac{8\pi}{75(2\ell_a+1)} \left(\frac{1}{n_a^2} - \frac{1}{n_b^2}\right) \left(\frac{I_H^2}{WW_i}\right) \frac{|(n_b \ell_b \|T(2)\| n_a \ell_a)|^2}{a_o^4} \psi(\beta_o)(\pi a_o^2) \qquad (4.2.2)$$

with

$$W = W_i - \Delta E/2$$

$$\beta_o = \frac{1}{2}\sqrt{\frac{W_i}{I_H}}\left(\frac{\Delta E}{W}\right)\left(\frac{R_o}{a_o}\right) . \qquad (4.2.3)$$

In order to obtain the cut-off parameter R_o for the transitions induced by electron impact we normalize our cross sections to existing first Born approximation calculations (see §1.3) at the highest energies for which they are available ($\sim$1000 eV). Knowing one value of the cross section and the energy at which this occurs we can solve (4.2.2) for $\Psi(\beta_o)$. The corresponding value of β_o is obtained by interpolation in a table of $\Psi(\beta)$ and R_o is then calculated from (4.2.3). The values of R_o calculated in this way are given in Table 4.4 for the various transitions under investigation. We also list values of $\bar{r}_a$, $\bar{r}_b$ and $\bar{R}$ where $\bar{r}_a$ and $\bar{r}_b$ are the expectation values of r in the initial and final states, respectively (i.e. $\bar{r}_a = \langle n_a \ell_a | r | n_a \ell_a \rangle$) and

$$\bar{R} = \frac{(2\ell_> + 1)\bar{r}_< + (2\ell_< + 1)\bar{r}_>}{(2\ell_> + 1) + (2\ell_< + 1)} \qquad (4.2.4)$$

Here $\ell_>$, $\ell_<$ are the greater and lesser of ℓ_a, ℓ_b, respectively, and $\bar{r}_>$, $\bar{r}_<$ the greater and lesser of $\bar{r}_a$, $\bar{r}_b$. We shall make use of these quantities in §4.5.

Table 4.4.

Cut-off parameters for transitions in hydrogen (in units of a_o).

$n_a \ell_a$	$n_b \ell_b$	$\bar{r}_a$	$\bar{r}_b$	$\bar{R}$	R_o
		$\Delta \ell = 2$			
1s	3d	1.5	10.5	3.0	3.5
2s	3d	6.0	10.5	6.8	6.7
2p	4f	5.0	18.0	8.9	7.8
3s	4d	13.5	21.0	14.8	14.9
3p	4f	12.5	18.0	14.2	11.9
3d	4s	10.5	24.0	12.8	14.5
		$\Delta \ell = 0$			
2p	3p	5.0	12.5	8.8	3.5
3p	4p	12.5	23.0	17.8	7.2
3d	4d	10.5	21.0	15.8	5.5

The results of calculations using these values of R_o in (4.2.2) are listed in Table 4.5.

Cross sections were calculated from the strong coupling formula as follows. Using the values of $R_{ji}^{(2)}$ from Table 4.3 and choosing a value for β_1, (2.8.2) was solved for the corresponding value of W. Hence W_i can be found from (2.4.3) and the cross section evaluated by means of (2.8.4). Table 4.6 lists representative values of the cross sections for various transitions calculated in this way.

Table 4.5.

Cross sections for transitions in hydrogen induced by electron impact (in units of πa_o^2).

W_i(eV)	Q(1s-3d)	Q(2s-3d)	Q(2p-4f)
2	-	1.408, 1	-
3	-	3.158, 1	-
4	-	3.470, 1	1.203, 0
5	-	3.321, 1	1.572, 0
7	-	-	1.747, 0
10	-	2.164, 1	1.598, 0
15	6.45 , -3	-	1.256, 0
20	1.243, -2	1.161, 1	1.007, 0
30	1.613, -2	-	7.03 , -1
40	1.562, -2	-	5.40 , -1
50	1.425, -2	4.70 , 0	4.35 , -1
75	1.096, -2	-	2.91 , -1
100	8.72 , -3	2.33 , 0	2.13 , -1
200	4.63 , -3	1.156, 0	1.078, -1
500	1.862, -3	4.58 , -1	4.25 , -2
946	-	2.41 , -1	2.23 , -2
1360	6.73 , -4	-	-

Table 4.5 (contd.)

W_i(eV)	Q(3s-4d)	Q(3p-4f)	Q(3d-4s)
0.8	-	1.677, 2	1.001, 0
0.9	1.124, 2	2.157, 2	1.430, 0
1.0	1.417, 2	2.498, 2	1.771, 0
1.5	2.077, 2	-	-
2	2.091, 2	2.751, 2	2.545, 0
5	1.227, 2	1.424, 2	1.437, 0
10	6.58 , 1	7.41 , 1	7.66 , -1
20	3.33 , 1	3.71 , 1	3.86 , -1
50	1.313, 1	1.467, 1	1.527, -1
100	6.49 , 0	7.27 , 0	7.55 , -2
200	3.23 , 0	3.61 , 0	3.74 , -2
500	1.277, 0	1.437, 0	1.486, -2
1360	4.67 , -1	5.27 , -1	5.44 , -3

Table 4.5 (contd.)

W_i(eV)	Q(2p-3p)	Q(3p-4p)	Q(3d-4d)
0.7	-	1.649, 2	1.780, 2
0.8	-	1.975, 2	1.953, 2
0.9	-	2.134, 2	1.999, 2
1	-	2.191, 2	1.979, 2
2	1.582, 1	1.631, 2	1.324, 2
3	1.807, 1	-	-
5	1.370, 1	7.35 , 1	5.81 , 1
10	7.65 , 0	3.74 , 1	2.96 , 1
15	5.21 , 0	-	-
20	3.94 , 0	1.867, 1	1.482, 1
30	2.64 , 0	-	-
40	1.990, 0	-	-
50	1.587, 0	7,44 , 0	5.93 , 0
75	1.058, 0	-	-
100	7.94 , -1	3.71 , 0	2.96 , 0
200	3.96 , -1	1.848, 0	1.478, 0
500	1.58 , -1	7.38 , -1	5.90 , -1
946	8.36 , -2	-	-
1360	-	2.71 , -1	2.17 , -1

The figure after the comma in the entries for the cross sections indicates the power of ten by which the entries are to be multiplied.

Table 4.6

Cross sections for transitions in hydrogen induced by electron impact (in units of πa_o^2). (Strong coupling formula).

W_i(eV)	Q(1s-3d)	W_i(eV)	Q(2s-3d)
17.15	0.930	3.80	51.6
24.79	0.845	16.3	35
33.31	0.756		
52.51	0.620		

W_i(eV)	Q(2p-4f)	W_i(eV)	Q(3s-4d)
5.95	18.1	2.03	279
12.6	12.3	9.1	175

W_i(eV)	Q(3p-4f)	W_i(eV)	Q(3d-4s)
1.17	219	2.36	34.8
1.34	231		
1.57	240		
1.85	245		
2.25	245		
2.80	238		
8.51	157		

W_i(eV)	Q(2p-3p)	W_i(eV)	Q(3p-4p)
3.05	19.4	0.91	112
3.79	19.2	1.04	119
6.17	16.6	1.21	124
7.92	15.0	1.57	127
11.09	12.9	2.24	119
		3.11	107
		5.03	87

Table 4.6 (contd.)

W_i(eV)	Q(3d-4d)
0.71	72.1
0.78	78.8
0.88	84.7
1.01	89.4
1.43	92.2
2.49	80.9
3.97	66.5
9.36	43.9

Figures 4.1 to 4.9 show graphically the results of Table 4.5 and Table 4.6 when possible. Also plotted are the available Born cross sections for these transitions.

In the case when the incident particle has mass Mm and charge Z'e where $Z'=\pm 1$ we see from (2.5.6) and (2.10.5) that

$$Q^M(MW_i{}^e-(M-1)\Delta E/2) = \frac{1}{1-(1-1/M)\Delta E/(2W_i{}^e)}\, Q^e(W_i{}^e) \qquad (4.2.5)$$

where the superscripts M and e refer to quantities pertaining to collisions involving particles of mass Mm and electrons, respectively. If $M \gg 1$ then

$$W_i{}^M = MW_i{}^e-(M-1)\Delta E/2 \cong MW^e \qquad (4.2.6)$$

and (4.2.5) becomes

$$Q^M(W_i{}^M) \cong \frac{W_i{}^e}{W^e}\, Q^e(W_i{}^e) \qquad (4.2.7)$$

For transitions in hydrogen the cross sections corresponding

to $Q^M(W_i{}^M)$ and $Q^e(W_i{}^e)$ calculated in the first Born approximation also satisfy the approximate relationships (4.2.6) and (4.2.7) when $\Delta E/4W_i{}^e$ is small compared to one (i.e. when $W_i{}^e \gtrsim 5\Delta E$). (Bates and Griffing,(1953), Carew and Milford,(1963)).

Carew and Milford,(1963) have calculated cross sections for excitation by proton impact of forbidden transitions in hydrogen by means of the approximate formula analagous to (4.2.7) but involving the Born cross sections. They have used the electron impact cross sections of McCoyd et al,(1960) and Scanlon and Milford,(1961). Hence the relation between the proton impact cross sections calculated via (4.2.7) and the Born calculations of Carew and Milford,(1963) will be the same as between the corresponding electron impact cross sections shown in Figure 4.2 and Figures 4.4 to 4.9. For this reason we have not calculated the proton impact cross section for those transitions considered by Carew and Milford,(1963). However we have calculated the cross section for the 1s-3d transition since Bates and Griffing,(1953) have done an exact calculation for this transition. The results are given in Table 4.7 and shown in Figure 4.10

We also note that, when $W_i{}^e \gg \Delta E$ (and $M>1$), (4.2.5) becomes (since $W_i{}^e \cong W^e$)

$$Q^M(MW_i{}^e) \cong Q^e(W_i{}^e) \qquad (4.2.8)$$

i.e the cross sections Q^M and Q^e are equal for equal values of the velocity of the incident particles. The first Born approximation cross sections also satisfy (4.2.8) at high impact energies. (Mott and Massey,(1949)).

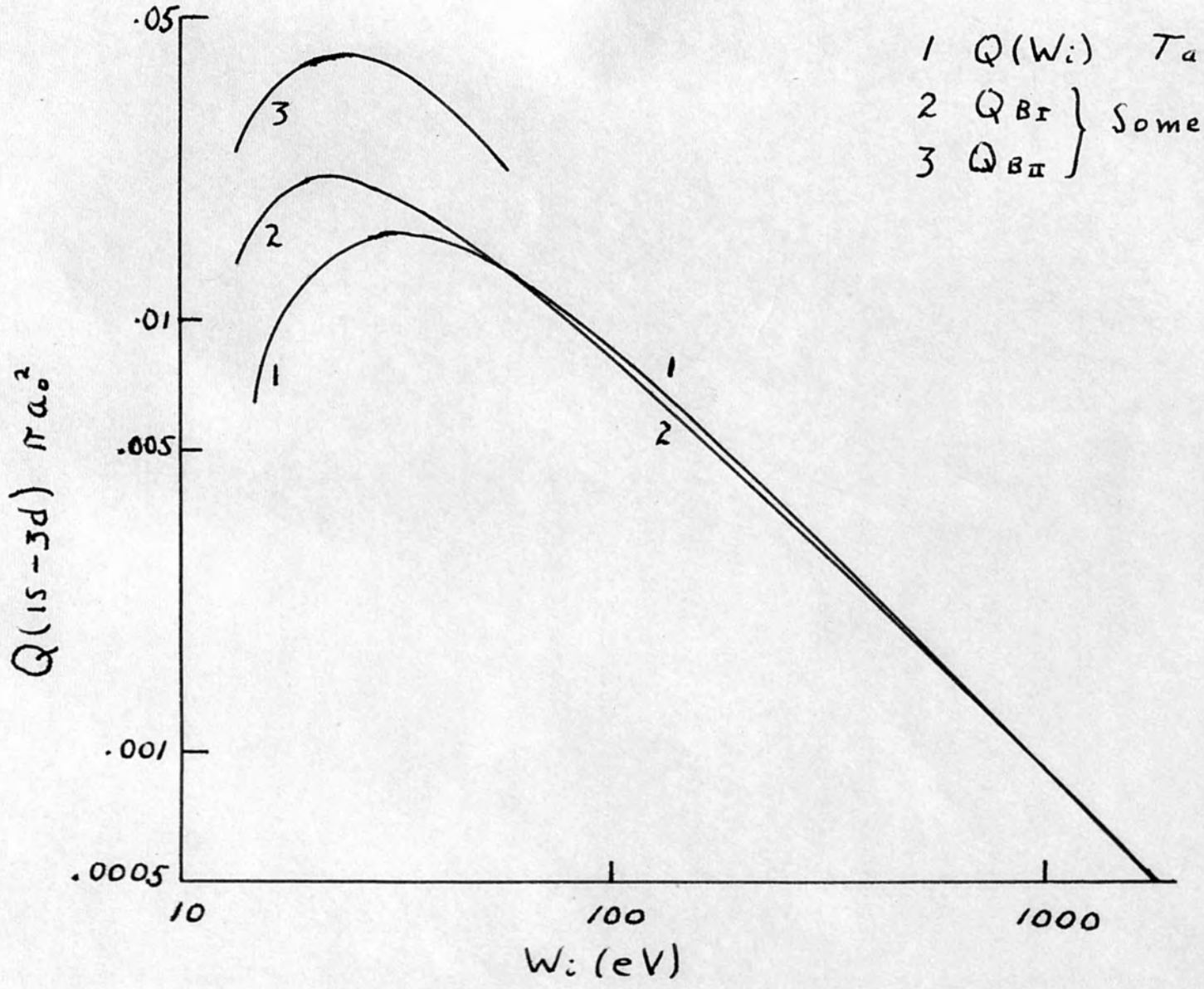
1 Q(Wi) Table 4·5
2 QBI } Somerville, (1963)
3 QBII
.05
.01
.005
.001
.0005
Q(1S-3d) πa0²
10
100
1000
Wi (eV)
1
2
3

Fig. 4·1

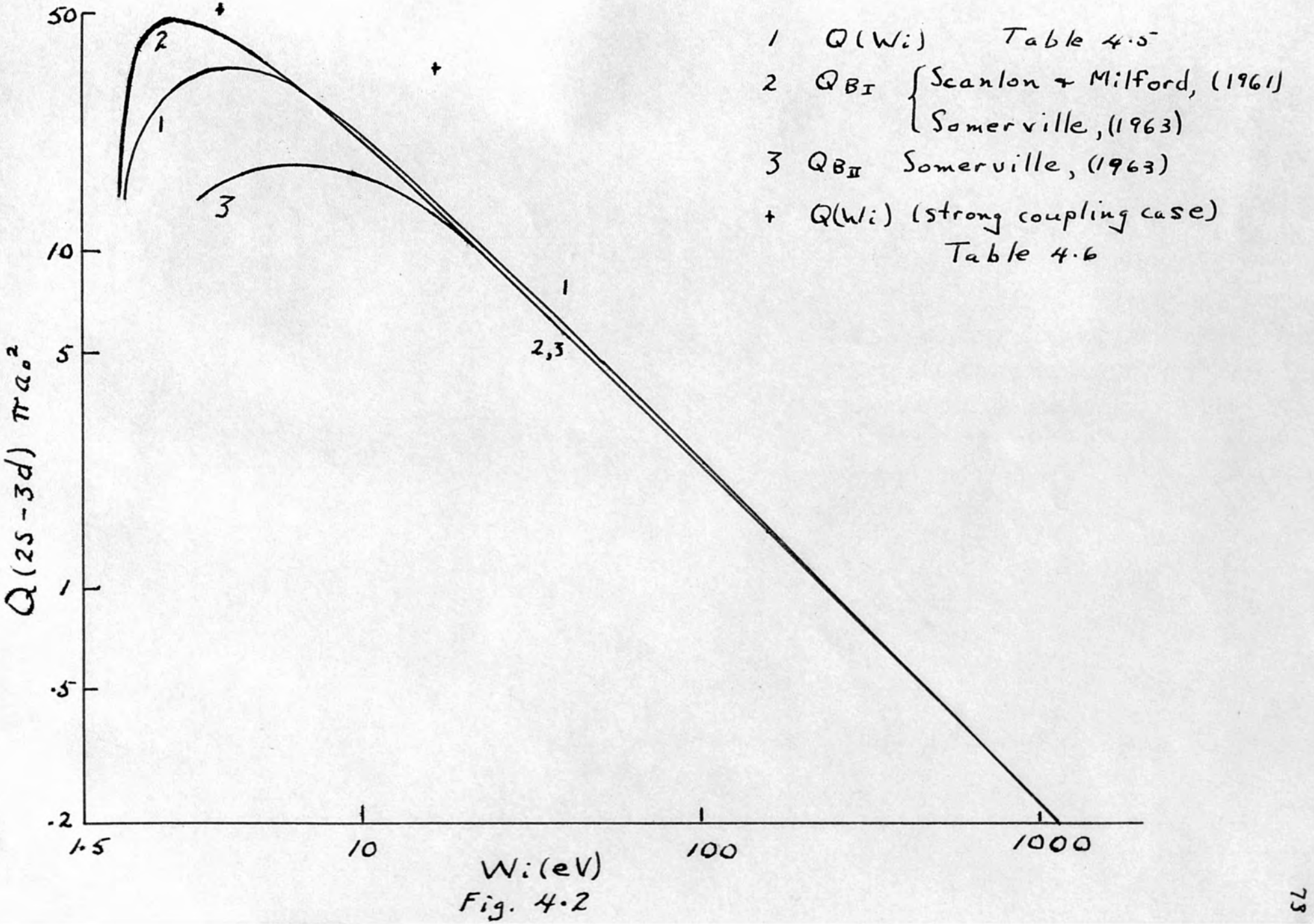
1 Q(Wi) Table 4.5
2 Q_{B_I} {Scanlon + Milford, (1961) Somerville, (1963)
3 $Q_{B_{II}}$ Somerville, (1963)
+ Q(Wi) (strong coupling case) Table 4.6
50
10
5
1
.5
.2
1.5
10
100
1000
Wi(eV)
$Q(2S-3d)\ \pi a_0^2$
1
2,3
2
1
3

Fig. 4.2

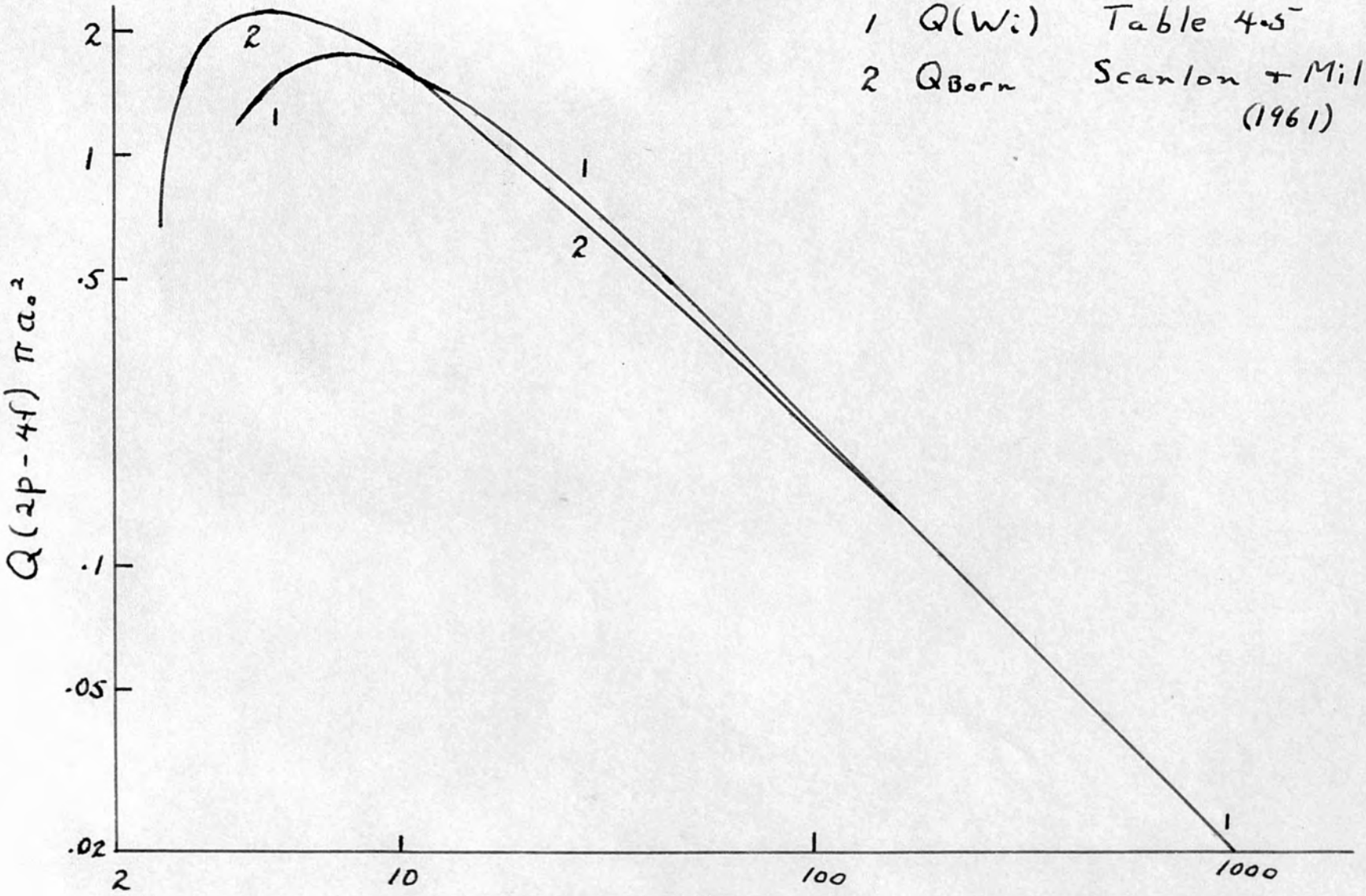
1 Q(Wi) Table 4.5
2 QBorn Scanlon + Milford, (1961)
Q(2p-4f) πa0²
2
1
.5
.1
.05
.02
2
10
100
1000
Wi (eV)

