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EXCITATION AND IONIZATION OF ATOMS BY ELECTRON IMPACT—THE BORN AND OPPENHEIMER APPROXIMATIONS

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CONTENTS

It is important, for many applications, to have reliable data on the magnitudes of the cross-sections for excitation and ionization of atoms and ions by electrons. In part I the usual approximations (those of Born and of Oppenheimer) which are made to obtain theoretical values are critically examined. It is pointed out that the assumption of separable bound wave functions may often lead to considerable errors. In the case of the Oppenheimer approximation the errors may even be such as to give results violating the principle of detailed balancing. Circumstances in which these errors are likely to be serious are analyzed, and precautions which may be taken to reduce them are proposed. The conditions under which the approximations are likely to fail, even when exact bound wave functions are used, appear to be related to the magnitude of certain coupling terms which are ignored in obtaining the approximations. The usefulness of certain conservation theorems which limit the possible size of collision cross-sections is also pointed out. A summary of those general properties of inelastic cross-sections which are reliably given by the theory is included.

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In part II the available experimental data are compared with the predictions of the Born and Oppenheimer approximations. The collision processes studied include the following: excitation of H, He, Na, Ne and Hg; ionization of H_2, He, Ne, Hg, Ni (K) and Ag (K and L_{III}).

The investigation shows that the Born approximation is the one that should generally be used in the treatment of transitions which can take place without electron exchange having to be invoked. For these the approximation achieves a considerable degree of success. As far as can be judged from the comparison data available, the main defects are that the maxima of the predicted cross-section energy curves tend to be too pronounced, and to be located too close to the critical potentials.

In the case of transitions involving a reversal of electron spin the Oppenheimer approximation must be used. Unfortunately, it proves to be very unsatisfactory. Thus for non-hydrogenic systems it may give very different results according to whether a prior or a post interaction is adopted. It leads to frequent violations of the conservation theorem and cannot be relied upon even to give the detailed shape of cross-section against energy curves.

By generalizing from the evidence collected, an attempt is made to specify the conditions under which the Born and Oppenheimer approximations are most reliable; on this basis, proposals for systemization are made.

Attention is drawn to the fact that some (but by no means all) of the observed excitation functions possess an extremely sharp peak just beyond the critical potential. The theory seems unable to reproduce this peculiar feature. It does not appear in the observed ionization functions.

INTRODUCTION

In numerous geophysical and astrophysical problems it is important to have quantitative information on the cross-sections associated with excitation and ionization by electrons. Thus, data of this kind are required before the significance of the observed spectral characteristics of aurorae may be properly understood (Bates, Massey & Pearse 1948). They are also wanted in connexion with investigations on the chemical composition of the solar corona (Hoyle 1949) and of the gaseous nebulae (Aller & Menzel 1945). An accurate knowledge of these inelastic cross-sections, besides being necessary for the development of a detailed theory of gas discharges, would be useful in connexion with certain of their industrial applications.

It is true that inelastic collisions of electrons with atoms have been studied experimentally in a number of laboratories and data on the associated cross-sections have been obtained. However, experimental measurement, particularly of the absolute value of the excitation cross-sections, is difficult. Furthermore, in many cases of most interest in applications, the experimental method encounters exceptional difficulties. The particles concerned may not be readily obtainable in an adequate and controlled concentration. This will be so if they are atoms of an element which, under normal conditions, exists only as a solid or a molecular gas, or if they are positive ions. In other cases the transitions involved may give rise to metastable particles of long radiative lifetime, so that the usual optical methods of measurement cannot be applied. These difficulties characterize the following reactions, all of which are of geophysical or astrophysical interest:

$$\left.\begin{aligned} \mathrm{N}({}^4S)+e&\rightarrow\mathrm{N}({}^3P\,3p)\,({}^4P)+e,\\ \mathrm{S}^{++}({}^3P)+e&\rightarrow\mathrm{S}^{++}({}^1D)+e,\\ \mathrm{Fe}^{14+}({}^2P_{\frac{1}{2}})+e&\rightarrow\mathrm{Fe}^{14+}({}^2P_{\frac{3}{2}})+e,\\ \mathrm{O}({}^3P)+e&\rightarrow\mathrm{O}^{+}({}^2P)+2e. \end{aligned}\right\} \qquad (1)$$

Theoretical determination of the cross-sections also meets with difficulty. An exact quantal treatment is not possible. Approximate methods such as those of Born and of Oppenheimer must be used, and these are least satisfactory for low-energy collisions, which are usually those concerned in applications. It is clearly important to extend the range of reliable theoretical estimates, and the first step is to assess as precisely as possible how accurate the approximations really are. In part I of this paper we examine the approximations critically from the theoretical aspect. A detailed comparison of calculated and laboratory data is then carried out in part II, attention being paid to the general features which might be expected to appear from the considerations of part I. The effectiveness of the comparison is reduced by the uncertain validity of many of the measurements revealed by the inconsistency of results found by different observers and, in certain cases, by the inherent impossibility of the values given. Nevertheless, on the basis of the comparison, an attempt is made to determine the conditions of validity of the theoretical approximations and the type of error to be expected when they become inaccurate. This is unavoidably incomplete at present, and the directions in which further experimental work would help to produce clarification are pointed out.

Throughout the paper we shall specify all the cross-sections in multiples of πa_0^2, i.e. in units of $8{\cdot}8\times10^{-17}$ cm.^{2}. One or more of three characteristic components appear in cross-section against energy curves. In agreement with theory (cf. § 3) the well-known broad direct-term maxima and narrow exchange-term maxima are found (cf. figures 2*a* and 8*b*, *c*). There is evidence also for the occurrence in some cases of an extremely sharp peak located just beyond the excitation threshold (cf. figures 6*b*, *c*). For brevity, these features will occasionally be referred to as *F*-, *G*- and *X*-type maxima respectively.

PART I. THE BORN AND OPPENHEIMER APPROXIMATIONS—GENERAL THEORY

1. Maximum cross-section for given angular momentum

Before proceeding to discuss in detail the Born and Oppenheimer approximations it is convenient to mention briefly a general conservation theorem due to Mott and to Bohr, Peierls and Placzek (cf. Mott & Massey 1949) which we will have occasion to employ.

The electron wave incident on the scattering centre may be resolved into a series of partial waves of angular momentum $\dfrac{\boldsymbol{h}}{2\pi}\{l(l+1)\}^{\frac{1}{2}}$, $\boldsymbol{h}$ being Planck's constant and l any integer. For any collision process, i, each of these partial waves gives a contribution Q_l^i to the total cross-section. It may be shown that

$$\sum_i^{\text{inelastic}} Q_l^i \leqslant \frac{\pi}{k^2}(2l+1), \tag{2}$$

where

$$k = 2\pi mv/\boldsymbol{h}, \tag{3}$$

and m is the mass and v is the velocity of the electrons.

Condition (2) is of great value in that it provides conclusive evidence on defects in theoretical approximations, since it is sufficiently exacting to be violated by the calculated partial cross-sections in a number of cases (cf. § 4·6). Sometimes for even a single member, j, of the series the calculated value of Q_l^j exceeds the limit. In this connexion it is useful to notice that Q_l^{AB} and Q_l^{BA}, the partial cross-sections associated with transitions from level A to level B, and from level B to level A, respectively, are related by the equation

$$\omega_A k_A^2 Q_l^{AB} = \omega_B k_B^2 Q_l^{BA}, \tag{4}$$

where the ω's are statistical weights and the subscripts on them and on the k's denote the level concerned. It follows at once that the inequality

$$Q_l^{AB} < \frac{\pi}{k_A^2}(2l+1) \tag{5}$$

must be replaced by what is sometimes a more powerful inequality,

$$Q_l^{AB} < \gamma \frac{\pi}{k_A^2}(2l+1), \tag{6}$$

γ being either unity or ω_B/ω_A whichever is the smaller. If l changes to l' during the transition, ω_B/ω_A must be multiplied by $(2l'+1)/(2l+1)$.

2. Basis of Born and Oppenheimer approximations

Though the collision theory method of deriving the Born and the Oppenheimer approximations is well known (Born 1926; Oppenheimer 1928), we will give an outline of it here so that we may draw attention to the assumptions involved.

For simplicity we will consider the case of the excitation or ionization of a hydrogen atom. Neglecting the very small spin-orbital interaction, the wave equation for the complete system (in Hartree units) is

$$\left\{\nabla_1^2 + \nabla_2^2 + 2\left(E + \frac{1}{r_1} + \frac{1}{r_2} - \frac{1}{r_{12}}\right)\right\} \mathrm{X}(1,2) = 0, \tag{7}$$

r_1 and r_2 being the distance of the electrons from the nucleus, r_{12} the distance between them, and E the sum of $\frac{1}{2}k_p^2$, the energy of the incident electron, and E_p, the energy of the atomic electron in the initial state p. The wave function X can of course be written as

$$\Omega(\sigma_1, \sigma_2)\, \Psi(\mathbf{r}_1, \mathbf{r}_2), \tag{8}$$

where Ω depends only on the spin co-ordinates σ_1 and σ_2, and Ψ depends only on the spatial co-ordinates $\mathbf{r}_1$ and $\mathbf{r}_2$. To calculate the various collision cross-sections it is necessary to determine the asymptotic form of the X appropriate to the problem. We will consider the Born and the Oppenheimer approximations separately.

2·1. *Born approximation*

2·1·1. *Hydrogen-like atoms*

In the Born approximation the indistinguishability of the electrons is ignored, and one of the two reference numbers (say 1) is taken to refer to the incident electron, and the other (2) is taken to refer to the atomic electron. Ω is assumed to have the form

$$\delta(s_1 \mid \sigma_1)\, \delta(s_2 \mid \sigma_2), \tag{9}$$

where s_1 and s_2 are the spin-quantum numbers and where the δ-functions have the property

$$\left.\begin{aligned} \delta(s \mid \sigma) &= 0 \quad \text{for} \quad \sigma \neq s \\ \text{and} \qquad &= 1 \quad \text{for} \quad \sigma = s. \end{aligned}\right\} \tag{10}$$

s_1 and s_2 have either of two values α and β, and they remain unaltered throughout the collision. No special symmetry properties are associated with Ψ. It is expanded in terms of the complete set of eigenfunctions $\psi_m(\mathbf{r}_2)$ of the hydrogen atom; thus

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_m \psi_m(\mathbf{r}_2)\, F_m(\mathbf{r}_1), \tag{11}$$

the summation sign including integration over the continuum. By substituting in (7) and making use of the fact that ψ_m satisfies the equation

$$\left\{\nabla_2^2 + 2\left(E_m + \frac{1}{r_2}\right)\right\} \psi_m(\mathbf{r}_2) = 0, \tag{12}$$

by then multiplying by $\psi_q^*(\mathbf{r}_2)$ and integrating over the spatial co-ordinates of the atomic electron it can be shown that

$$\{\nabla_1^2 + 2(E - E_q)\} F_q(\mathbf{r}_1) = 2\int \left(\frac{1}{r_{12}} - \frac{1}{r_1}\right) \Psi(\mathbf{r}_1, \mathbf{r}_2)\, \psi_q^*(\mathbf{r}_2)\, d\tau_2. \tag{13}$$

Hence using (11) again

$$\{\nabla_1^2 + 2(E - E_q - V_{qq}(\mathbf{r}_1))\} F_q(\mathbf{r}_1) = 2 \sum_{m \neq q} V_{mq}(\mathbf{r}_1)\, F_m(\mathbf{r}_1), \tag{14}$$

where

$$V_{mq}(\mathbf{r}_1) = \int \left(\frac{1}{r_{12}} - \frac{1}{r_1}\right) \psi_m(\mathbf{r}_2)\, \psi_q^*(\mathbf{r}_2)\, d\tau_2 \tag{15}$$

$$= \int \left(\frac{1}{r_{12}}\right) \psi_m(\mathbf{r}_2)\, \psi_q^*(\mathbf{r}_2)\, d\tau_2 \quad \text{for} \quad m \neq q, \tag{16}$$

owing to the orthogonality of ψ_q and ψ_m.

To simplify this infinite set of coupled differential equations Born assumes:

(i) that $V_{qq}(\mathbf{r}_1)$ (which is the electrostatic potential appearing on the left-hand side of (14)) can be neglected;

(ii) that $V_{mq}(\mathbf{r}_1)\, F_m(\mathbf{r}_1)$ (on the right-hand side of (14)) can be neglected for $m \neq p$ (so that the coupling terms disappear);

(iii) that $F_p(\mathbf{r}_1)$ (again on the right-hand side of (14)) can be replaced by $\exp(ik_p \mathbf{n}_p . \mathbf{r}_1)$, $\mathbf{n}_p$ being a unit vector in the direction of the incident wave (that is, that $F_p(\mathbf{r}_1)$ is undistorted by the interaction—as follows from (i) and (ii)).

These assumptions are, of course, equivalent to representing Ψ in (13) by

$$\exp(ik_p \mathbf{n}_p . \mathbf{r}_1)\, \psi_p(\mathbf{r}_2), \tag{17}$$

and lead to the equation

$$\{\nabla_1^2 + 2(E - E_q)\} F_q(\mathbf{r}_1) = 2\int \left(\frac{1}{r_{12}}\right) \psi_p(\mathbf{r}_2)\, \psi_q^*(\mathbf{r}_2)\, d\tau_2 \exp(ik_p \mathbf{n}_p . \mathbf{r}_1). \tag{18}$$

Following the standard procedure (Mott & Massey 1949) the asymptotic form of the relevant solution of this equation can be shown to be

$$r_1^{-1} \exp(ik_q r_1)\, f_{pq}(\theta, \phi; k_p), \tag{19}$$

where

$$f_{pq}(\theta, \phi; k_p) = -\frac{1}{2\pi} \iint \frac{\exp\{i(k_p \mathbf{n}_p - k_q \mathbf{n}_q) . \mathbf{r}_1'\}}{|\mathbf{r}_1' - \mathbf{r}_2|}\, \psi_p(\mathbf{r}_2)\, \psi_q^*(\mathbf{r}_2)\, d\tau_1'\, d\tau_2, \tag{20}$$

$$k_q^2 = k_p^2 + 2(E_p - E_q), \tag{21}$$

and $\mathbf{n}_q$ is a unit vector in the direction of the scattered wave.

The cross-section associated with the scattering in a direction (θ, ϕ) of those incident electrons which have caused a transition from state p to state q is termed the differential cross-section and is given simply by

$$I_{pq}(\theta, \phi; k_p) = \frac{k_q}{k_p} \,|\, f_{pq}(\theta, \phi; k_p) \,|^2. \tag{22}$$

The total cross-section associated with the transition is then

$$Q_{pq}(k_p) = \int_0^{2\pi} \int_0^{\pi} I_{pq}(\theta, \phi, k_p) \sin\theta \, d\theta \, d\phi. \tag{23}$$

It can be determined most readily by changing from angular to momentum variables (Mott & Massey 1949). Choosing the axis of polar co-ordinates parallel to the change of momentum vector $(k_q \mathbf{n}_q - k_p \mathbf{n}_p)$ we have,

$$(k_q \mathbf{n}_q - k_p \mathbf{n}_p) \,.\, \mathbf{r}_1' = K_{pq} z', \tag{24}$$

where

$$K = |\, k_q \mathbf{n}_q - k_p \mathbf{n}_p \,|. \tag{25}$$

Using (20) to (25) it may be shown that

$$I_{pq}(K, k_p) \, dK = \frac{8\pi}{k_p^2} \left| \int \exp(-iKz) \, \psi_p(\mathbf{r}) \, \psi_q^*(\mathbf{r}) \, d\tau \right|^2 \frac{dK}{K^3} \tag{26}$$

and

$$Q_{pq}(k_p) = \int_{K_{\text{min.}}}^{K_{\text{max.}}} I_{pq}(K, k_p) \, dK, \tag{27}$$

where

$$K_{\text{max.}} = k_p + k_q, \tag{28}$$

$$K_{\text{min.}} = k_p - k_q. \tag{29}$$

If the final state q lies in the continuum it is of course necessary to integrate over all possible energies of the ejected electron to obtain the total ionization cross-section.

2·1·2. *Application to complex atoms*

As can readily be verified, the hydrogenic formulae given above can be applied immediately to complex atoms if simple product-type wave functions are employed. Thus the contribution from each electron in a subshell can be obtained by using its initial and final wave functions for ψ_p and ψ_q in (26), the other electrons being ignored; and the full cross-section can then be found by summing the contributions from all the equivalent electrons.

Exact wave functions for complex atoms cannot be derived, and the necessity of employing approximations such as those of Slater (1932), Hartree (1946–7) or Fock (1930) introduces uncertainties distinct from those inherent in the Born treatment.

If ψ_p and ψ_q (in (26)) overlap considerably and are not too crudely represented, the additional error will in general be relatively unimportant. In some cases it may be worth taking advantage of the fact that by making use of the equations satisfied by the ψ's the original formula may be transformed to

$$I_{pq}(K, k_p) \, dK = \frac{2\pi}{k_p^2} \left| \int \exp(-iKz) \left\{ \psi_p(\mathbf{r}) \frac{\partial \psi_q^*(\mathbf{r})}{\partial z} - \psi_q^*(\mathbf{r}) \frac{\partial \psi_p(\mathbf{r})}{\partial z} \right\} d\tau \right|^2 \frac{dK}{K(E_q - E_p)^2}. \tag{30}\dagger$$

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† This transformation is closely analogous to that introduced by Chandrasekhar (1945) in his work on the calculation of the cross-section associated with photo-detachment from H^-.

While (26) and (30) are formally equivalent they are not necessarily the same in practical computations, since they weight the various regions of co-ordinate space differently. In consequence, by evaluating the cross-sections, using each separately, some information may be obtained on the inaccuracies caused by defects in the ψ's. Both formulae have their weaknesses; that of (26) is that a considerable contribution to the integral appearing in it comes from large radial distances where the wave functions are usually poorly determined; and that of (30) (which unfortunately has not yet been applied) is that it involves derivatives of the wave functions.

In many transitions (particularly where there is little overlap between the main parts of ψ_p and ψ_q), the positive and negative portions of the integrals to be evaluated almost completely cancel each other. This occurs, for example, in transitions between the ground state and most of the higher excited states of the alkali atoms. Experience with the calculation of spontaneous transition probabilities (for which the essential integrals are of the form

$$\left.\begin{aligned} &\int \psi_p(\mathbf{r})\,\mathbf{r}\psi_q^*(\mathbf{r})\,d\tau \\ \text{or}\qquad &\int (\psi_p(\mathbf{r})\,\nabla\psi_q^*(\mathbf{r})-\psi_q^*(\mathbf{r})\,\nabla\psi_p(\mathbf{r}))\,d\tau, \end{aligned}\right\} \tag{31}$$

and are thus rather similar to those appearing in (26) and (30) respectively) indicates that in these instances little reliance can be placed on any results obtained.†

Another difficulty that may arise is that the wave functions of the active electron, ψ_p and ψ_q, may not be orthogonal‡; for the wave functions of the passive electrons may be appreciably affected by the change in the orbit of the active electron so that there may be a significant alteration in the potential field in which this latter moves. In view of the derivation of (26) the use of non-orthogonal wave functions is clearly inconsistent. The procedure would indeed lead to discrepancies; for example, in conflict with the observational data, it would yield cross-sections not falling to zero at high-impact energies. A device commonly employed is to replace ψ_q by

$$\psi_q(\mathbf{r})-\left(\int \psi_p^*(\mathbf{r})\,\psi_q(\mathbf{r})\,d\tau\right)\psi_p(\mathbf{r}) \tag{32}$$

or by some other function which is of necessity orthogonal to ψ_p. Though this is without theoretical justification it at least avoids absurdities in the results. Fock functions, which are sometimes used, do of course form a proper orthogonal set. It must be stressed, however, that as far as the present problem is concerned they are no less artificial (though they may well be more accurate) than functions like (32) which have arbitrarily been made to conform to the orthogonality condition. The reason for this is that the equation they satisfy is of a more complicated form than (12), and since the additional terms included do not disappear on carrying out the integration yielding (13), formula (26) is not consistent with them.

The fundamental origin of the difficulty just discussed lies in the employment of separable wave functions for the atomic or ionic electrons. Such separation results in an invaluable

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† Cf. Bates & Damgaard (1949).

‡ This difficulty is naturally confined to transitions involving no change in the azimuthal quantum number; for other transitions the angular parts of the wave functions ensure orthogonality.

simplification; but, as we shall see, both it, and the further separation of the wave function of the free electron, are a frequent source of trouble.

Finally, it is perhaps worth drawing specific attention here to the selection rules for the atomic electron. These are that no change occurs in (*a*) the spin quantum number, and (*b*) the magnetic quantum number (the axis being chosen as indicated). The first of these has been mentioned earlier in this section; the second follows at once from formula (26).

2·1·3. *The omitted terms*

Equation (14) can also be solved by what is known as the distorted wave approximation. We will content ourselves with indicating very briefly the basis of the method. The essential difference from the Born approximation is that the ordinary atomic potential terms V_{qq} are retained (i.e. assumption (i) is not made and the related assumption (iii) is consequently modified). Thus (14) reduces to

$$\{\nabla_1^2+2(E-E_q-V_{qq}(\mathbf{r}_1))\}F_q(\mathbf{r}_1) = 2V_{pq}(\mathbf{r}_1)\,F_p(\mathbf{r}_1), \tag{33}$$

where F_p on the right-hand side is the relevant solution of

$$\{\nabla_1^2+2(E-E_p-V_{pp}(\mathbf{r}_1))\}F_p(\mathbf{r}_1) = 0. \tag{34}$$

The procedure for obtaining the asymptotic form of F_q and hence the cross-section is discussed by Mott & Massey (1949).

It must be emphasized that the distorted wave approximation does *not* necessarily yield more accurate results than the Born approximation. If assumptions (i) and (iii) and assumption (ii) cause errors of the same sense, the elaboration would certainly lead to an improvement; but if they cause errors of the opposite sense it would lead to a deterioration.

The significance of the coupling terms can be discussed from several aspects. Perhaps the simplest approach is to note that their absence from equations (18) and (33) arises directly from the assumption that $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ in (13) can be represented by a single product of functions of $\mathbf{r}_1$ and of $\mathbf{r}_2$. Now such separation of the variables does not take proper account of the repulsion between the two electrons. Equation (33) is apparently superior to (18) in that it makes allowance for the influence of the *average static potential* of the atom or ion on the wave function of the incident electron. For many problems this would certainly be an adequate approximation. However, for the calculation of collision cross-sections (especially if neutral atoms are involved) the effect of the *actual instantaneous interaction* is likely to be of greater importance.† This unusual contingency arises because part of the integrand on the right-hand side of (13) contains the factor $\frac{1}{r_{12}}\Psi(\mathbf{r}_1, \mathbf{r}_2)$; and it is precisely in the region where $1/r_{12}$ tends to infinity that the $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ assumed is most in error, its value there (no less with distorted waves than with plane waves) being seriously overestimated. Apart from the

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† Ionization of a neutral atom provides an obvious example of this. The average static potential of the ejected electron is zero. Hence on the distorted wave approximation the potential acting on the scattered electron would be that of the ion formed. In fact, the potential must be much less. For in general the ejected electron has much lower velocity than the scattered electron (Mott & Massey 1949) and thus it cannot move far in the effective duration of the collision. The Born approximation in contrast assumes that the Coulomb potential of the ion is completely screened. This probably does not introduce significant error at high-impact energies, but at low-impact energies (when the difference in the velocities of the ejected and scattered electrons is least pronounced) the position is very uncertain.

possibility of a variational treatment the defect can only be removed by taking account of the full expansion for $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ given in (11); and clearly, the introduction of the higher terms (which can be regarded as representing both the inelastically scattered waves and the polarization of the atom or ion) automatically produces coupling.

It is of course impossible to solve the general equations exactly. However, by studying the single pair of equations relating to two states of an atom which are in resonance, Massey & Mohr (1933*b*) have been able to obtain qualitative information on the type of effect to which coupling gives rise. Ignoring all states other than p and q, the two in resonance, writing

$$\left.\begin{aligned} k_p = k_q &= k, \\ V_{pp} = V_{qq} &= V, \\ V_{pq} &= \lambda v_{pq}, \end{aligned}\right\} \tag{35}$$

(where λ is a constant and v_{pq} is a shape factor) and assuming, for simplicity, that the potentials are spherically symmetrical, the equations become

$$\{\nabla^2 + k^2 - 2V(r)\} F_p(\mathbf{r}) = 2\lambda v_{pq}(r)\, F_q(\mathbf{r}), \tag{36}$$

$$\{\nabla^2 + k^2 - 2V(r)\} F_q(\mathbf{r}) = 2\lambda v_{pq}(r)\, F_p(\mathbf{r}). \tag{37}$$

London (1932) has derived the exact solutions of this and has hence shown that the cross-section associated with the transition is

$$\frac{\pi}{k^2} \Sigma(2l+1) \sin^2(\eta^l - \delta^l), \tag{38}$$

where the phases η^l and δ^l are determined in the standard way from the equations

$$\{\nabla^2 + k^2 - 2(V(r) \pm \lambda v_{pq}(r))\} \mathscr{F}(\mathbf{r}) = 0. \tag{39}$$

This result is to be compared with the expression for the cross-section on the distorted wave approximation, which is

$$\frac{\pi}{k^2} \Sigma(2l+1) \left\{4k \int_0^\infty \lambda v_{pq}(r)\, (rF_p^l(r))^2\, dr\right\}^2, \tag{40}$$

$F_p^l(r)$ being the bounded function satisfying

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{dF_p^l(r)}{dr}\right) + \left(k^2 - 2V(r) - \frac{l(l+1)}{r^2}\right) F_p^l(r) = 0, \tag{41}$$

and being normalized as usual. Now it may be shown that

$$\sin^2(\eta^l - \delta^l) = \left\{4k\lambda \int_0^\infty v_{pq}(r)\, (rF_p^l(r))^2\, dr\right\}^2, \tag{42}$$

provided λ is such that the right-hand side is small compared with unity. This implies that, for sufficiently weak coupling, expansions (38) and (40) are equivalent. Massey & Mohr, point out however, that as the coupling parameter λ is strengthened the two sides of (42) eventually separate, the rate of growth of the left-hand side being less than that of the right-hand side; and if λ is large the extent of the separation is clearly very serious, since the left-hand side is an oscillatory function whereas the right-hand side is a monotonically increasing function. For strong coupling therefore the cross-section given by the distorted wave approximation is much too great.†

The reason why the inclusion of both coupling terms in the resonance equations leads to there being a *limitation* on the cross-section can readily be appreciated physically. Just as the term $2\lambda v_{pq}(r)\,F_p(\mathbf{r})$ in (36) gives rise to transitions $p \rightarrow q$, so the term $2\lambda v_{pq}(\mathbf{r})\,F_q(\mathbf{r})$ in (37) gives rise to transitions $q \rightarrow p$; and it is these reverse transitions (neglected in the Born and distorted wave approximations) that prevent $F_q(\mathbf{r})$, and hence the cross-section, from increasing indefinitely.

It is now possible to understand in general the effect of the infinity of coupling terms that appear in the equations relating to an actual atom or ion. Clearly each such term corresponds to the possibility of a transition between the two connected states. The incident electron must therefore be regarded as making not a *single* but rather a *multiple* collision. In an extreme case of very strong coupling (probably never realized or even approached in practice except in nuclear collisions), the scattering centre is surrounded by what may be termed a collision zone, an incident electron emerging from which will leave the atom or ion in a state determined solely by statistical considerations. It is clear that for any particular transition the coupling effects ultimately decrease with increase in the energy or the azimuthal quantum number of the incident electron.

Massey & Mohr (1933 *b*) have adduced interesting evidence favouring the picture presented from a comparison of the observed and calculated angular distributions of electrons elastically scattered by helium.

Finally, we will indicate the type of correction that, according to the model just described, should be applied to the cross-sections derived using the Born or distorted wave approximations. There are two principal cases to be considered.

Case I. V_{pq} *strong.* Simple theory tends to overestimate the cross-section of the transition $p \rightarrow q$, as it ignores the reverse transition $q \rightarrow p$. Further, as the state q may be regarded as overpopulated, the balance of such transitions as $r \rightarrow q$ and $q \rightarrow r$, where r is any other state, is also likely to lead to a reduction in the cross-section. These remarks have less applicability to ionizing collisions, as leakage transitions out of the continuum are relatively infrequent.

Case II. V_{pq} *weak.* The effect of the reverse transition $q \rightarrow p$ is here slight. If there is another state s with V_{ps} strong (as there will be in general), then the balance of the transitions $s \rightarrow q$ and $q \rightarrow s$ is likely to increase the cross-section, the extent to which it does so depending on V_{sq}.

The situation may be summarized as follows: the neglected transitions have a tendency to bring about both some degree of equalization of the individual inelastic cross-sections and some reduction in their sum (with, of course, a corresponding increase in the elastic cross-section).

In the study of a particular atom or ion it is useful to be able to estimate rapidly the approximate value of the coupling terms. The magnitude of any V_{pq} at small radial distances can readily be assessed from the amount of overlap between the relevant wave functions.

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† The replacement of $F_p^l(r)$ in (40) by the corresponding component of a plane wave reduces the value of the expression in many instances. Born's approximation is thus often rather more accurate than the distorted wave approximation. It must be emphasized, however, that the conclusion that the latter approximation *always* overestimates the electron collision cross-section applies only to the simplified resonance transition discussed.

Perhaps of greater significance is the asymptotic form. Fortunately, this depends only on the type of the orbitals involved (i.e. on whether they are S, P, D or F, etc.†) and in table 1 we give it for the more important transitions (the multiplying constant is not, of course, included).

TABLE 1. ASYMPTOTIC FORM OF V_{pq}

connected orbitals	S	P	D	F
S	$\exp(-\gamma r)$	r^{-2}	r^{-3}	r^{-4}
P	r^{-2}	r^{-3}	r^{-2}	r^{-3}
D	r^{-3}	r^{-2}	r^{-3}	r^{-2}
F	r^{-4}	r^{-3}	r^{-2}	r^{-3}

It will be noted that for all optically allowed transitions V_{pq} falls off only as r^{-2}, but that for optically disallowed transitions it falls off as r^{-3} or faster. This difference is of considerable importance, particularly in connexion with the calculation of the cross-sections of the transitions from the ground to the lower excited states. After evaluating the $p \to q$ cross-section by the simple theory as a first approximation, it is natural as a second approximation to attempt next to allow for the reverse $q \to p$ transitions. We cannot yet do this quantitatively, but the asymptotic form of the V_{pq}'s at least suggests that the correction is greater for optically allowed transitions than for optically disallowed transitions; and that of these latter it is least for S–S transitions.‡

2·2. *Oppenheimer approximation*

2·2·1. *Atomic hydrogen*

In the Oppenheimer approximation proper account is taken of the indistinguishability of the electrons. For singlet and triplet states of the complete system, Ω is

$$\frac{1}{\sqrt{2}}\{\delta(\alpha_1 \mid \sigma_1)\,\delta(\beta_2 \mid \sigma_2) - \delta(\beta_1 \mid \sigma_1)\,\delta(\alpha_2 \mid \sigma_2)\}, \tag{43}$$

and

$$\left.\begin{array}{c} \delta(\alpha_1 \mid \sigma_1)\,\delta(\alpha_2 \mid \sigma_2), \\ \dfrac{1}{\sqrt{2}}\{\delta(\alpha_1 \mid \sigma_1)\,\delta(\beta_2 \mid \sigma_2) + \delta(\beta_1 \mid \sigma_1)\,\delta(\alpha_2 \mid \sigma_2)\}, \\ \delta(\beta_1 \mid \sigma_1)\,\delta(\beta_2 \mid \sigma_2), \end{array}\right\} \tag{44}$$

respectively. The Ψ associated with the former must be symmetrical with respect to electron interchange, and that associated with the latter must be anti-symmetrical. Such functions may be expanded in the form

$$\sum_m \psi_m(\mathbf{r}_2)\,H_m(\mathbf{r}_1) \pm \sum_m \psi_m(\mathbf{r}_1)\,H_m(\mathbf{r}_2) \quad \left\{\begin{array}{l} +\text{ve sign: symmetrical} \\ -\text{ve sign: anti-symmetrical} \end{array}\right. \tag{45}$$

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† To avoid possible confusion we adopt capitals here instead of the customary small letters (some of which we use for other purposes).

‡ It will be shown in part II that these predictions are in fair agreement with observation. Nevertheless consideration of the contributions from electrons with different relative angular momenta shows that the phenomena are rather more complex than the simple picture given above would suggest. Thus a considerable part of the cross-section arises from the action of electrons of high azimuthal quantum number for which the right-hand side of (42) is so small that the Born approximation should treat them accurately. The failure of the approximation would only arise then in determining the contributions of low azimuthal quantum number. These should be relatively insensitive to the asymptotic form of the interaction.

(cf. (11)). Now the second sum may also be expanded in terms of $\psi_m(\mathbf{r}_2)$,

$$\sum_m \psi_m(\mathbf{r}_1)\, H_m(\mathbf{r}_2) = \sum_m \psi_m(\mathbf{r}_2)\, G_m(\mathbf{r}_1). \tag{46}$$

Hence
$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_m \psi_m(\mathbf{r}_2)\, \{H_m(\mathbf{r}_1) \pm G_m(\mathbf{r}_1)\}. \tag{47}$$

Carrying through exactly the same procedure as in § 2·1·1 we obtain (corresponding to (13))

$$\{\nabla_1^2 + 2(E-E_q)\}\,(H_q(\mathbf{r}_1) \pm G_q(\mathbf{r}_1)) = 2\int\left(\frac{1}{r_{12}} - \frac{1}{r_1}\right) \Psi(\mathbf{r}_1, \mathbf{r}_2)\, \psi_q^*(\mathbf{r}_2)\, d\tau_2. \tag{48}$$

Substitution of the first expansion for Ψ (i.e. (45)) yields

$$\{\nabla_1^2 + 2(E-E_q)\}\,(H_q(\mathbf{r}_1) \pm G_q(\mathbf{r}_1)) = 2\{\sum_m V_{mq}(\mathbf{r}_1)\, H_m(\mathbf{r}_1) \pm \sum_m U_{mq}(\mathbf{r}_1)\, \psi_m(\mathbf{r}_1)\}, \tag{49}$$

where $V_{mq}(\mathbf{r}_1)$ is as in (15) and (16), and where

$$U_{mq}(\mathbf{r}_1) = \int\left(\frac{1}{r_{12}} - \frac{1}{r_1}\right) H_m(\mathbf{r}_2)\, \psi_q^*(\mathbf{r}_2)\, d\tau_2. \tag{50}$$

The ordinary atomic potential does not appear explicitly because of the use of (45) (which involves *both* $\psi_m(\mathbf{r}_1)$ *and* $\psi_m(\mathbf{r}_2)$).

Equations (48) are exact. Simplifications have of course to be introduced to render them soluble. Analogous to the assumptions of Born ((i), (ii) and (iii) of § 2·1·1), Oppenheimer takes $H_p\begin{pmatrix}\mathbf{r}_1\\ \mathbf{r}_2\end{pmatrix}$ to be $\exp\begin{pmatrix} ik_p \mathbf{n}_p . \begin{matrix}\mathbf{r}_1\\ \mathbf{r}_2\end{matrix}\end{pmatrix}$ and ignores all other terms on the right-hand side; that is, he takes

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \exp\,(ik_p \mathbf{n}_p . \mathbf{r}_1)\, \psi_p(\mathbf{r}_2) \pm \psi_p(\mathbf{r}_1)\, \exp\,(ik_p \mathbf{n}_p . \mathbf{r}_2). \tag{51}†$$

This reduces (49) to

$$\begin{aligned}\{\nabla_1^2 + 2(E-E_q)\}\,(H_q(\mathbf{r}_1) \pm G_q(\mathbf{r}_1)) = 2\Bigg\{&\left(\int \frac{1}{r_{12}}\, \psi_p(\mathbf{r}_2)\, \psi_q^*(\mathbf{r}_2)\, d\tau_2\right) \exp\,(ik_p \mathbf{n}_p . \mathbf{r}_1)\\ &\pm \left(\int\left(\frac{1}{r_{12}} - \frac{1}{r_1}\right) \exp\,(ik_p \mathbf{n}_p . \mathbf{r}_2)\, \psi_q^*(\mathbf{r}_2)\, d\tau_2\, \psi_p(\mathbf{r}_1)\right)\Bigg\}.\end{aligned} \tag{52}$$

An unsatisfactory feature of the approximation must be pointed out at this stage. The *general nature* of the wave function is doubtless reasonably well represented by (51). But what is actually required is that a *refined property* of it should be given accurately. Thus to yield the $1/r_1$ term of the integral in (48) precisely, the multiple of $\psi_q(\mathbf{r}_2)$ contained in Ψ must be

$$H_q(\mathbf{r}_1) \pm G_q(\mathbf{r}_1). \tag{53}$$

In fact with the adopted Ψ the value of this component is

$$\left(\int \exp\,(ik_p \mathbf{n}_p . \mathbf{r}_2)\, \psi_q^*(\mathbf{r}_2)\, d\tau_2\right) \psi_p(\mathbf{r}_1), \tag{54}$$

which is clearly incorrect. The similarity of the $1/r_{12}$ term suggests that it is also poorly determined. In view of this it is best to retain the second integral in (52) as given, in the

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† The vital difference between the Born and Oppenheimer approximations is that between equations (17) and (51) rather than that between (11) and (45) (which is formal only).

hope that the error in the two terms partially cancel; merely to replace the coefficient of $1/r_1$ by (53), or to neglect it altogether, would probably lead to a worsening of the situation. It is important to note that the first integral in (52) is not open to objection, as it arises from the part of Ψ^s which is specifically expanded in a $\psi_m(\mathbf{r}_2)$ series.†

Returning to the completion of the analysis, it can be shown from (52) that

$$(H_q(\mathbf{r}_1) \pm G_q(\mathbf{r}_1)) \sim r_1^{-1} \exp(ik_q r_1)\,(h_{pq}(\theta, \phi; k_p) \pm g_{pq}(\theta, \phi; k_p)), \tag{55}$$

where
$$h_{pq}(\theta, \phi; k_p) = -\frac{1}{2\pi}\iint \frac{\exp\{i(k_p\mathbf{n}_p - k_q\mathbf{n}_q)\,.\,\mathbf{r}_1'\}}{|r_1' - r_2|}\,\psi_p(\mathbf{r}_2)\,\psi_q^*(\mathbf{r}_2)\,d\tau_1'\,d\tau_2, \tag{56}$$

and
$$g_{pq}(\theta, \phi; k_p) = \frac{1}{2\pi}\iint\left(\frac{1}{r_1'} - \frac{1}{|\mathbf{r}_1' - \mathbf{r}_2|}\right)\exp(-ik_q\mathbf{n}_q\,.\,\mathbf{r}_1')\,\psi_p(\mathbf{r}_1')\exp(ik_p\mathbf{n}_p\,.\,\mathbf{r}_2)\,\psi_q^*(\mathbf{r}_2)\,d\tau_1'\,d\tau_2. \tag{57}$$

h_{pq} is thus identical with f_{pq} of (20) (which designation will be used in future) and is hence referred to as the *direct* function; g_{pq} is referred to as the *exchange* function. It can be proved that the ratio f_{pq}/g_{pq} is real.

On introducing the spin-wave functions, it can readily be seen from the significance of the various terms of the complete asymptotic wave function, that the differential cross-section, $I_{pq}(\theta, \phi; k_p)$, is given by

$$\frac{k_q}{2k_p}\{|f_{pq}(\theta, \phi; k_p)|^2 + |f_{pq}(\theta, \phi; k_p) - g_{pq}(\theta, \phi; k_p)|^2\}, \tag{58}$$

for transitions in which the spin of the atomic electron does not change; and by

$$\frac{k_q}{2k_p}\{|g_{pq}(\theta, \phi; k_p)|^2\} \tag{59}$$

for transitions in which the spin of the atomic electron is reversed. The total cross-section $Q_{pq}(k_p)$ is of course obtained by integrating over all angles. It may be mentioned that Yavorsky (1944, 1945*b*) has succeeded in deriving explicit expressions for f_{pq} and g_{pq} for excitation and ionization from, and to, any state. These are exceedingly complicated and need not be given here.

2·2·2. *Hydrogen-like positive ions*

We will now consider collisions with the hydrogen-like positive ions (e.g. He$^+$, Be^{2+}, etc.) of nuclear charge Z. An analysis identical to that given above yields an equation similar to (49) but with $V_{mq}(\mathbf{r}_1)$ and $U_{mq}(\mathbf{r}_1)$ replaced by $V_{mq}^Z(\mathbf{r}_1)$ and $U_{mq}^Z(\mathbf{r}_1)$, which are defined as follows:

$$V_{mq}^Z(\mathbf{r}_1) = \int\left(\frac{1}{r_{12}} - \frac{Z}{r_1}\right)\psi_m(\mathbf{r}_2)\,\psi_q^*(\mathbf{r}_2)\,d\tau_2 \tag{60}$$

$$= \int\left(\frac{1}{r_{12}}\right)\psi_m(\mathbf{r}_2)\,\psi_q^*(\mathbf{r}_2)\,d\tau_2 \quad \text{for} \quad m \neq q, \tag{61}$$

and
$$U_{mq}^Z(\mathbf{r}_1) = \int\left(\frac{1}{r_{12}} - \frac{Z}{r_1}\right)H_m(\mathbf{r}_2)\,\psi_q^*(\mathbf{r}_2)\,d\tau_2. \tag{62}$$

Naturally $\psi_q(\mathbf{r}_2)$ is here an eigenfunction of the ion concerned.

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† This is also true of the integral in (18) of §2·1·1.

No comment need be made regarding $V_{mq}^{Z}(\mathbf{r}_1)$ beyond pointing out that it is of the same form as $V_{mq}(\mathbf{r}_1)$ except when m is equal to q. With $U_{mq}^{Z}(\mathbf{r}_1)$, however, a difficulty arises. The $1/r_{12}$ and the Z/r_1 terms *do not balance*, and the lack of balance of course subsequently appears in the second integral of the equation corresponding to (52). In view of the earlier discussion (§ 2·2·1) it would therefore appear likely that this introduces serious error.