Fig. 4.3

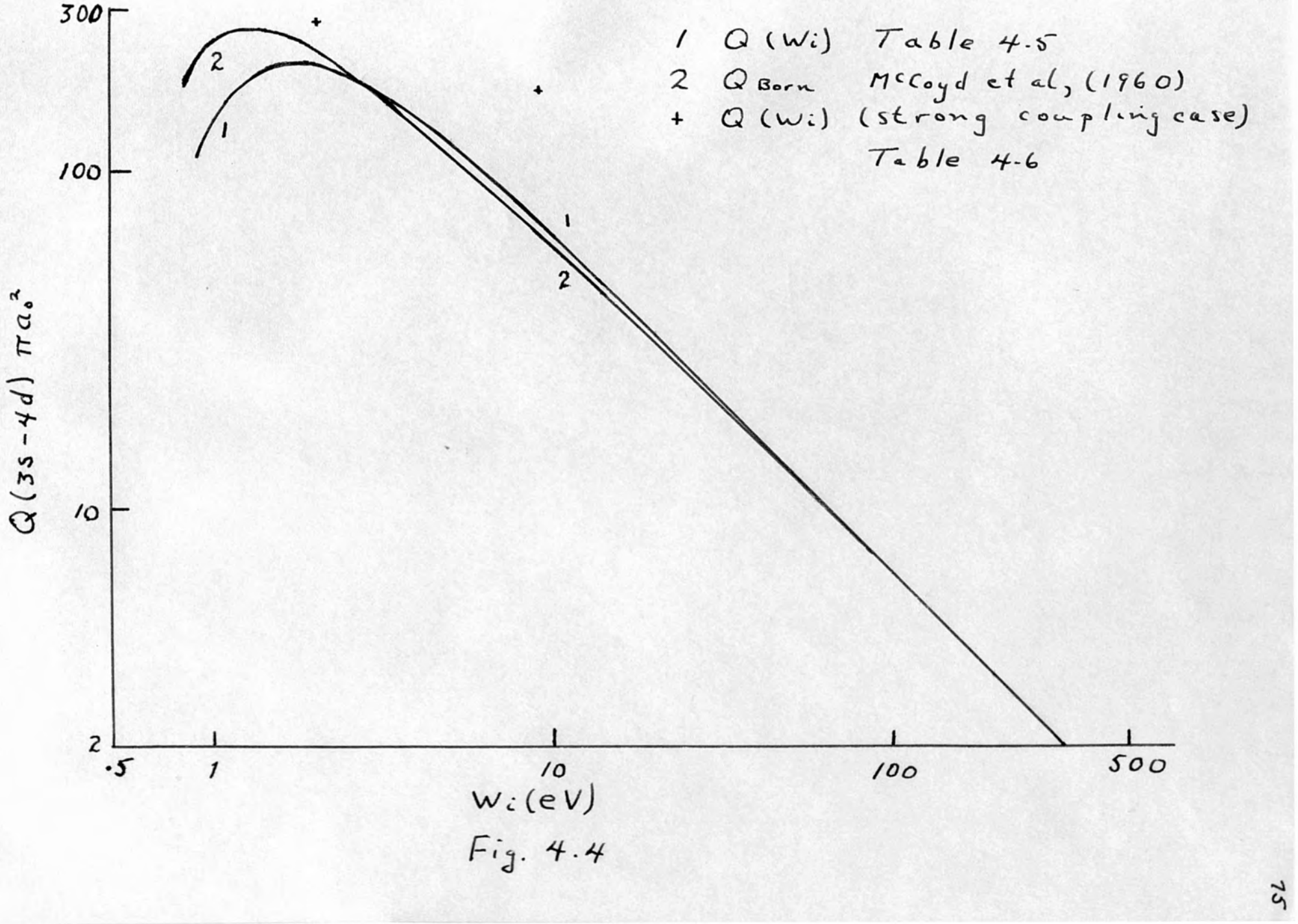
1 Q (Wi) Table 4.5
2 Q Born McCoyd et al, (1960)
+ Q (Wi) (strong coupling case)
Table 4-6
300
100
10
2
Q(3S-4d) πa₀²
.5
1
10
100
500
Wi (eV)

Fig. 4.4

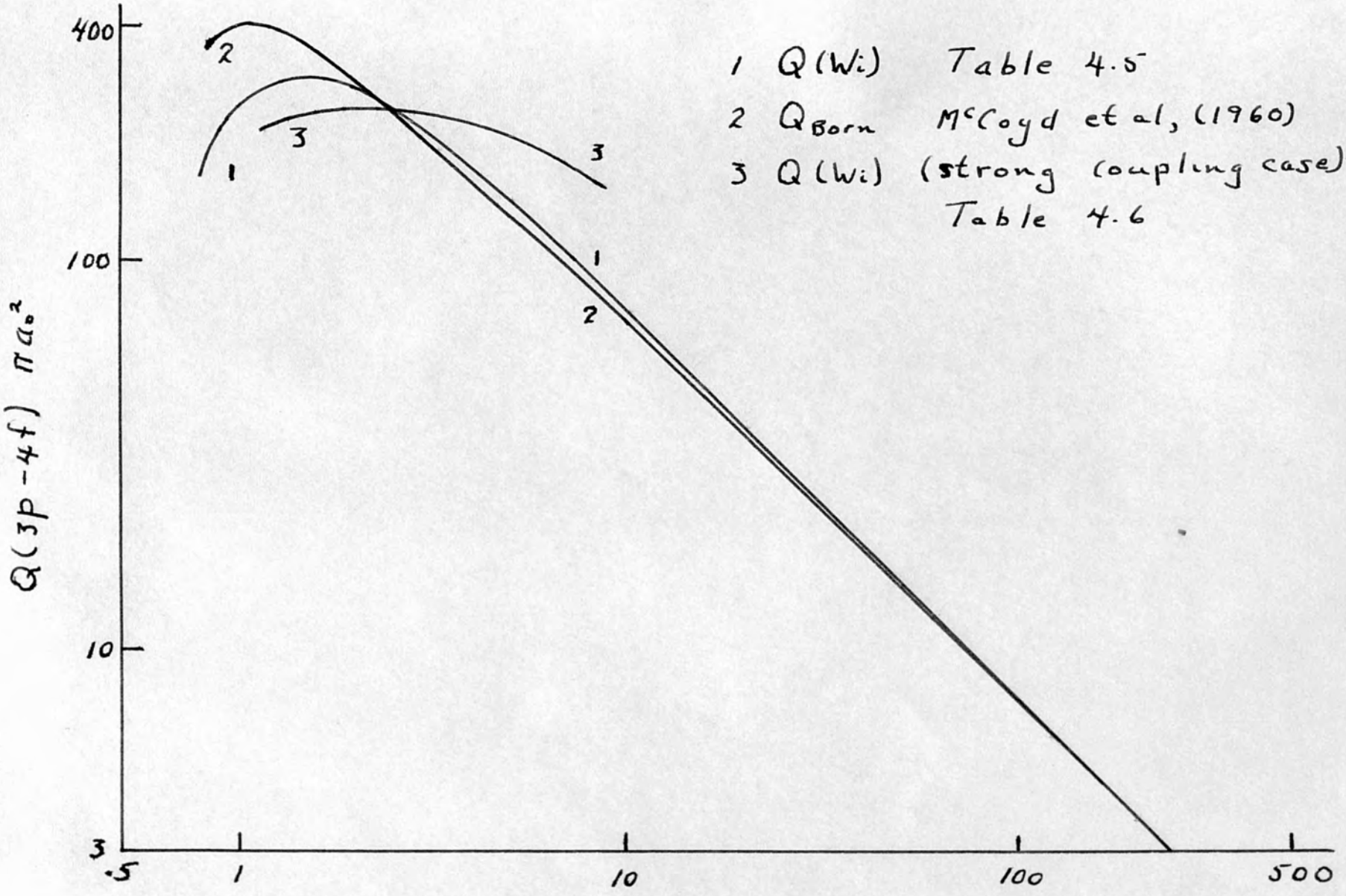
400
100
10
3
.5
1
10
100
500
Q(3p-4f) πa₀²
Wi(eV)
1 Q(Wi) Table 4.5
2 Q Born McCoyd et al, (1960)
3 Q(Wi) (strong coupling case)
Table 4.6
1
2
3
1
2
3

Fig. 4.5

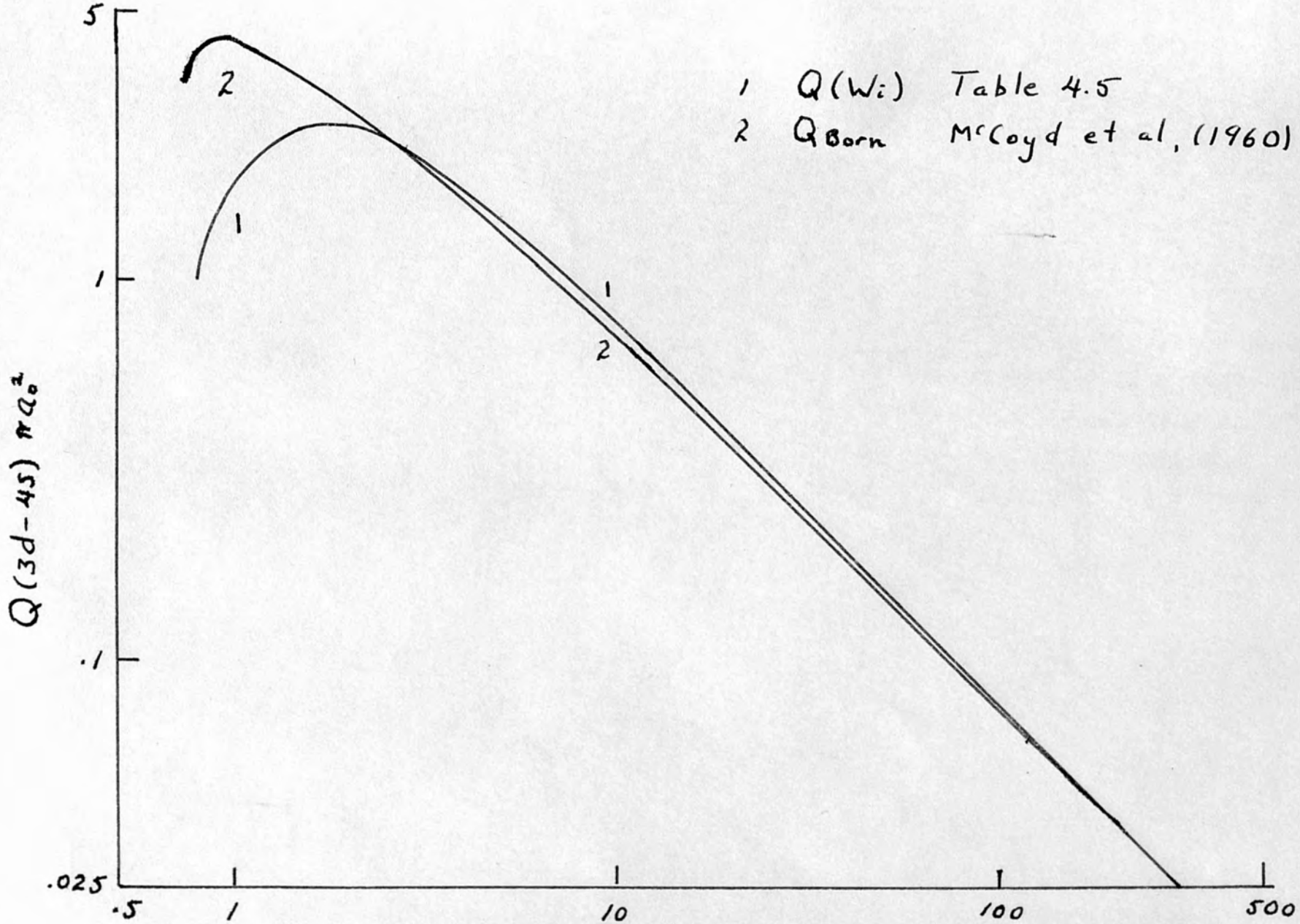
1 Q(Wi) Table 4.5
2 QBorn McCoyd et al, (1960)
5
1
.1
.025
.5
1
10
100
500
Wi (eV)
Q(3d-45) πa0²
1
2
1
2

Fig. 4.6

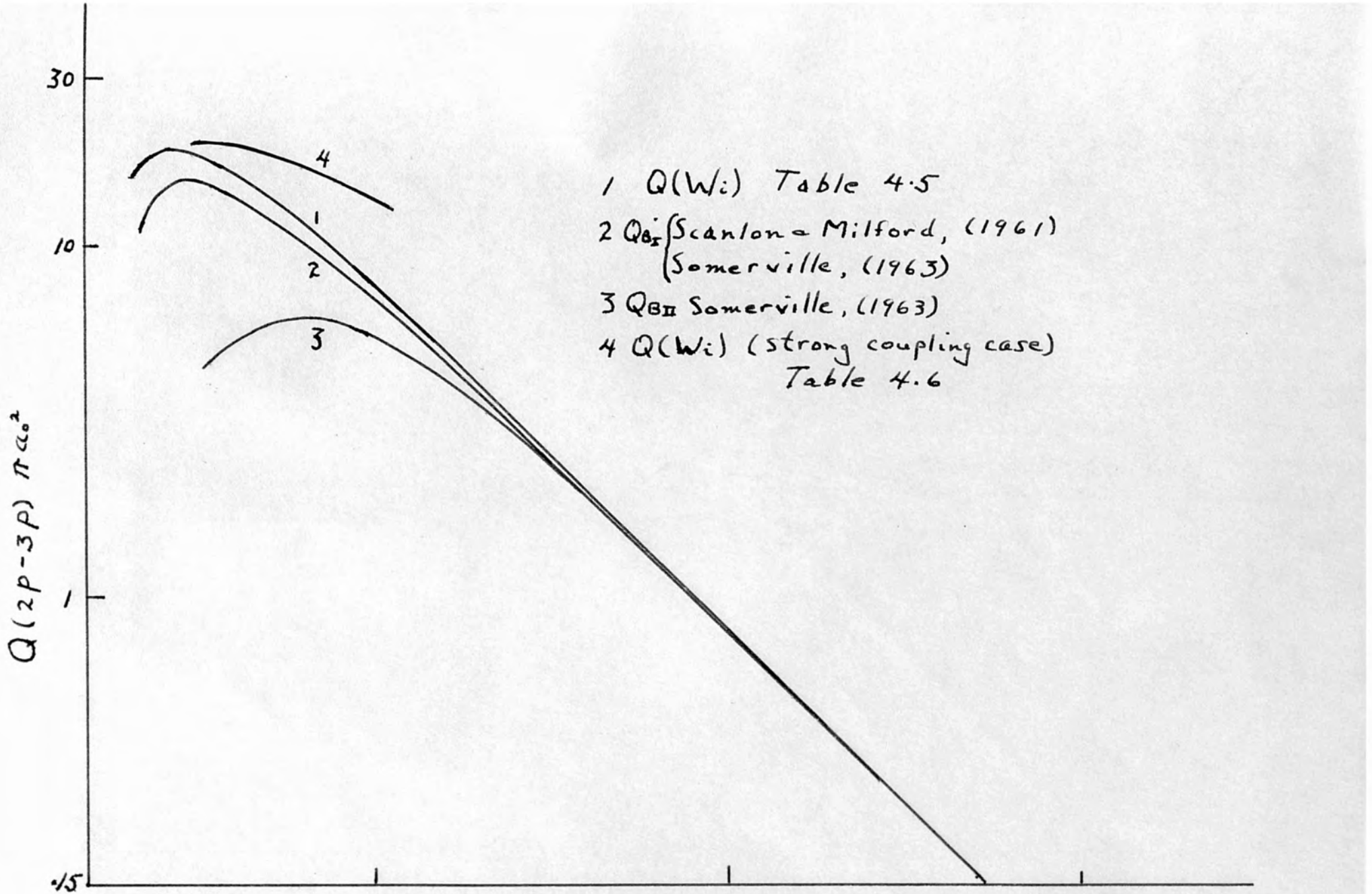
30
10
1
.15
1.5
10
100
1000
Q(2p-3p) πa₀²
Wi(eV)
1 Q(Wi) Table 4.5
2 QBI {Scanlon & Milford, (1961) Somerville, (1963)
3 QBII Somerville, (1963)
4 Q(Wi) (strong coupling case) Table 4.6

Fig. 4.7

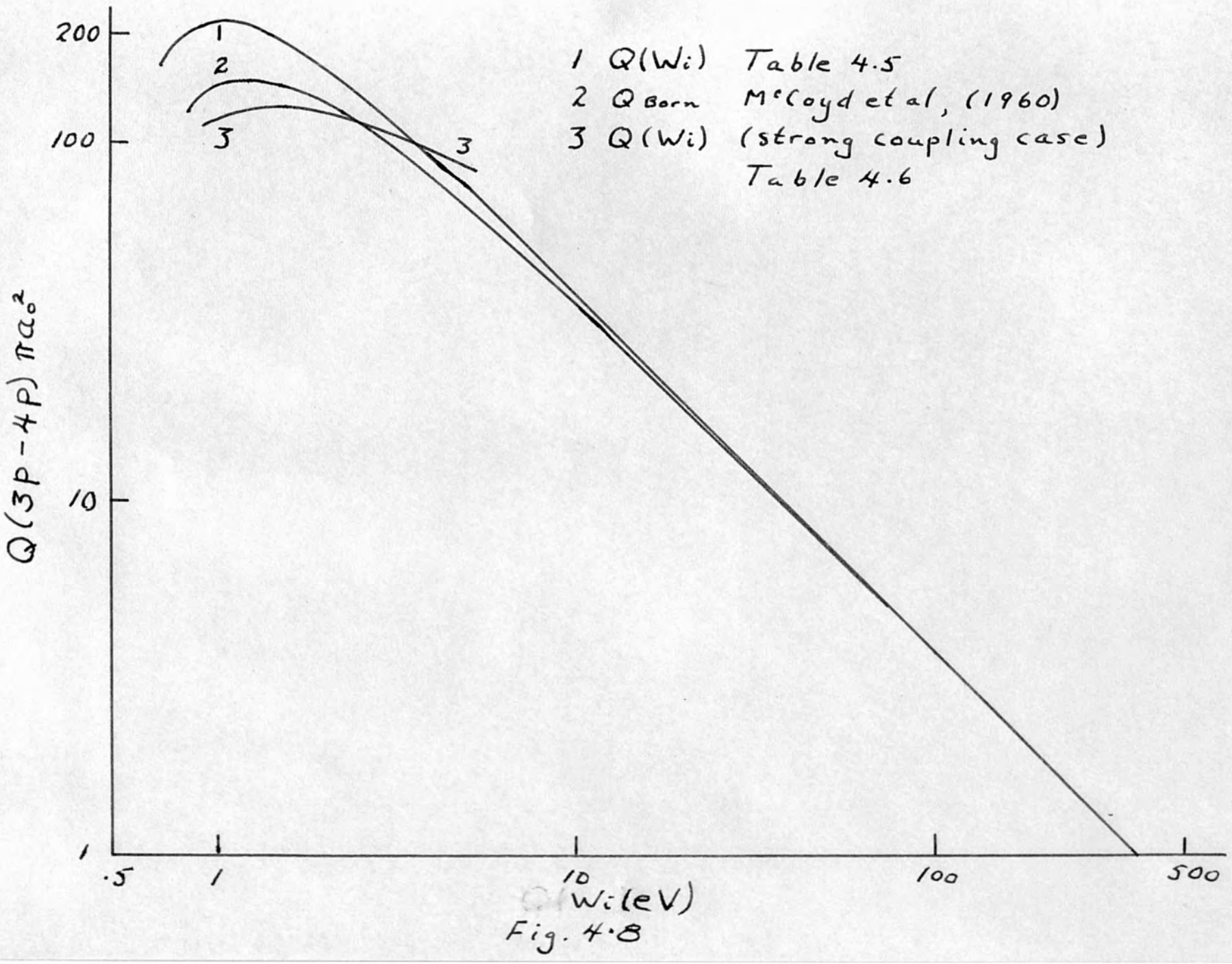
200
100
10
1
Q(3P-4P) πa₀²
1
2
3
3
1 Q(Wi) Table 4.5
2 Q Born McCoyd et al, (1960)
3 Q(Wi) (strong coupling case)
Table 4.6
.5
1
10
100
500
Wi(eV)