Perhaps the most satisfactory procedure is to write the basic equation in the form

$$\{\nabla_1^2+2(E-E_q)\}\,(H_q(\mathbf{r}_1)\pm G_q(\mathbf{r}_1)) = 2\int \frac{-(Z-1)}{r_1}\,\Psi(\mathbf{r}_1,\mathbf{r}_2)\,\psi_q^*(\mathbf{r}_2)\,d\tau_2 \\ +2\int\left(\frac{1}{r_{12}}-\frac{1}{r_1}\right)\Psi(\mathbf{r}_1,\mathbf{r}_2)\,\psi_q^*(\mathbf{r}_2)\,d\tau_2. \qquad (63)$$

If, in the first integral, Ψ is expanded by (47), and if, in the second integral, it is expanded as before by (45), we obtain

$$\left\{\nabla_1^2+2\left(E-E_q+\frac{Z-1}{r_1}\right)\right\}(H_q(\mathbf{r}_1)\pm G_q(\mathbf{r}_1)) = 2\left\{\left(\int\frac{1}{r_{12}}\,\psi_p(\mathbf{r}_2)\,\psi_q^*(r_2)\,d\tau_2\right)H_p(\mathbf{r}_1)\right. \\ \left.\pm\left(\int\left(\frac{1}{r_{12}}-\frac{1}{r_1}\right)H_p(\mathbf{r}_2)\,\psi_q^*(\mathbf{r}_2)\,d\tau_2\right)\psi_p(\mathbf{r}_1)\right\}, \qquad (64)$$

the usual coupling terms being neglected. As can be seen, the right-hand side is of the standard form. The left-hand side, however, contains a Coulomb potential $(Z-1)/r_1$. For consistency, therefore, we shall adopt as the zero-order approximation for H_p not plane waves but Coulomb waves, $\mathscr{C}_p^{(Z-1)}$. If these are used (64) is essentially a distorted wave extension of the Oppenheimer approximation.† Doubts were expressed in § 2·1·3 as to whether taking account of distortion yields a real advantage. However, the long range of the Coulomb potential places it in a special category, and, as will be shown later, there are here fundamental objections to the employment of plane waves.

2·2·3. *Alkali-like systems*

Transitions involving the outer electron of alkali-like systems can be treated by an obvious modification of the formulae in §§ 2·2·1 and 2·2·2. Thus for the neutral alkali atoms it is only necessary to replace $1/r_1'$ in (57) by $v(r_1')$, the core potential; alternatively (to avoid the lack of balance effect), it is possible to retain $1/r_1'$ and to introduce a distorting potential $(v(r_1)-1/r_1)$.

Neither procedure takes account of exchange with the inner electrons. To allow for this and to deal with more complex systems the formula given must be generalized. The method of analysis is the same as for the simpler cases, but naturally the algebra is rather lengthy and some additional complication is caused by the spatial and spin co-ordinates not being separable. The result finally obtained is that

$$I_{pq}(\theta,\phi;\,k_p) = \frac{1}{4\pi^2}\frac{k_q}{k_p}\left|\int_{\text{(space and spin)}} \mathrm{X}_p\,V\mathrm{X}_q^*\,d\tau\right|^2, \qquad (65)‡$$

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† It will be noted that it does not contain a term allowing explicitly for distortion by the bound electron. With the Oppenheimer approximation such a term cannot be separated (as mentioned in § 2·2·1).

‡ This formula was first given by Dirac (1926).

V being an interaction potential (see below). If the space and spin co-ordinates of the electrons are represented by the arguments $1, 2, \ldots, N, N+1$, and if the wave functions of the initial and final states of the atom or ion are denoted by $\Phi_p\ (1, 2, \ldots, N-1, N)$ and $\Phi_q\ (1, 2, \ldots, N-1, N)$, respectively, and those of the incident and scattered electron by $\mathscr{H}_p(N+1)$ and $\mathscr{H}_q(N+1)$,† then

$$\mathrm{X}_p = \frac{1}{\surd N}\Sigma\mathbf{P}(\Phi_p(1, 2, \ldots, N-1, N)\,\mathscr{H}_p(N+1)), \tag{66}$$

and

$$\mathrm{X}_q = \frac{1}{\surd N}\Sigma\mathbf{P}(\Phi_q(1, 2, \ldots, N-1, N)\,\mathscr{H}_q(N+1)), \tag{67}$$

where $\mathbf{P}$ is an operator which successively interchanges the argument $N+1$ with each of the arguments $1, 2, \ldots, N-1, N$ and at the same time multiplies by ± 1, so that when the arguments are adjusted in cyclic order the resulting terms are of the same sign if N is even, and are of alternating sign if N is odd. V can now be defined. It is a function whose form depends on the term of X_q with which it is associated. For the term in which the argument of $\mathscr{H}_q$ is j,

$$V = \frac{S}{r_j} - \sum_{k \neq j} \frac{1}{r_{kj}}, \tag{68}$$

with either $$S = Z \quad \text{(the nuclear charge)} \tag{69}$$

or $$S = N \quad \text{(the number of atomic or ionic electrons)}. \tag{70}$$

The first alternative arises from the generalization of the equation with the *unbalanced* exchange integral, and the second from the generalization of the more satisfactory equation with the *balanced* exchange integral (§ 2·2·2). For neutral atoms Z and N are of course equal.

What is usually of interest is the cross-section for transition between two *terms*. This can be obtained in the usual way by averaging over all states of the initial term and summing over all states of the final term. Apart from the trivial one that the total spin of the atomic or ionic electrons does not change by more than 1, there are no selection rules.

2·2·4. *Detailed balancing and the Oppenheimer formula*

Inspection of the formulae in the three preceding subsections shows at once that the incident and scattered electrons are not treated on the same basis. Thus V as defined in (68) involves the interactions of the scattered electron of momentum k_q; it may be regarded as a *post* interaction with respect to the transition $p \rightarrow q$ and may conveniently be designated by $V(q)$. However, the principle of detailed balancing clearly requires that it must be permissible to use $V(p)$ the interactions of the incident electron of momentum k_p; with respect to the transition $p \rightarrow q$ this alternative is a *prior* interaction.

On inserting $V(p)$ and $V(q)$ in (65) it is apparent that the only terms of the resulting two expressions that are identical are those for which the arguments appearing in $\mathscr{H}_p$ and $\mathscr{H}_q$ are the same (i.e. the direct terms). The other terms (i.e. the exchange terms) are formally different. It can be shown, however, that this difference is only apparent *provided* that suitable wave functions are employed. The conditions to be satisfied by these may be stated briefly as follows.

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† The Φ's are of course anti-symmetrical functions, and the $\mathscr{H}$'s are simply products of a spatial part (which is a plane or Coulomb wave) and a spin part (which is a delta function).

(*a*) *Many-electron systems.* The Φ's must be solutions of the exact wave equation. This implies in particular that the co-ordinates of the different electrons must not be separated. Hartree and Fock wave functions are thus unsatisfactory.

For neutral atoms, plane waves must be used for the spatial part of the $\mathscr{H}$'s, and for positive ions Coulomb waves must be used (except with the objectionable unbalanced interaction (69) which requires plane waves).

(*b*) *Single-electron systems* (including alkali-like systems when treated by the approximation mentioned in § 2·2·3). The Φ's must be solutions of the wave equation formed with a *static* core potential $v(r)$. In this respect Hartree† but *not* Fock wave functions are suitable.

If $v(r)$ is used in the exchange integral the $\mathscr{H}$'s must be as in (*a*),‡ but if an r^{-1} term is used allowance must be made for the distortion associated with the departure of $v(r)$ from its asymptotic form (cf. § 2·2·3).

To demonstrate how the statements made in (*a*) and (*b*) can be proved we will consider as a particular case a two-electron system with nuclear charge Z. Using (65), (66), (67), (70) and the prior interaction, and rearranging the arguments so as to combine together as many terms as possible, the matrix elements can be simplified to

$$2\left|\int \Phi_p(1,2)\,\mathscr{H}_p(3)\left\{\frac{1}{r_3}-\frac{1}{r_{13}}\right\}\Phi_q^*(1,2)\,\mathscr{H}_q^*(3)\,d\tau+\int \Phi_p(1,2)\,\mathscr{H}_p(3)\left\{\frac{1}{r_3}-\frac{1}{r_{13}}\right\}\Phi_q^*(2,3)\,\mathscr{H}_q^*(1)\,d\tau\right.$$
$$\left.+\int \Phi_p(1,2)\,\mathscr{H}_p(3)\left\{\frac{1}{r_3}-\frac{1}{r_{13}}\right\}\Phi_q^*(3,1)\,\mathscr{H}_q^*(2)\,d\tau\right|. \qquad (71)$$

The corresponding expression using the post interaction is

$$2\left|\int \Phi_p(1,2)\,\mathscr{H}_p(3)\left\{\frac{1}{r_3}-\frac{1}{r_{13}}\right\}\Phi_q^*(1,2)\,\mathscr{H}_q^*(3)\,d\tau+\int \Phi_p(1,2)\,\mathscr{H}_p(3)\left\{\frac{1}{r_1}-\frac{1}{r_{13}}\right\}\Phi_q^*(2,3)\,\mathscr{H}_q^*(1)\,d\tau\right.$$
$$\left.+\int \Phi_p(1,2)\,\mathscr{H}_p(3)\left\{\frac{1}{r_2}-\frac{1}{r_{21}}\right\}\Phi_q^*(3,1)\,\mathscr{H}_q^*(2)\,d\tau\right|. \qquad (72)$$

It will be noted that the same direct integral occurs in both. We will examine the conditions for which the sums of the exchange integrals are equal by supposing that $\Phi_{p\text{ or }q}(i,j)$ is a solution of

$$\left\{\nabla_i^2+\nabla_j^2+2\left(\frac{Z}{r_i}+\frac{Z}{r_j}-\frac{1}{r_{ij}}+u(r_i,r_j,r_{ij})+E_{p\text{ or }q}\right)\right\}\Phi(i,j)=0, \qquad (73)$$

u being any function (symmetrical in r_i and r_j), and that $\mathscr{H}_{p\text{ or }q}(k)$ is a solution of

$$\left\{\nabla_k^2+2\left(\frac{Z-2}{r_k}+f(r_k)+E-E_{p\text{ or }q}\right)\right\}\mathscr{H}(k)=0, \qquad (74)$$

f being any function. These equations are not completely general but they are adequate for the present discussion.

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† With Hartree wave functions it is necessary for consistency to employ the computed, and not the actual, term energies.

‡ Actually with true hydrogen-like systems (H itself, He^+, Be^{2+}, etc.) plane or Coulomb waves can be used with either (69) or (70). This peculiarity arises because the central potential is itself of the Coulomb form. The magnitude of the cross-section obtained will of course depend on the choice made, illustrating that merely satisfying the principle of detailed balancing does not ensure accuracy.

We have that

$$\int \Phi_p(1,2)\, \mathscr{H}_p(3) \left\{ \nabla_2^2 + \nabla_3^2 + 2\left(\frac{Z}{r_2} + \frac{Z}{r_3} - \frac{1}{r_{23}} + u(r_2, r_3, r_{23}) + E_q \right) \right\} \Phi_q^*(2,3)\, \mathscr{H}_q^*(1)\, d\tau \equiv 0. \tag{75}$$

By successive application of Green's theorem, and the repeated use of (73) and (74), the Laplacian operators can be eliminated, yielding

$$\int \Phi_p(1,2)\, \mathscr{H}_p(3) \left\{ \left(\frac{2}{r_3} - \frac{1}{r_{23}} + u(r_2, r_3 r_{23}) - f(r_3) \right) \right.$$
$$\left. - \left(\frac{2}{r_1} - \frac{1}{r_{12}} + u(r_1, r_2, r_{12}) - f(r_1) \right) \right\} \Phi_q^*(2,3)\, \mathscr{H}_q^*(1)\, d\tau \equiv 0. \tag{76}$$

With the aid of this identity the difference between the sum of the exchange terms of (71) and (72) can readily be reduced to

$$2\int \Phi_p(1,2)\, \mathscr{H}_p(3) \left\{ \left(u(r_1, r_3, r_{13}) - u(r_1, r_2, r_{12}) \right) - \left(f(r_3) - f(r_2) \right) \right\} \Phi_q^*(3,1)\, \mathscr{H}_q^*(2)\, d\tau. \tag{77}$$

If $u = 0$ and $f = 0$, so that Φ is exact and $\mathscr{H}$ is Coulombian $(Z \neq 2)$, this difference obviously vanishes; but if $f = -(Z-2)/r$, so that $\mathscr{H}$ is plane, it becomes

$$2(Z-2) \int \Phi_p(1,2)\, \mathscr{H}_p(3) \left\{ \frac{1}{r_3} - \frac{1}{r_2} \right\} \Phi_q^*(3,1)\, \mathscr{H}_q^*(2)\, d\tau. \tag{78}$$

Apart from coincidental cancelling this is zero only for $Z = 2$, that is, for the case of a neutral atom. Doubtless there are other u's and f's that satisfy detailed balancing, but the form of (77) is not such as to suggest any of physical significance.

It is possible to investigate the prior-post discrepancy for wave functions satisfying more complicated equations than (73) and (74). In general, the expressions corresponding to (77) that are obtained are too cumbersome to be of value. One-electron systems, however, are of special simplicity. If the Φ's are assumed to be solutions of

$$\{\nabla^2 + 2(E_{p \text{ or } q} + v(r))\}\, \Phi = \Theta_{p \text{ or } q} \tag{79}$$

(where the Θ's are the Fock terms arising from exchange effects between the outer and the core electrons (Fock 1930)), and if the $\mathscr{H}$'s are taken as in (*b*) above, then it can be shown that the difference between the prior- and post-matrix elements reduces to

$$\frac{1}{2}\left\{ \left(\int \Phi_p \mathscr{H}_q^*\, d\tau \right) \left(\int \Theta_q^* \mathscr{H}_p\, d\tau \right) - \left(\int \Phi_q^* \mathscr{H}_p\, d\tau \right) \left(\int \Theta_p \mathscr{H}_q^*\, d\tau \right) \right\}. \tag{80}$$

With the Hartree approximation (in which the Θ's are ignored), (80) vanishes, but with the Fock approximation it will not in general do so—indeed, it may be comparable with either of the two matrix elements. This must not be taken to imply that Hartree wave functions are preferable to Fock wave functions. It only indicates that they alone are consistent with the other approximations made; but there is no obvious reason for supposing that the neglect of exchange between the outer and core electrons compensates for the neglect of the corresponding effect between the free and core electrons. If Fock wave functions are used it is probably best to adopt a mean of the prior- and post-matrix elements, as this at least ensures that the maximum error is not made. However, the *true* matrix element is not necessarily a mean—it is quite conceivable that the required corrections to the prior- and post-matrix elements are of the *same* sign (but of different magnitude). Similar remarks apply to many electron systems (for which, of course, both Hartree and Fock wave functions lead to inconsistencies).

2·2·5. *Further remarks*

The remaining comments on the Oppenheimer approximation are an extension of those already made on the Born approximation. We will therefore be very brief and will give back-references as far as possible.

(i) *The uncertainties caused by the necessity of using approximate wave functions for complex atoms or ions.* The discussion in § 2·1·2 applies without modification to the direct integral. As we have just seen, the values obtained for the exchange integrals depend on whether prior or post interactions are adopted. In addition, they are usually very sensitive to the details of the wave functions employed and must hence be regarded with the greatest reserve.

It is perhaps worth drawing attention to one particular feature that shows directly that the use of separated wave functions for the atomic or ionic electrons may result in serious error. In expressions (71) and (72) (to take for simplicity the case of a two electron system) the integrand of the last term contains the quantities $\frac{1}{r_{31}}\Phi_q^*(3,1)$ and $\frac{1}{r_{12}}\Phi_p(1,2)$. Products of this type have already been discussed† (§ 2·1·3), and it has been pointed out that they cannot be properly treated if separated wave functions are used, as these lead to an overestimation of the contributions from the regions where r_{31} and r_{12} are small.

(ii) *The effect of the omitted coupling terms.* The errors likely to be caused by the neglect of coupling can be studied as in § 2·1·3. We will again take as our standard example the case of the hydrogen atom. The necessary investigation is facilitated by using expansion (47) on *both* sides of (48), and by subdividing the resultant equation as follows:

$$\{\nabla_1^2+2(E-E_q)\}\,H_q(\mathbf{r}_1) = 2\sum_m V_{mq}(\mathbf{r}_1)\,H_m(\mathbf{r}_1), \tag{81}$$

$$\{\nabla_1^2+2(E-E_q)\}\,(H_q(\mathbf{r}_1)-G_q(\mathbf{r}_1)) = 2\sum_m V_{mq}(\mathbf{r}_1)\,(H_m(\mathbf{r}_1)-G_m(\mathbf{r}_1)), \tag{82}$$

$$\{\nabla_1^2+2(E-E_q)\}\,G_q(r_1) = 2\sum_m V_{mq}(\mathbf{r}_1)\,G_m(\mathbf{r}_1). \tag{83}$$

As is readily apparent (81), (82) and (83) describe the collisions

atom (p,α) + incident electron $(k_p,\beta)\rightarrow$ atom (q,α) + scattered electron (k_q,β), (84)

atom (p,α) + incident electron $(k_p,\alpha)\rightarrow$ atom (q,α) + scattered electron (k_q,α), (85)

atom (p,α) + incident electron $(k_p,\beta)\rightarrow$ atom (q,β) + scattered electron (k_q,α), (86)

respectively, the components of spin being denoted by α and β. The solutions of (81) and (82) yield the first and second terms of (58), and that of (83) yields the single term of (59).

Oppenheimer's basic assumption (51) is exactly equivalent to taking as the zero-order approximation on the right-hand side of the rearranged equations

$$\left.\begin{aligned} H_p(\mathbf{r}_1) &= \exp(ik_p\mathbf{n}_p\,.\,\mathbf{r}_1),\\ H_m(\mathbf{r}_1) &= 0 \quad (m\neq p),\\ G_m(\mathbf{r}_1) &= \left(\int\exp(ik_p\mathbf{n}_p\,.\,\mathbf{r}_2)\,\psi_m^*(\mathbf{r}_2)\,d\tau_2\right)\psi_p(\mathbf{r}_1) \quad (\text{all } m).\end{aligned}\right\} \tag{87}$$

---

† Previously however, the pair have not been *atomic or ionic* electrons.

Thus (81) is identical with Born's equation (18), and the omitted coupling terms have precisely the same effect as previously discussed (§ 2·1·3); it will be recalled that the omission implies effectively that the reverse transition $q \rightarrow p$ is neglected and that all other transitions $m \rightarrow q$ and $q \rightarrow m$ are taken to balance. Owing to the adoption, in (87), of non-zero G_m, the position with regard to (82) and (83) is completely different. Instead of a balance between the transitions $m \rightarrow q$ and $q \rightarrow m$ being assumed, allowance is made for *all* of the former and for *none* of the latter. It is clear that in many cases this will result in the cross-section being over-estimated. The danger is rendered particularly acute, since (see below) the contribution from the G_m's is concentrated in a few of the earlier terms (corresponding to low azimuthal quantum numbers) in the expansion of the solutions of the equations in partial waves. And, indeed, as will be seen later, the calculated cross-sections actually exceed the theoretical upper limit (§ 1) in a number of instances.

It is important to notice that the coupling corrections that should be applied to (82) and to (83) will *not* in general be equal. At least for transitions with V_{pq} strong the correction to (82) is likely to be the greater; for the existence of the large H_p term on the right-hand side tends to increase the extent of the over-population of state q and hence tends to magnify the effect of the leakage transitions away from q that are neglected.

The total cross-section associated with all possible transitions between two given terms is often of interest. We will first consider transitions not involving a change of spin. In the important group for which V_{pq} is strong, the Oppenheimer approximation gives too great a value for *each* individual cross-section. The Born approximation, however, *over* estimates in some respects and *under* estimates in other respects, so the errors partially cancel.† Obviously, therefore, the introduction of the allowance for exchange does not necessarily lead to increased accuracy. In practice it is found that the apparent refinement is usually detrimental and that the simple Born approximation is often remarkably successful. The neglect of exchange is of course an arbitrary device which should only be used with caution, particularly if V_{pq} is weak.

Unfortunately, no procedure such as we have just described can be applied to transitions between terms of differing multiplicity. For these the Oppenheimer approximation must be used, as it is only because of exchange effects that the cross-sections do not vanish. We have suggested that the coupling corrections may, in certain cases, be less than those that are associated with transitions that can occur directly. However, they may often be far from negligible and in consequence any calculated results must be treated with reserve.

2·2·6. *Formulae for helium*

Later we shall have occasion to discuss in some detail calculations on transitions between different terms of the helium atom, and it will be convenient to have available the formulae used. For this reason (and to illustrate, for a many-electron system, the type of expression obtained on integrating over the spin co-ordinates) we will conclude by quoting them here.

The differential cross-section is given by

$$\frac{k_q}{k_p} \left| f_{pq}(\theta, \phi; k_p) - g_{pq}(\theta, \phi; k_p) \right|^2 \tag{88}$$

---

† For example, it *over* estimates the cross-section of (84) but *under* estimates that of (86) (actually giving it as zero).

for singlet → singlet transitions; by

$$3\frac{k_q}{k_p}\,|\,g_{pq}(\theta,\phi;k_p)\,|^2 \tag{89}$$

for singlet → triplet transitions; by

$$\frac{k_q}{k_p}\,|\,g_{pq}(\theta,\phi;k_p)\,|^2 \tag{90}$$

for triplet → singlet transitions; and by

$$\frac{k_q}{k_p}\{|\,f_{pq}(\theta,\phi;k_p)-g_{pq}(\theta,\phi;k_p)\,|^2+2\,|\,g_{pq}(\theta,\phi;k_p)\,|^2\} \tag{91}$$

for triplet → triplet transitions. The functions f_{pq} and g_{pq} are defined as follows:

$$f_{pq}(\theta,\phi;k_p) = -\frac{1}{2\pi}\int\left(\frac{1}{r_{23}}+\frac{1}{r_{13}}\right)\Phi_p(\mathbf{r}_1,\mathbf{r}_2)\exp\left(i(k_p\mathbf{n}_p-k_q\mathbf{n}_q)\,.\,\mathbf{r}_3\right)\Phi_q^*(\mathbf{r}_1,\mathbf{r}_2)\,d\tau, \tag{92}$$

and $$g_{pq}(\theta,\phi;k_p) = \frac{1}{2\pi}\int\left(\frac{2}{r_3}-\frac{1}{r_{23}}-\frac{1}{r_{13}}\right)\Phi_p(\mathbf{r}_1,\mathbf{r}_2)\exp\left(ik_p\mathbf{n}_p\,.\,\mathbf{r}_3-ik_q\mathbf{n}_q\,.\,\mathbf{r}_2\right)\Phi_q^*(\mathbf{r}_1,\mathbf{r}_3)\,d\tau, \tag{93}$$

the prior interaction being adopted.

The Φ's are, of course, symmetrical or anti-symmetrical according to whether they represent a singlet or a triplet state.

3. General properties of inelastic collision cross-sections

3·1. *Cross-sections at high impact energies—direct excitation*

The asymptotic form of the direct term in the expression for the cross-section has been derived by Bethe (1930). Expansion of the exponential in (26) by means of a power series yields

$$Q_{pq}(k_p) = \frac{8\pi}{k_p^2}\int_{K_{\text{min.}}}^{K_{\text{max.}}}\left|\sum_{n=0}^{\infty}\frac{(iK)^n}{n!}M_{pq}^n\right|^2\frac{dK}{K^3}, \tag{94}$$

where M_{pq}^n is given by

$$\int z^n\psi_p(\mathbf{r})\,\psi_q^*(\mathbf{r})\,d\tau. \tag{95}$$

As can be seen M_{pq}^n vanishes unless the states p and q have identical magnetic quantum numbers (§ 2·1·2). Clearly, in addition, it also vanishes for n zero (owing to orthogonality), and for either n even or n odd according to whether p and q are of different, or are of the same, parity. Now, if their energy is sufficiently high, the incident electrons are usually deviated but very slightly; the fraction of collisions involving a large momentum change is negligible (Mott & Massey 1949). This enables us to obtain Bethe's approximation to formula (94). Instead of carrying the necessary integration through to $K_{\text{max.}}$ it may be terminated at some much lower value K_T; and if K_T is small, only the first non-zero term in the expansion need be taken into account. We thus have that

$$Q_{pq}(k_p) \simeq \left\{\frac{8\pi}{k_p^2}\log\left(\frac{K_T}{K_{\text{min.}}}\right)\right\}|\,M_{pq}^1\,|^2 \tag{96}$$

for optically allowed transitions, and that

$$Q_{pq}(k_p) \simeq \left\{\frac{\pi}{k_p^2}(K_T^2-K_{\text{min.}}^2)\right\}|\,M_{pq}^2\,|^2 \tag{97}$$

for optically forbidden transitions (with a quadrupole moment). In these $K_{\text{min.}}$ is of course known (cf. (29)), and for large k_p it clearly approximates to

$$(E_q - E_p)/k_p. \tag{98}$$

There is, however, no simple expression for K_T. Fundaminsky (1949) has performed a number of detailed calculations. Amongst the representative cases he investigated are the $1\,^2S$–$2\,^2S$ and the $1\,^2S$–$2\,^2P$ transitions of atomic hydrogen for which he found K_T to be 0·67 and 0·48 respectively. In general the custom is simply to assume that K_T is of order $(E_q - E_p)^{\frac{1}{2}}$. The precise value is fortunately of little moment in (96) owing to the fact that $K_{\text{min.}}$ ultimately dominates the logarithmic term; but without it (97) yields only the asymptotic variation, not the absolute magnitude. As can be seen the cross-sections for optically allowed transitions fall off rather more slowly than those for optically forbidden transitions. Similar conclusions are valid in the case of ions for which, of course, Coulomb waves may be used.

The range of k_p for which Bethe's formula is applicable extends down to some limit $k_p(B)$ whose value is determined by certain detailed properties of the particular transition concerned. For optically allowed transitions the second non-zero term of the expansion for the cross-section has a dependence on k_p which is essentially similar to that occurring in (97) and thus differs from that of the first term. Clearly therefore $k_p(B)$ is at least partially controlled by the magnitude of the ratio $\{M^1_{pq}/M^3_{pq}\}$; formula (96) may not be grossly inaccurate even at quite low impact energies if the ratio is large, but it will only be valid at very high impact energies if the ratio is small. The $3\,^2S$–$3\,^2P$ and $3\,^2S$–$4\,^2P$ transitions of atomic sodium exemplify the position, $\{M^1_{pq}/M^3_{pq}\}$ being large for the former and small for the latter. Using Born's approximation, Fundaminsky has shown that the cross-sections actually tend to

$$\frac{57\pi a^2}{k_p^2}(\log k_p + 1{\cdot}3), \tag{99}$$

and to

$$\frac{0{\cdot}45\pi a^2}{k_p^2}(\log k_p + 4{\cdot}5), \tag{100}$$

respectively. The impact energies above which the logarithmic terms effectively control the variation are obviously very different. It is interesting to compare the rates of diminution of the cross-sections in the energy range just beyond where each has its maximum. Fundaminsky found that between 10 and 100 eV, the cross-section of the $3\,^2S$–$3\,^2P$ transition falls off by a factor of 0·21 and that of the $3\,^2S$–$4\,^2P$ transition falls off by a factor of 0·14; the corresponding Bethe factor is 0·20, which is closer to the former than to the latter in agreement with expectation. For optically forbidden transitions all terms in the expansion have the same dependence on k_p, so that the effect just described does not enter. The decay of the cross-section just after the maximum is passed is usually rather slower than that attained at high-impact energies owing to there being a tendency for K_T to increase initially. Figure 1 shows the Bethe and Born cross-section curves for some transitions of atomic hydrogen (Fundaminsky 1949).

The same dipole-moment elements M^1_{pq} appearing in (96) also arise in the calculation of radiative transition probabilities. For this reason Bates & Damgaard (1949) have recently prepared tables giving their values systematically for a wide range of cases. These obviously have immediate applications in the present problem. Apart from their use in determining the absolute cross-sections at high impact energies they also give at least an indication of the relative magnitudes of the maxima of different cross-sections. From them it would appear that in a given optically allowed series, the most important single parameter on which the cross-section of a transition depends is the difference in the effective principal quantum numbers of the two connected states. The cross-sections in general fall rapidly as this difference is increased. There is no simple expression for the rate of the fall (which varies greatly from series to series), but in any particular case information on it can be obtained by consulting the tables mentioned.

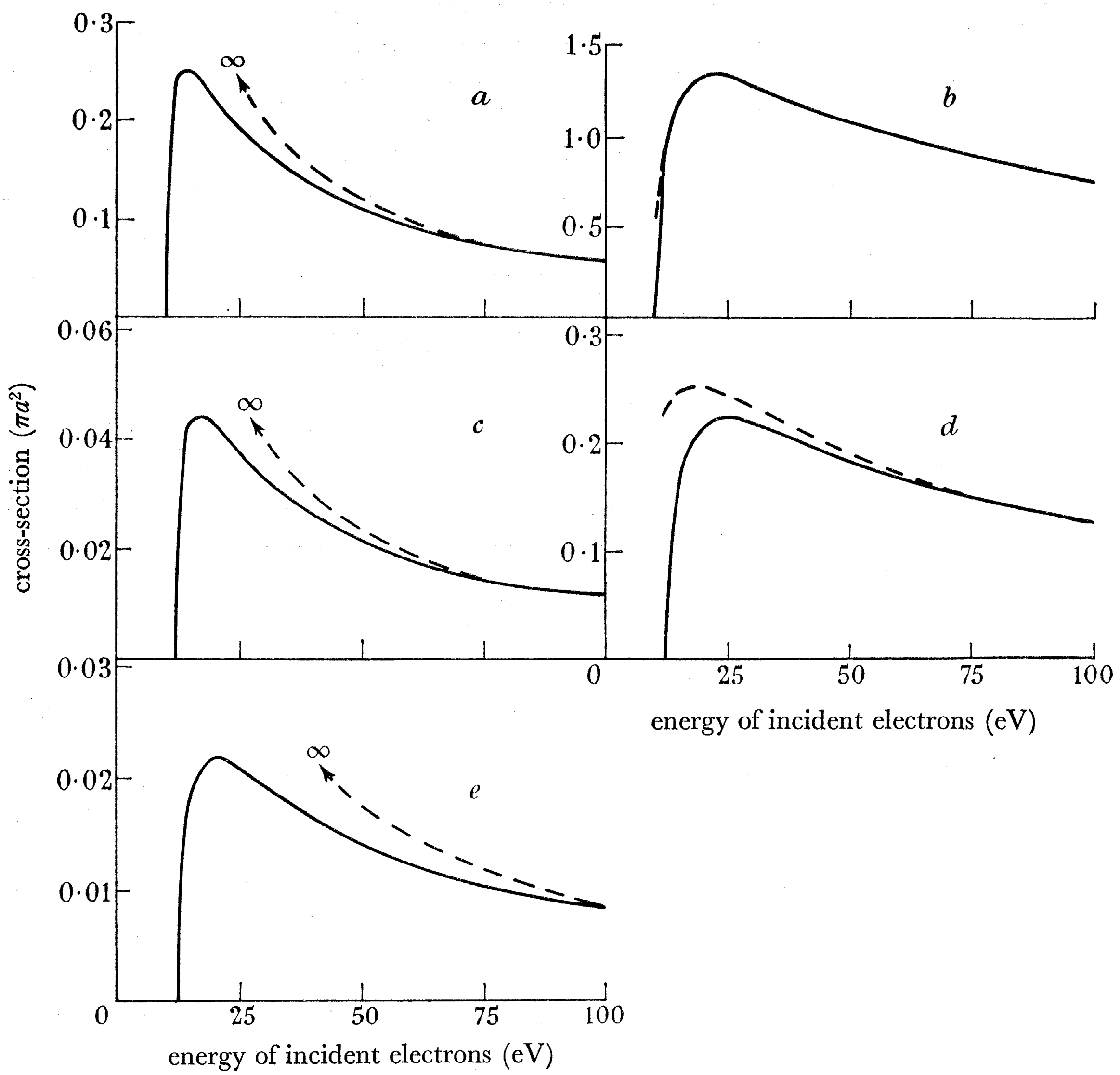

FIGURE 1. Comparison of Born (1926) and Bethe (1930) approximations for some transitions of atomic hydrogen. (—, Born; ---, Bethe.)

curve	excitation to	K_T
a	2^2S	0·67
b	2^2P	0·48
c	3^2S	0·81
d	3^2P	0·62
e	3^2D	0·50

Optically forbidden transitions involve the quadrupole moment elements M^2_{pq}, octopole moment elements M^4_{pq}, etc., comprehensive data on which are not available. It is to be expected, however, that the relative cross-sections of different members of a series will exhibit a trend qualitatively similar to that described in the preceding paragraph.

3·2. *Cross-sections at high impact energies—exchange terms*

It is well known that the exchange term ultimately falls rapidly towards zero as the impact energy increases. Unfortunately, no simple asymptotic formula corresponding to (96) and (97) can be developed. The $1\,^2S$–$2\,^2S$ and $1\,^2S$–$2\,^2P$ transitions of atomic hydrogen, however, illustrate the position adequately. It may be shown (Fundaminsky 1949) that over a wide range the exchange terms for these decay as about k_p^{-4} and as k_p^{-6} respectively. Since the corresponding direct terms decay and only as k_p^{-2} and as $k_p^{-2}\log k_p$, they alone are of importance at high impact energies.

Consideration of the constitution of the two overlap integrals suggests that in a spectral series the exchange term decreases with increase of separation of the connected levels. No prediction about the variation of its magnitude relative to that of the direct term seems possible.

3·3. *Cross-sections near the threshold*

The investigation of the behaviour of the cross-section at low impact energies presents no difficulty. If we restrict ourselves to a small energy range just above the threshold the wave functions representing the incident, scattered and (for ionizing collisions) ejected electrons, can be written in the form

$$A(k)\,\mathscr{P}(\mathbf{r})\,; \tag{101}$$

that is, the dependence on k, the momentum of the particular electron concerned can be entirely confined to a multiplying factor. Hence the general expression (cf. § 2·2·3) for excitation and ionization cross-sections can be reduced to

$$\left\{\frac{k_q}{k_p}\,(A_{\text{incident}}(k_p))^2\,(A_{\text{scattered}}(k_q))^2\right\}\mathscr{I}_{pq} \quad (\text{with } 2E_p+k_p^2 = 2E_q+k_q^2), \tag{102}$$

and to

$$\left\{\int_0^{k_{\epsilon\,(\text{max.})}}\left(\frac{k_q}{k_p}\,(A_{\text{incident}}(k_p))^2\,(A_{\text{scattered}}(k_q))^2\,(A_{\text{ejected}}(k_\epsilon))^2\,dk_\epsilon\right)\right\}$$
$$(\text{with } 2E_p+k_p^2 = k_\epsilon^2+k_q^2 \text{ and } k_{\epsilon(\text{max.})} = (2E_p+k_p^2)^{\frac{1}{2}}), \tag{103}$$

respectively, k_p and k_q having their usual significance, k_ϵ being the momentum of the ejected electron and $\mathscr{I}_{pq}$ being an integral whose value does not depend on k_p, k_q or k_ϵ in the energy range specified.

The $A(k)$'s can be obtained at once from the standard expressions for normalized plane and Coulomb wave functions. For certain purposes, it is useful also to have available the corresponding individual coefficients $A^l(k)$, associated with the separate terms in the expansion of the wave in components of differencing angular momentum. We therefore give the $A^l(k)$'s in table 2; it is, of course, unnecessary to give the $A(k)$'s in addition.

TABLE 2

	type of wave	plane	attractive Coulomb	repulsive Coulomb
$A^l_{\text{incident}}(k_p)$	k_p small	k_p^l	$k_p^{-\frac{1}{2}}$	$k_p^{-\frac{1}{2}} \exp(-\pi Z/k_p)$
	k_p not small but k_q small	const.	const.	const.
$A^l_{\text{scattered}}(k_q)$	k_q small	k_q^l	$k_q^{-\frac{1}{2}}$	$k_q^{-\frac{1}{2}} \exp(-\pi Z/k_q)$
	k_q not small but k_p small	const.	const.	const.
$A^l_{\text{ejected}}(k_\epsilon)$	k_ϵ small	$k_\epsilon^{l+\frac{1}{2}}$	const.	—

Substitution in (102) and (103) from table 2 yields the results shown in table 3.

TABLE 3. VARIATION OF COLLISION CROSS-SECTIONS NEAR THRESHOLD ENERGY

	system: and wave functions adopted		
	neutral atom: incident and scattered electron, plane waves; ejected electron, attractive Coulomb wave†	positive ion: all electrons, attractive Coulomb waves	negative ion: incident and scattered electrons, repulsive Coulomb waves, ejected electron, plane wave
type of collision	Q_{pq} variation		
(i) excitation $(\lvert E_p\rvert > \lvert E_q\rvert)$ k_p not small, k_q small	k_q	const.	—
(ii) de-excitation $(\lvert E_p\rvert < \lvert E_q\rvert)$ k_p small, k_q not small	k_p^{-1}	k_p^{-2}	—
(iii) ionization or detachment k_p not small, k_q and k_ϵ small‡	$k^2_{\epsilon\,(\text{max.})}$	$k_{\epsilon\,(\text{max.})}$	$k^3_{\epsilon\,(\text{max.})} \exp(-2\pi/k_{\epsilon\,(\text{max.})})$

† The entries (i) and (ii) in this column do not apply to all exchange transitions, as in some cases the contribution from free *s* electrons vanishes; for these an additional factor $k_p^{2l} k_q^{2l'}$ must be included, l and l' being the azimuthal quantum numbers of the partial waves giving the first non-zero term in the expression for the cross-section.

‡ Cf. first footnote to §3·1·3.

The Born and Oppenheimer approximations are known to lead to very grave inaccuracies at low impact energies. Consequently, it is by no means obvious that they predict correctly even the variation of the cross-sections near the thresholds. However, the work of Wigner (1948) shows that in this respect they actually are satisfactory.† The results in table 3 are therefore of real significance. An interesting feature of them is the marked distinction between neutral atoms and positive ions; for example, with the former the ordinary excitation cross-section is zero at the threshold whereas with the latter it is finite.

The cross-section variations given apply equally to the direct and to the exchange contributions. It must be emphasized that they refer only to the immediate neighbourhood of the threshold. Even at moderate energies the two contributions behave dissimilarly. In the excitation of neutral atoms for instance, the former rises less rapidly towards its maximum than does the latter.

3·4. *Analysis of cross-sections in terms of relative angular momenta*

It is useful, finally, to discuss collision cross-sections from another aspect. They may be regarded as the sums of partial cross-sections, each of which arises from a pair of the various

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† It should be noted that in the case of ions fallacious conclusions are reached if account is not taken of the Coulomb distortion of the incident and scattered waves (cf. §2·2·2).

angular momentum components into which the incident and scattered waves can be resolved. By using the well-known Legendre polynomial expansion for the electronic interaction potentials appearing in the general expression for the cross-section (§ 2·2·3), the following deductions can readily be made:

(i) During a collision the total angular momentum is conserved. This means that there is equality between (*a*) the difference of the azimuthal quantum numbers of those paired components of the incident and scattered waves that contribute appreciably to the cross-section and (*b*) the difference of the azimuthal quantum numbers of the initial and final states.

(ii) The direct terms are made up of the contributions from a very large number of the paired components. To illustrate the effect we will consider the experimental data on the excitation of the $4\,^2P$ level of the potassium atom. Fabrikant (1939) finds that at its maximum (which occurs at some 6 or 7 eV impact energy) the cross-section is $2{\cdot}0\times10^{-14}\,\mathrm{cm.}^2$. Hence, from the formulae quoted in § 1, it is apparent that

$$\Sigma(2l+1)$$

is at least 100 and is probably even greater.

(iii) In contrast the exchange terms are closely represented by a few of the paired components; indeed, at low impact energies a single one is usually adequate. For example, the calculations of Hebb & Menzel (1940) on the excitation of the various terms of the ground configuration of O^{++} show that the components of the incident and scattered waves having azimuthal quantum number other than unity are responsible for only about a hundredth of the cross-section at the threshold in any particular case. There is no difficulty in predicting the pair yielding the dominant contribution; with neutral atoms the form of the coefficients (cf. § 3·3, particularly table 2) is usually decisive; with positive ions consideration has to be given to the relative overlaps with the wave functions of the initial and final states and to the influence of the associated term of the expansion of the electronic interaction potential; in both cases (but more so in the former than in the latter) components of low azimuthal quantum number are strongly favoured.

As a consequence of the results just described the theorem in § 1 is of particular value for transitions that can arise only through exchange; clearly for those it not merely gives the maximum permissible *partial* cross-sections, but also gives the maximum permissible *total* cross-section.

PART II. THE BORN AND OPPENHEIMER APPROXIMATIONS—COMPARISON WITH EXPERIMENT

4. Excitation

4·1. *Hydrogen*

Extensive and accurate measurements on the excitation cross-sections of hydrogen would clearly be of the utmost service in the development of the theory since it is an atom for which exact wave functions are available, and for which, therefore, the formulae of Born and Oppenheimer can be evaluated precisely; such measurements, too, are urgently required for various astrophysical applications.

In spite of the difficulties arising from the fact that the element is in the molecular state under normal laboratory conditions Ornstein & Lindeman (1933) have succeeded in obtaining some important results. They bombarded hydrogen atoms with electrons of controlled energy (ranging from 15 to 75 eV) and measured the variation in the intensity of the emitted Balmer lines $H(\alpha)$, $H(\beta)$ and $H(\gamma)$; on applying a correction for cascading they hence derived the forms of the cross-section curves associated with transitions from the ground level to the levels of principal quantum numbers 3, 4 and 5. As is generally the case with excitation functions of a given series, the three curves obtained exhibit close similitude. The first of them is reproduced in figure 2*a*, together with the corresponding curve based on the Born approximation (i.e. using the direct terms only). Though the maxima are slightly displaced the agreement as a whole is remarkably good. It is rendered considerably less satisfactory if the exchange terms are included, as in the Oppenheimer approximation, for these lead to a great enhancement of the theoretical cross-sections at low energies. The necessary computations have not been performed for the 1→3 transition under discussion, but the effect is sufficiently well illustrated by the combination of figure 2*b*, which compares

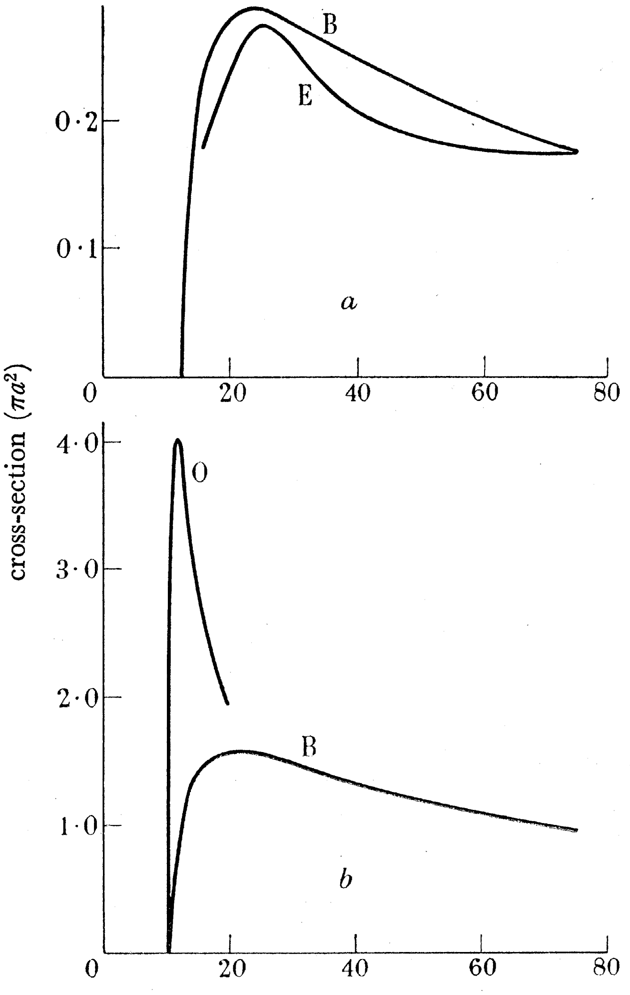

FIGURE 2. Excitation functions of atomic hydrogen. *a*, transition 1→3; B, Born approximation (Fundaminsky 1949); E, experimental (Ornstein & Lindeman 1933), arbitrary units. *b*, transition 1→2; O, Oppenheimer approximation; B, Born approximation (both from Fundaminsky 1949).

the curves given by the Born and the Oppenheimer approximations for the 1 → 2 transition, and of table 4, which contains complete data on both transitions at their critical potentials (Fundaminsky 1949). Further evidence that the Oppenheimer approximation overestimates the cross-sections is provided by the conservation theorem of Mott and of Bohr, Peierls and Placzek (cf. § 1); thus for the 1 → 2 transition *alone* the calculated contribution from the incident *s*-partial wave reaches a maximum of $1\cdot7\pi a^2$ at 11·2 eV, whereas $1\cdot2\pi a^2$ is the greatest permissible value at this energy.