Fig. 4·8

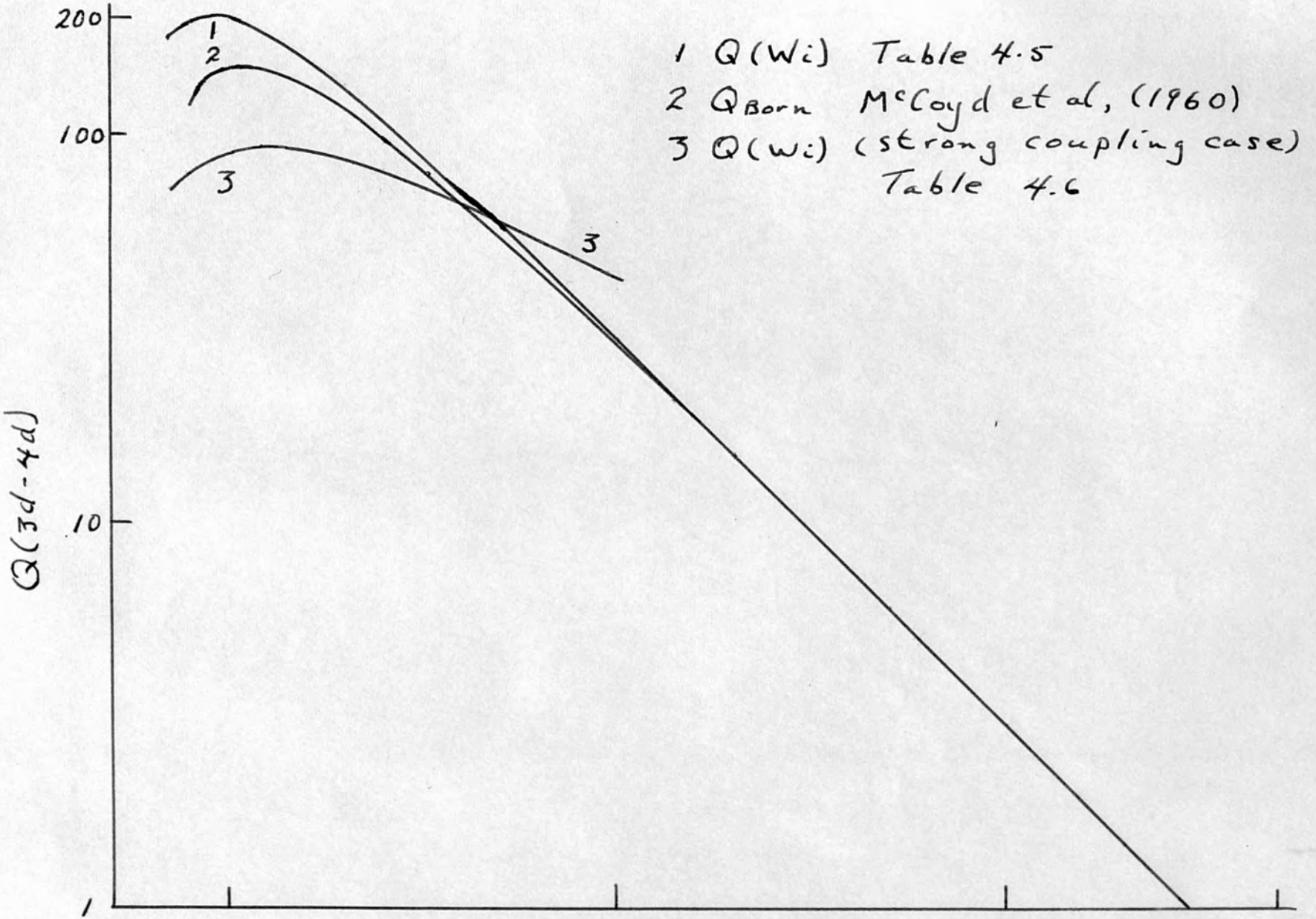
200
100
10
1
Q(3d-4d)
1
2
3
3
1 Q(Wi) Table 4.5
2 QBorn McCoyd et al, (1960)
3 Q(Wi) (strong coupling case)
Table 4.6
.5
1
10
100
500
Wi (eV)

Fig 4.9

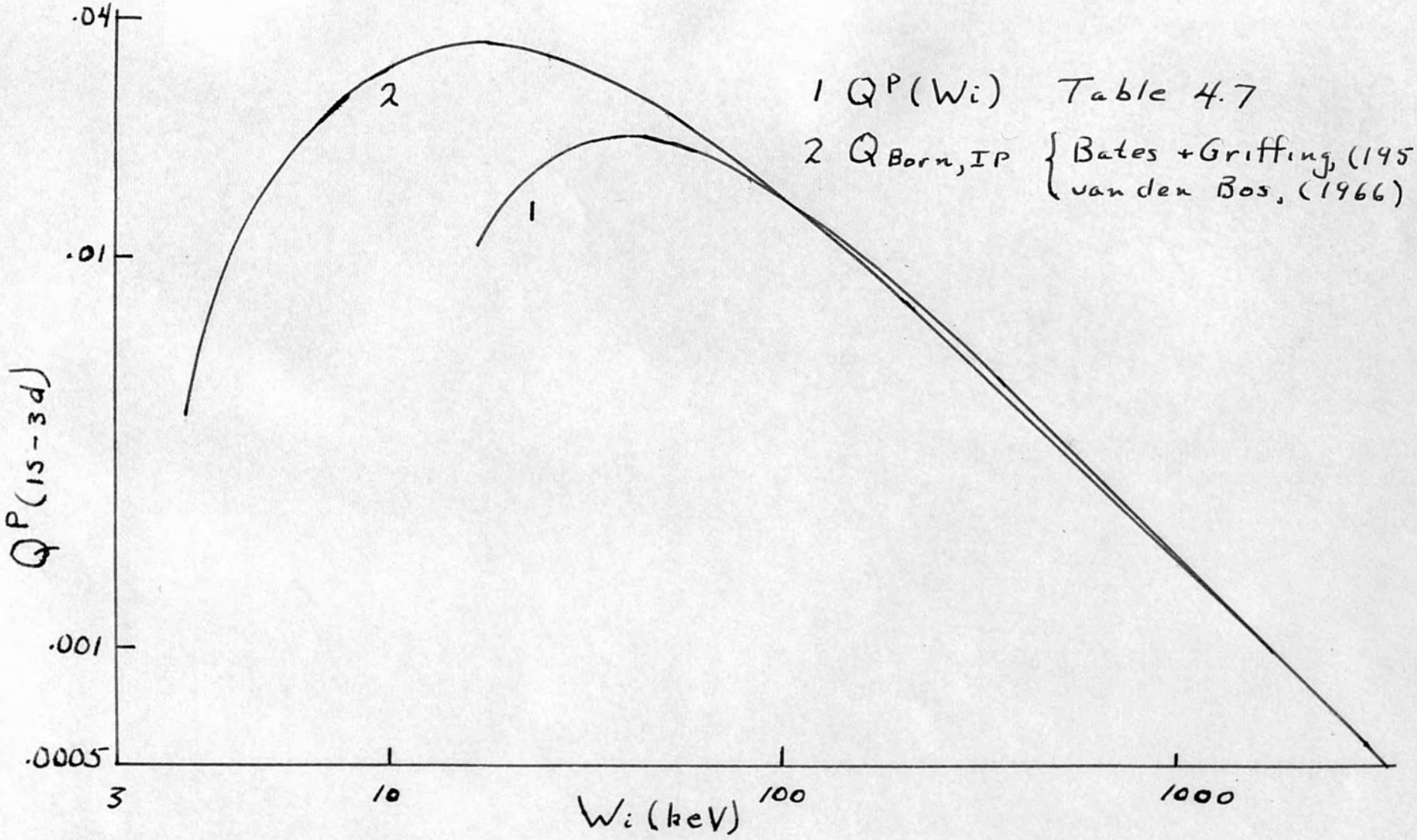
.04
.01
.001
.0005
$Q^P(15-3d)$
2
1
1 $Q^P(W_i)$ Table 4.7
2 $Q_{Born,IP}$ { Bates + Griffing, (1953)
van den Bos, (1966)
3
10
100
1000
W_i (keV)

Fig 4.10

Table 4.7

Q(1s-3d) (in units of πa_o^2) for proton impact on hydrogen.

W_i^p(keV)	Q(1s-3d)
16.4	1.08, -2
25.6	1.79, -2
44.0	2.02, -2
62.4	1.84, -2
80.6	1.58, -2
126.6	1.19, -2
172.6	9.3 , -3
356	4.8 , -3
906	1.89, -3
2490	6.8 , -4

The figure after the comma in each entry of the second column indicates the power of ten by which the entry is to be multiplied.

§ 4.3. Results for Helium.

The evaluation of reduced matrix elements for transitions in helium is not a straightforward matter since exact wave functions for the atomic states are not known. Hence we must make do with approximate ones. There are two conditions that these wave functions must satisfy, viz. they must be completely antisymmetric and the initial and final state wave functions must be orthogonal. We also require that the wave functions are normalized. For the transitions in question (1'S → n'D) the orthogonality

condition is automatically satisfied via the angular parts of the wave function since the initial and final states have different angular momentum quantum numbers. We must however ensure that the wave functions are antisymmetric. Since we are dealing with singlet states this means that the spin part of the wave functions are antisymmetric and hence the space parts must be symmetric.

There are a great many approximate wave functions available for the ground state (1'S) of helium. We have chosen five of these wave functions which are of sufficiently simple form to allow the integrations that are required to evaluate the reduced matrix elements to be done analytically. These wave functions can be written as

$$\Psi^{(k)}_{1'S} = \frac{N_k}{a_o^3}\left(e^{-(a_k r_1 + b_k r_2)/a_o} + e^{-(b_k r_1 + a_k r_2)/a_o}\right) \times (1 + c_k r_{12}/a_o) \qquad (4.3.1)$$

for k=1,3,4,5. $\Psi^{(2)}_{1'S}$ is the analytic Hartree-Fock function of Roothaan et al,(1960) and is of the form

$$\Psi^{(2)}_{1'S} = F(r_1)F(r_2)$$

The values of the parameters which appear in (4.3.1) are listed in Table 4.8.

There do not seem to exist any calculations of wave functions for the n'D excited states of helium. However from the energy levels and quantum defects (which are very small; see Moore,(1949)) of the excited states it appears as though these states can be reasonably well described by a (1s) electron in the field of a nucleus of charge 2e plus an (nd) electron in the field of a nucleus of charge e. Thus we write

$$\Psi_{n'D} = \frac{1}{\sqrt{2}}\left(\psi_{1s}(2|r_1)\psi_{nd}(1|r_2) + \psi_{1s}(2|r_2)\psi_{nd}(1|r_1)\right) \qquad (4.3.2)$$

Table 4.8.

Values of the parameters which appear in (4.3.1)

k	a_k	b_k	c_k	N_k	ΔE_k
1	27/16	27/16	0	$3^9/(2^{13}\pi)$	0.05606(a)
2	-	-	-	-	0.04204(b)
3	2.18	1.19	0	$8.9/(4\pi)$	0.02830(a)
4	1.850	1.850	0.366	0.6952	0.01260(c)
5	1.436	2.208	0.292	0.6767	0.00230(c)

ΔE_k is the difference between the experimentally determined energy of the ground state of the atom and the energy calculated from the wave function. It is given in atomic units (27.2eV).

(a) Coulson and Neilson, (1961).
(b) Roothaan et al, (1960).
(c) Roothaan and Weiss, (1960).

where $\psi_{n\ell}(z|r)$ is the wave function of a hydrogenic system with nuclear charge z. n and ℓ are the principal and orbital angular momentum quantum numbers, respectively.

In order to evaluate the reduced matrix elements we use (3.3.9) with $T(\lambda\mu)=-r^{\lambda}Y_{\lambda\mu}(\theta,\varphi)$ and the approximate initial and final state wave functions as discussed above. However we can calculate the matrix element on the l.h.s. of (3.3.9) in two ways, viz. as it stands or using the alternate form (E.5). In analogy with the different forms of the dipole matrix element we call these forms the quadrupole length (Q.L.) and quadrupole velocity (Q.V.) forms, respectively. If the wave functions used were exact

these two forms would give us identical results. Hence the difference between these two results will be a measure of the goodness of the approximate wave functions (a small difference implying that the wave functions are good). Results of calculations using the various approximate wave functions are given in Table 4.9. The values for ΔE used for calculations in this section are the experimentally determined energy differences (Moore,(1949)) and are

$$\Delta E(1'S\text{-}3'D) = 1.6962 \text{ Ryd.}$$
$$\Delta E(1'S\text{-}4'D) = 1.7449 \text{ Ryd.} \qquad (4.3.3)$$

Table 4.9

Values for $(4\pi/5)R_{ji}^{(2)}$ (in units of a_o^4). The number k refers to the approximate wave function used (c.f. Table 4.8).

k	$(4\pi/5)R_{ji}^{(2)}$(Q.L.)	$(4\pi/5)R_{ji}^{(2)}$(Q.V.)
	1'S-3'D	
1	0.02090	0.03759
2	0.05471	0.05993
3	0.12934	-
4	0.02207	-
5	0.07139	0.06506
	1'S-4'D	
1	0.01107	0.01947
2	0.02701	0.02957
5	0.03510	-

The smallest difference between the Q.L. and Q.V. forms for the 1'S-3'D transition occurs with the Hartree-Fock wave function (k=2). The next smallest difference is obtained with the wave function k=5. This behaviour seems to be the case for the 1'S-4'D transition as well. The numerical values of the reduced matrix elements seem to be converging to a value in the neighbourhood $R_{ji}^{(2)}$(Q.V.) calculated with the k=2 wave function and we have used the values of $R_{ji}^{(2)}$ calculated in this way in evaluating cross sections for both transitions.

We note from Tables 4.8 and 4.9 that there is no correlation between the smallness of the ΔE_k values and the smallness of the difference between $R_{ji}^{(2)}$(Q.L.) and $R_{ji}^{(2)}$(Q.V.). In particular allowance for correlation ($c_k \neq 0$) and allowance for open shell behaviour ($a_k \neq b_k$) seem to be about equally important.

Calculations of cross sections were carried out using (2.7.5) with ω_i=1 and N=2. The values of ΔE are given in (4.3.3) and the values for $R_{ji}^{(2)}$ were chosen as discussed above. The cut-off R_o is obtained by normalizing our cross sections to the experimental data of St.John et al, (1964) at 450eV. Since the experimental data is uncertain by at least 10% (part of this is due to the fact that the results we used were read from a graph) the values of R_o and hence the cross section are uncertain by at least this amount. (See §5.1 for a discussion of the effect of errors in R_o). Table 4.10 gives these values of R_o along with values of $\bar{r}_i$, $\bar{r}_j$ and $\bar{R}$. (For a definition of these quantities see §4.2). Cross section results are given in Table 4.11 and presented graphically in Figures 4.11 and 4.12 along with experimental results.

Table 4.10

Values for the cut-off parameter R_o for transitions in helium.

i	j	$\bar{r}_i$	$\bar{r}_j$	$\bar{R}$	R_o
1'S	3'D	0.928	5.63	1.71	1.74
1'S	4'D	0.928	10.88	2.59	1.64

Table 4.11

Cross sections for transitions in helium induced by electron impact (in units of $\pi a_o^2 \times 10^{-3}$)

W_i(eV)	Q(1'S-3'D)	Q(1'S-4'D)
25	2.02	1.10
30	3.02	1.69
40	3.81	2.11
45	3.89	2.15
50	3.84	2.13
75	3.25	1.79
100	2.66	1.47
150	1.90	1.05
200	1.44	0.802
250	1.18	0.650
300	0.990	0.543
350	0.851	0.466
400	0.742	0.408
450	0.660	0.364

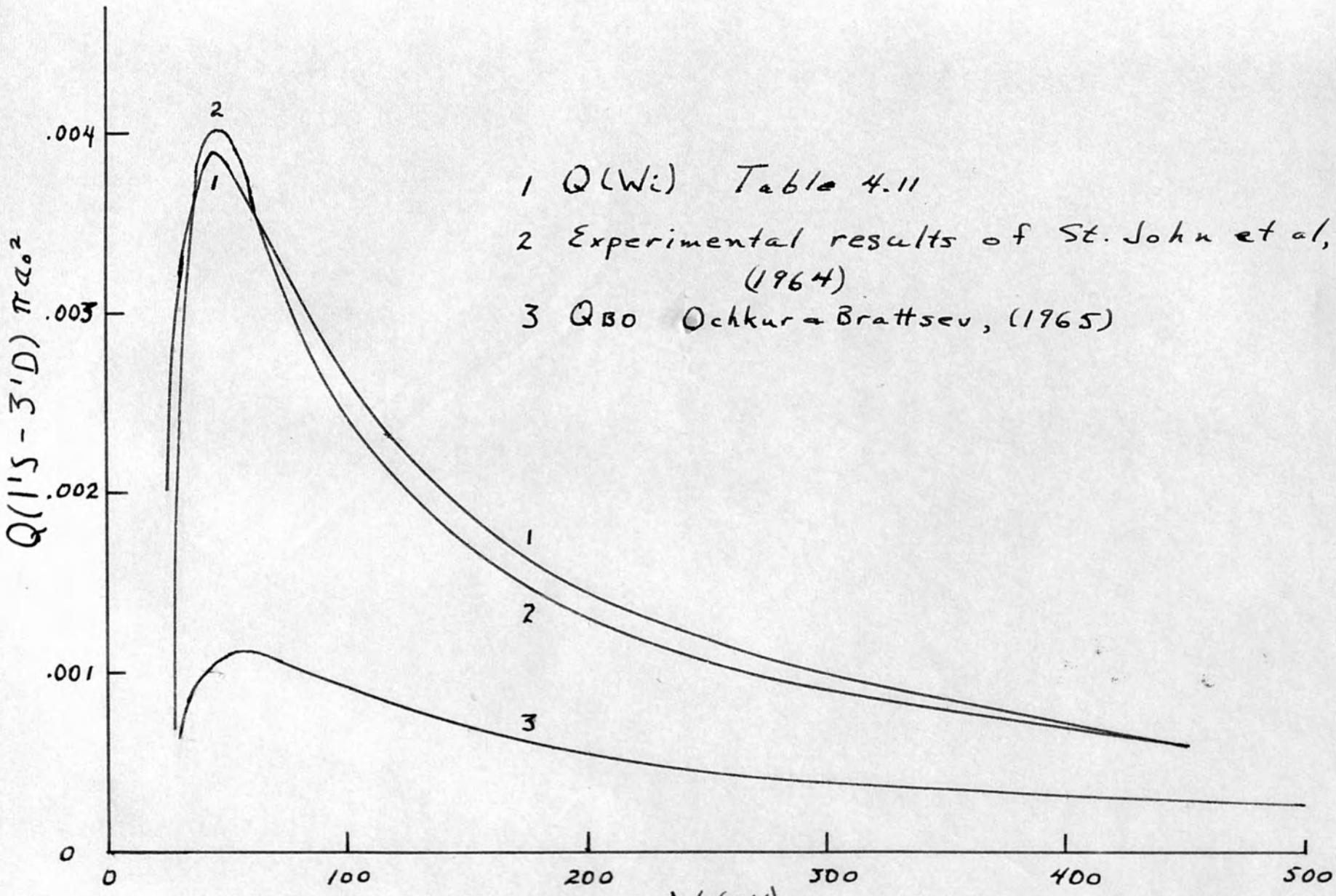
1 Q(Wi) Table 4.11
2 Experimental results of St. John et al, (1964)
3 QBO Ochkur + Brattsev, (1965)
Q(1'S - 3'D) πa0²
.004
.003
.002
.001
0
0
100
200
300
400
500
Wi(eV)
1
2
3

Fig. 4.11

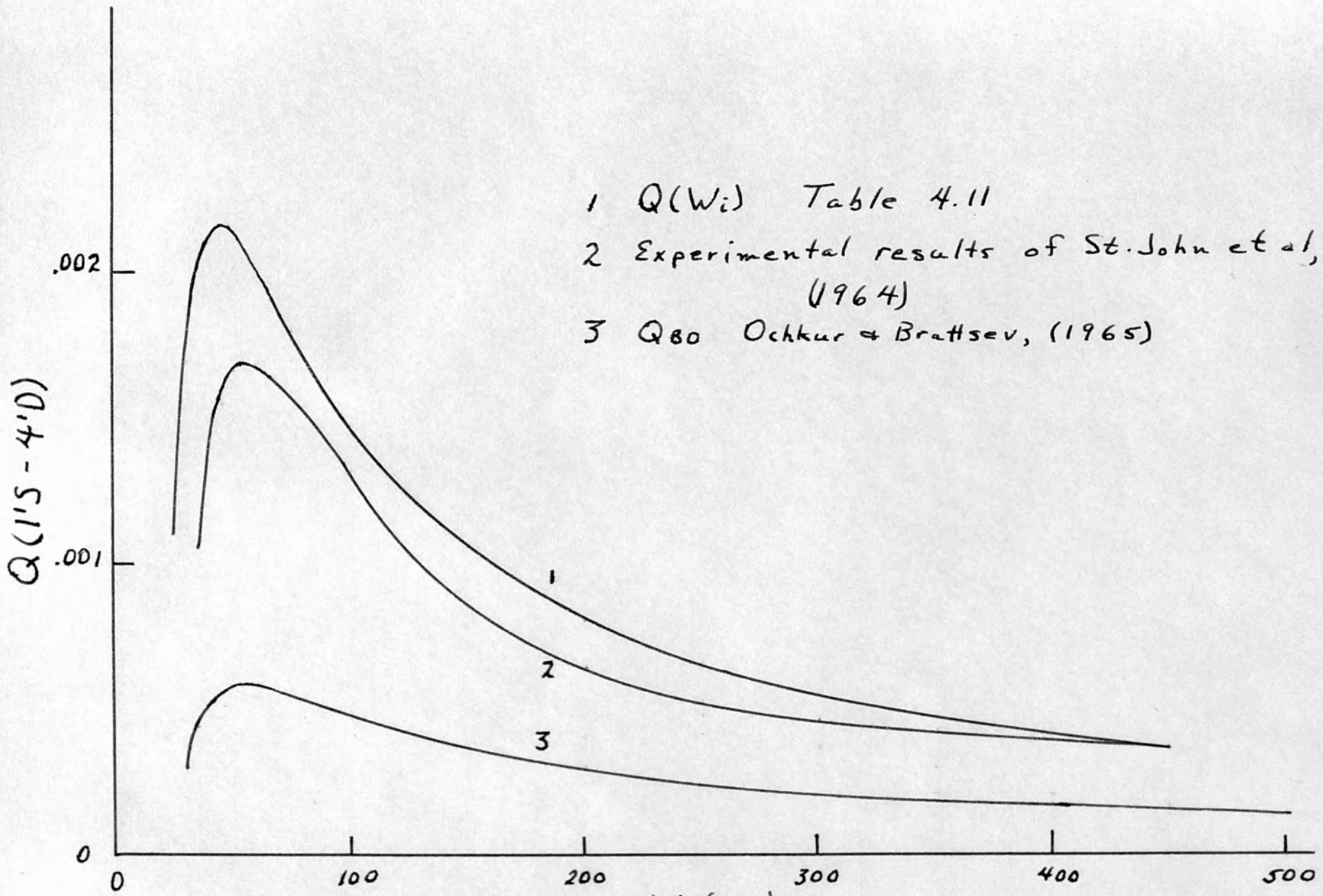
1 Q(Wi) Table 4.11
2 Experimental results of St. John et al, (1964)
3 Q80 Ochkur & Brathsev, (1965)
.002
.001
0
Q(1'S - 4'D)
1
2
3
0
100
200
300
400
500
Wi(eV)

Fig 4.12

No strong coupling calculations were done for transitions in helium in view of their general unreliability in the case of hydrogen.