TABLE 4. DATA RELATING TO SOME TRANSITIONS OF HYDROGEN.
(ENERGY OF INCIDENT ELECTRONS EQUALS THAT CORRESPONDING TO CRITICAL POTENTIAL)

transition	direct integral (f)†	exchange integral (g)†	ratio of Oppenheimer to Born cross-section (R)
$1\,^2S$–$2\,^2S$	$-0\cdot42$	$+1\cdot3$	14
$1\,^2S$–$2\,^2P$	$-0\cdot72i$	$+1\cdot1i$	4·8
$1\,^2S$–$3\,^2S$	$-0\cdot18$	$+0\cdot65$	18
$1\,^2S$–$3\,^2P$	$-0\cdot31i$	$+0\cdot57i$	6·2
$1\,^2S$–$3\,^2D$	$+0\cdot10$	$-0\cdot15$	4·7

† For definitions of f and g see § 2·2·1. *Note.* At the critical potential these functions become spherically symmetrical (account being taken of possible degenerate states).

On referring again to figure 2*a*, it will be observed that while the theoretical cross-sections tend to zero at high energies the experimental cross-sections tend to a constant. In commenting on this discrepancy Ornstein & Lindeman appeared sufficiently confident of the accuracy of their results to regard it as significant. They suggested, indeed, that their excitation functions might be analogous with a well-known one of mercury which certainly exhibits the peculiarity†. However, it has since been proven that the form of this latter excitation function is due to spin-orbital interaction which is of course negligible for hydrogen. As there is no doubt that the trend predicted by theory is correct, some effect not taken into account by Ornstein & Lindeman (such as, perhaps, emission following recombination) must enter. Allowance should be made for this in assessing the success achieved by the Born approximation which may be either rather better, or rather worse, than is suggested at present. The fixing of the scale of the experimental curve by even a single absolute measurement would obviously be of great value. It is also important to investigate the region near the critical potential so as to determine whether a type X peak occurs.

The reliability of the theory may depend on the azimuthal quantum numbers of the connected levels and in particular on whether the transition is optically allowed or forbidden (cf. § 2·1·3). In this connexion attention may be drawn to the fact that, though the 1 → 3 transition is a combination of $1\,^2S \rightarrow 3\,^2S$, $1\,^2S \rightarrow 3\,^2P$ and $1\,^2S \rightarrow 3\,^2D$, the calculated contribution from $1\,^2S \rightarrow 3\,^2P$ is *considerably larger* than that from the others; for example, at the maximum it is about 5 times that from $1\,^2S \rightarrow 3\,^2S$ and about 10 times that from $1\,^2S \rightarrow 3\,^2D$. This adds to the significance of the comparison made in figure 2*a*, since the agreement shown suggests that the Born approximation yields accurate results for the dominant *optically allowed* transition. Such a conclusion must, however, be treated with reserve, as it is contrary to a general rule indicated by the bulk of the evidence to be presented.

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† Actually though the gradient of the mercury curve diminishes markedly at moderate energies it does not vanish.

Information on the possible differences between optically allowed and forbidden transitions could be obtained by the study of the fine structure of the Balmer lines. Ornstein, Lindeman & Vreeswijk (1935) have measured the ratio, r, of the intensities of the short and long wave-length components of $H(\alpha)$,

$$\{(3\,^2P_{\frac{1}{2}} \rightarrow 2\,^2S_{\frac{1}{2}}) + (3\,^2P_{\frac{3}{2}} \rightarrow 2\,^2S_{\frac{1}{2}}) + (3\,^2S_{\frac{1}{2}} \rightarrow 2\,^2P_{\frac{1}{2}}) + (3\,^2D_{\frac{3}{2}} \rightarrow 2\,^2P_{\frac{1}{2}})\}$$

and

$$\{(3\,^2S_{\frac{1}{2}} \rightarrow 2\,^2P_{\frac{3}{2}}) + (3\,^2D_{\frac{3}{2}} \rightarrow 2\,^2P_{\frac{3}{2}}) + (3\,^2D_{\frac{5}{2}} \rightarrow 2\,^2P_{\frac{3}{2}})\}$$

respectively, the energy of the bombarding electrons being varied between 15 and 100 eV. They found it to be about 1·2 throughout the whole range, whereas according to calculations using the Born approximation it should increase steadily from 1·17 at the lowest energy to 1·81 at the highest.† Processes other than simple excitation probably affected the populations in the three-quantum levels; collisions, for example, would tend to produce statistical equilibrium for which the value of r is 0·80. Such complications of interpretation, inevitable in exploratory work, could doubtless be eliminated by a suitable modification of the experimental technique.

4·2. *Sodium*

Fundaminsky (1949) has performed calculations on the $3\,^2S \rightarrow 3\,^2P$, $3\,^2S \rightarrow 3\,^2D$, $3\,^2S \rightarrow 4\,^2S$ and $3\,^2S \rightarrow 4\,^2P$ transitions of sodium, using Fock wave functions to describe the bound electrons. At the critical potentials he applied both the Born approximation and a simplified‡ Oppenheimer approximation. The magnitudes of the essential quantities evaluated are given in table 5. As can be seen, allowance for exchange leads in all cases but one to an increase in the cross-section. It will be noticed too that the prior and post interactions do not yield identical results.§ The differences indeed are very great; thus $|g\,(\text{prior})/g\,(\text{post})|^2$, which gives the ratio of the cross-sections associated with partial transition involving a reversal of spin of the valency electron, is actually 160 for $3\,^2S \rightarrow 4\,^2S$; and even $R\,(\text{prior})/R\,(\text{post})$, which gives the ratio of the total cross-sections, is as high as 7·5 for $3\,^2S \rightarrow 4\,^2P$. This serious disagreement is stressed because in the past many workers have contented themselves with using *either* prior *or* post interactions. In view of it, extensive computations on the Oppenheimer approximation did not seem justified, and Fundaminsky employed only the Born approximation for energies above the critical potentials.

TABLE 5. DATA RELATING TO SOME TRANSITIONS OF SODIUM.
(ENERGY OF INCIDENT ELECTRONS EQUALS THAT CORRESPONDING TO CRITICAL POTENTIAL)

transition	direct integral (f)	exchange integral (g)		$\left\lvert \dfrac{g\,(\text{prior})}{g\,(\text{post})} \right\rvert^2$	ratio of Oppenheimer to Born cross-section (R)		$\dfrac{R\,(\text{prior})}{R\,(\text{post})}$
		prior	post		prior	post	
$3\,^2S$–$3\,^2P$	$-7·5i$	$+8·8i$	$+1·3i$	48	3·6	1·2	3·0
$3\,^2S$–$3\,^2D$	$+2·0$	$-3·1$	$+0·71$	19	4·9	0·77	6·4
$3\,^2S$–$4\,^2S$	$-1·5$	$+2·8$	$+0·22$	160	6·1	1·2	5·1
$3\,^2S$–$4\,^2P$	$+1·5i$	$-4·0i$	$-0·52i$	59	11	1·5	7·5

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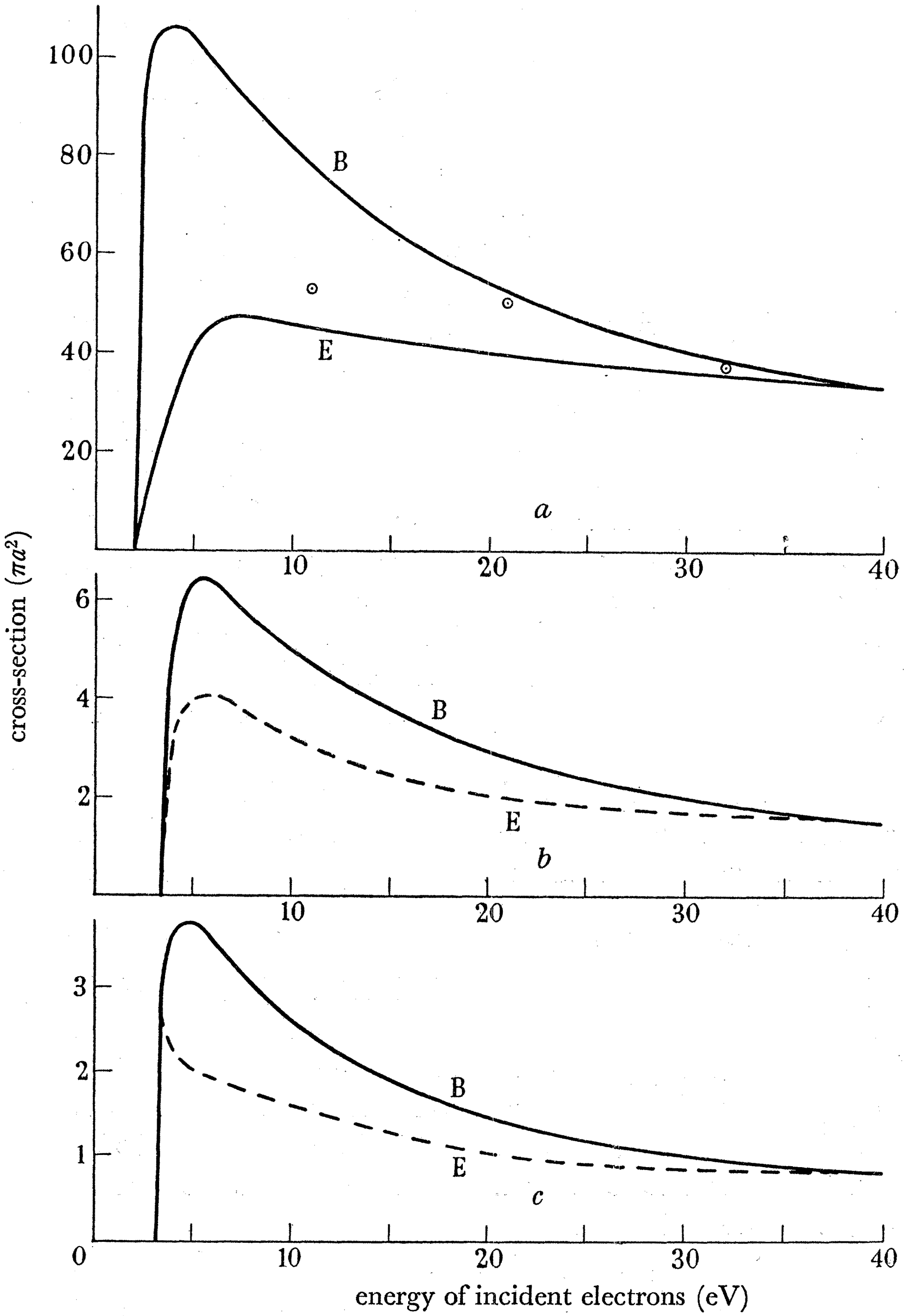
† In considering the discrepancy it should be noted that the cross-section associated with the transition $1\,^2S \rightarrow 3\,^2P$ largely controls the numerator of the theoretical expression for r, and only those associated with the transitions $1\,^2S \rightarrow 3\,^2S$ and $1\,^2S \rightarrow 3\,^2D$ appear in the denominator.

‡ Exchange between the *free* and *core* electrons (which is relatively unimportant) was neglected and an unbalanced interaction was adopted (cf. §2·2·3).

§ The cause of the disparity is discussed in §2·2·4.



a, transition $3\,^2S \rightarrow 3\,^2P$; B, Born approximation (Fundaminsky 1949); E, experimental (Haft 1933), arbitrary units; ⊙, Christoph (1935), absolute units.

b, B, Born approximation (Fundaminsky 1949)

$(3\,^2S \rightarrow 3\,^2D)$;

E, experimental (Haft 1933), displaced $3\,^2S$–$4\,^2D$, arbitrary units.

c, B, Born approximation (Fundaminsky 1949)

$(3\,^2S \rightarrow 4\,^2S)$;

E, experimental (Haft 1933), displaced $3\,^2S$–$5\,^2S$, arbitrary units.

Figure 3. Excitation functions of atomic sodium.

Haft (1933) has determined the form of the excitation function associated with the $3\,^2S \rightarrow 3\,^2P$ transition, and Christoph (1935) has measured the absolute cross-section† at three points. Both used optical methods. Their results, together with the corresponding curve computed by Fundaminsky, are illustrated in figure 3*a*.‡ The transitions $3\,^2S \rightarrow 3\,^2D$

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† In the reduction of his measurements Christoph did not allow for the temperature of the sodium vapour; but by using information he gives it was possible to apply the necessary correction.

‡ Entirely different results have been reported by Michels (1931), who claimed that type X peaks occur for this and for other transitions. His work is ignored, since his technique is rendered extremely suspect by the fact that it gave vanishingly small cross-sections at energies slightly above the critical potentials.

and $3\,^2S \rightarrow 4\,^2S$ have not been studied experimentally, but Haft has investigated the emission from the $4\,^2D$ and $5\,^2S$ levels. In view of the general similitude law already mentioned, the excitation functions obtained are adopted in figures 3 *b*, *c* as suitable for comparison with those calculated; they are, of course, in arbitrary units, and are displaced by the energy differences between the $3\,^2D$ and $4\,^2D$ levels, and between the $4\,^2S$ and $5\,^2S$ levels, respectively. No laboratory data on the $3\,^2S \rightarrow 4\,^2P$ transition is available; in any event the theoretical cross-sections are so sensitive to details of the wave functions involved that great reliance cannot be placed upon them.

For the allowed $3\,^2S \rightarrow 3\,^2P$ transition the Born approximation clearly gives excellent accord with Christoph's absolute measurements at moderate energies. But it yields much too pronounced a maximum; and the extent of this characteristic discrepancy would certainly be increased if the apparently more refined Oppenheimer approximation were used. As can be seen, better agreement is achieved for the forbidden $3\,^2S \rightarrow 3\,^2D$ and $3\,^2S \rightarrow 4\,^2S$ transitions. It is interesting to note that the sharpness of the maximum found by Haft could be interpreted as indicating that in the case of the latter transition there may be a small effect attributable to electron exchange. The evidence is not conclusive and confirmatory measurements near the critical potential are required; but it is suggestive that according to theory it is just for this type of transition that exchange effects should be most important. A further and more striking example of what is, perhaps, the same phenomenon will be mentioned later (§ 4·5).

Finally, it may be remarked that the Born approximation may actually be rather more successful than would appear from the comparisons made; for the experimental curves fall off so slowly at high energies† that it is probable that some subsidiary process contributes.

4·3. *Helium*

Massey & Mohr (1931, 1933) have carried out extensive calculations on inelastic collisions between electrons and helium atoms. Their work has recently been extended, and in part repeated, by Fundaminsky (1949) and Leech (1949). Screened hydrogenic wave functions were employed. As a result of these investigations information is now available on the excitation functions associated with transitions from the ground, $1\,^1S$, level to the 2 and $3\,^1S$, 2, 3 and $4\,^1P$, 3, 4 and $5\,^1D$, $2\,^3S$, $2\,^3P$ and $3\,^3D$ levels; and, in addition, there are data on a number of other transitions at moderate and high energies only.

The main results are based on the Born approximation, in the case of singlet-singlet transitions, and on the Oppenheimer approximation (with usually only a prior *or* a post interaction‡) in the case of singlet-triplet transitions. Before proceeding to the consideration of them, mention may be made of the interesting exploratory work by Fundaminsky and Leech on the consequences of including exchange terms in the singlet-singlet calculations (they cannot of course be excluded in the singlet-triplet calculations), and on the difference between the cross-sections obtained with the two alternative interactions. Figure 4 *a*, *b* shows the excitation functions for the transitions $1\,^1S \rightarrow 2\,^1S$ and $1\,^1S \rightarrow 2\,^1P$, as computed

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† For instance, the ratio of the measured excitation cross-section at 200 eV to that at 100 eV is 0·77 for $3\,^2P$, 0·71 for $4\,^2D$ and 0·78 for $5\,^2S$, whereas the predicted ratios (which in the energy region concerned cannot be appreciably in error) are 0·58 in the first case and 0·50 in the other two.

‡ The choice of interaction was to some extent fortuitous.

from the Born approximation, and from the Oppenheimer approximation with both interactions; and table 6 gives the values of some basic quantities relating to these and a few other transitions. It will be noted that in most instances the inclusion of exchange increases the cross-section at low energies; the effect is much the greatest for ${}^1S\to{}^1S$ transitions and in general is a decreasing function of the total angular momentum of the excited level. As for sodium the results obtained with the prior and post interactions are far from identical; however, in the present case it appears that it is not in general the former, but the latter, which yields the larger cross-sections.

Table 6. Data relating to some transitions of helium
(Energy of incident electrons equals that corresponding to critical potential)

transition	direct integral (f)	exchange integral (g)		$\left\lvert\dfrac{g\,(\text{prior})}{g\,(\text{post})}\right\rvert^2$	ratio of Oppenheimer to Born cross-section (R)		$\dfrac{R\,(\text{prior})}{R\,(\text{post})}$
		prior	post		prior	post	
$1\,{}^1S\to 2\,{}^1S$	$-0{\cdot}13$	$+0{\cdot}085$	$+0{\cdot}37$	0·052	2·8	15	0·18
$2\,{}^1P$	$-0{\cdot}24i$	$+0{\cdot}078i$	$+0{\cdot}18i$	0·18	1·7	3·1	0·55
$3\,{}^1P$	$-0{\cdot}12i$	$+0{\cdot}054i$	$+0{\cdot}10i$	0·30	2·1	3·3	0·64
$3\,{}^1D$	$+0{\cdot}021$	$+0{\cdot}031$	$-0{\cdot}020$	2·4	0·23	3·8	0·061
$1\,{}^1S\to 2\,{}^3S$	0	$+0{\cdot}30$	$+0{\cdot}52$	0·33	—	—	—
$2\,{}^3P$	0	$+0{\cdot}19i$	$+0{\cdot}20i$	0·91	—	—	—
$3\,{}^3P$	0	$+0{\cdot}10i$	$+0{\cdot}10i$	1·0	—	—	—
$3\,{}^3D$	0	$-0{\cdot}051$	$-0{\cdot}020$	6·5	—	—	—

The results of the experimental investigations on helium can be divided into two main groups which, though they overlap to some extent, can conveniently be discussed separately.

We will first consider the optical measurements of Thieme (1932) and of Lees (1932) on the shape of the excitation functions of the singlet-singlet transitions.† Actually the original papers merely give the intensity-energy curves for various spectral lines; but by making use of the spontaneous transition probabilities computed by Hylleraas (1937) and by Bates & Damgaard (1949), these can be corrected for cascading and reduced to the form required.‡

Neither Thieme nor Lees studied the emission from any of the ${}^1S$ levels covered by the theoretical research. However, the relative excitation functions derived from their work are almost identical for all members of the series investigated. It would thus appear legitimate to compare, as in figure 4*c*, the computed $3\,{}^1S$ results and the observed $4\,{}^1S$ results, the latter being displaced by the difference between the critical potentials concerned. In the case of the other principal classes of singlet-singlet transition a direct collation of the excitation functions can be made. The curves for $1\,{}^1S\to 3\,{}^1P$ and $1\,{}^1S\to 4\,{}^1D$ are depicted in figures 4 *d*, *e*; those for $1\,{}^1S\to 4\,{}^1P$ and $1\,{}^1S\to 5\,{}^1D$ are also known but are not illustrated, as they are essentially similar.

The Born approximation clearly meets with the same kind of failures and successes in the treatment of helium as in the treatment of sodium. Thus for the allowed ${}^1S\to{}^1P$ transitions

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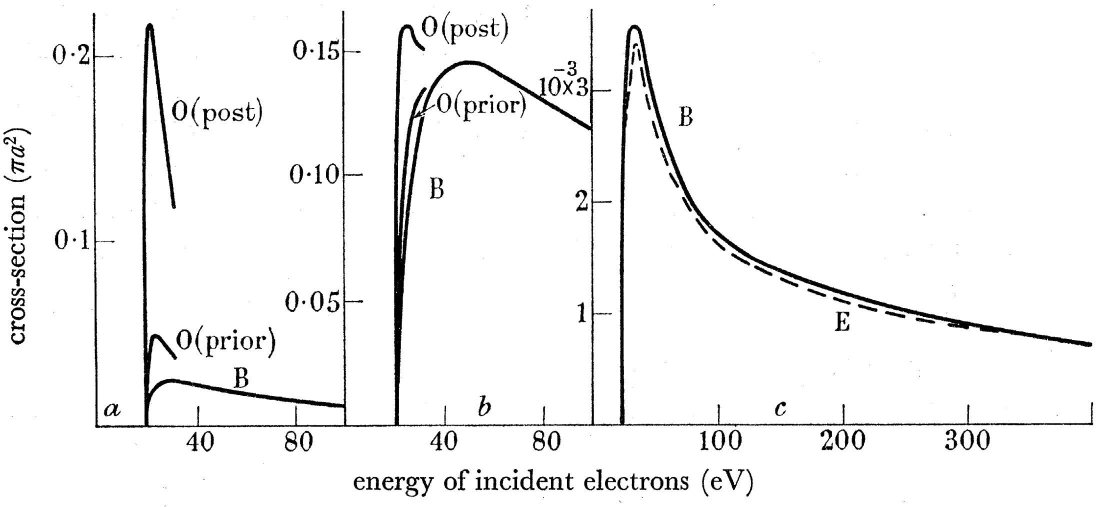
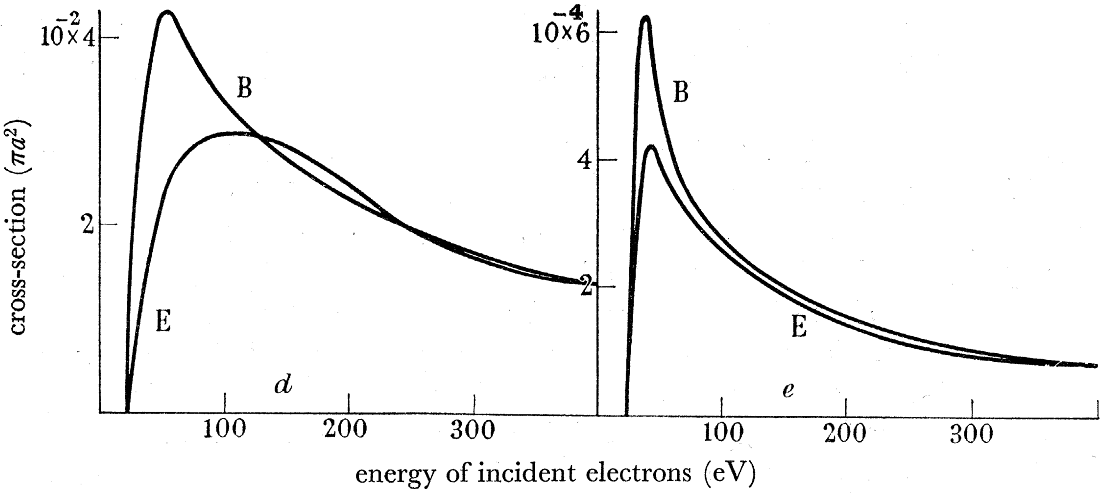
† We usually adopt the results of Thieme in preference to those of Lees as they were obtained at a lower gas pressure.

‡ Massey & Mohr (1933*b*) had to adopt crude estimates of the spontaneous transition probabilities, as the necessary detailed calculations had not been performed at the time of their original work. In consequence, their results differ somewhat from those given in the present paper.



a, transition 1^1S–2^1S; *b*, transition $1^1S \rightarrow 2^1P$; O, Oppenheimer approximation post and prior; B, Born approximation (all from Fundaminsky 1949).

c, B, Born approximation $1^1S \rightarrow 3^1S$ (Massey & Mohr 1931, 1933*b*); E, experimental (Thieme 1932), displaced $1^1S \rightarrow 4^1S$, arbitrary units.



d, $1^1S \rightarrow 3^1P$; B, Born approximation (Fundaminsky 1949); E, experimental (Thieme 1932), arbitrary units.

e, $1^1S \rightarrow 4^1D$; B, Born approximation (Massey & Mohr 1933*b*); E, experimental (Thieme 1932), arbitrary units.

FIGURE 4. Excitation functions of atomic helium.

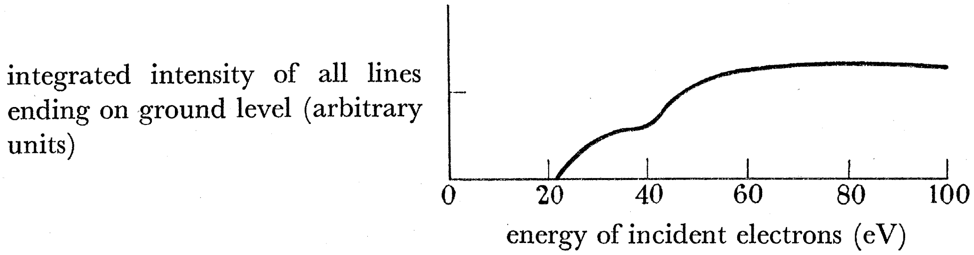


FIGURE 5. Photon yield function of atomic helium (after Dorrestein 1942).

it yields an excitation function with a maximum both too high and too close to the critical potential; but for the forbidden ^1S–^1S and $^1S \rightarrow {}^1D$ transitions it is much more satisfactory—the agreement with the observational data is indeed almost perfect in the case of the $^1S \rightarrow {}^1S$ transitions and is remarkably good even in the case of the $^1S \rightarrow {}^1D$ transitions.

Lees and Thieme also studied the singlet-triplet transitions. For these theory and experiment agree to the extent that both give excitation functions which are markedly different from those characteristic of singlet-singlet transitions, the maxima being much sharper and being located at much lower energies. There is little certain evidence on which a detailed comparison of theoretical and observed shapes can be made. The cross-sections fall so rapidly from the maximum as the electron energy increases that it is very difficult to exclude contributions from secondary effects.

Photon emission rates are extremely difficult to determine accurately, and reliance cannot be placed upon the data presented by Thieme and Lees on absolute intensities. At 100 eV the cross-section for the transition $1\,{}^1S \rightarrow 3\,{}^1P$ is $0{\cdot}39\pi a^2$, according to the measurements of the former, and $0{\cdot}49\pi a^2$, according to those of the latter. In spite of the reasonable agreement between them it is difficult to accept these values. Both would appear to be too high, since, at the same energy, the contribution to the total cross-section from *all* discrete excitations is estimated to be only about $0{\cdot}3\pi a^2$;† indeed, the amount by which they are in excess would seem to be considerable in view of the fact that the transition concerned is not the major one, its cross-section being certainly several times smaller than that of $1\,{}^1S \rightarrow 2\,{}^1P$. However, it is worth attempting to extract as much information as possible from the results, as they form the most comprehensive set that have been published; and even though the absolute scale is untrustworthy the *relative* measurements on the different spectral lines should be approximately correct.

To facilitate comparison with theory the excitation functions derived from the intensity data were reduced in magnitude so as to bring about coincidence at moderate energies in some particular case; the transition $1\,{}^1S \rightarrow 3\,{}^1D$ was chosen as most suitable for this fitting. Table 7 gives the maxima of the cross-sections thus obtained together with the corresponding calculated values. As can be seen there are serious differences between the columns relating to Thieme and to Lees; and, quite apart from the presumed inaccuracies in the basic experimental data the derived cross-sections may be in error by factors of perhaps between 0·7 and 1·3, because of uncertainties in the cascade corrections applied, and in the spontaneous transition probabilities assumed.

Though in consequence of the limitations mentioned it is not possible to reach any precise conclusions, it would seem that for the singlet-singlet transitions the theory is reasonably successful. Some supporting evidence is provided by the experiments of Mohr & Nicoll (1932) and of Whiddington & Woodroofe (1935) on inelastic scattering at small angles. From these it is possible to estimate the relative partial cross-sections for the excitation of the 2, 3 and 4 ^1P levels by undeviated electrons. The agreement with the calculated results is excellent; thus for the ratio of the three cross-sections at 100 eV Mohr & Nicoll give (–):2·7:1·0, Whiddington & Woodroofe give 10:2:1, and Massey & Mohr obtain

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† This figure was obtained by subtracting from the Ramsauer cross-section ($1{\cdot}1\pi a^2$; Normand 1930), the elastic cross-section ($0{\cdot}37\pi a^2$; Massey & Mohr 1931) and the ionization cross-section ($0{\cdot}40\pi a^2$; Smith 1930).

11·5:2·7:1·0 by applying the Born approximation. However, the measurements of Dorrestein (1942) on the integrated intensity of all lines ending on the ground level reveal a possible discrepancy. As can readily be verified from an inspection of a table of spontaneous transition probabilities these give essentially the sum of the excitation functions associated with the 3 and higher ^1S levels, the 2 and higher ^1P levels, and the 3 and higher ^1D levels. The intensity energy curve (figure 5) at first seems in general accord with expectation; thus it shows in addition to the main maximum, due to the dominant ^1P excitations, a ledge between 30 and 40 eV which might plausibly be attributed to the ^1S and ^1D excitations (cf. figure 4). But quantitative considerations show that the position is actually far from satisfactory; for according to theory (cf. table 7) the ^1S and ^1D excitations are much too weak compared with the ^1P excitations to be responsible for the ledge. The implication that the calculated cross-sections for the ^1S and ^1D transitions are greatly underestimated relative to those for the ^1P transitions cannot easily be accepted. It may, instead, be that the observed ledge (if indeed real) is associated with the latter transitions, in which case the possibility of there being an appreciable contribution due to exchange would have to be reconsidered carefully.

Unfortunately table 5 does not contain sufficient data to enable an assessment to be made of the validity of the theory in the case of singlet-triplet transitions. The only other absolute optical measurements relating to such transitions are those carried out by Woudenberg & Milatz (1941), who determined the intensity of the emission from the $2\,^3P$ and $3\,^3P$ levels when helium atoms are bombarded with 60 V electrons. It should be noted that owing to one of the spectral lines studied being in the infra-red and to the other being in the ultra-violet different techniques had to be employed, so that the two intensity determinations are

TABLE 7. CROSS-SECTIONS OF HELIUM TRANSITIONS AT THEIR MAXIMA (UNITS $10^{-3}\pi a^2$)

			experiment	
level excited	theory	Born approximation	Thieme	Lees
$2\,^1S$	24	(F)	—	—
$3\,^1S$	3·6	(MM)	—	—
$4\,^1S$	—		0·38	—
$5\,^1S$	—		0·23	0·17
$6\,^1S$	—		0·11	0·070
$2\,^1P$	150	(F)	—	—
$3\,^1P$	43	(F)	48	120
$4\,^1P$	15	(MM)	11	27
$5\,^1P$	(8·3)	(MM)	—	4·9
$3\,^1D$	0·82	(L)	—	—
$4\,^1D$	0·63	(MM)	0·42	0·42
$5\,^1D$	0·37	(MM)	0·25	0·26
$6\,^1D$	—		0·11	—
	Oppenheimer approximation ((pr) prior and (pt) post interaction)			
$2\,^3S$	220 (pr) 660 (pt)	(F)	—	—
$3\,^3S$	—		—	—
$4\,^3S$	—		0·50	0·95
$5\,^3S$	—		—	0·26
$2\,^3P$	76 (pt)	(F)	—	—
$3\,^3P$	—		26	1·7
$3\,^3D$	0·81 (pt)	(L)	0·49	—

((F), Fundaminsky (1949); (L), Leech (1949); (MM) Massey & Mohr (1933*b*)).

independent. By assuming that the excitation functions of all ^3P levels are the same shape, and adopting Thieme's curve, it can be deduced from the measurements that the maximum cross-section associated with $1\,^1S \rightarrow 2\,^3P$ is $1{\cdot}0\pi a^2$, and that the maximum cross-section associated with $1\,^1S \rightarrow 3\,^3P$ is $0{\cdot}012\pi a^2$. The value for $1\,^1S \rightarrow 2\,^3P$ is more than an order greater than that obtained from the Oppenheimer approximation (cf. table 7); while it is probably an overestimate, as it exceeds a limit set by an experiment considered in the next paragraph, it at least suggests that the true cross-section cannot be minute. In the case of $1\,^1S \rightarrow 3\,^3P$ theoretical results are not available.†

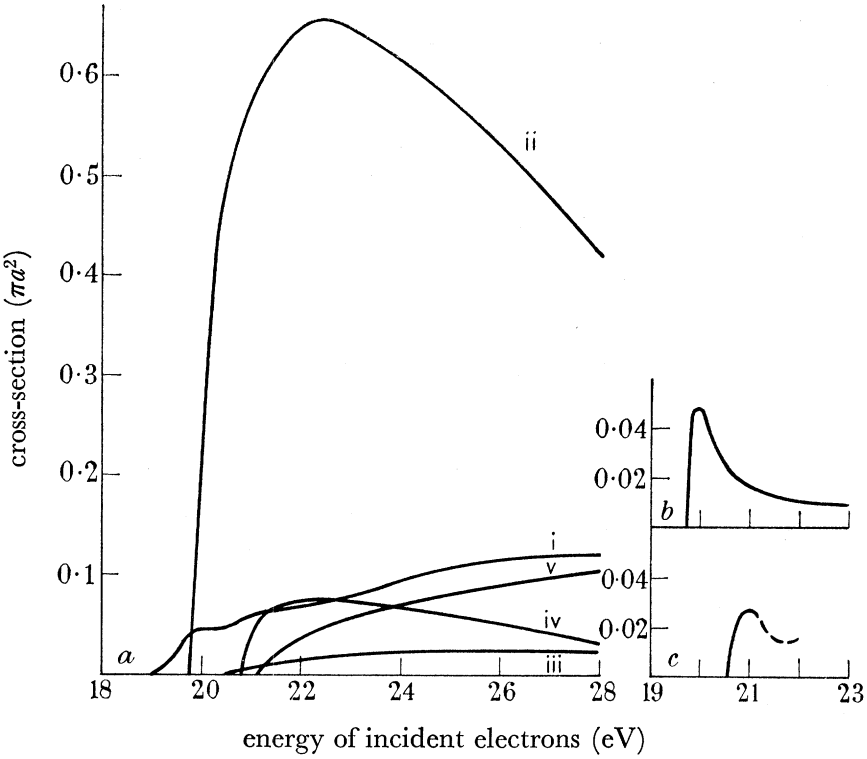

FIGURE 6. Excitation functions of atomic helium.

	curve		
a	i	experimental (Maier-Leibnitz 1935; Smith 1930), sum of *all* discrete transitions	
	ii	Oppenheimer approximation, post interaction (Fundaminsky 1949)	transition to $2\,^3S$
	iv		transition to $2\,^3P$
	iii	Born approximation (Fundaminsky 1949)	transition to $2\,^1S$
	v		transition to $2\,^1P$
b		experimental (Maier-Leibnitz 1935)	transition to $2\,^3S$
c			transition to $2\,^1S$

The investigations that remain to be discussed have nothing in common as far as the experimental methods employed are concerned, but the results they yield are closely related.

By a carefully conducted series of purely electrical measurements Maier-Liebnitz (1935) succeeded in determining the total inelastic cross-section of helium in the energy region below 28 eV. Now, from the work of Smith (1930) the contribution due to ionizing collisions is accurately known. Hence by subtraction the excitation function for the *sum of all discrete transitions* can be found. This is depicted in figure 6*a* with, for comparison, the calculated

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† It is suspected that some early calculations published may contain a numerical error.

excitation functions associated with the four lowest levels $2\,^3S$, $2\,^1S$, $2\,^3P$ and $2\,^1P$; for the singlets the excitation functions chosen are those obtained from the Born approximation,† and for the triplets they are those obtained from the Oppenheimer approximation using a post interaction.‡ There is clearly a serious discrepancy between theory and experiment. In particular, the computed cross-section for transitions to $2\,^3S$ alone is many times that observed for transitions to all levels. This is the most important and decisive illustration of the inadequacy of the treatment of electron exchange so far presented.

In addition to his measurement of the total inelastic cross-section Maier-Leibnitz resolved the contributions from some individual transitions. His results are of the greatest interest, for, in confirmation of the early work of Dymond (1925) and of Glockler (1929), he found that type X peaks occur with both $1\,^1S \rightarrow 2\,^1S$ and $1\,^1S \rightarrow 2\,^3S$, and perhaps with other transitions. The excitation functions he gives are reproduced in figure 6 *b*, *c*; in inspecting them the very extended energy scale used should be borne in mind.

Dorrestein (1942) has provided independent evidence supporting the existence of the type X peaks just mentioned. Instead of making the customary energy-loss measurements he studied the yield of metastable $2\,^1S$ and $2\,^3S$ helium atoms by determining the number of electrons liberated when a fraction of them were allowed to strike a platinum plate.§ The procedure does not give directly the separate cross-sections $q(2\,^1S)$ and $q(2\,^3S)$; it only gives $(sq(2\,^1S)+tq(2\,^3S))$, where s and t are the efficiencies with which the metastable atoms concerned free electrons from the plate on colliding with it. This function, however, is of considerable interest, for it shows unmistakably the two type X peaks (figure 7 *a*, *b*).

To test the consistency of his results with other data, and to derive what further information he could, Dorrestein conducted the following analysis:

(i) He assumed that above about 25 eV the form of $q(2\,^1S)$ is the same as found by Thieme in the case of the higher ^1S levels, and that at 100 eV its magnitude is as calculated by Massey & Mohr (allowance being made for indirect excitation).

(ii) Next he chose the constant s so that on combining the adopted $q(2\,^1S)$ with the measured $(sq(2\,^1S)+tq(2\,^3S))$, the deduced $tq(2\,^3S)$ agreed in shape with Thieme's triplet excitation function. (Though for arbitrary curves exact fitting is of course only possible at a limited number of points, the coincidence achieved in the present case, on taking s to be 0·40, is almost perfect over the entire energy range 30 to 100 eV.)

(iii) Finally, he fixed the constant t as about 0·24 by comparing his measurements with those of Maier-Leibnitz in the region below the critical potential of the $2\,^1S$ level; and hence he derived $q(2\,^3S)$.

It will be observed from figure 7 *c* that after passing through the small type X peaks $q(2\,^1S)$ and $q(2\,^3S)$ rise to major maxima of types F and G respectively. For the former such a subsequent rise is also suggested by Maier-Leibnitz's investigation; but for the latter, though it is probably not excluded, it is certainly not favoured. The only other work on excitation to $2\,^3S$ is that of Woudenberg & Milatz (1941), whose results (based on the determination of the concentration of helium atoms in this level by measurements on the absorp-

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† Cf. figure 4 *a*, *b* for the corresponding results based on the Oppenheimer approximation.

‡ A prior interaction gives excitation functions of much the same shape but about three times smaller.

§ He had, of course, to correct for the photo-electric emission. The measurements made on this are actually the source of figure 5.

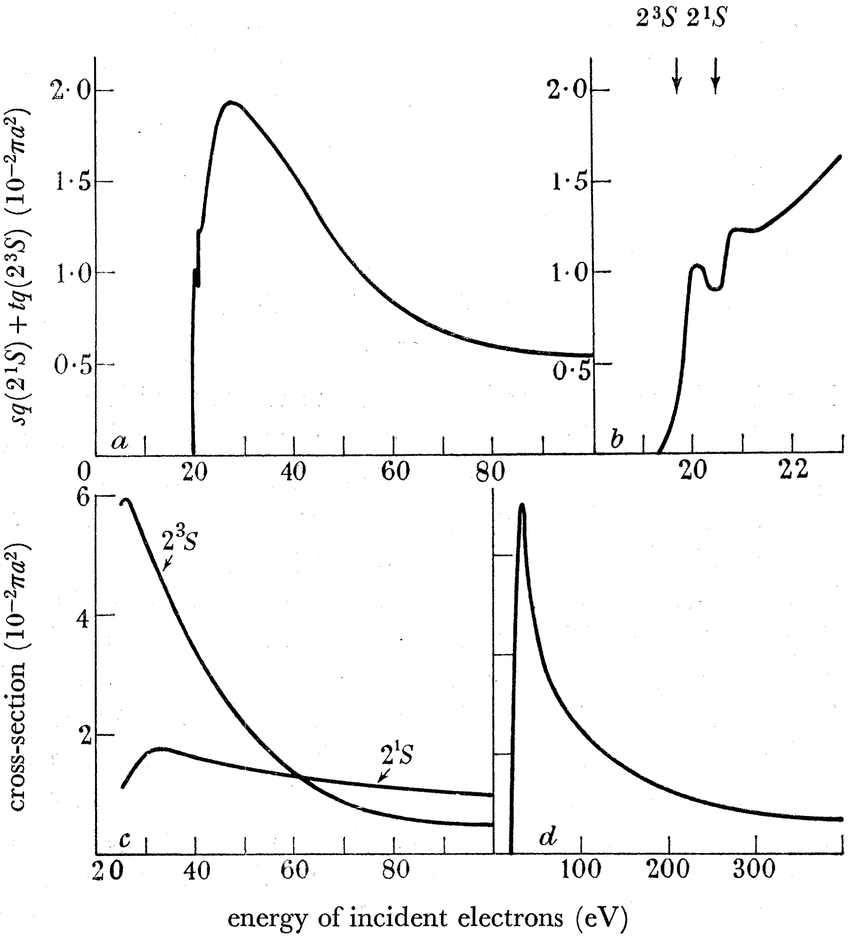

FIGURE 7. Excitation functions of atomic helium; the values of the constants s and t are about 0·40 and 0·24 respectively (see text). No cascade corrections have been applied.
a and *b*, experimental (Dorrestein 1942), $2\,^3S$ and $2\,^1S$ combined.
c, $2\,^3S$ and $2\,^1S$ separated from *a* and *b*.
d, experimental (Woudenburg & Milatz 1941), $2\,^3S$, arbitrary units.

tion of the line $2\,^3P \rightarrow 2\,^3S$), are given in figure 7*d*. Unfortunately, they are of limited value, since, as was pointed out by the authors themselves, the gas pressure was not sufficiently low to ensure that the process

$$\left.\begin{array}{c} \mathrm{He}\,(1\,^1S) + e \rightarrow \mathrm{He}\,(n\,^1P) + e, \\ \mathrm{He}\,(n\,^1P) + \mathrm{He}\,(1\,^1S) \rightarrow \mathrm{He}\,(n^3\,D) + \mathrm{He}\,(1\,^1S), \\ \mathrm{He}\,(n\,^3D) \rightarrow \mathrm{He}\,(2\,^3S) + 2h\nu, \end{array}\right\}$$

did not enter appreciably,† but, nevertheless, they give at least some support to the view that the excitation is not confined to a narrow energy range just beyond the critical potential.‡

A serious reservation regarding the interpretation of the experimental data must be made at this stage. Both Dorrestein, and Woudenberg & Milatz measured essentially, not the rate of the transition $1\,^1S \rightarrow 2\,^3S$, but the rate of formation of He $(2\,^3S)$. Now transitions to *any* triplet level will contribute to this. Hence it is conceivable that at moderate energies

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† Attention was first drawn to the possible influence of such interatomic collisions by Lees & Skinner (1932).