Cross sections for excitation of the 1'S-n'D transitions in helium by proton impact were calculated by means of (4.2.7). The results are given in Table 4.12 and in Figures 4.13 and 4.14.

§ 4.4. Additional Calculations.

In this section we report on additional calculations done by other workers and ourselves using formulae derived in this thesis. Dr. M.R.C.McDowell has calculated cross sections using (3.5.6) for the following transitions excited by electron impact:

$$\mathrm{He}(1s2p\,{}^1P) \rightarrow \mathrm{He}(1snd\,{}^1D) \quad n=3,4,5,6 \qquad (4.4.1)$$

$$\mathrm{N}((1s)^2(2s)^2(2p)^3\,{}^2P) \rightarrow \mathrm{N}((1s)^2(2s)^2(2p)^3\,{}^2D) \qquad (4.4.2)$$

$$\mathrm{O}((1s)^2(2s)^2(2p)^4\,{}^1D) \rightarrow \mathrm{O}((1s)^2(2s)^2(2p)^4\,{}^1S) \qquad (4.4.3)$$

$$\mathrm{O}((1s)^2(2s)^2(2p)^4\,{}^3P) \rightarrow \mathrm{O}((1s)^2(2s)^2(2p)^3(3s)\,{}^3S) \qquad (4.4.4)$$

The transitions (4.4.1) and (4.4.4) are allowed transitions and in the case of (4.4.4), (3.5.6) reduces to the formula given by Seaton, (1962). There are no experimental or other theoretical results available with which we may compare. However from the work of Seaton, (1962) we would expect these results to be quite reasonable and comparison with similar transitions in hydrogen indicates that they are of the right order of magnitude.

The maximum values of the cross sections for the transitions (4.4.1) are (in units of πa_o^2) approximately 40, 4.9, 0.27 and 0.008 for n=3,4,5 and 6, respectively. The transition (4.4.4) was calculated in two ways corresponding to the choice of $\bar{r}_i$ and $\bar{R}$ for the cut-off R_o.

Table 4.12

Cross sections for transitions in helium induced by proton impact (in units of $\pi a_o^2 \times 10^{-3}$).

W_i(keV)	Q(1'S-3'D)	W_i(keV)	Q(1'S-4'D)
24.8	3.76	24.2	2.10
34.0	4.87	33.6	2.65
52.2	5.36	51.7	3.00
61.5	5.24	60.8	2.92
70.7	4.99	70.1	2.80
116.7	3.84	116.1	2.13
162	3.01	162	1.67
255	2.06	254	1.140
346	1.530	346	0.855
438	1.238	438	0.681
530	1.030	530	0.565
622	0.882	622	0.486
713	0.765	713	0.422
805	0.678	805	0.374

Maximum values of the cross section for these two choices are (in units of πa_o^2) 2 and 0.9, respectively.

The transitions given by (4.4.2) and (4.4.3) are forbidden transitions with $\Delta l = 0$. Thus from the discussion in §2.2 and the results of §4.2 for these types of transition we would not expect to obtain good results in these cases. Comparisons of the values for the collision strengths for these transitions can be made with those obtained by Seaton, (1955) and (1958) and they differ by a factor of more than 100.

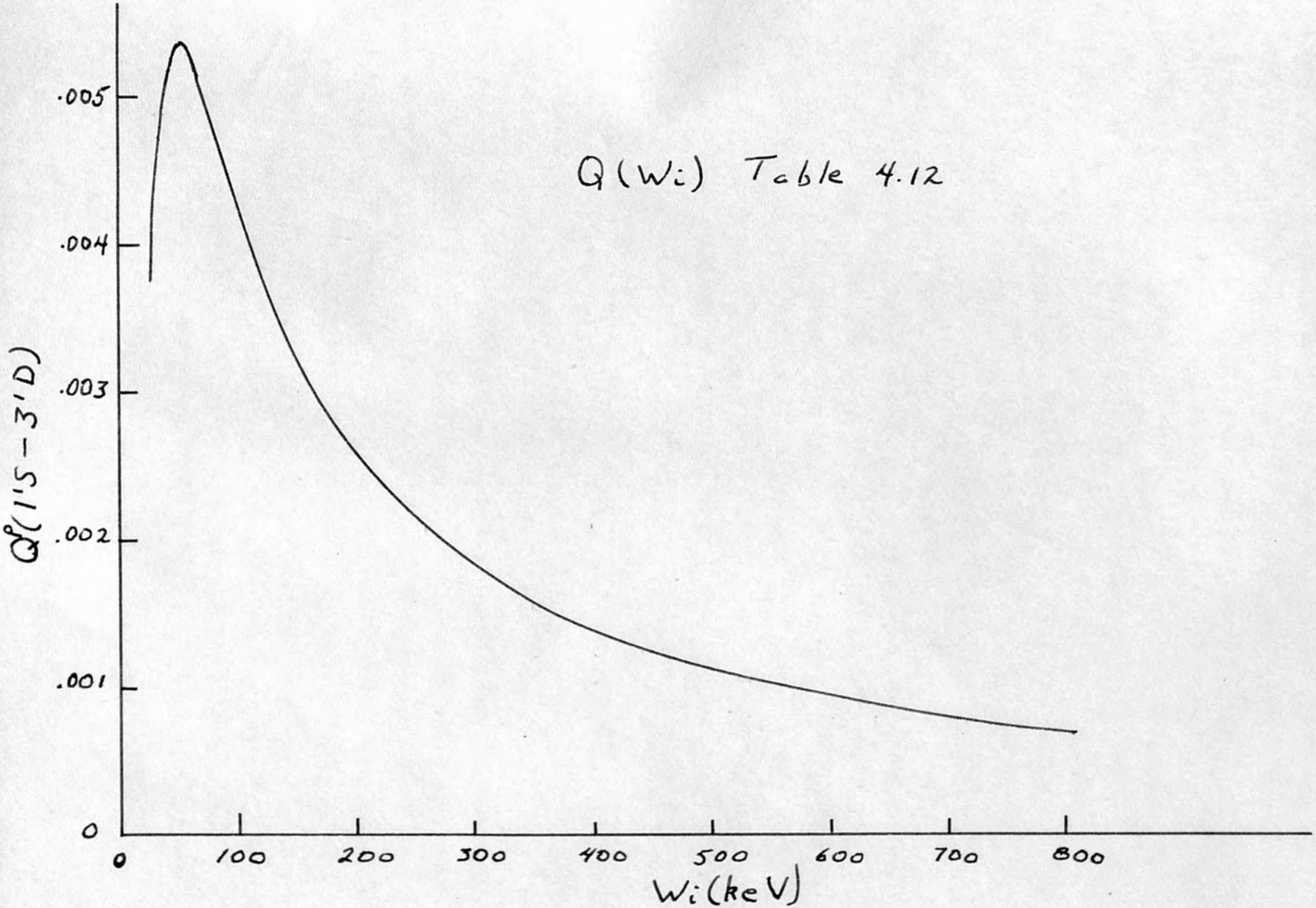
Q(Wi) Table 4.12
.005
.004
.003
.002
.001
0
$Q^0(1'S-3'D)$
0
100
200
300
400
500
600
700
800
Wi(keV)

Fig. 4.13

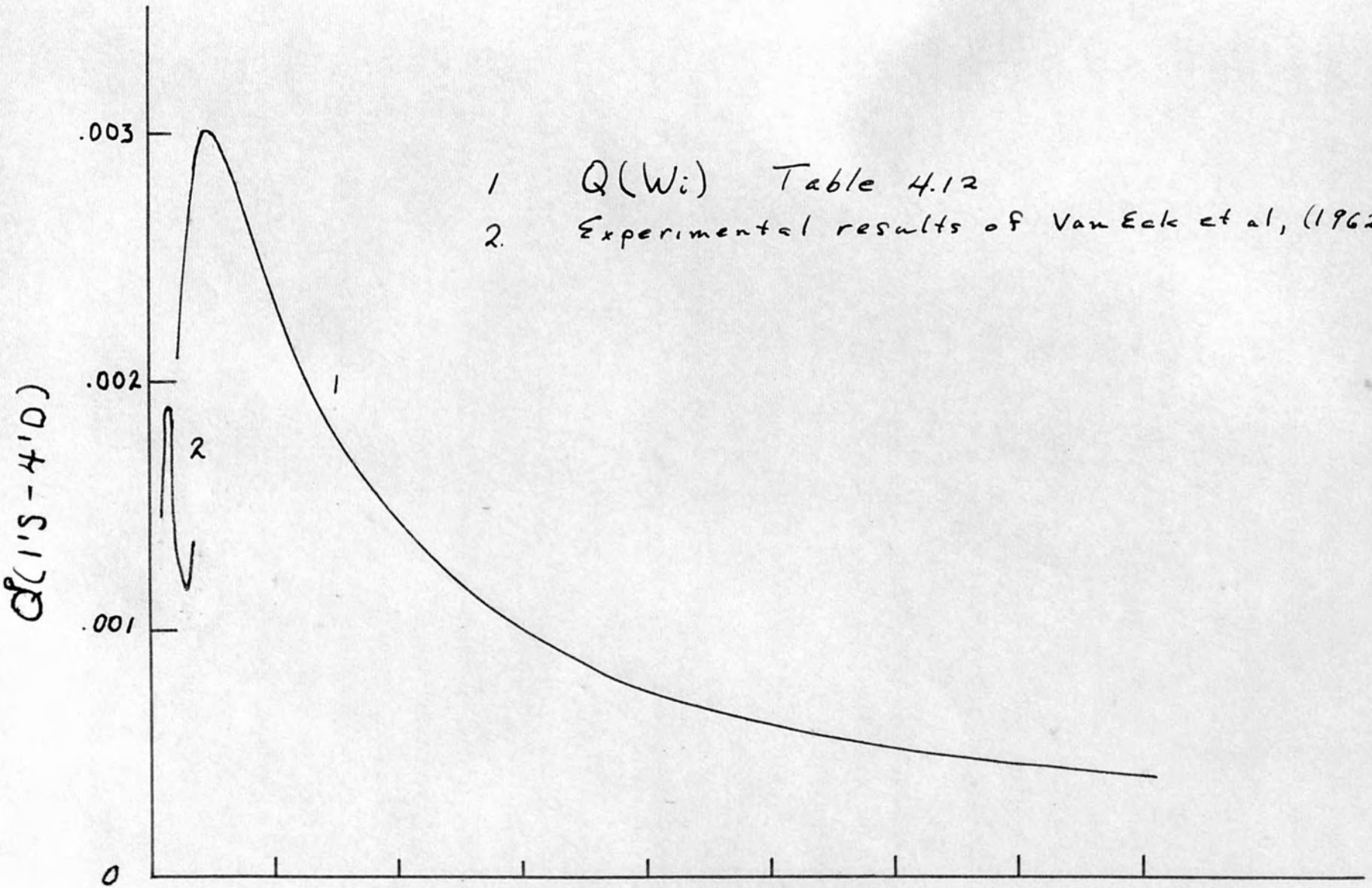
1 Q(Wi) Table 4.12
2. Experimental results of Van Eck et al, (1962)
Q(1'S - 4'D)
.003
.002
.001
0
1
2
0
100
200
300
400
500
600
700
800
Wi (keV)

Fig. 4.14

Calculations have also been done for transitions in hydrogen using (3.5.6), i.e. including all multipoles which contribute to the cross section. The inclusion of all the pertinent multipoles will result in the addition of a non-negative quantity to the cross section calculated using the dominant multipole only. For allowed transitions the dipole contributes the dominant term to the cross section and this behaves as $\ln W_i/W_i$ at large impact energies. The rest of the multipoles contribute terms which behave as W_i^{-1}. Thus we would not expect the use of (3.5.6) instead of (2.5.6) to appreciably change the values of the cross sections for large impact energies. Calculations for the transitions 2p-3d, 3p-4d and 3p-5d bear this out as the additional term amounts to 2% or less of the total cross section at these energies. At the maximum of the cross section the additional term contributes about 10% and 15% of the total for the first two transitions, respectively.

For forbidden transitions all the pertinent multipoles give rise to terms in the cross section which behave as W_i^{-1} for large W_i. For the 2p-4f transition the exact term contributes about 25% of the total cross section at high impact energies and about 30% at the maximum of the cross section.

Thus for allowed transitions the values of R_o which are obtained by normalizing our cross sections to other theoretical or experimental results will not be appreciably affected by which formula is used to calculate the cross sections. For forbidden transitions, however, the values of R_o obtained in this way will generally be different for the two different methods.

Miss K.Pluta has calculated numerous transitions in hydrogen via (3.5.6) using $R_o=\bar{R}$. Typical results are shown in Figure 4.15.

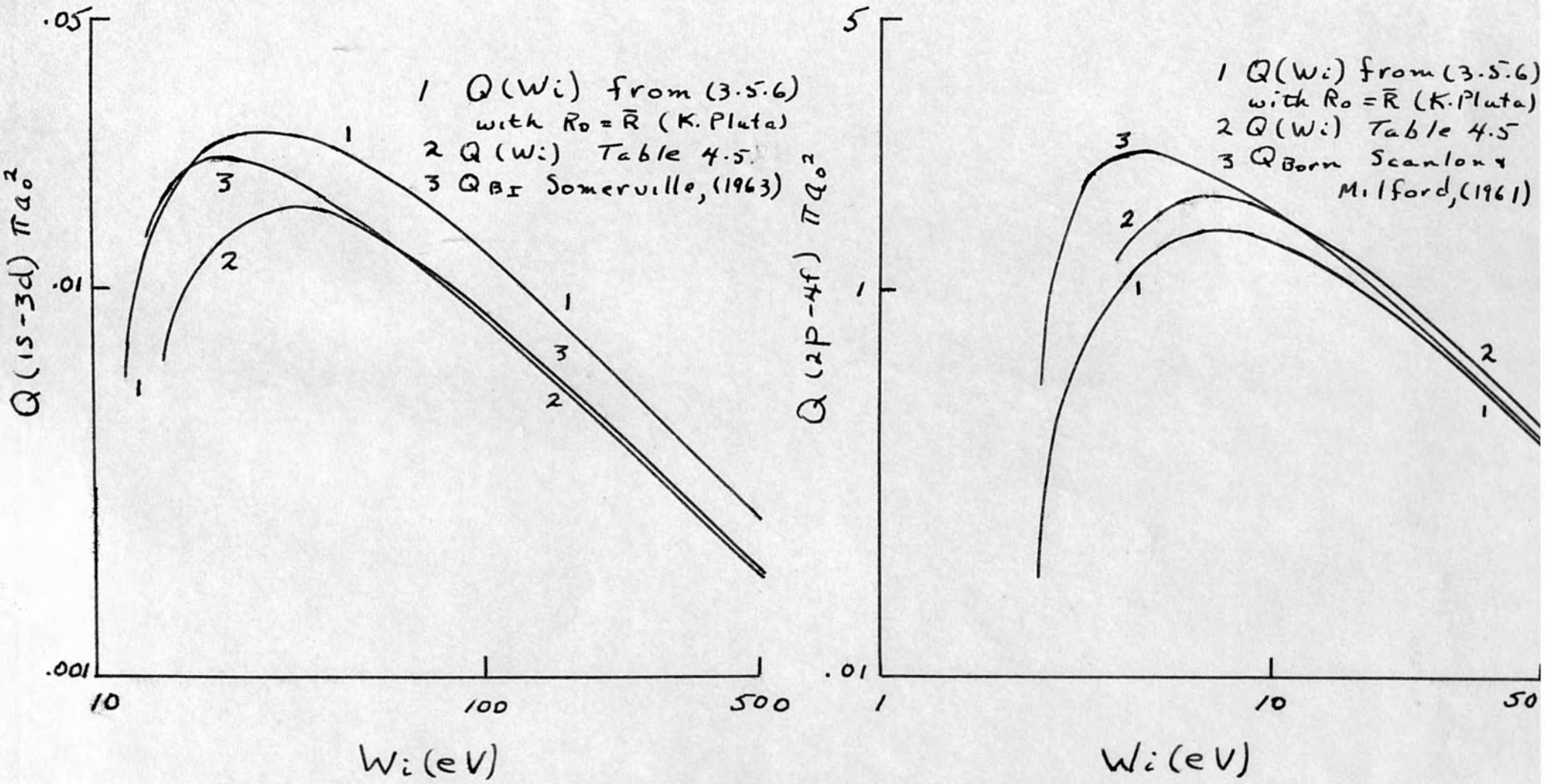
1 Q(Wi) from (3.5.6) with R0 = R̄ (K. Pluta)
2 Q (Wi) Table 4.5
3 Q BI Somerville, (1963)
Q (1S-3d) πa0²
.05
.01
.001
10
100
500
Wi (eV)
1 Q(Wi) from (3.5.6) with R0 = R̄ (K. Pluta)
2 Q(Wi) Table 4.5
3 Q Born Scanlon & Milford, (1961)
Q (2P-4f) πa0²
5
1
.01
1
10
50
Wi (eV)

Fig. 4-15

§ 4.5. Validity of the Approximations.

In this section we investigate the validity of the approximations made in the course of deriving our formulae.

First of all we consider the assumptions made in the general impact parameter method. Classically the assumption that the incident particle travels in a straight line with constant velocity is valid under almost all conditions (see §1.2). The only check we make on this assumption is the overall agreement of our cross sections with experimental and other theoretical results. Concerning the assumption that first order time-dependent perturbation theory is valid we can make a check to see whether the condition $\sum_{j\neq i} P_{ji} \ll 1$ is likely to be satisfied. We list some representative values of P_{ji} for hydrogen in Table 4.13 calculated from (2.3.7) using (2.4.6). From this table it would appear that the above condition will be satisfied for almost all values of W_i and R_i when the initial state is 1s. When the initial state is 2s the condition appears to be satisfied except when W_i and R_i are both small. However when the initial state is 2p the probabilities for the 2p-3p transition alone violate this condition over a fairly large region of energies and impact parameters. This explains in part the poor results we have obtained for the $\Delta l = 0$ cross sections.

It should be noted that the impact parameter method itself is not necessarily invalid in these regions where our probabilities do not fulfill the requisite condition since our probabilities are only approximate even within the context of the impact parameter method.

Table 4.13.

Values of P_{ji} for transitions in hydrogen induced by electron impact.

W_i(Ryd.)	R_i/a_o	P(1s-2p)	P(1s-3p)	P(1s-3d)
1.44	3.5	0.036	0.0034	0.0020
	5.6	-	-	0.00011
	8.4	-	-	0.0000033
4.00	3.5	0.033	0.0045	0.0014
	5.2	-	-	0.00025
	10.0	-	-	0.0000084

W_i(Ryd.)	R_i/a_o	P(2s-3p)	P(2s-3d)
0.25	7.8	0.23	0.57
	13.0	-	0.035
	20.8	-	0.0094
3.35	8.39	0.054	0.047
	10.1	-	0.022
	20.3	-	0.0015

W_i(Ryd.)	R_i/a_o	P(2p-3p)
0.25	3.5	4.6
	7.8	0.16
	20.8	0.00027
3.35	3.5	0.42
	7.6	0.019
	12.7	0.0026

From Table 4.13 we can reasonably conclude that, excluding $\Delta\ell = 0$ transitions, the method should be valid for $W_i \gtrsim 5\,\Delta E$ (and $R_i \gtrsim R_o$).

We are justified in introducing a cut-off for the impact parameter only if a sufficiently large contribution to the cross section actually comes from the region $R_i \geq R_o$. In order to verify this we calculate the collision strengths for some transitions in hydrogen and compare them with the Born results of Somerville,(1963). In quantum mechanical partial wave theory the collision strengths $\Omega_\ell(j,i)$ are defined such that

$$Q(i \rightarrow j) = \frac{I_H}{\omega_i W_i} \sum_{\ell=0}^{\infty} \Omega_\ell(j,i)\ (\pi a_o^2) \qquad (4.5.1)$$

(c.f. Somerville,(1963)). Following Seaton,(1962) we put $L^2 = \ell(\ell+1)\hbar^2$ where L^2 is the magnitude of the angular momentum of the incident particle. Then the impact parameter R_ℓ is given by

$$R_\ell = \frac{L}{mv_i} = \frac{h\sqrt{\ell(\ell+1)}}{mv_i} \qquad (4.5.2)$$

and

$$d\left(\frac{R_\ell^2}{2}\right) = \frac{\hbar^2}{2m^2 v_i^2}(2\ell+1)d\ell \qquad (4.5.3)$$

so that

$$\begin{aligned} Q(i \rightarrow j) &= 2\pi \int_o^\infty P_{ji}(R_\ell)\, d\left(\frac{R_\ell^2}{2}\right) \\ &= \frac{\pi\hbar^2}{m^2 v_i^2} 2 \int_o^\infty P_{ji}(R_\ell)(2\ell+1)d\ell \ . \end{aligned} \qquad (4.5.4)$$

Comparing (4.5.1) and (4.5.4) and treating the sum as an integral with $1 = d\ell$ we have

$$\Omega_\ell(j,i) = \omega_i(2\ell+1)\ P_{ji}(R_\ell). \qquad (4.5.5)$$

Values of Ω_ℓ are listed in Table 4.14 for certain transitions in hydrogen induced by electron impact and are compared graphically with the Born calculations of Somerville,(1963) in Figures 4.16, 4.17 and 4.18. We see

Table 4.14.

Collision strengths for transitions in hydrogen induced by electron impact. ($(k_i a_o)^2 = W_i/I_H$).

$\Omega_\ell(3d,1s)$

$k_i a_o = 1.2$		$k_i a_o = 2.0$	
R_ℓ/a_o	Ω_ℓ	R_ℓ/a_o	Ω_ℓ
3.50	1.72, -2	3.50	1.94, -2
4.11	7.94, -3	4.00	1.29, -2
4.67	4.29, -3	5.20	5.48, -3
5.60	1.48, -3	6.40	2.57, -3
6.53	5.19, -4	7.60	1.27, -3
7.47	1.85, -4	8.80	6.20, -4
8.40	6.6 , -5	10.00	3.36, -4

$\Omega_\ell(3d,2s)$

$k_i a_o = 0.5$		$k_i a_o = 1.803$	
R_ℓ/a_o	Ω_ℓ	R_ℓ/a_o	Ω_ℓ
6.7	7.79, 0	6.70	2.77, 0
7.8	4.51, 0	7.62	1.89, 0
10.4	1.45, 0	8.39	1.43, 0
13.0	4.59, -1	9.40	1.03, 0
15.6	1.58, -1	10.16	8.21, -1
18.2	5.6 , -2	10.93	6.66, -1
20.8	1.9 , -2	11.94	5.16, -1
		15.25	2.56, -1
		20.33	1.11, -1

The figure after the comma in the entries for Ω_ℓ indicates the power of ten by which the entry is to be multiplied.

Table 4.14 cont'd.

$\Omega_\ell(3p,2p)$

$k_i a_o = 0.5$		$k_i a_o = 1.803$	
R_ℓ/a_o	Ω_ℓ	R_ℓ/a_o	Ω_ℓ
3.5	1.67, 1	3.50	5.35, 0
5.2	5.02, 0	5.08	1.76, 0
7.8	1.27, 0	6.35	9.05, -1
10.4	4.07, -1	7.62	5.33, -1
13.0	1.29, -1	8.89	3.40, -1
15.6	4.44, -2	10.16	2.31, -1
18.2	1.56, -2	11.43	1.64, -1
20.8	5.6 , -3	12.71	1.21, -1

The figure after the comma in each entry for Ω_ℓ indicates the power of ten by which the entry is to be multiplied.

from these figures that a majority of the Born cross section does come from $R_\ell > R_o$ for the 1s-3d and 2s-3d transitions but not for the 2p-3p transition. (It is probable that in fact a larger proportion of the contributions to the cross sections comes from the region $R_\ell > R_o$ than is indicated by the Born results. This is because the Born cross sections tend to overestimate the contributions from the region of small R_ℓ). This indicates that the introduction of the cut-off R_o is justified for $\Delta\ell = 2$ transitions but not for $\Delta\ell = 0$ transitions. This is borne out by the cross section results given in §§4.2 and 4.3.

We note that the collision strengths calculated in

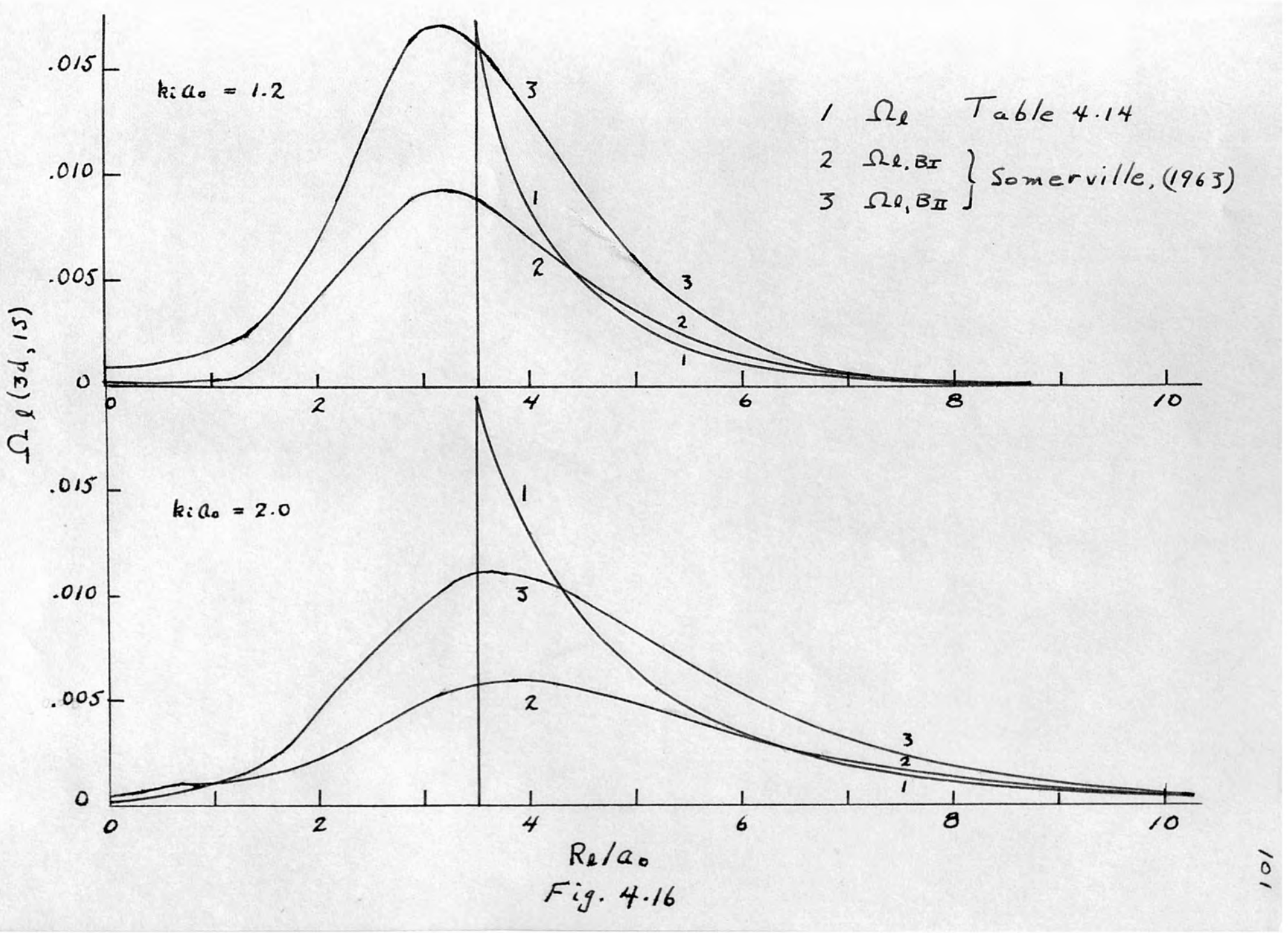
.015
.010
.005
0
$ki a_o = 1.2$
3
1
2
3
2
1
$\Omega_l(34,15)$
0
2
4
6
8
10
.015
.010
.005
0
$ki a_o = 2.0$
1
3
2
3
2
1
0
2
4
6
8
10
R_l/a_o
1 Ω_l Table 4.14
2 $\Omega_{l,BI}$
3 $\Omega_{l,BII}$
Somerville, (1963)

Fig. 4.16

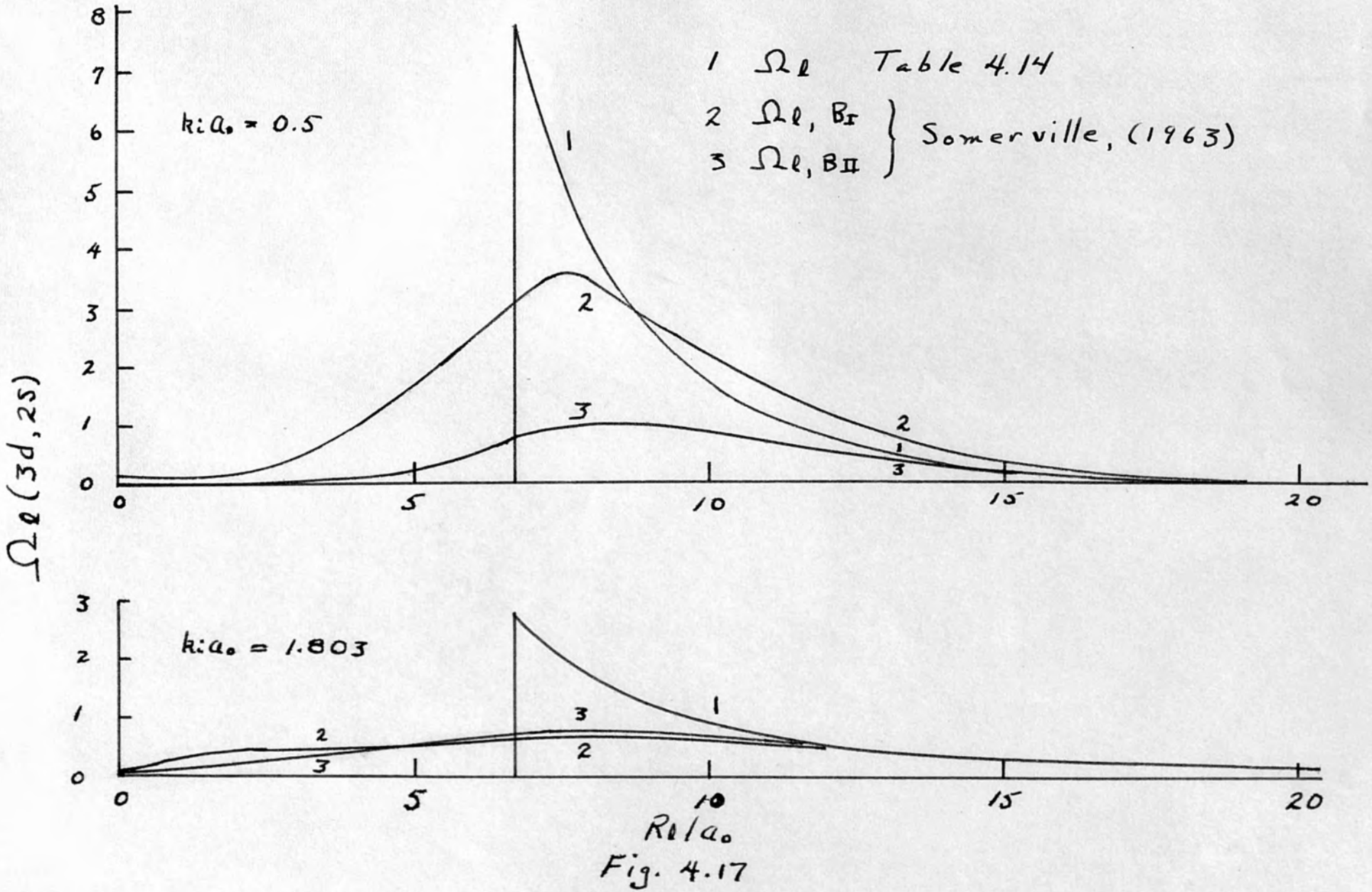
1 Ω_ℓ Table 4.14
2 Ω_ℓ, B_I
3 Ω_ℓ, B_{II}
Somerville, (1963)
$ka_0 = 0.5$
$ka_0 = 1.803$
$\Omega_\ell(3d,25)$
R_ℓ/a_0

Fig. 4.17

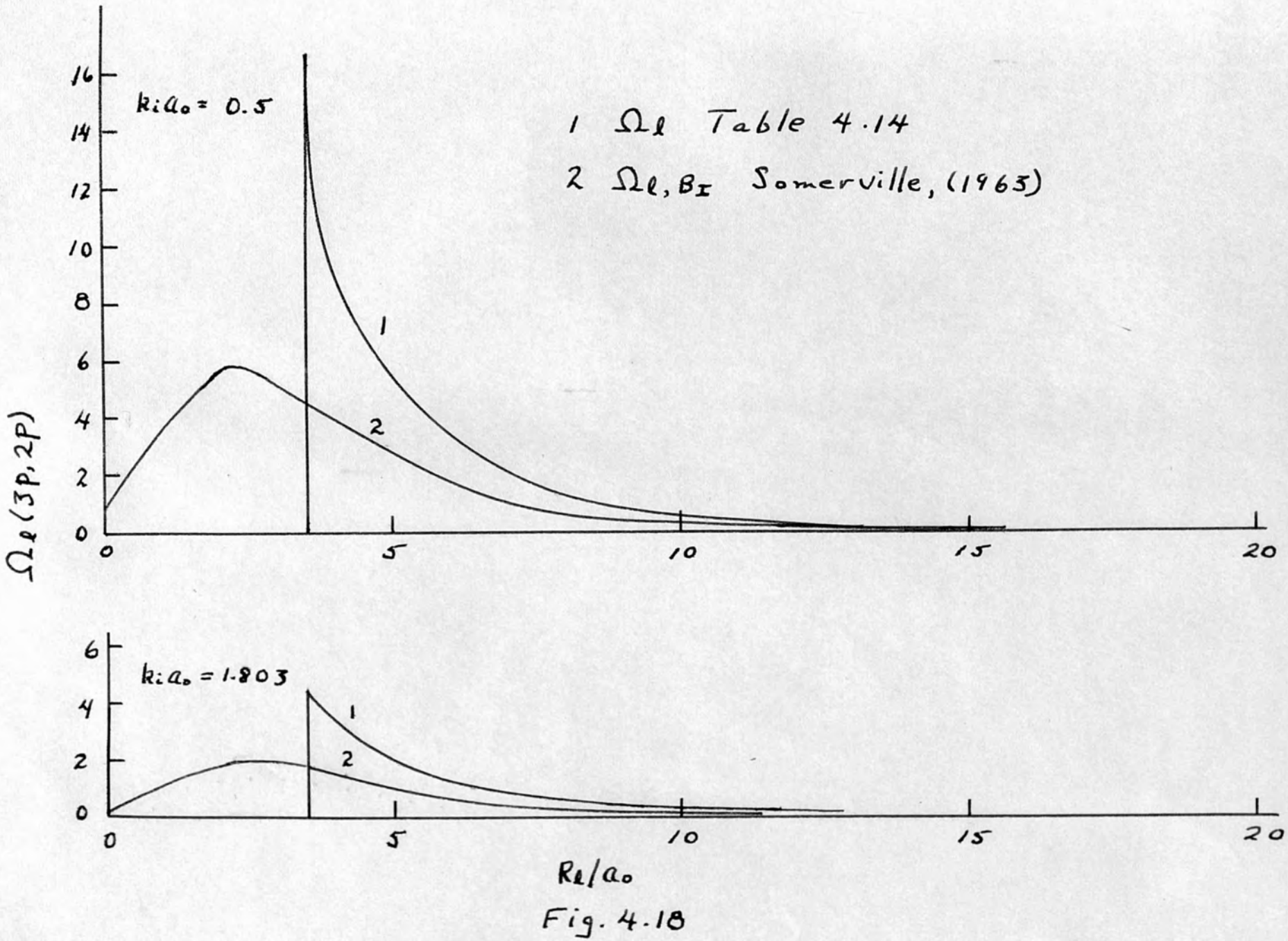
1 Ω_l Table 4.14
2 Ω_l, B_I Somerville, (1965)
$k_i a_o = 0.5$
$k_i a_o = 1.803$
$\Omega_l(3P, 2P)$
R_l/a_o
0
2
4
6
8
10
12
14
16
5
10
15
20
1
2

Fig. 4.18

the Born approximation and by the impact parameter method have the same values for sufficiently high values of R_1. It is interesting to note that for the 2s-3d transition the impact parameter collision strengths are in agreement with the B_{II} results (improved Born approximation; Somerville, (1963)) over a wider range of values than with the B_I results (ordinary Born approximation). We would not expect the same to hold true for the 1s-3d transition as it appears that the B_{II} cross sections are greater than the B_I cross sections even at large impact energies (i.e. in the region where we have normalized our cross sections to the B_I results). For the 2s-3d transition the B_I and B_{II} cross sections agree for $W_i \gtrsim 50$eV.

We now consider the effect of using the asymptotic form of the potential instead of the actual potential, i.e. the effect of the assumption that r', the coordinate of the incident particle, is always greater than r, the coordinate of the atomic electron. We note that this assumption requires the introduction of a cut-off since, if we let R_o tend to zero our formulae give infinite values for the cross sections (and for the transition probabilities). That this is so can be seen from (2.5.6) or (3.4.7) since as R_o (and hence β_o) tends to zero, $K_\mu \sim \beta^{-\mu}$.

Of course, even if our results did not diverge in the limit $R_o \to 0$, we would still be justified in introducing a cut-off if we obtained "better" results by using this method. In fact, the motive for the introduction of the cut-off was to avoid the region of small impact parameters where the general assumptions of the semi-classical impact parameter method were likely to be invalid and, on the basis of the results of the first Born approximation, likely to overestimate the transition probabilities (Seaton, (1962)). From this point of view it is the introduction of the cut-off which allows us to use the asymptotic

form of the potential and not the use of this form of the potential which necessitates the cut-off.

Seaton, (1962) has given a qualitative argument (reproduced in §1.4) to justify the use of the asymptotic form of the potential if R_o is large enough ($R_o \gtrsim \bar{r}_<$). We have shown above that the majority of the contribution to the cross section comes from $R_i > R_o$ and that R_o satisfies the requisite condition for all transitions except those with $\Delta l = 0$ (c.f. Tables 4.4 and 4.10). This indicates that we are justified in using this approximation to evaluate cross sections and this conclusion is supported by the results obtained (c.f.§§4.2, 4.3).

In addition to these qualitative arguments we can make a few quantitative comparisons between the exact semi-classical impact parameter method (i.e. no cut-off is introduced and the exact form of the potential is used) and our approximate method. Note that we are comparing the results of calculations of cross sections and not of transition probabilities. In introducing a cut-off we assume that the transition probabilities are zero for $R_i < R_o$ and thus we would not expect the transition probabilities calculated by the exact method and by our approximate method to agree over the whole range of impact parameters. In this context the two approximations of introducing a cut-off and of using the asymptotic form of the potential must be considered together.

The following calculations have been made of cross sections for the excitation of hydrogen by proton impact by means of the exact semi-classical impact parameter method: Bates, (1961), 1s-2s; van den Bos, (1966), all transitions from the ground state to states with n=2 and 3. These results have been compared with cross sections for the above transitions calculated by means of the first Born approximation (Bates and Griffing, (1953)) in the energy range 1 to 100 keV. For the s-s and s-d transitions

no differences between the cross sections calculated in these two ways could be found. For the 1s-2p transition the Born cross section was slightly above (~20%) the impact parameter cross section for $W_i > 50$ keV. and for the 1s-3p transition the Born cross section was above the impact parameter cross section for $W_i < 30$ keV. At 1 keV. it was twice as large.

Dr. M.R.C.McDowell has calculated cross sections for the 1'S-n'D, n=3,4, transitions in helium for both electron and proton impact using the exact impact parameter method and has obtained results which are 30% to 40% lower than the experimental electron impact results of St.John et al, (1964). The proton impact results are in fairly good agreement with some recent unpublished results of de Heer and van den Bos. The use of more accurate wave functions in this calculation might lower these cross section results by a factor of two bringing them into agreement with the recent calculations of Ochkur and Brattsev,(1965) for electron impact. Ochkur and Brattsev have used a modified Born-Oppenheimer approximation which makes allowance for exchange and their results agree fairly well with the calculations of Fox (see Seaton,(1962a)) at 108 eV.

In view of these results we have done a rough calculation of the 1'S-4'D transition by means of our approximate impact parameter method, normalizing our results to those of Ochkur and Brattsev,(1965) at 400 eV. Our results behave in much the same way with respect to the Born-Oppenheimer results in helium as they did with respect to the Born results in hydrogen; that is, they agree quite well at high and moderate energies but drop below the Born-Oppenheimer results near the peak of the cross section and have a maximum at an energy some 50% higher than that at which the Born-Oppenheimer results have a maximum. The cut-off for both the n=3 and 4 transitions

when normalized in this way is $R_o \cong 2.8$. (c.f. Table 4.10).

Because of the relation between the electron and proton excitation cross sections, both in the Born approximation and in the impact parameter method, as given in §4.2, we can reasonably conclude that the cross sections for electron excitation calculated by means of the exact impact parameter method will agree with those calculated in the first Born approximation, at least for $W_i \geq 5\Delta E$. On the basis of the results discussed above we are led to the following statement. If a cut-off is introduced and the asymptotic form of the potential used in the impact parameter method, and if the cut-off is chosen to make the cross section agree with the first Born cross section at high energies, then there is no significant difference from the exact impact parameter method at high and moderate energies. Near the peak the approximate impact parameter method cross sections are below those obtained with the exact method and the maximum of the cross section occurs at higher energies. This statement must of course, be regarded as tentative until further evidence for or against it is available.