‡ It will be recalled too that Lees and Thieme obtained similar results for the case of excitation to the higher ^1S and ^3S levels.

almost the entire effect observed by these workers arises from cascading, and that after the brief initial increase from zero the cross-section for $1\,^1S \rightarrow 2\,^3S$ actually decreases monotonically, as is indicated by the results of Maier-Leibnitz. Experiments to elucidate the matter are urgently required; for theoretically it is very important to know if both a type X peak *and* type G maximum can be associated with a purely exchange transition, as this may assist in determining whether or not these features are really fundamentally distinct in origin; and if it should transpire that the excitation function consists *only* of a type X peak the Oppenheimer approximation would appear to fail utterly.

4·4. *Neon*

The calculations that have been carried out on neon are very incomplete and consequently scarcely merit reporting in detail. Reference may, however, be made to those of Fundaminsky (1949) on the transition $(2p^6)\,^1S \rightarrow (2p^5\,3s)\,^1P$. Briefly he found that the cross-section given by the Born approximation reaches its maximum at about 40 eV, and that its value there is some $5{\cdot}0 \times 10^{-2}\pi a^2$. Now, Dorrestein (1942) has shown that the maximum of the integrated intensity of all lines ending on the ground level is located beyond 100 eV. Since it is probable that the transition treated by Fundaminsky is the major one, and since in any event the maxima of the others likely to be appreciable cannot occur at higher energies, it would seem that there is a discrepancy similar in nature to that encountered in the cases of the optically allowed transitions of sodium and helium considered earlier (cf. figures 3*a* and 4*d*). Reliable absolute measurements would provide a useful further test of the theory.

In view of the interest attached to type X peaks it is perhaps worth concluding this short section by mentioning that Maier-Leibnitz and Dorrestein (using the same experimental methods as in their work on helium) have established that these features appear in the excitation functions associated with transitions to the groups of levels arising from the $3s$ and $3p$ orbitals.

4·5. *Mercury*

A great deal of work has been done on mercury, and from various comments that appear in the literature it might be thought that there is very close accord between theory and experiment. In fact, however, the agreement is only fair—which is scarcely surprising in view of the complexity of the system.

Calculations have been performed by Penney (1932) on the transitions $6\,^1S \rightarrow 6\,^1P$ and $6\,^1S \rightarrow 6\,^3P$ and by Yavorsky (1945, 1946) on the transitions $6\,^1S \rightarrow 7\,^3S$, $6\,^3P \rightarrow 7\,^3S$ and $6\,^3P_1 \rightarrow 6\,^3P_2$. The wave functions employed were of the crude Slater type except that allowance was made for the strong coupling between the spin and orbital motion; as evidence of their limitations it may be mentioned that the oscillator strengths that have been computed using them are several times too great. For all transitions (even those not necessitating exchange) the approximation applied was that of Oppenheimer.† Unfortunately, only a prior interaction was adopted and no results based on a post interaction are available for comparison.

Schaffernicht (1930) has investigated the emission from the $8\,^1P$ level, and his results were later fully confirmed by Thieme (1932). In figure 8*a* the excitation function obtained

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† The approximation was simplified as for sodium (§4·2), except that a balanced interaction (without, however, the associated modification of the wave functions of the incident and scattered electrons) was used (cf. §2·2·3).

(displaced as usual) is compared with that given by the Oppenheimer approximation for the $6\,^1S\rightarrow 6\,^1P$ transition; a cascade correction was not applied, but in spite of this the form of the experimental curve is unlikely to be in error. As can be seen the theory over-estimates the cross-section at low energies in the customary manner. It is important, however, to notice that the failure is almost certainly partially due to the inclusion of the exchange terms in the computations. If the Born approximation had been used the agreement might possibly have been appreciably better than that found for comparable transitions of the other systems that have been discussed, which suggests that there may be a tendency for the theory to be more successful in the treatment of heavy than of light systems. Further evidence is, of course, required before this can be regarded as other than speculation.

The measurements of Schaffernicht and of Thieme did not extend down to the region just above the critical potential. Seiler (1929), however, has covered the complete energy range, using an electrical method. He found that the $6\,^1S\rightarrow 6\,^1P$ excitation function began with a type X peak. This feature is reproduced in figure 8*a*, the scale being such that the ordinary maximum occurring at higher energies (which is not shown as its shape is probably not very accurate) is of the same magnitude as the maximum of the theoretical curve. The measurements of Brattain (1929) and Foard (1930) also lend support to the existence of a type X peak; but Arnot & Baines (1935), in describing their own more recent work, make no reference to it. In order to place the matter beyond doubt it is desirable that the early experiments should be repeated using modern techniques.

In figure 8*b*, *c* the calculated excitation functions of the $6\,^1S\rightarrow 6\,^3P_1$ and $6\,^1S\rightarrow 7\,^3S$ transitions are compared with the observations of Ornstein, Lindeman & Oldeman (1933) and of

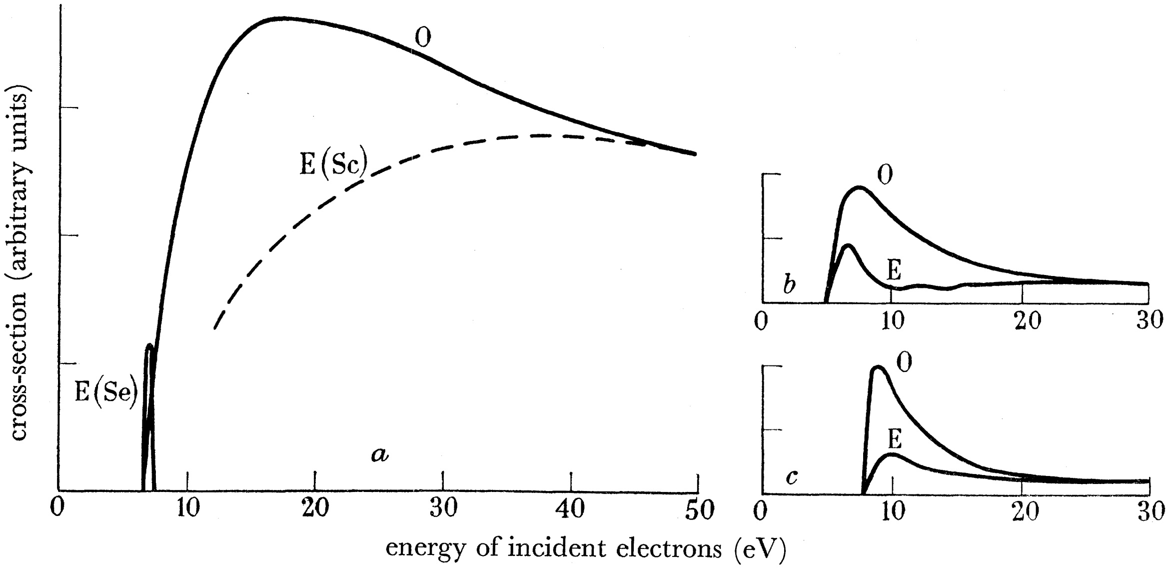

FIGURE 8. Excitation functions of atomic mercury. In *a* and *c* allowance has not been made for cascading.

a, $6\,^1S_0\rightarrow 6\,^1P_1$, O, Oppenheimer approximation, prior (Penney 1932); E (Sc), experimental (Schaffernicht 1930), displaced $6\,^1S_0\rightarrow 8\,^1P_1$; *E* (Se), experimental (Seiler 1929).

b, $6\,^1S_0\rightarrow 6\,^3P_1$; O, Oppenheimer approximation, prior (Penney 1932); E, experimental (Ornstein, Lindeman & Oldeman 1933).

c, O, Oppenheimer approximation, prior (Yavorsky 1945*a*, *b*, 1946); E, experimental (Schaffernicht 1930).

Schaffernicht (1930), respectively, the former but not the latter being corrected for cascading. Because of the use of wave functions in which allowance is made for the spin-orbital interaction the theory naturally gives for each curve a type G maximum followed by a slow (type F) fall off at high energies. This is of the general form obtained experimentally. As usual, however, the predicted maxima are too pronounced—though the discrepancy is less serious than in the corresponding helium transition, suggesting, perhaps, that the Oppenheimer approximation (like the Born approximation) is most reliable for heavy systems.

No precise laboratory measurements are available on the transitions $6\,^3P \rightarrow 7\,^3S$ and $6\,^3P_1 \rightarrow 6\,^3P_2$, but Yavorsky finds at least some confirmation for the correctness of his calculated excitation functions from results deduced by Fabrikant (1937) from discharge-tube data.

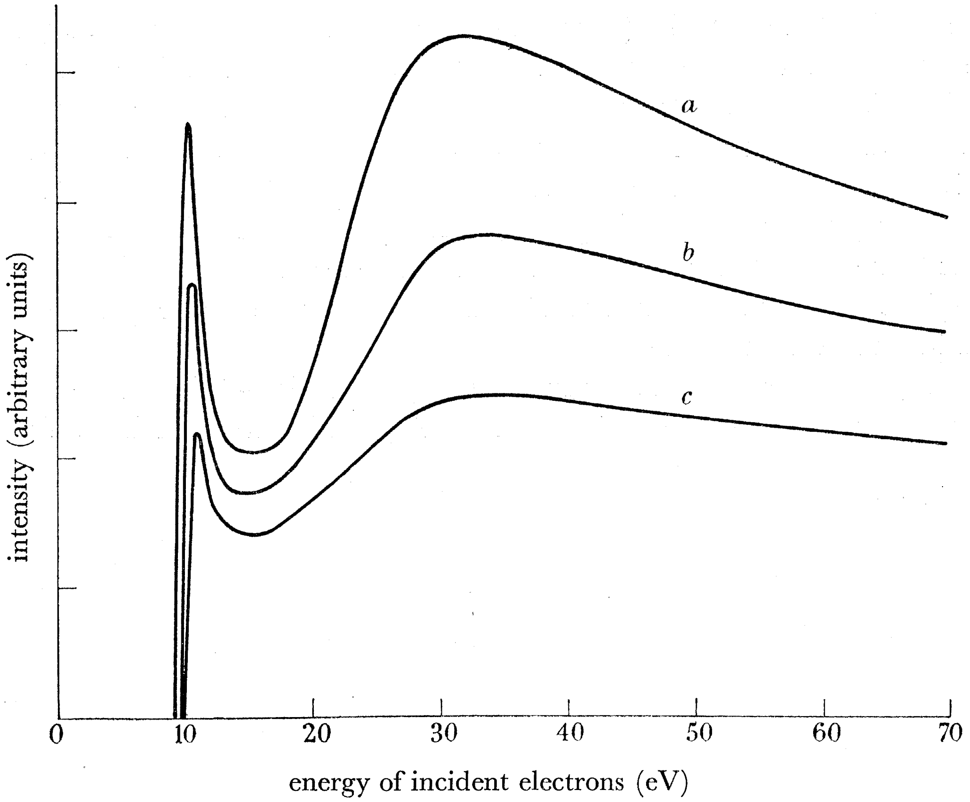

FIGURE 9. Excitation of lines of $6\,^1P_1$–$n\,^1S_0$ series of mercury (after Schaffernicht 1930). a, $6\,^1P_1$–$8\,^1S_0$: λ, 4916; b, $6\,^1P_1$–$9\,^1S_0$: λ, 4108; c, $6\,^1P_1$–$10\,^1S_0$: λ, 3801.

Though a theoretical investigation of the relevant transitions has not been carried out, it is worth drawing attention to the remarkable results obtained by Schaffernicht (1930) and Thieme (1932) on the emission arising from the $n\,^1S$ levels. Some of the intensity-energy curves concerned are illustrated in figure 9; it is reasonable to assume provisionally that they give the approximate form of the excitation functions associated with the transitions $6\,^1S \rightarrow n\,^1S$. In addition to the normal-type F maximum between 30 and 40 eV it will be observed that there is another and much sharper maxima, *possibly* of type G, near the critical potential. If the proposed interpretation of this latter is correct† it would appear that

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† A possible alternative interpretation is that interatomic collisions (involving transfer of excitation energy from triplet to singlet levels) are responsible. It is desirable that the matter be elucidated by further work.

exchange effects are sometimes of major importance, even for transitions which have a non-vanishing cross-section on the Born approximation. Caution must therefore be exercised in assuming, as a generalization of the evidence given earlier, that for *all* such transitions exchange is best neglected. It is interesting to note (cf. § 4·2) that it is the ${}^1S \rightarrow {}^1S$ transitions which are abnormal, and that the numerous other transitions of mercury which have been studied exhibit no marked peculiarity.

TABLE 8. EXCITATION CROSS-SECTIONS OF MERCURY (ABSOLUTE VALUES)

	theory		experiment		
			cross-section		
transition	cross-section at maximum (πa^2)	reference	at type X peak (πa^2)	at main maximum (πa^2)	reference
$6\,{}^1S \rightarrow 6\,{}^1P$	10†	Penney (1932)	1·9	—	Brattain (1929)
			0·35	1·1	Seiler (1929)
			—	4·8	Arnot & Baines (1935)
$6\,{}^1S \rightarrow 6\,{}^3P_1$	2·3†	Penney (1932)	—	2·0	Bricout (1928)
			—	3·5§	Ornstein, Lindeman & Oldeman (1933)
$6\,{}^1S \rightarrow 6\,{}^3P_{0,1,2}$	7·3†	Penney (1932)	—	1·0	Sponer (1921) (revised Hertz (1925))
			—	1·4	Seiler (1929)
			—	4·7	Arnot & Baines (1935)
$6\,{}^1S \rightarrow 7\,{}^3S$	0·57‡	Yavorsky (1945, 1946)	—	0·73§	Hanle & Schaffernicht (1930)

† Unfortunately, Penney does not attach a scale to the diagram in his paper which covers the region of interest (near the maxima) and extends to about 50 eV. However, he gives the absolute cross-sections for the $6\,{}^1S \rightarrow 6\,{}^1P$ transition at 200 and 400 eV, and from these it can be estimated roughly by using the Bethe formula (§3·1).

‡ The figure quoted in the table is taken from the text of Yavorsky's paper. A slightly smaller value, $0{\cdot}53\pi a^2$, appears to be given by the graph that is also shown. The units used in the latter are stated to be $\pi a^2 \times 10^{16}$; we interpreted these as being $\pi a^2 \times 10^{16}/\text{cm.}^3$ (1 mm. Hg; 0° C).

§ The results given by Ornstein, Lindeman & Oldeman on $6\,{}^1S \rightarrow 6\,{}^3P_1$, and by Hanle & Schaffernicht on $6\,{}^1S \rightarrow 7\,{}^3S$ are based on the same absolute measurement and are thus not independent. Both are probably high; for if $3{\cdot}5\pi a^2$ were the maximum cross-section for the former transition, that for $6\,{}^1S \rightarrow 6\,{}^3P_{0,1,2}$ would, from Penney's ratio, be approximately $11\pi a^2$, which is about twice the theoretical upper limit. The calculated cross-section for $6\,{}^1S \rightarrow 6\,{}^3P_{0,1,2}$ also appears to violate the conservation theorem (cf. table 10).

Thus far we have confined ourselves to the discussion of the form of the excitation functions, as the scale of the experimental curves is not known accurately. The absolute measurements available are summarized in table 8 and compared with the theoretical predictions. Unfortunately, their scatter and uncertainty is such that little can be said regarding the calculated cross-sections except that it is probable that they are correct to well within an order of magnitude. Some suggestive indirect evidence supporting this can be obtained by considering the *relative* cross-sections associated with *different* transitions. Thus table 9 gives the observed (Tate 1932) and computed (Penney 1932) cross-sections for excitation to the $6\,{}^3P_0$, $6\,{}^3P_1$ and $6\,{}^3P_2$ levels expressed as fractions of the cross-section for excitation to the $6\,{}^1P$ level, the energy in each case being 10 eV; clearly the agreement is extremely satisfactory. Again, without making use of the doubtful absolute measurements, it can be shown from the experimental data published by Hanle & Schaffernicht (1930) and by Ornstein *et al.* (1933) that the ratio of the maximum cross-section of the transition $6\,^1S \rightarrow 6\,^3P_1$ to that of the transition $6^1S \rightarrow 7\,^3S$ is about 4·8, which is in fair accord with the value of 4·0 deduced from the calculations of Penney (1932) and of Yavorsky (1945*a*, 1946).† It cannot, of course, be assumed from these successes that the theoretical cross-sections are accurate in magnitude, since perhaps all are too great by the same extent: but at least it would seem reasonable to conclude that the factor by which they are in error is not unduly large.

TABLE 9. EXCITATION CROSS-SECTIONS OF MERCURY (RELATIVE VALUES AT 10 eV)

	cross-section	
transition	theory (Penney 1932)	experiment (Tate 1932)
($6\,^1S \rightarrow 6\,^1P$	1·0	1·0)
$6\,^1S \rightarrow 6\,^3P_0$	0·06	small
$6\,^1S \rightarrow 6\,^3P_1$	0·27	0·34
$6\,^1S \rightarrow 6\,^3P_2$	0·50	0·53

4·6. *The conservation theorem*

The conservation theorem of Mott and of Bohr, Peierls and Placzek (see Mott & Massey 1949 and § 1) is of considerable value in exposing the inability of the Oppenheimer approximation to deal successfully with many exchange transitions. To enable the general position to be surveyed, all cases known to have been investigated have been collected together and are listed either in table 10*a* or in table 10*b* according to whether the calculated cross-section is greater or less than the theoretical upper limit. For some of the examples cited a brief account has already been given of the wave functions employed in the computational work; as regards the others, details need not be reported here, though it should perhaps be mentioned that the incident and scattered electrons were represented by distorted plane waves in the case of atomic oxygen and by Coulomb waves in the case of the various ions.

It will be noticed that if a transition connects levels of the same principal quantum number it usually appears in table 10*a*,‡ and conversely if it does not do so, it usually appears in table 10*b*; indeed, the only exceptions to the rule are He, $1\,^1S \rightarrow 2\,^3S$, and H_2, $^1\Sigma_g^+ \rightarrow {}^3\Sigma_u^+$ (with post interaction) and Hg, $6\,^3P_1 \rightarrow 6\,^3P_2$ (with prior interaction). Such a division is, of course, only to be expected and is merely a manifestation of the fact that the cross-sections associated with the former group are normally larger than those associated with the latter group; conclusions cannot be drawn on the relative accuracy of the calculations for the two classes of transition. The apparently anomalous cases are, however, of interest; for it is the very light atom, helium, and molecule, hydrogen, that provide the exceptional transitions in table 10*a*, and it is the very heavy atom, mercury, that provides the exceptional transition in table 10*b*. Once again there is the suggestion that the Oppenheimer approximation is worst suited to light systems and best suited to heavy systems.

It is natural to inquire whether, if for a particular transition the Oppenheimer approximation yields a cross-section in excess of the limit, the true cross-section is actually only slightly below the limit. The rather crude laboratory data on H_2, $^1\Sigma_g \rightarrow {}^3\Sigma_u$ (Poole 1937) and on

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† Cf. footnote to table 8.

‡ Further, the most striking failures occur with transitions not involving a change in the electron configuration.

Hg, $6\,^1S \rightarrow 6\,^3P$ (cf. § 4·5) suggests that for these the limit is indeed approached; and for the O^{++} transitions it can at least be said that the use of the calculated cross-sections in astrophysical applications leads to results reasonably consistent with those obtained in other ways.[†] However, for He, $1\,^1S \rightarrow 2\,^3S$ the position is entirely different; thus while the cross-section derived from the post interaction is greater than the limit by a factor of 1·1 the true cross-section (as judged from the work of Maier-Leibnitz; cf. § 4·3) is less than the limit by a factor of at least 8 (and probably by considerably more). Though the conservation theorem was not violated grossly in this last example, the inference is that it is unwise to rely on the Oppenheimer approximation even to indicate the transitions for which the limiting cross-section is almost reached.

5. Ionization

5·1. *Outer-shell ionization*

The Born approximation has been applied to a number of cases of outer-shell ionization. Computations on molecular hydrogen and on helium have been carried out by Massey & Mohr (1933 *b*), on neon by Ledsham (1949) and on mercury by Yavorsky (1946). The wave functions used were briefly as follows:

Bound electrons: H_2 and He, hydrogenic; Ne, Hartree type; Hg, Slater type;

Ejected electron: H_2, He and Hg, simple Coulomb (with nuclear charge that effective for ground level): Ne, distorted Coulomb (based on self-consistent core field).

Ionization cross-sections can be measured in the laboratory with much greater precision than can excitation cross-sections and, due to the work of Bleakney (1930), Smith (1930), Tate & Smith (1932) and Nottingham (1939), reliable information is available concerning the four substances which have been treated theoretically. The calculated and observed results are shown in figures 10 *a*, *b*, *c*, *d*, the ionization potentials being adopted as the units of energy. Though there is the usual tendency for the predicted maxima to be over-estimated, the accord is quite good considering that absolute magnitudes are compared. It will be noted that mercury is the *s*-shell system treated most successfully, and that the improvement over hydrogen and helium arises from a change in the shape of the experimental curves rather than from a change in the shape of the theoretical curves which indeed are remarkably similar and, what is even more striking, are remarkably similar to the corresponding curves associated with *K*-shells (cf. figure 11 *a*, *b*). A natural generalization to propose is that the Born approximation yields essentially the same form of ionization function for all such systems and that, on proceeding from light to heavy systems, the true form tends towards this.[‡]

In order to provide further evidence on the hypothesis, the observed ionization functions of sodium (Tate & Smith 1934) and of argon (Smith 1930; Bleakney 1930) are plotted in figure 10 *a*, *c* respectively, arbitrary units being used. The agreement between the former

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[†] We are indebted to Dr L. H. Aller for this information and for sending us the results of the calculations on O^+ and N^+ (see table 10 *a*, footnote) before publication.

[‡] The fact that the most serious failure occurs with neon (which occupies a central position in the group studied) is of course in no way contradictory since *s*- and *p*-shell systems are not strictly comparable; and furthermore the difference in the representation of the ejected electron (see above) may introduce complications.

TABLE 10*a*. CALCULATIONS VIOLATING THE CONSERVATION THEOREM

	transition	matrix element employed	energy of incident electrons for greatest p/q ratio (eV)	azimuthal quantum number of dominant incident partial wave (l)	k^2Q (atomic units)		ratio p/q	reference
					(p) calculated	(q) theoretical upper limit		
H_2,	${}^1\Sigma_g^+ \to {}^3\Sigma_u^+$	post	10·0	1	4·0	3·0	1·3	Massey & Milford (1950)
He,	$1\,{}^1S \to 2\,{}^3S$	post	22·5	0	1·1	1·0	1·1	Fundaminsky (1949)
O,	$2\,{}^3P \to 2\,{}^1D$	prior (with nuclear part of interaction neglected)†	8·7	1	150	1·7	89	Yamanouchi, Inui & Amemiya (1940)
	$2\,{}^3P \to 2\,{}^1S$		11·0	1	22	0·33	66	
O^+,	$2\,{}^4S \to 2\,{}^2D$	prior (with nuclear part of interaction neglected)†	3·4	1	25	3·0	8·3	Aller (1949)
O^{++},	$2\,{}^3P_0 \to 2\,{}^3P_2$	geometric mean of prior and post	a few units‡	1	4·1	3·0	1·4	Hebb & Menzel (1940)§
	$2\,{}^3P_1 \to 2\,{}^3P_2$			1	3·7	3·0	1·2	
	$2\,{}^3P_0$ → all other levels of ground configuration			1	8·4	3·0	2·8	
	$2\,{}^3P_1$ → all other levels of ground configuration			1	6·9	3·0	2·3	
	$2\,{}^3P_2$ → all other levels of ground configuration			1	5·7	3·0	1·9	
	$2\,{}^1D_2$ → all other levels of ground configuration			1	4·5	3·0	1·5	
	$2\,{}^1S_0$ → all other levels of ground configuration			1	6·2	3·0	2·1	
Hg,	$6\,{}^1S \to 6\,{}^3P_{0,1,2}$	prior	8·2	1	4·4	3·0	1·5	Penney (1932)‖

† The undesirability of omitting the nuclear term when computing exchange integrals is discussed in §2·2·1.

‡ k^2Q (calculated) is almost constant up to energies of several electron-volts.

§ Aller & White (1950) have calculated the cross-sections associated with the ${}^3P_0 \to {}^1D_2$ and ${}^3P_0 \to {}^1S_0$ transitions of N^+, using exactly the same method as did Hebb & Menzel. The values they derived are about 0·5 time the computed cross-sections of the corresponding transitions of O^{++} and individually do not violate the conservation theorem; but if, as seems probable, the cross-sections associated with the remaining ground configuration transitions are in the same ratio as for the case of O^{++} their sum would be slightly in excess of the theoretical limit.

‖ Cf. footnote to table 8 regarding the uncertainty of the value of the cross-section we attribute to Penney.

TABLE 10*b*. CALCULATIONS CONSISTENT WITH THE CONSERVATION THEOREM

transition	matrix element employed	energy of incident electrons for greatest p/q ratio (eV)	azimuthal quantum number of dominant incident partial wave (l)	k^2Q (atomic units)		ratio p/q	reference
				(p) calculated	(q) theoretical upper limit		
He, $1\,^1S\rightarrow 2\,^3S$	prior	22·5	0	0·33	1·0	0·33	Fundaminsky (1949)
$1\,^1S\rightarrow 2\,^3P$	post	22·6	1	0·13	3·0	0·043	Fundaminsky (1949)
$1\,^1S\rightarrow 3\,^3D$							Leech (1949)
Ne, $(p^6)\,^1S\rightarrow(p^5 3s)\,^3P$	prior and post	19·0	1	0·01	3·0	0·003	Fundaminsky (1949)
Hg, $6\,^1S\rightarrow 7\,^3S$	prior	9·0	0	0·42	1·0	0·42	Yavorsky† (1945*a*, 1946)
$6\,^3P_1\rightarrow 6\,^3P_2$	prior	1·0	1	1·7	3·0	0·56	Yavorsky (1945*a*, 1946)

† The cross-section given in the text of the original paper is used here (cf. table 8, footnote).

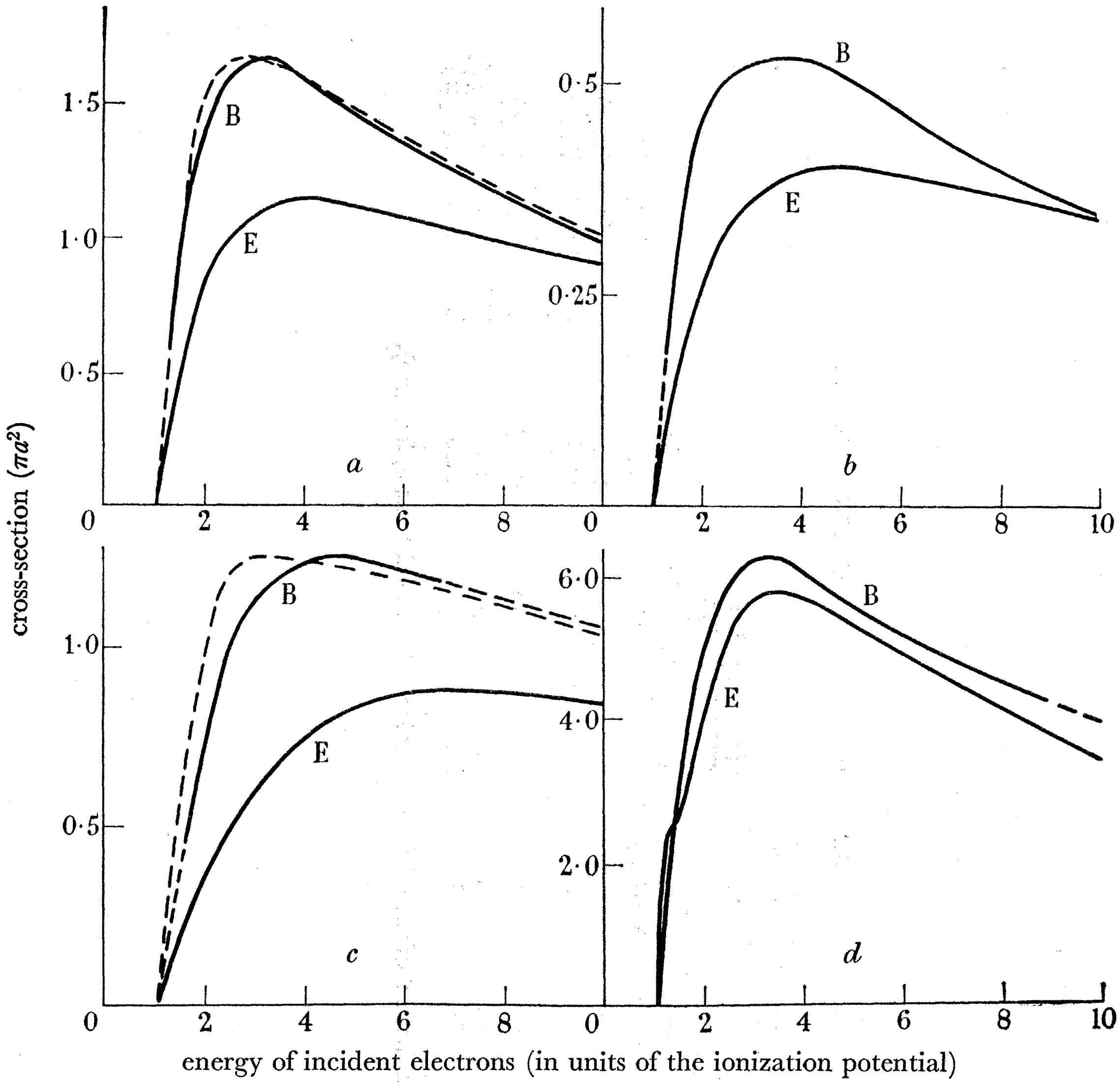

FIGURE 10. Some outer shell ionization functions.

a, H_2 [except --- Na, experimental (arbitrary units) (Tate & Smith 1932, 1934)]. B, Born approximation (Massey & Mohr 1933 *b*); E, experimental (Tate & Smith 1932, 1934).

b, He; B, Born approximation (Massey & Mohr 1933); E, experimental (Smith 1930).

c, Ne [except --- A, experimental (arbitrary units) (Smith 1930)]; B, Born approximation (Ledsham 1949); E, experimental (Bleakney 1930).

d, Hg; B, Born approximation (Yavorsky 1946); E, experimental (Nottingham 1939).

and the theoretical hydrogen curve is almost perfect; and that between the latter and the theoretical neon curve, though not so noteworthy,[†] is, nevertheless, encouraging, particularly as the nature of the discrepancy is such as to suggest that if calculations on argon itself were carried out the results obtained would be but little in error.[‡]

[†] Actually the agreement may be within the accuracy of the experimental measurements. Stevenson & Hipple (1942) given an appreciably flatter curve than does Smith.

[‡] The theoretical curve for argon would be expected to lie between that for neon and that for an L_{II} or L_{III} shell (cf. figure 11*c*). It may be remarked that the similitude between these is rather less marked than that shown by the theoretical curves for hydrogen, helium, mercury and a K-shell. Whether this is a real characteristic, or whether it is simply due to the use of a distorted Coulomb wave function in the case of neon, is uncertain.

The observed ionization functions of the heavier alkali metals, potassium, rubidium and caesium (Tate & Smith 1934), are not of the standard simple form; thus they possesss double maxima, and the ultimate fall-off does not become appreciable until an energy of ten or more times the ionization potential is reached. It is probable that this apparently anomalous behaviour arises largely because the mechanism studied in the laboratory includes the removal of electrons other than the valency electron; the *d*-shell especially may well con-

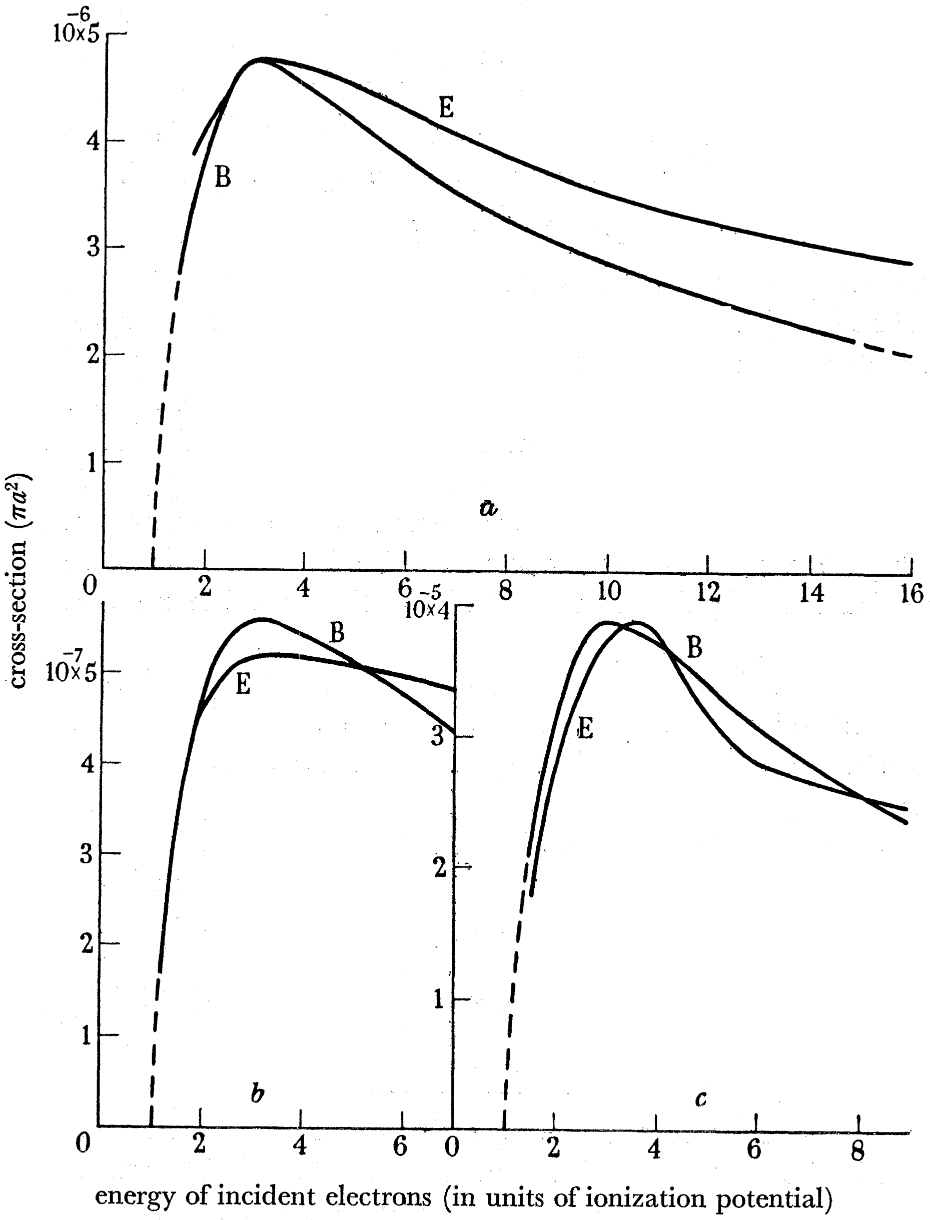

FIGURE 11. Some inner shell ionization functions.

a, Ni, *K*; B, Born approximation (Burhop 1940); E, experimental (absolute units) (Smick & Kirkpatrick 1945; Pockman, Webster, Kirkpatrick & Harworth 1947).

b, Ag, *K*; B, Born approximation (Burhop 1940); E, experimental (absolute units) (Clark 1935; Webster, Hansen & Duveneck 1933).

c, Ag, L_{II}; B, Born approximation (Burhop 1940); E, experimental (arbitrary units) (McCue 1944).

tribute to the measured cross-section.† In the case of the heavier inert gases, krypton and xenon, for which this complication is less likely to influence seriously the shape of the ionization function, there is, as for argon, fair agreement with the theoretical neon curve.

Little need be said regarding exchange effects as they seem of minor direct importance—though they may conceivably be the cause of certain irregularities such as that appearing in the ionization function of mercury (cf. figure 10*d*). It is interesting to note that the experimental investigations provide no evidence for the existence of type X peaks. On the contrary, indeed, Stevenson & Hipple (1942) claim that careful measurements show that for neon and argon the cross-section energy curve is *concave upwards* for about 1 eV. beyond the ionization potential. Yavorsky apparently finds a similar behaviour with mercury; the other quantal investigators did not carry out the calculations at sufficiently close intervals to establish the exact form of the predicted curve in the region concerned.

5·2. *Inner-shell ionization*

Using the same type of wave functions as adopted by Massey & Mohr in their work on hydrogen and helium (cf. § 5·1), Burhop (1940) evaluated the Born approximation for the ionization functions associated with the inner shells Ni (K), Ag ($K, L_{\mathrm{I}}, L_{\mathrm{II}}, L_{\mathrm{III}}$) and Hg ($K, L_{\mathrm{I}}, L_{\mathrm{II}}, L_{\mathrm{III}}$). He found them to be almost identical in shape. In figure 11 *a*, *b*, *c* some of his results are compared with experimental data obtained by Smick & Kirkpatrick (1945) Pockman, Webster, Kirkpatrick & Harworth (1947), Clark (1935), Webster, Hansen & Duveneck (1933) and McCue (1944). The agreement is excellent except as regards the rate of fall-off at high energies; and no concern need be felt about this discrepancy, as some preliminary calculations by Fundaminsky indicate that it is due merely to the neglect of relativistic effects.

The inner-shell investigations thus suggest that the Born approximation deals successfully with systems having strong fields. This may be because the perturbations of an atomic electron by the incident electron is relatively much smaller compared with the binding field in these cases.

As has been mentioned in § 4·5 there is also some evidence that the approximation is a good one for dealing with excitation of heavy atoms, irrespective of whether the excited electron is initially bound by a strong force or not. An explanation of such an effect is not so obvious. Caution must be exercised regarding both generalizations. On seeking for regularities amongst a limited selection of results it is easy to be misled by chance.

6. CONCLUSIONS

For compactness and to avoid undue repetition we present our main conclusions in the form of a table. In the last column of this we list some systems and transitions on which work might usefully be done in the future. Little comment is necessary on the suggestions made. Clearly, hydrogen and helium should be studied extensively, since they provide the simplest examples of the two main classes of excitation. In the case of H it may be recalled that some measurements of Ornstein and Lindeman on a composite, but dominantly allowed, transition seemed anomalous in that they did not show the customary divergence from the results obtained using the Born approximation (figure 2*a*); it is particularly desirable that these

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† The observed ionization function of mercury may unfortunately also be composite.

should be repeated. Further research on the $1\,^1S \rightarrow 2\,^3S$ transition of He would also be of special value in view of the significance attached to the question of whether the excitation function consists of a type X peak only or whether this is followed by a type G maximum. A study of representative transitions of the other atoms suggested should enable a final decision to be reached on the hypothesis we have advanced that the reliability of the theory improves in going from light to heavy and from weak field to strong field systems. It is felt that the evidence at present available, though quite convincing as regards ionization, is rather tentative as regards excitation. The investigation is one of considerable practical importance: for if the hypothesis could be firmly established the cross-sections of a number of transitions arising in astrophysical applications could be calculated with some confidence. Finally, it is to be hoped that in the experimental investigations care will be taken to explore in each case the region just beyond the critical potential so as to provide as much information as possible on the incidence of the peculiar type X peaks which theory seems unable to reproduce.

TABLE 11. SUMMARY OF CONCLUSIONS

process and most suitable approximation	remarks on agreement with observation (omitting type X peaks)	systems and transitions meriting study (or further study)
1. EXCITATION		
1·1. *Transitions not involving a reversal of spin*		
Born (Oppenheimer generally leads to gross errors at low energies)		
1·1·1. *Optically allowed*	fair (cf. figures 3*a*, 4*d*)	H (exp.), He (exp. and calc.) Na (exp.), K (exp. and calc.) Zn, Cd and Tl (calc.)† any group of transitions of the type: $P \rightarrow S$, $P \rightarrow P$, $P \rightarrow D$ (exp. and calc.)‡
1·1·2. *Optically forbidden*	good (cf. figures 3*b*, *c*, 4*c*, *e*); some *s*-*s* transitions possibly show exchange effects (cf. figures 3*c*, 9)	
1·2. *Transitions involving a reversal of spin* Oppenheimer (Born gives a zero cross-section) *Note.* Prior and post interactions may yield very different results (cf. figure 4*a*, *b*; tables 5, 6)	except for Hg (cf. figure 8*b*, *c*, table 9) very poor both as regards shape and absolute magnitude (cf. figure 6); conservation theorem frequently violated (cf. table 10*a*)	He (exp. and calc.) Zn and Cd (calc.)† any transition not involving change of electron configuration (exp. and calc.)
2. IONIZATION		
Born (Oppenheimer never been applied)		
2·1. *Outer shell*	fair-good (cf. figure 10); contain irregularities which possibly indicate minor exchange effects (cf. figure 10*d*)	Na and A (calc.) § any transition which can occur only by electron exchange (exp. and calc.)
2·2. *Inner shell*	excellent (cf. figure 11)	—

† For comparison with experimental results of Larché (1931) (Zn and Cd) and Ströhmeier (1937) (Tl).

‡ To obtain further evidence on the suggested difference between optically allowed and optically forbidden transitions.

§ For comparison with experimental results of Tate & Smith (1934), Smith (1930) and Stevenson & Hipple (1942).

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