The above statement implies that the exact impact parameter method and the first Born approximation give identical results at high energies. This is reasonable in the light of the discussion of §1.2. If R_o is not chosen to obtain agreement with the first Born cross sections at high energies there is, in general, no agreement between the results of the exact and approximate impact parameter methods. However, by regarding R_o as a parameter which we can adjust to obtain the "best" results, the approximate impact parameter method may be superior to the exact method in predicting cross sections, especially as there is a discrepancy between the first Born cross sections and the experimental results for the 1'S-n'D

series of transitions in helium. This brings up the whole question of the choice of R_o which we discuss in the next section.

Finally we consider the effect of requiring that the transition probabilities satisfy the reciprocity condition. In §2.4 we have given arguments to show that this requirement will not introduce appreciable errors except perhaps when R_i and W_i are both small. Since $R_i \geq R_o$ the only possible time when this approximation will be invalid is when W_i is small, in which case our cross sections are likely to be unreliable for other reasons given above. The fact that our transition probabilities (or equivalently, collision strengths) agree with those calculated in the first Born approximation at high energies (see Figs. 4.16, 17, 18) bears this out.

Before we leave the question of the validity of the approximations we should make the following remark. The approximation of using the asymptotic form of the potential becomes progressively worse as the value of λ, which designates the dominant term in the expansion of the interaction potential V(t), increases; (We note that $\lambda = \Delta\ell$ if $\Delta\ell \neq 0$). To put it another way, as λ increases, so must the value of the cut-off R_o increase in order that the approximation be valid. It would appear from Seaton, (1962) and from the above results that the method is valid for transitions for which $\Delta\ell = 1$ or 2. We stress that the above discussion is based on results of transitions for which $\Delta\ell \leq 2$. While we would expect the method to be generally valid if $\Delta\ell$ is not too large, more direct evidence is needed if we are able to say this with certainty for the cases $\Delta\ell > 2$. (See also §5.1).

§ 4.6. Choice of the cut-off R_o.

In order to calculate cross sections by means of the formulae (2.5.6) or (3.4.7) a value of the cut-off R_o must be chosen. If reliable experimental or theoretical data are available for high impact energies, a value of R_o may be obtained by normalizing our cross sections to these data as we did above. However if our formulae are to be used to calculate cross sections for transitions for which no previous data are available, a prescription for choosing R_o is necessary.

Seaton,(1962) has suggested that R_o be taken equal to $\bar{r}_a$, the mean atomic radius of the initial state. We suggest as an alternative that R_o be taken as $\bar{R}$ as defined by (4.2.4). Reference to Table 4.4 shows that for hydrogen (excluding $\Delta l = 0$ transitions) the choice $R_o = \bar{R}$ is closer to the value of R_o obtained by normalization than the choice $R_o = \bar{r}_a$ in all cases but one. The maximum error introduced by the former choice is 20%; by the latter, 60%. In the case of allowed transitions in hydrogen, Table 3 of Seaton,(1962) shows that the choice $R_o = \bar{R}$ is closer to the normalized value than Seaton's choice in slightly less than half the cases and the maximum error introduced by our choice is greater. The picture may be altered somewhat if (3.4.7) were used to calculate the cross sections rather than (2.5.6).

For the two transitions in helium which we have considered $\bar{R}$ is always closer to the normalized value of R_o than $\bar{r}_a$, whether we normalize to experimental results or to the Born-Oppenheimer cross sections.

In §2.9 we have derived an expression for the value of the energy at which the maximum of the cross section, as given by (2.7.5), occurs. The values of ε, as given

by (2.9.4), are displayed in Table 4.15 and shown in Fig. 4.19. By comparing the two curves for ε as given by (2.9.4) and (2.9.5) and shown in Figs 2.2 and 4.19 we see that they will intersect in at most one point and this point will give the value of ε (and hence (W_i) max) at which the maximum of the cross section occurs. Similar expressions for the energy at which the maximum in the cross section occurs could be derived for the more general cross section formula (3.4.7), at least for specific transitions.

If one knew the value of (W_i) max, say from relative experimental data, then one could obtain the corresponding value of R_o via (2.9.4). However, this method of choosing R_o is not very satisfactory as the maximum of our cross sections do not necessarily coincide with those of the experimental data (c.f. Figs. 4.13, 14).

Alternately one may think of using some empirical formula such as (W_i) max = $2\Delta E$ but this would give only a rough estimate for R_o.

Table 4.15

Values for ε as given by (2.9.4)

β_o	ε
0.4	< 0
0.5	0.0490
0.6	0.1227
0.7	0.223
0.8	0.353
0.9	0.520
1.0	0.736
1.1	1.024
1.2	1.405
1.3	1.950
1.4	2.756
1.5	4.145
1.6	6.864
1.7	14.99
1.8	830.
1.9	< 0

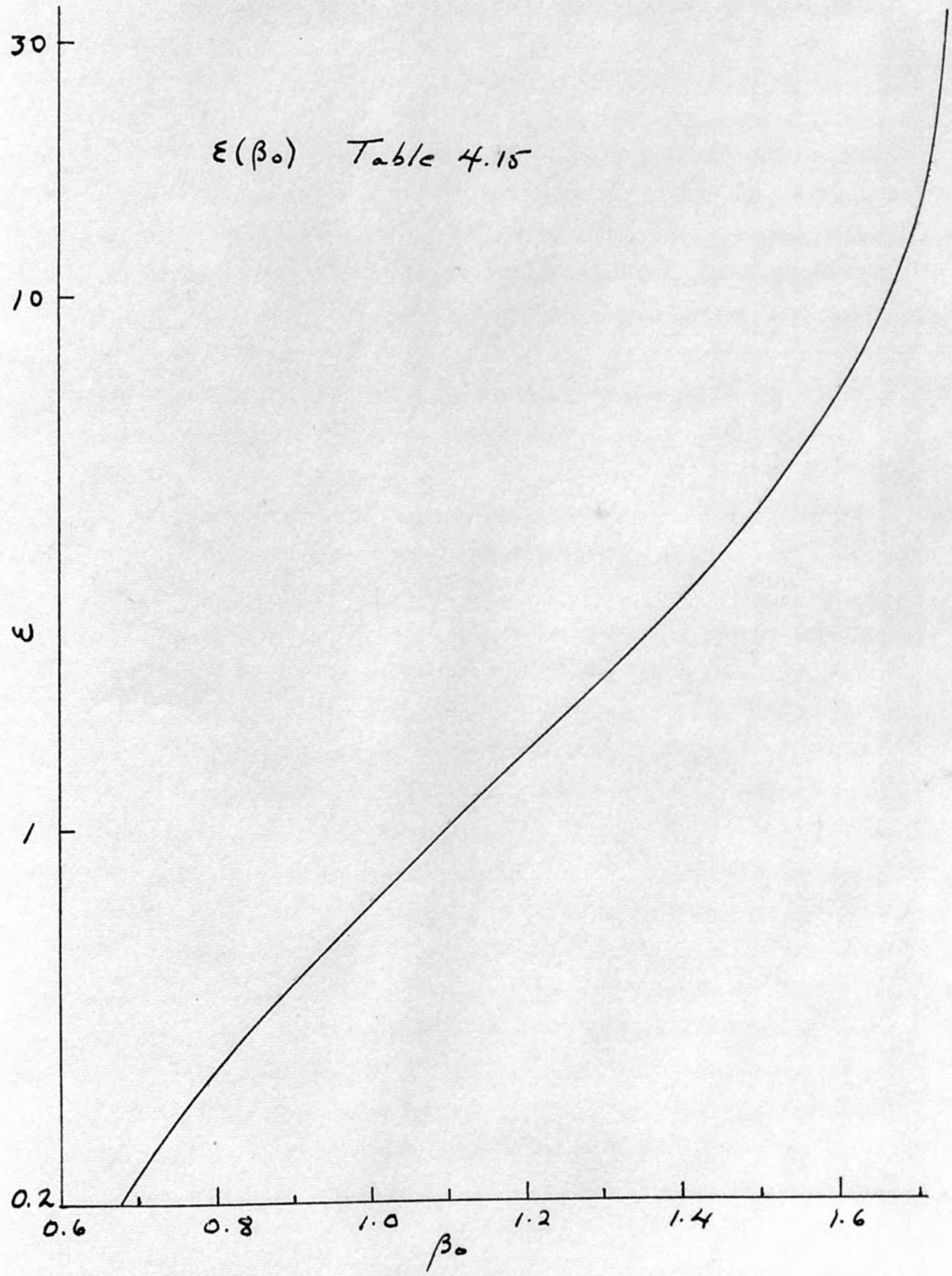

Fig 4.19

Chapter 5.

§ 5.1. Evaluation of the semi-classical impact parameter method.

We have used the formulae derived in Chapters 2 and 3 to calculate cross sections for transitions in various atoms for which $\Delta\ell=0$ or 2. The results of the calculations were presented in Chapter 4. Here we wish to try and draw some general conclusions about the usefulness and reliability of these formulae.

Comparing our results with those obtained from the first Born approximation (c.f. Figs. 4.1 to 4.10) we remark that,

a) our formulae are unreliable for transitions in which $\Delta\ell=0$. (This is not surprising in view of the discussion in §2.2);

b) the strong coupling formulae (2.8.4) does not give reliable results for $\Delta\ell=0,2$ transitions;

c) our formulae are likely to be unreliable very near threshold where the assumptions made are most likely to break down.

On the other hand cross sections for $\Delta\ell=2$ transitions calculated from (2.5.6) or (3.4.7), if normalized to agree with the first Born cross sections at one (large) value of the energy, agree well with these Born calculations at high and moderate energies. Near the peak of the cross section our results are always lower than the first Born results and the value of the energy at which the peak occurs is some 50% higher than that for the Born cross sections. In view of the fact that the first Born approximation usually overestimates the cross section

near the peak, our results may well be superior to the first Born cross sections in this region. Also our results lie above the modified Born calculations of Somerville, (1963) except for the 1s-3d transition in hydrogen in which case the modified Born results are always higher than the first Born results.

In the case of the 1'S-n'D series of transitions in helium, normalization of our results to the experimental data at 450eV means that our cross sections agree with the experimental results to within 20% everywhere except very near threshold. In view of experimental errors this agreement can be considered satisfactory though it does not imply that our cross sections are necessarily correct (see below).

We should also mention that our formulae (2.3.7) or (3.4.6) for $P_{ji}(R_i)$ give results which are in good agreement with the first Born results for large and medium values of the impact parameter R_i (c.f. Figs 4.16, 17, 18).

Since our impact parameter method seems to give reasonable results for $\Delta\ell=2$ transitions if the "correct" value of R_o is chosen, we must investigate the errors introduced into the cross section for a given error in the choice of R_o. From (3.4.7) the dependence of Q on R_o is via the $\Omega_\lambda(\beta_o)$ (see (2.6.12)). But for W_i large, i.e. β_o small, $\Omega_\lambda(\beta_o)\sim\beta_o^{-2\lambda+2}$ if $\lambda\neq1$ and $\Omega_1\sim\ln\beta_o$ (c.f. §3.7) and β_o varies directly as R_o (see (2.5.1)). Thus if there is an error ΔR_o in R_o, at high energies we have

$$\frac{Q(R_o+\Delta R_o)}{Q(R_o)} \sim \left(1+\frac{\Delta R_o}{R_o}\right)^{-2\lambda+2}, \quad \lambda\neq1$$

$$\sim \frac{\ln(R_o+\Delta R_o)}{\ln R_o}, \quad \lambda=1 \qquad (2.5.1)$$

where the value of λ refers to the dominant term in (3.4.7). For allowed transitions $\lambda=1$ and for $\Delta\ell=0,2$ transitions $\lambda=2$. Thus, while allowed transitions depend logarithmically on the cut-off at high energies and hence are relatively insensitive to errors in R_o, $\Delta\ell=0,2$ transitions have an error $\sim -2\Delta R_o/R_o$ and are rather sensitive to the choice of cut-off. It should be noted that for transitions for which $\lambda > 2$ (i.e. $\Delta\ell > 2$), the sensitivity to errors increases rapidly as λ increases and hence the cross section results become progressively more unreliable.

Near the peak of the cross section errors in R_o have two effects. One is to change the magnitude of the cross section in that region and the other is to change the energy at which the peak occurs. In all the cases we have investigated, in the region of the peak $\beta_o \cong 1$. If we consider cross sections given by (2.7.5) for $\Delta\ell=0,2$ transitions then the dependence of the cross section on R_o is via the function $\psi(\beta_o)$. By examining the values of $\psi(\beta_o)$ in the region of $\beta_o=1$ (see Table 4.2) we see that

$$\frac{Q(R_o+\Delta R_o)}{Q(R_o)} \sim \left(1+\frac{\Delta R_o}{R_o}\right)^{-3} \qquad (2.5.2)$$

in this region. Thus the error in the magnitude of the cross section is $\sim -3\Delta R_o/R_o$.

Near the peak $\sqrt{\frac{\Delta E}{I_H}}\,\frac{R_o}{a_o} \cong 3$ for all transitions investigated so that $\beta_o \cong 3x$ where x is defined in §2.9. Thus by plotting (2.9.5) on Fig. 4.19 with $\beta_o=3(1+\Delta R_o/R_o)x$ for various values of $\Delta R_o/R_o$ we find that

$$\frac{W_i \text{ max } (R_o+\Delta R_o)}{W_i \text{ max } (R_o)} \sim \left(1+\frac{\Delta R_o}{R_o}\right) \qquad (2.5.3)$$

Thus the percentage shift in the energy at which the peak occurs is approximately equal to the percentage error in R_o.

Since we assume that the cross sections are unreliable near threshold we do not consider the effects of errors in R_o in this region.

For $\Delta l = 2$ transitions in hydrogen $\Delta R_o/R_o$ is less than 20% in all cases investigated if we put $R_o = \bar{R}$. Hence it would appear that the cross section for any $\Delta l = 2$ transition in hydrogen, calculated with $R_o = \bar{R}$, should differ from the first Born results by less than a factor of two everwhere except near threshold.

The position for helium, the other atom which we have studied, is not as clear. Because of a discrepancy of a factor of three or four between the first Born approximation calculations and experimental results for the 1'S-n'D series of transitions we cannot say with certainty what are the correct values of the cross sections for these transitions.

Uncertainty is also introduced into our calculations because we do not know the exact value of the reduced matrix elements (c.f.Table 4.9) although we would expect the values we have chosen to be within 30% of the correct ones.

These two sources of uncertainty make it difficult to estimate the "correct" value of R_o and hence we cannot judge whether or not putting $R_o = \bar{R}$ is a good approximation. We can say one thing however. Whether we normalize to experiment or to the Born approximation, the values of R_o for the n=3 and n=4 transition are approximately equal. In view of the suggestion made by Gabriel and Heddle, (1960) that the shape of the cross section is independent of n (which is substantially borne out by the results of St.John

et al, (1964)) we might expect this behaviour for the following reason. From (2.7.5), Q(1'S-4'D)/Q(1'S-3'D) is independent of energy if the value of β_o is equal in the two cases for equal values of the energy. This implies that $R_o\Delta E$ is independent of n and since the variation in ΔE is small between these two transitions (~5%) we would expect the value of R_o in these two cases to be roughly equal.

If the experimental results are reasonably accurate then it would appear that the value of R_o for the series of transitions 1'S-n'D is approximately the value of $\bar{R}$ for the n=3 transition (perhaps modified to keep $R_o\Delta E$ constant).

Thus, on the basis of our results, $R_o=\bar{R}$ seems to be a reasonable choice for $\Delta\ell=2$ transitions but the question of the choice of cut-off for arbitrary transitions in arbitrary atoms is far from settled and needs further investigation.

One line of attack on this problem is to calculate the value of the cross section at one (large) value of the energy via the exact impact parameter method and normalize our approximate cross section to this result. This will give a definite value of R_o which should make our results agree fairly closely with the first Born results.

§ 5.2. Better approximations.

In this section we briefly consider ways in which our impact parameter method might be improved. The most obvious way is to carry out the method exactly i.e. without using a cut-off or the asymptotic form of the potential. This would mean using the exact form for the

reduced matrix elements in §3.4. (It might still be useful to require that reciprocity be satisfied). This would remove any difficulty about the choice of cut-off but the results could not be given in an analytical form applicable to arbitrary atoms as the present results are. In fact it may not be possible to carry out exactly the integrations involved in this method (c.f. van den Bos, (1966)). It would also mean the loss of any flexibility that the parameter R_o introduced into the method.

In order to include the effects of coupling to intermediate states, the transition probabilities could be calculated up to the second order in the perturbation using either the approximate or the exact first order probabilities. This corresponds to a second Born calculation.

Alternately one could use the impact parameter version of the distortion approximation (Bates, (1961)). This approximation appears to give cross sections which are considerably lower than the first Born results in the region of the maximum (c.f.Bates, (1961)).

§ 5.3. Further applications.

We list here further applications of the formulae we derived which would be of interest.

Obviously calculations of cross sections for arbitrary non-exchange transitions in atoms could be carried out provided that the reduced matrix elements for the transitions in question could be obtained. The results should give a reasonable indication of the true cross section. Calculations of this type would enable one to further assess the reliability of the method, especially for transitions in which $\Delta l > 2$. They would also provide more

information on methods of choosing the cut-off R_o.

One could also use this method to calculate ionization cross sections. By decomposing the final state wave function into a sum of partial waves, formulae for the cross sections could be derived by methods similar to those used for excitation. Since in this case there would be an infinity of non-zero terms in the interaction potential matrix elements, only a finite number of the most important would probably be retained. Since the most important terms would be those corresponding to allowed transitions (at least at high energies) the method should give fairly reliable results as long as the interaction between the incident electron and the ejected electron could be neglected.

The impact parameter method could also be used to calculate excitation and ionization cross sections for ions. In this case the orbit of the incident particle would not be rectilinear but rather hyperbolic. In the case of heavy incident particles, e.g. protons, the actual orbit could probably be approximated by a rectilinear orbit.

Finally, the cross sections obtained by the methods developed in this thesis could be used to calculate the polarization of the light emitted from an atom which is decaying radiatively after being excited by electron or proton impact. The results should be good for high and moderate energies of the incident particle. Since exact threshold values are known theoretically, extrapolation of our results to threshold would probably give reasonable results over the whole range of energies.

Appendix A

We wish to prove

$$|T^{\lambda\mu}(R_i)|^2 = \frac{2\lambda+1}{\pi v_i^2}\left(\frac{p}{v_i}\right)^{2\lambda}\frac{K_\mu^2(\beta_i)}{(\lambda+\mu)!\,(\lambda-\mu)!} \quad . \tag{A.1}$$

We first prove the result

$$\frac{d^m}{d\beta^m}\left[\beta^n K_n(\beta)\right] = \sum_{r=0}^{[m/2]}(-1)^{m+r}\frac{m!}{2^r r!\,(m-2r)!}\,\beta^{n-r}K_{n-m+r}(\beta) \tag{A.2}$$

for m a non-negative integer where $\left[\frac{m}{2}\right]$ is the greatest integer contained in $\frac{m}{2}$ and $K_n(\beta)$ is the modified Bessel function of the second kind. We make use of the fact that

$$\frac{d}{d\beta}\left[\beta^n K_n(\beta)\right] = -\beta^n K_{n-1}(\beta) \tag{A.3}$$

(McLachlan, 1946, p.165). Thus (A.2) is obviously true for m=0 and m=1. We prove the general result by induction. Assume (A.2) is true for some $m \geq 1$. Then

$$\begin{aligned}\frac{d^{m+1}}{d\beta^{m+1}}\left[\beta^n K_n(\beta)\right] &= \sum_{r=0}^{[m/2]}(-1)^{m+r}\frac{m!}{2^r r!\,(m-2r)!} \\ &\quad\times\frac{d}{d\beta}\left[\left(\beta^{n-m+r}K_{n-m+r}(\beta)\right)\left(\beta^{m-2r}\right)\right] \\ &= \sum_{r=0}^{[m/2]}(-1)^{m+r+1}\frac{m!}{2^r r!\,(m-2r)!}\,\beta^{n-r}K_{n-m+r-1}(\beta) \\ &\quad+\sum_{s=0}^{[m/2]}(-1)^{m+s}\,\frac{m!\,(m-2s)}{2^s s!\,(m-2s)!}\,\beta^{n-s-1}K_{n-m+s}(\beta)\end{aligned} \tag{A.4}$$

using (A.3). In the second summation of (A.4) we replace s by r-1 to get

$$\begin{aligned}\frac{d^{m+1}}{d\beta^{m+1}}\left[\beta^n K_n(\beta)\right] &= \sum_{r=0}^{[m/2]}(-1)^{(m+1)+r}\frac{m!}{2^r r!\,(m-2r)!}\,\beta^{n-r}K_{n-(m+1)+r}(\beta) \\ &\quad+\sum_{r=1}^{[(m+1)/2]}(-1)^{(m+1)+r}\frac{m!\,(m-2r+2)}{2^{r-1}(r-1)!\,(m-2r+2)!}\,\beta^{n-r}K_{n-(m+1)+r}(\beta) \quad .\end{aligned} \tag{A.5}$$

We have replaced the upper limit of the second summation in (A.5), $\left[\frac{m}{2}\right] + 1$, by $\left[\frac{m+1}{2}\right]$ since if m is even then the last term in this summation is that with $r = \frac{m}{2} + 1$. But this term disappears because of the factor $(m-2r+2)$. Thus the last non-zero term is that with $r = \frac{m}{2} = \left[\frac{m+1}{2}\right]$. For m odd the last term is that with $r = \frac{m-1}{2} + 1 = \frac{m+1}{2} = \left[\frac{m+1}{2}\right]$ and hence our replacement is justified.

Let the coefficient of $\beta^{n-r} K_{n-(m+1)+r}(\beta)$ in (A.5) be C_r. Then for $1 \leq r \leq \frac{m}{2}$

$$C_r = (-1)^{(m+1)+r}\left[\frac{m!}{2^r\, r!\,(m-2r)!} + \frac{m!}{2^{r-1}(r-1)!\,(m-2r+1)!}\right]$$

$$= (-1)^{(m+1)+r}\,\frac{(m+1)!}{2^r\, r!\,(m-2r+1)!}\,. \qquad \text{(A.6)}$$

Also $C_0 = (-1)^{m+1}$ which is identical with (A.6) for r=0. With m odd

$$C_{(m+1)/2} = (-1)^{3(m+1)/2}\,\frac{m!}{2^{(m-1)/2}\left((m-1)/2\right)!} = (-1)^{3(m+1)/2}\,\frac{(m+1)!}{2^{(m+1)/2}\left((m+1)/2\right)!}$$

which is identical with (A.6) for $r = \frac{m+1}{2}$. Hence (A.6) is valid for all possible values of r and we have

$$\frac{d^{m+1}}{d\beta^{m+1}}\left[\beta^n K_n(\beta)\right] = \sum_{r=0}^{[(m+1)/2]} (-1)^{(m+1)+r}\,\frac{(m+1)!}{2^r\, r!\,(m+1-2r)!}\,\beta^{n-r} K_{n-(m+1)+r}(\beta)$$

which is just the formula given in (A.2). Thus (A.2) is true for m+1 if it is true for m and since it is true for m=1 we conclude (A.2) is valid for all finite, non-negative values of m.

From (2.3.1) and (2.3.6)

$$T^{\lambda\mu}(R_i) = \int_{-\infty}^{\infty} \frac{e^{ipt}}{r'(t)^{\lambda+1}}\, Y_{\lambda\mu}(\Theta, 0)\, dt \qquad \text{(A.7)}$$

and $\cos\Theta = v_i t \Big/ \sqrt{R_i^2 + v_i^2 t^2}$. (A.8)

Thus from (E 2.5.29)

$$T^{\lambda\mu}(R_i) = (-1)^{\mu}\sqrt{\frac{(2\lambda+1)(\lambda-\mu)!}{4\pi\,(\lambda+\mu)!}}\int_{-\infty}^{\infty} \frac{e^{ipt}}{(R_i^2+v_i^2t^2)^{(\lambda+1)/2}} P_\lambda^\mu(\cos\Theta)\,dt$$

$$= 2(-1)^{\mu}\sqrt{\frac{(2\lambda+1)(\lambda-\mu)!}{4\pi\,(\lambda+\mu)!}}\int_{0}^{\infty} \frac{\left\{\begin{matrix}\cos\\ i\sin\end{matrix}\right\} pt}{(R_i^2+v_i^2t^2)^{(\lambda+1)/2}} P_\lambda^\mu(\cos\Theta)\,dt \qquad \text{(A.9)}$$

for $\lambda+\mu$ $\left\{\begin{matrix}\text{even}\\ \text{odd}\end{matrix}\right\}$ since (E 2.5.18).

$$P_\lambda^\mu(-x) = (-1)^{\lambda+\mu} P_\lambda^\mu(x) . \tag{A.10}$$

Also (Menzel, 1960, Ch.1)

$$P_\lambda^\mu(x) = \frac{(1-x^2)^{\mu/2}}{2^\lambda} \sum_{q=0}^{[(\lambda-\mu)/2]} \frac{(-1)^q (2\lambda-2q)!}{q!(\lambda-q)!(\lambda-\mu-2q)!} x^{\lambda-\mu-2q} \tag{A.11}$$

Putting $v_i t = z$ and assuming $\lambda+\mu$ even, (A.9) becomes using (A.11)

$$T^{\lambda\mu}(R_i) = \frac{(-1)^\mu}{2^{\lambda-1}} \sqrt{\frac{(2\lambda+1)(\lambda-\mu)!}{4\pi(\lambda+\mu)!}} \sum_{q=0}^{(\lambda-\mu)/2} \frac{(-1)^q (2\lambda-2q)!}{q!(\lambda-q)!(\lambda-\mu-2q)!}$$
$$\times \frac{R_i^\mu}{v_i} \int_0^\infty \frac{\cos(pz/v_i)\, z^{\lambda-\mu-2q}}{(R_i^2+z^2)^{\lambda-q+1/2}} dz . \tag{A.12}$$

Since $\lambda-\mu-2q \geq 0$ and is even and $\frac{\lambda-\mu-2q}{2} < \lambda-q+1/2$,

$$\int_0^\infty \frac{\cos(pz/v_i)\, z^{\lambda-\mu-2q}}{(R_i^2+z^2)^{\lambda-q+1/2}} dz = \frac{(-1)^{(\lambda-\mu)/2-q}\sqrt{\pi}}{2^{\lambda-q} R_i^{\lambda+\mu} \Gamma(\lambda-q+1/2)}$$
$$\times \frac{d^{\lambda-\mu-2q}}{d\beta_i^{\lambda-\mu-2q}} \left[\beta_i^{\lambda-q} K_{\lambda-q}(\beta_i)\right] \tag{A.13}$$

(Erdélyi, 1954, p. 14) where we have put $\beta_i = \frac{pR_i}{v_i}$.

$\Gamma(\lambda-q+1/2)$ is the usual gamma function. Using (A.2) in (A.13) and substituting in (A.12) we get

$$T^{\lambda\mu}(R_i) = \frac{(-1)^{(\lambda+\mu)/2}}{(4R_i)^\lambda v_i} \sqrt{(2\lambda+1)\frac{(\lambda-\mu)!}{(\lambda+\mu)!}} \sum_{q=0}^{(\lambda-\mu)/2} \frac{2^q (2\lambda-2q)!}{q!(\lambda-q)!(\lambda-\mu-2q)!}$$
$$\times \frac{1}{\Gamma(\lambda-q+1/2)} \sum_{r=0}^{(\lambda-\mu)/2+q} (-1)^{\lambda-\mu+r} \frac{(\lambda-\mu-2q)!\,\beta_i^{\lambda-q-r} K_{\mu+q+r}(\beta_i)}{2^r r!(\lambda-\mu-2q-2r)!}$$

or putting $q + r = t$ and rearranging our two finite summations so that we are summing over t and q instead of r and q we get

$$T^{\lambda\mu}(R_i) = \frac{(-1)^{(\lambda+\mu)/2}\, 2^{2\lambda}}{\Gamma(1/2)\,(4R_i)^{\lambda}\,\nu_i}\sqrt{(2\lambda+1)\frac{(\lambda-\mu)!}{(\lambda+\mu)!}}$$
$$\times \sum_{t=0}^{(\lambda-\mu)/2} \frac{(-1)^t \beta_i^{\lambda-t} K_{\mu+t}(\beta_i)}{2^t(\lambda-\mu-2t)!} \sum_{q=0}^{t} \frac{(-1)^q}{q!\,(t-q)!} \qquad (A.14)$$

where we have used the result

$$\Gamma(\lambda - q + 1/2) = \frac{(2\lambda-2q)!}{2^{2\lambda-2q}(\lambda-q)!}\,\Gamma(1/2)\,.$$

But

$$\sum_{q=0}^{t} \frac{(-1)^q}{q!\,(t-q)!} = \frac{1}{t!}\sum_{q=0}^{t}(-)^q\binom{t}{q} = \begin{cases} 0, & t \neq 0 \\ 1, & t = 0 \end{cases}$$

(Feller, 1957, p. 61) where $\binom{t}{q}$ is the usual binomial coefficient. Thus (A.14) becomes

$$T^{\lambda\mu}(R_i) = \frac{(-1)^{(\lambda+\mu)/2}}{\Gamma(1/2)\,R_i^{\lambda}\,\nu_i}\sqrt{\frac{2\lambda+1}{(\lambda-\mu)!\,(\lambda+\mu)!}}\,\beta_i^{\lambda} K_{\mu}(\beta_i) \qquad (A.15)$$

for $\lambda + \mu$ even which is equivalent to (A.1).

The result for $\lambda + \mu$ odd follows similar lines and we merely sketch the proof. For $\lambda + \mu$ odd (A.9) becomes using (A.11)

$$T^{\lambda\mu}(R_i) = \frac{i\,(-1)^{\mu}}{2^{\lambda-1}}\sqrt{\frac{(2\lambda+1)\,(\lambda-\mu)!}{4\pi\;(\lambda+\mu)!}}\sum_{q=0}^{(\lambda-\mu-1)/2}\frac{(-1)^q\,(2\lambda-2q)!}{q!\,(\lambda-q)!\,(\lambda-\mu-2q)!}$$
$$\times \frac{R_i^{\mu}}{\nu_i}\int_0^{\infty}\frac{\sin(pz/\nu_i)\, z^{\lambda-\mu-2q}}{(R_i^2+z^2)^{\lambda-q+1/2}}\,dz\,. \qquad (A.16)$$

Now

$$\int_0^{\infty}\frac{\sin(pz/\nu_i)\, z^{\lambda-\mu-2q}}{(R_i^2+z^2)^{\lambda-q+1/2}}\,dz = -\frac{d}{d(p/\nu_i)}\int_0^{\infty}\frac{\cos(pz/\nu_i)\, z^{\lambda-\mu-1-2q}}{(R_i^2+z^2)^{\lambda-q+1/2}}\,dz$$
$$= \frac{(-1)^{(\lambda-\mu+1)/2-q}\sqrt{\pi}}{2^{\lambda-q}\,R_i^{\lambda+\mu}\,\Gamma(\lambda-q+1/2)}\,\frac{d^{\lambda-\mu-2q}}{d(\beta_i^{\lambda-\mu-2q})}\left[\beta_i^{\lambda-q}K_{\lambda-q}(\beta_i)\right] \qquad (A.17)$$

using (A.13) since $\lambda - \mu - 1 - 2q$ is even. The simplification of (A.16) using (A.17) follows exactly as in the previous case except that $\frac{\lambda-\mu}{2}$ is replaced by $\frac{\lambda-\mu-1}{2}$ in the upper

limit of the summation. Hence we obtain

$$T^{\lambda\mu}(R_i) = \frac{i(-1)^{(\lambda+\mu+1)/2}}{\Gamma(1/2)\, R_i^{\lambda}\, v_i} \sqrt{\frac{2\lambda+1}{(\lambda-\mu)!\,(\lambda+\mu)!}}\, \beta_i^{\lambda} K_{\mu}(\beta_i) \qquad \text{(A.18)}$$

for $\lambda + \mu$ odd which is equivalent to (A.1).

Appendix B

To show that

$$\frac{1}{8\pi^2}\int_0^{2\pi}\int_0^{\pi}\int_0^{2\pi} \mathcal{D}^{(J_a)}_{M_{J_a}M'_{J_a}}(\alpha\beta\gamma)\,\mathcal{D}^{(J_b)*}_{M_{J_b}M'_{J_b}}(\alpha\beta\gamma)\,\mathcal{D}^{(J_a)*}_{M''_{J_a}M'_{J_a}}(\alpha\beta\gamma)$$

$$\times \mathcal{D}^{(J_b)}_{M''_{J_b}M'_{J_b}}(\alpha\beta\gamma)\,d\alpha\sin\beta\,d\beta\,d\gamma$$

$$= \sum_{J_c M_{J_c} M'_{J_c}} (2J_c+1)\begin{pmatrix} J_a & J_b & J_c \\ M_{J_a} & M''_{J_b} & M_{J_c}\end{pmatrix}\begin{pmatrix} J_a & J_b & J_c \\ M''_{J_a} & M_{J_b} & M_{J_c}\end{pmatrix}\begin{pmatrix} J_a & J_b & J_c \\ M'_{J_a} & M'_{J_b} & M'_{J_c}\end{pmatrix}^2 \qquad \text{(B.1)}$$

where $\begin{pmatrix} J_a & J_b & J_c \\ M_{J_a} & M_{J_b} & M_{J_c}\end{pmatrix}$ are the Wigner 3-j symbols (see Edmonds, 1957, Ch.3). The sum over M_{J_c} and M'_{J_c} is from $-J_c$ to J_c, and the sum over J_c is from $|J_a-J_b|$ to J_a+J_b.

Using (E4.3.2)

$$\mathcal{D}^{(J_a)}_{M_{J_a}M'_{J_a}}(\alpha\beta\gamma)\,\mathcal{D}^{(J_b)}_{M''_{J_b}M'_{J_b}}(\alpha\beta\gamma) = \sum_{J_c M_{J_c} M'_{J_c}} (2J_c+1)\begin{pmatrix} J_a & J_b & J_c \\ M_{J_a} & M''_{J_b} & M_{J_c}\end{pmatrix}$$

$$\times \begin{pmatrix} J_a & J_b & J_c \\ M'_{J_a} & M'_{J_b} & M'_{J_c}\end{pmatrix}\mathcal{D}^{(J_c)*}_{M_{J_c}M'_{J_c}}(\alpha\beta\gamma) \qquad \text{(B.2)}$$

and

$$\mathcal{D}^{(J_a)*}_{M''_{J_a}M'_{J_a}}(\alpha\beta\gamma)\,\mathcal{D}^{(J_b)*}_{M_{J_b}M'_{J_b}}(\alpha\beta\gamma) = \sum_{J'_c \mu_{J_c}\mu'_{J_c}} (2J'_c+1)\begin{pmatrix} J_a & J_b & J'_c \\ M''_{J_a} & M_{J_b} & \mu_{J_c}\end{pmatrix}$$

$$\times \begin{pmatrix} J_a & J_b & J'_c \\ M'_{J_a} & M'_{J_b} & \mu'_{J_c}\end{pmatrix}\mathcal{D}^{(J'_c)}_{\mu_{J_c}\mu'_{J_c}}(\alpha\beta\gamma) \qquad \text{(B.3)}$$

taking the complex conjugate of (E4.3.2) since the 3-j symbols are real. Hence the l.h.s. of (B.1) becomes using (B.2) and (B.3)

$$\sum_{\substack{J_c M_{J_c} M'_{J_c} \\ J'_c \mu_{J_c}\mu'_{J_c}}} (2J_c+1)(2J'_c+1)\begin{pmatrix} J_a & J_b & J_c \\ M_{J_a} & M''_{J_b} & M_{J_c}\end{pmatrix}\begin{pmatrix} J_a & J_b & J_c \\ M'_{J_a} & M'_{J_b} & M'_{J_c}\end{pmatrix}$$

$$\times \begin{pmatrix} J_a & J_b & J'_c \\ M''_{J_a} & M_{J_b} & \mu_{J_c}\end{pmatrix}\begin{pmatrix} J_a & J_b & J'_c \\ M'_{J_a} & M'_{J_b} & \mu'_{J_c}\end{pmatrix}\frac{1}{8\pi^2}\int_0^{2\pi}\int_0^{\pi}\int_0^{2\pi}\mathcal{D}^{(J_c)*}_{M_{J_c}M'_{J_c}}(\alpha\beta\gamma)$$

$$\times \mathcal{D}^{(J'_c)}_{\mu_{J_c}\mu'_{J_c}}(\alpha\beta\gamma)\,d\alpha\sin\beta\,d\beta\,d\gamma$$

$$= \sum_{J_c M_{J_c} M'_{J_c}} (2J_c+1) \begin{pmatrix} J_a & J_b & J_c \\ M_{J_a} & M''_{J_b} & M_{J_c} \end{pmatrix} \begin{pmatrix} J_a & J_b & J_c \\ M''_{J_a} & M_{J_b} & M_{J_c} \end{pmatrix} \begin{pmatrix} J_a & J_b & J_c \\ M'_{J_a} & M'_{J_b} & M'_{J_c} \end{pmatrix}^2$$

using (E 4.6.1).

Appendix C

To prove

$$J_{l,m}(\gamma) \equiv \int_0^{\pi} P_l^m(\cos\theta)\, e^{i\gamma\cos\theta}\, I_m(\gamma\sin\theta)\sin\theta\, d\theta$$

$$= \begin{cases} \dfrac{2(-1)^{(l-m)/2}\,\gamma^l}{(2l+1)(l-m)!} & \text{for } l+m \text{ even} \quad (C.1a) \\ \dfrac{2i(-1)^{(l-m-1)/2}\,\gamma^l}{(2l+1)(l-m)!} & \text{for } l+m \text{ odd} \quad (C.1b) \end{cases}$$

where l, m are non-negative integers, $P_l^m(x)$ is the associated Legendre polynomial, $I_m(z)$ is the modified Bessel function of the first kind and γ is any complex number. (For the purposes of § 3.6 we need only consider γ real. However we are able to prove this more general result without any additional difficulty).

We define the binomial coefficient $\binom{n}{p}$ for all real numbers n and non-negative integers p as

$$\binom{n}{p} \equiv \frac{n(n-1)\cdots(n-p+1)}{p!} = \frac{\Gamma(n+1)}{p!\,\Gamma(n-p+1)} \quad (C.2)$$

where $\Gamma(x)$ is the gamma function. From (C.2) we have that

$$\binom{-n}{p} = (-1)^p \binom{n+p-1}{p}. \quad (C.3)$$

First of all we prove the following results:

$$\sum_{p=0}^{t} (-1)^p \binom{2n+2p}{2p}\binom{n+t}{t-p} = (-1)^t \frac{2^{2t}\,\Gamma(n+t+1)}{(2t)!\,\Gamma(n-t+1)} \quad (C.4a)$$

and

$$\sum_{p=0}^{t} (-1)^p \binom{2n+2p}{2p+1}\binom{n+t}{t-p} = (-1)^t \frac{2^{2t+1}\,\Gamma(n+t+1)}{(2t+1)!\,\Gamma(n-t)}. \quad (C.4b)$$

Consider the identity for t a non-negative integer

$$\frac{(1-x^2)^{n+t}}{(1-x)^{2n+1}} \equiv \frac{(1+x)^{n+t}}{(1-x)^{n-t+1}}. \quad (C.5)$$

The l.h.s. of (C.5) can be expanded to give

$$\sum_{r=0}^{\infty} (-1)^r \binom{n+t}{r} x^{2r} \sum_{s=0}^{\infty} (-1)^s \binom{-2n-1}{s} x^s. \quad (C.6)$$

Using (C.3) we find the coefficient of x^{2t} in (C.6) to be (putting $2r+s = 2t$)

$$\sum_{r=0}^{t}(-1)^r \binom{n+t}{r}\binom{2n+2t-2r}{2t-2r}$$

$$=(-1)^t\sum_{p=0}^{t}(-1)^p\binom{n+t}{t-p}\binom{2n+2p}{2p} \qquad (C.7)$$

where $p=t-r$. Expanding the r.h.s. of (C.5) yields

$$\sum_{r=0}^{\infty}\binom{n+t}{r}x^r\sum_{s=0}^{\infty}(-1)^s\binom{-n+t-1}{s}x^s \qquad (C.8)$$

and the coefficient of x^{2t} in (C.8) is (putting $r+s=2t$ and using (C.3))

$$\sum_{r=0}^{2t}\binom{n+t}{r}\binom{n+t-r}{2t-r}$$

$$=\sum_{r=0}^{2t}\frac{\Gamma(n+t+1)\,\Gamma(n+t-r+1)}{r!\,\Gamma(n+t-r+1)\,(2t-r)!\,\Gamma(n-t+1)} \quad \text{by (C.2)}$$

$$=\frac{\Gamma(n+t+1)}{\Gamma(n-t+1)(2t)!}\sum_{r=0}^{2t}\binom{2t}{r}=\frac{2^{2t}\Gamma(n+t+1)}{(2t)!\,\Gamma(n-t+1)}. \qquad (C.9)$$

But (C.7) and (C.9) must be equal since they are both the coefficient of x^{2t} in (C.5). Hence we have proved (C.4a).

By considering the coefficient of x^{2t+1} on both sides of

$$\frac{(1-x^2)^{n+t}}{(1-x)^{2n}}\equiv\frac{(1+x)^{n+t}}{(1-x)^{n-t}} \qquad (C.10)$$

we prove (C.4b) in a similar manner.

Secondly we prove the results:

$$\sum_{p=0}^{t}\frac{(-1)^p 2^{2p}\Gamma(n+p+1/2)}{(2p)!\,(t-p)!\,\Gamma(n+1/2)}=(-1)^t\frac{2^{2t}\Gamma(n+1)}{(2t)!\,\Gamma(n-t+1)} \qquad (C.11a)$$

and

$$\sum_{p=0}^{t}\frac{(-1)^p 2^{2p}\Gamma(n+p+1/2)}{(2p+1)!\,(t-p)!\,\Gamma(n+1/2)}=(-1)^t\frac{2^{2t}\Gamma(n)}{(2t+1)!\,\Gamma(n-t)}. \qquad (C.11b)$$

The l.h.s. of (C.11a) becomes

$$\sum_{p=0}^{t}\frac{(-1)^p 2^{2p}}{(2p)!\,(t-p)!}(n+p-1/2)(n+p-3/2)\cdots(n+1/2)$$

$$=\sum_{p=0}^{t}\frac{(-1)^p(2n+2p)(2n+2p-1)\cdots(2n+1)}{(2p)!\,(t-p)!\,(n+p)(n+p-1)\cdots(n+1)}$$

$$=\frac{\Gamma(n+1)}{\Gamma(n+t+1)}\sum_{p=0}^{t}(-1)^p\binom{2n+2p}{2p}\binom{n+t}{t-p} \qquad (C.12)$$

which is equal to the r.h.s. of (C.11a) using (C.4a).

The proof of (C.11b) follows similar lines making use of (C.4b).

Thirdly we prove

$$\sum_{q=0}^{(l-m)/2-t} \frac{(-1)^q (2l-2q)!\,((l+m)/2-q+t)!}{q!\,(l-q)!\,((l-m)/2-q-t)!\,(l+m-2q+2t+1)!}$$

$$= \begin{cases} \dfrac{1}{2l+1} & \text{if } t=\dfrac{l-m}{2}, \qquad \text{(C.13a)} \\ 0 & \text{otherwise} \qquad \text{(C.13b)} \end{cases}$$

for t, $\frac{l-m}{2}$ non-negative integers such that $\frac{l-m}{2} \geq t$.

If $t=\frac{l-m}{2}$ (C.13a) follows by direct substitution. Otherwise put $\frac{l-m}{2} - t - q = s$, $m+2t=u$. Then the l.h.s. of (C.13b) becomes

$$(-1)^{(l-u)/2} \sum_{s=0}^{(l-u)/2} (-1)^s \left\{ \frac{2s(2s+2u+1)}{(l+u+1)(l-u)} + \frac{(2s+l+u+1)(l-u-2s}{(l+u+1)(l-u)} \right\}$$

$$\times \frac{(2s+l+u)!\,(s+u)!}{((l-u)/2-s)!\,((l+u)/2+s)!\;s!\,(2s+2u+1)!} \qquad \text{(C.14)}$$

where the expression in curly brackets is just equal to unity. The first part of the s^{th} term in (C.14) cancels the last part of the $(s-1)^{th}$ term as can be verified. The first part of the s=0 term vanishes as does the last part of the $s=\frac{l-u}{2}$ term. Hence (C.13b) follows.

We shall also need this result when m is replaced by m+1 and $\frac{l-m-1}{2}$ is a non-negative integer.

We are now in a position to prove (C.1). Making the substitution $\cos\theta = x$ we have

$$J_{l,m}(\gamma) = 2\int_0^1 P_l^m(x) \left\{ \begin{matrix} \cos \\ i\sin \end{matrix} \right\} (\gamma x)\, I_m\left(\gamma\sqrt{1-x^2}\right) dx \qquad \text{(C.15)}$$

for $l+m$ $\left\{ \begin{matrix} \text{even} \\ \text{odd} \end{matrix} \right\}$ since $P_l^m(x)$ is an even or odd function of x according as $(l+m)$ is even or odd (A.10). Consider the case $l+m$ even and expand $P_l^m(x)$ by (A.11). Expanding also the cosine term and putting $y^2=1-x^2$ we find that

$$J_{l,m}(\gamma) = \frac{1}{2^{l-1}} \sum_{q=0}^{(l-m)/2} \frac{(-1)^q (2l-2q)!}{q!\,(l-q)!\,(l-m-2q)!} \sum_{p=0}^{\infty} (-1)^p \frac{\gamma^{2p}}{(2p)!}$$

$$\times \int_0^1 y^{m+1} (1-y^2)^{\nu} I_m(\gamma y)\, dy \qquad \text{(C.16)}$$

where $2\nu = l-m-2q+2p-1$. But (M^{c}Lachlan, 1934, p.159)

$$\int_0^1 y^{m+1} (1-y^2)^{\nu} I_m(\gamma y)\, dy = \frac{2^{\nu}}{\gamma^{\nu+1}} \Gamma(\nu+1) I_{m+\nu+1}(\gamma) \qquad \text{(C.17)}$$

for $m > -1$, $\nu > -1$. Since $l-m-2q \geq 0$, $m \geq 0$, $p \geq 0$ we may use (C.17) to evaluate (C.16). Expanding $I_{m+\nu+1}(\gamma)$ (M^{c}Lachlan, 1934, p. 163) we have

$$J_{l,m}(\gamma) = \frac{1}{2^{l-1}} \sum_{q=0}^{(l-m)/2} \frac{(-1)^q (2l-2q)!}{q!\,(l-q)!\,(l-m-2q)!} \sum_{p=0}^{\infty} (-1)^p \frac{\gamma^{2p}}{(2p)!}$$

$$\times \frac{\gamma^m}{2^{m+1}} \Gamma(\nu+1) \sum_{r=0}^{\infty} \frac{(\gamma/2)^{2r}}{r!\,\Gamma(m+\nu+r+2)} . \qquad \text{(C.18)}$$

Since $\cos\gamma$ and $\frac{2^{\nu}}{\gamma^{\nu+1}} \Gamma(\nu+1) I_{m+\nu+1}(\gamma)$ both have an infinite radius of convergence (see for instance, Hille, 1959, p.119) we may rearrange the two infinite series in (C.18) to yield

$$J_{l,m}(\gamma) = \frac{\gamma^m}{2^{l+m}} \sum_{q=0}^{(l-m)/2} \frac{(-1)^q (2l-2q)!}{q!\,(l-q)!\,(l-m-2q)!} \sum_{t=0}^{\infty} \left(\frac{\gamma}{2}\right)^{2t} \frac{1}{\Gamma(n+m+t+3/2)}$$

$$\times \sum_{p=0}^{t} \frac{(-1)^p\, 2^{2p}\, \Gamma(n+p+1/2)}{(2p)!\,(t-p)!} \qquad \text{(C.19)}$$

where $n = \frac{l-m}{2} - q$ is a non-negative integer. By (C.11a) the coefficient of γ^{2t} reduces to a single term which contains as a factor $1/\Gamma(n-t+1)$. Hence the series in t terminates with the term t=n. Interchanging the order of summation of the two remaining finite series we obtain

$$J_{l,m}(\gamma) = \frac{\gamma^m}{2^{l+m}} \sum_{t=0}^{(l-m)/2} (-1)^t \frac{\gamma^{2t}}{(2t)!}\, 2^{2m+2t+1}$$

$$\times \sum_{q=0}^{(l-m)/2-t} \frac{(-1)^q (2l-2q)!\, \left((l+m)/2 - q + t\right)!}{q!\,(l-q)!\,\left((l-m)/2 - q - t\right)!\,(l+m-2q+2t+1)!} \qquad \text{(C.20)}$$

since

$$\frac{\Gamma(n+1/2)}{\Gamma(n+m+t+3/2)} = 2^{2m+2t+1}\,\frac{(n+m+t)!(2n)!}{(2n+2m+2t+1)!\,n!}\,. \qquad (C.21)$$

Hence by (C.13), (C.20) is identical to (C.1a).

In the case when $\ell-m$ is odd the proof of (C.1b) follows similar lines and we will only outline it briefly. Expanding and making the same substitutions as before (C.1b) becomes

$$J_{\ell,m}(\gamma) = \frac{i}{2^{\ell-1}} \sum_{q=0}^{(\ell-m-1)/2} \frac{(-1)^q (2\ell-2q)!}{q!\,(\ell-q)!\,(\ell-m-2q)!} \sum_{p=0}^{\infty} (-1)^p \frac{\gamma^{2p+1}}{(2p+1)!}$$

$$\times \int_0^1 y^{m+1} (1-y^2)^{\nu+1/2}\, I_m(\gamma y)\, dy\,. \qquad (C.22)$$

Using (C.17) to evaluate the integral, expanding the resultant Bessel function and rearranging as before, we obtain

$$J_{\ell,m}(\gamma) = \frac{i\gamma^{m+1}}{2^{\ell+m}} \sum_{q=0}^{(\ell-m-1)/2} \frac{(-1)^q (2\ell-2q)!}{q!\,(\ell-q)!\,(\ell-m-2q)!}$$

$$\times \sum_{t=0}^{\infty} \left(\frac{\gamma}{2}\right)^{2t} \frac{1}{\Gamma(n'+m+t+3/2)} \sum_{p=0}^{t} \frac{(-1)^p 2^{2p}\,\Gamma(n'+p+1/2)}{(2p+1)!\,(t-p)!} \qquad (C.23)$$

where $n' = \frac{\ell-m+1}{2} - q$ is a positive integer. The sum over p in (C.23) is given by (C.11b) and hence the sum over t terminates with the term $t=n'-1$. Interchanging the order of summation of the two finite series we get using (C.21)

$$J_{\ell,m}(\gamma) = \frac{i\gamma^{m+1}}{2^{\ell+m}} \sum_{t=0}^{(\ell-m-1)/2} \frac{(-1)^t \gamma^{2t}}{(2t+1)!}\, 2^{2m+2t+1}$$

$$\times \sum_{q=0}^{(\ell-m-1)/2-t} \frac{(-1)^q (2\ell-2q)!\,((\ell+m+1)/2-q+t)!}{q!\,(\ell-q)!\,((\ell-m-1)/2-q-t)!\,(\ell+m+1-2q+2t+1)!}$$

$$= \frac{2i(-1)^{(\ell-m-1)/2}\,\gamma^{\ell}}{(2\ell+1)(\ell-m)!} \qquad (C.24)$$

by (C.13) with m replaced by m+1. But (C.24) is identical to (C.1b).

We may evaluate $J_{\ell,m}(\gamma)$ for negative integral values

of m as follows. From (E2.5.8)
$P_l^{-m}(\cos\theta) = (-1)^m \frac{(l-m)!}{(l+m)!} P_l^m(\cos\theta)$. Also $I_{-m(z)} = I_{m(z)}$ when m is an integer (M^{c}Lachlan, 1934, p.163).
Hence

$$J_{l,-m}(\gamma) = \int_0^\pi P_l^{-m}(\cos\theta)\, e^{i\gamma\cos\theta}\, I_{-m}(\gamma\sin\theta)\sin\theta\, d\theta$$

$$= (-1)^m \frac{(l-m)!}{(l+m)!} \int_0^\pi P_l^m(\cos\theta)\, e^{i\gamma\cos\theta}\, I_m(\gamma\sin\theta)\sin\theta\, d\theta$$

$$= (-1)^m \frac{(l-m)!}{(l+m)!} J_{l,m}(\gamma) \,. \qquad (C.25)$$

That is, (C.1) holds for both positive and negative integral values of m.

Appendix D

We wish to show that

$$K_{2n+1}(\beta) = \sum_{p=0}^{n} \frac{2^{2p}(n+p)!\,(n+p)!}{(2p)!\,(n-p)!\,(n-p)!}\,\beta^{-2p} K_1(\beta)$$

$$+ \sum_{p=0}^{n-1} \frac{2^{2p+1}(n+p+1)!\,(n+p)!}{(2p+1)!\,(n-p)!\,(n-p-1)!}\,\beta^{-2p-1} K_0(\beta) \qquad \text{(D.1a)}$$

and

$$K_{2n+2}(\beta) = \sum_{p=0}^{n} \frac{2^{2p}(n+p+1)!\,(n+p)!}{(2p)!\,(n-p+1)!\,(n-p)!}\,\beta^{-2p} K_0(\beta)$$

$$+ \sum_{p=0}^{n} \frac{2^{2p+1}(n+p+1)!\,(n+p+1)!}{(2p+1)!\,(n-p)!\,(n-p)!}\,\beta^{-2p-1} K_1(\beta) \qquad \text{(D.1b)}$$

for n a non-negative integer. Noting (2.6.7) the expressions are obviously true for n=0. We prove the general result by induction.

Assume that both (D.1a) and (D.1b) are true for some $n \geq 0$. Then from (2.6.7)

$$K_{2n+3}(\beta) = \frac{2(2n+2)}{\beta} K_{2n+2}(\beta) + K_{2n+1}(\beta)$$

$$= \sum_{p=0}^{n-1} \frac{2^{2p+1}(n+p+1)!\,(n+p)!}{(2p+1)!\,(n-p+1)!\,(n-p)!}$$

$$\times \left[(2n+2)(2p+1) + (n-p+1)(n-p)\right]\beta^{-2p-1} K_0(\beta)$$

$$+ \frac{2^{2n+1}(2n+2)!\,(2n)!}{(2n)!}\,\beta^{-2n-1} K_0(\beta)$$

$$+ \sum_{p=1}^{n} \frac{2^{2p}(n+p)!\,(n+p)!}{(2p)!\,(n-p+1)!\,(n-p+1)!}$$

$$\times \left[2p(2n+2) + (n-p+1)^2\right]\beta^{-2p} K_1(\beta)$$

$$+ \left[1 + 2^{2n+2}(2n+2)(2n+1)!\,\beta^{-2n-2}\right] K_1(\beta)$$

$$= \sum_{p=0}^{n+1} \frac{2^{2p}(n+p+1)!\,(n+p+1)!}{(2p)!\,(n-p+1)!\,(n-p+1)!}\,\beta^{-2p} K_1(\beta)$$

$$+ \sum_{p=0}^{n+1} \frac{2^{2p+1}(n+p+2)!\,(n+p+1)!}{(2p+1)!\,(n-p+1)!\,(n-p)!}\,\beta^{-2p-1} K_0(\beta) \qquad (D.2)$$

which is the expression given by (D.1a) when n is replaced by n+1. Thus if (D.1a) and (D.1b) are true for n then (D.1a) is true for n+1.

Hence

$$K_{2n+4}(\beta) = \frac{2(2n+3)}{\beta} K_{2n+3}(\beta) + K_{2n+2}(\beta)$$

$$= \sum_{p=1}^{n} \frac{2^{2p}(n+p+1)!\,(n+p)!}{(2p)!\,(n-p+2)!\,(n-p+1)!}$$

$$\times\left[2p(2n+3) + (n-p+2)(n-p+1)\right]\beta^{-2p} K_0(\beta)$$

$$+ \left[1 + 2^{2n+2}(2n+3)!\,\beta^{-2n-2}\right] K_0(\beta)$$

$$+ \sum_{p=0}^{n} \frac{2^{2p+1}(n+p+1)!\,(n+p+1)!}{(2p+1)!\,(n-p+1)!\,(n-p+1)!}$$

$$\times\left[(2p+1)(2n+3) + (n-p+1)^2\right]\beta^{-2p-1} K_1(\beta)$$

$$+ 2^{2n+3}(2n+3)!\,\beta^{-2n-3} K_1(\beta)$$

$$= \sum_{p=0}^{n+1} \frac{2^{2p}(n+p+2)!\,(n+p+1)!}{(2p)!\,(n-p+2)!\,(n-p+1)!}\,\beta^{-2p} K_0(\beta)$$

$$+ \sum_{p=0}^{n+1} \frac{2^{2p+1}(n+p+2)!\,(n+p+2)!}{(2p+1)!\,(n-p+1)!\,(n-p+1)!}\,\beta^{-2p-1} K_1(\beta) \qquad (D.3)$$

which is the expression given by (D.1b) when n is replaced by (n+1). Thus if (D.1) are true for n they are true for n+1 and since they are true for n=0 they are true for all non-negative integral n.

Appendix E

We seek alternate forms for the matrix elements $\langle \psi_n | T(\lambda\mu) | \psi_m \rangle$ where the ψ_n satisfy the eigenvalue equation

$$H\psi_n = E_n \psi_n$$

and H is the Hamiltonian operator, viz.

$$H = -\frac{\hbar^2}{2m} \sum_{j=1}^{N} \nabla_j^2 + V(\underline{r}_1, \ldots \underline{r}_N)$$

Consider $[H,f]$ where f is an arbitrary operator. Then

$$\langle \psi_n | [H,f] | \psi_m \rangle = \langle \psi_n | Hf - fH | \psi_m \rangle$$
$$= (E_n - E_m) \langle \psi_n | f | \psi_m \rangle \qquad \text{(E.1)}$$

since H is Hermitian. But

$$\langle \psi_n | [H,f] | \psi_m \rangle = -\frac{\hbar^2}{2m} \sum_{j=1}^{N} \langle \psi_n | [\nabla_j^2, f] | \psi_m \rangle + \langle \psi_n | [V, f] | \psi_m \rangle \qquad \text{(E.2)}$$

Hence comparing (E.1) and (E.2) we have

$$\langle \psi_n | f | \psi_m \rangle = \frac{-\hbar^2}{2m(E_n - E_m)} \sum_{j=1}^{N} \langle \psi_n | [\nabla_j^2, f] | \psi_m \rangle + \frac{1}{E_n - E_m} \langle \psi_n | [V, f] | \psi_m \rangle \qquad \text{(E.3)}$$

Now put $f = T(\lambda\mu) = -r^\lambda Y_{\lambda\mu}(\theta, \varphi)$ i.e. f depends only on the co-ordinates of one particle. Since the ψ_n are assumed to be completely antisymmetrized it is immaterial which particular set of co-ordinates $T(\lambda\mu)$ depends on. Also

$$\nabla^2 T(\lambda\mu) = 0$$

Thus for an arbitrary function φ

$$[\nabla^2, T(\lambda\mu)]\varphi = 2(\nabla T(\lambda\mu)) \cdot (\nabla \varphi) + \varphi \nabla^2 T(\lambda\mu) = 2(\nabla T(\lambda\mu)) \cdot (\nabla \varphi)$$

and $$[V, T(\lambda\mu)]\varphi = 0 \qquad \text{(E.4)}$$

so that from (E.3)

$$\langle \psi_n \mid T(\lambda\mu) \mid \psi_m \rangle = \frac{-\hbar^2}{m(E_n - E_m)} \langle \psi_n \mid \nabla\, T(\lambda\mu) \cdot \nabla \mid \psi_m \rangle$$

$$= -2a_0^2 \left(\frac{I_H}{E_n - E_m} \right) \langle \psi_n \mid \nabla\, T(\lambda\mu) \cdot \nabla \mid \psi_m \rangle \qquad \text{(E.5)}$$

Now put $f = (\nabla\, T(\lambda\mu)) \cdot \nabla$. Again f depends on the co-ordinates of one particle only and

$$[\nabla^2,\ (\nabla\, T(\lambda\mu)) \cdot \nabla]\, \varphi =$$

$$\nabla^2 \left(\frac{\partial T(\lambda\mu)}{\partial x} \frac{\partial \varphi}{\partial x} + \frac{\partial T(\lambda\mu)}{\partial y} \frac{\partial \varphi}{\partial y} + \frac{\partial T(\lambda\mu)}{\partial z} \frac{\partial \varphi}{\partial z} \right)$$

$$- (\nabla\, T(\lambda\mu)) \cdot \nabla (\nabla^2 \varphi)$$

But $$\nabla^2 \left[\frac{\partial T(\lambda\mu)}{\partial x} \frac{\partial \varphi}{\partial x} \right] = \frac{\partial}{\partial x} (\nabla^2 T(\lambda\mu)) \frac{\partial \varphi}{\partial x}$$

$$+ 2 \left(\nabla \frac{\partial T(\lambda\mu)}{\partial x} \right) \cdot \left(\nabla \frac{\partial \varphi}{\partial x} \right) + \frac{\partial}{\partial x} T(\lambda\mu) \frac{\partial}{\partial x} (\nabla^2 \varphi)$$

with similar expressions for the y - and z - terms so that

$$[\nabla^2,\ (\nabla\, T(\lambda\mu)) \cdot \nabla] = 2 \sum_{j=1}^{3} \left(\nabla \frac{\partial T(\lambda\mu)}{\partial x_j} \right) \cdot \left(\nabla \frac{\partial}{\partial x_j} \right)$$

$$= 2 \sum_{j,k=1}^{3} (D_{jk}\, T(\lambda\mu))\, D_{jk} \qquad \text{(E.6)}$$

where we have put $(x_1, x_2, x_3) = (x, y, z)$ and defined the operator $D_{jk} \equiv \frac{\partial^2}{\partial x_j \partial x_k}$. Also

$$[V,\ (\nabla\, T(\lambda\mu)) \cdot \nabla]\, \varphi = \sum_{j=1}^{3} V \frac{\partial T(\lambda\mu)}{\partial x_j} \frac{\partial \varphi}{\partial x_j} - \sum_{j=1}^{3} \frac{\partial T(\lambda\mu)}{\partial x_j} \frac{\partial (V\varphi)}{\partial x_j}$$

$$= - \sum_{j=1}^{3} \frac{\partial T(\lambda\mu)}{\partial x_j} \frac{\partial V}{\partial x_j} \varphi$$

that is $$[V,\ (\nabla\, T(\lambda\mu)) \cdot \nabla] = - (\nabla\, T(\lambda\mu)) \cdot (\nabla V) \qquad \text{(E.7)}$$

Thus from (E.3) and (E.5)

$$\langle \psi_n \mid T(\lambda\mu) \mid \psi_m \rangle = 4 a_0^4 \left(\frac{I_H}{E_n - E_m} \right)^2 \sum_{j,k=1}^{3} \langle \psi_n \mid (D_{jk}\, T(\lambda\mu)) D_{jk} \mid \psi_m \rangle$$

$$+ 2a_0^2 \frac{I_H}{(E_n - E_m)^2} \langle \psi_n \mid (\nabla T(\lambda\mu)) \cdot (\nabla V) \mid \psi_m \rangle \qquad \text{(E.8)}$$

Note that for $\lambda = 1$ (E.5) and (E.8) are equivalent to the usual identity between the dipole length, dipole velocity and dipole acceleration matrix elements.

Using spherical polar co-ordinates we have that

$$(\nabla T(\lambda\mu)) \cdot \nabla = \frac{\partial T(\lambda\mu)}{\partial r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial T(\lambda\mu)}{\partial \theta} \frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2\theta} \frac{\partial T(\lambda\mu)}{\partial \varphi} \frac{\partial}{\partial \varphi}$$

or noting the explicit form of $T(\lambda\mu)$

$$(\nabla T(\lambda\mu)) \cdot \nabla = \frac{\lambda}{r} T(\lambda\mu) \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial T(\lambda\mu)}{\partial \theta} \frac{\partial}{\partial \theta} + \frac{i\mu}{r^2 \sin^2\theta} T(\lambda\mu) \frac{\partial}{\partial \varphi} \qquad \text{(E.9)}$$

and from (E2.5.25) we can write

$$\frac{\partial}{\partial \theta} T(\lambda\mu) = -(\lambda+1) \cot\theta \; T(\lambda\mu) + \sqrt{\frac{2\lambda+1}{2\lambda+3} (\lambda-\mu+1)(\lambda+\mu+1)} \; \frac{T(\lambda+1,\mu)}{r \sin\theta}$$

$$= -\sqrt{\frac{2\lambda+1}{2\lambda-1} (\lambda-\mu)(\lambda+\mu)} \; \frac{r\, T(\lambda-1,\mu)}{\sin\theta} + \lambda \cot\theta \; T(\lambda\mu) \qquad \text{(E.10)}$$

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