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Theory of the Scattering of Slow Electrons

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1. INTRODUCTION

It is important at the outset to distinguish between fast and slow collisions of electrons with atoms. If v is the velocity of the incident electron and u a velocity of the order of that of the atomic electrons, we call the collision fast if $v\gg u$. Otherwise it will be regarded as slow. There is no difficulty in principle in developing a general theory of the scattering of fast electrons, valid for both elastic and inelastic collisions. This is the well-known first Born approximation. For slow collisions no such generally effective method is available, and it is the object of the present review to discuss what has so far been achieved under these circumstances. In order to avoid introducing irrelevant complication when discussing methods, detailed consideration will usually be confined to the collisions of electrons with hydrogen atoms. Most of the techniques which may be used are exemplified by this case, in which, because of its relative simplicity, most progress has been made. Generalization to more complex atoms usually presents no difficulty, apart from increased labor in numerical evaluation. Some attention will, however, be devoted to consideration of the collisions with atoms and ions which result in excitation of levels belonging to the ground configuration. A knowledge of the cross sections for these collisions is important for applications in astrophysics and in atmospheric physics.

The emphasis throughout this review will be on the problem of accurately calculating collision cross sections. It will not be possible to discuss general questions of collision theory; the existence of solutions which satisfy the boundary conditions demanded by the physical requirements will always be assumed, though it is realized that, from the mathematical point of view, it may often be very difficult to prove the appropriate existence theorems.

2. THE COLLISIONS OF ELECTRONS WITH HYDROGEN ATOMS

The wave equation for the two electron problem in this case takes the form

$$\left[\frac{\hbar^2}{2m}(\nabla_1^2+\nabla_2^2)+E-\frac{e^2}{r_{12}}+\frac{e^2}{r_1}+\frac{e^2}{r_2}\right]\Psi=0,\qquad(1)$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the coordinates of the two electrons. If the electron is incident with wave number k_0 on the atom in its ground state of energy E_0, the total energy E is given by

$$E=E_0+\frac{\hbar^2}{2m}k_0^2.\qquad(2)$$

To obtain an approximation to Ψ suitable for the determination of cross sections for elastic and inelastic collisions of the electron with the atom, it is usual to expand Ψ in the form

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=\left(\Sigma+\int\right)\psi_n(\mathbf{r}_1)F_n(\mathbf{r}_2),\qquad(3)$$

where, for the moment, we ignore the indistinguishability of the two electrons and designate electron 2 as the incident one. The functions ψ_n are those of the various states of the atom, and the integral sign allows for integration over the continuous spectrum. On substitution of (3) in (1), and using the fact that

$$\left(\frac{\hbar^2}{2m}\nabla_1^2+E_n+\frac{e^2}{r_1}\right)\psi_n(\mathbf{r}_1)=0,\qquad(4)$$

we obtain

$$\left(\Sigma_n+\int\right)\left\{\frac{\hbar^2}{2m}(\nabla_2^2+k_n^2)+\frac{e^2}{r_1}-\frac{e^2}{r_{12}}\right\}\psi_n(\mathbf{r}_1)F_n(\mathbf{r}_2)=0\qquad(5)$$

where

$$k_n^2=\frac{2m}{\hbar^2}(E-E_n).\qquad(6)$$

Multiplying by $\psi_n^*(\mathbf{r}_1)$ and integrating over $d\mathbf{r}_1$, we obtain the infinite set of simultaneous differential equations for the F_n,

$$(\nabla_2^2+k_n^2)F_n=\left(\Sigma_n+\int\right)U_{nm}F_m,\qquad(7)$$

where

$$U_{nm}=\frac{2me^2}{\hbar^2}\int\psi_n^*\left(\frac{1}{r_{12}}-\frac{1}{r_2}\right)\psi_m d\mathbf{r}_1.\qquad(8)$$

Solutions of these equations are now required which are well-behaved functions with asymptotic form

$$F_n\sim r_2^{-1}e^{ik_nr_2}f_n(\theta_2,\phi_2)+e^{i\mathbf{k}_0\cdot\mathbf{r}}\delta_{0n}.\qquad(9)$$

The differential cross section for the excitation of the nth state is now given by

$$I_n(\theta,\phi)d\omega=|f_n(\theta,\phi)|^2d\omega\qquad(10)$$

where $d\omega$ is the solid angle element about (θ,ϕ).

To make this procedure practicable it is necessary to develop methods of approximating to the solution of Eqs. (7). We now discuss the possibilities in this direction.

3. BORN'S APPROXIMATION

If we assume that the interaction of the electron with the atom is small, which will be true if the incident energy $k^2\hbar^2/2m \gg E_0$, Eqs. (7) may be solved by substituting on the right-hand sides

$$F_n = 0, \quad n \neq 0; \quad F_0 = e^{i\mathbf{k}_0 \cdot \mathbf{r}}, \tag{11}$$

so that

$$(\nabla_2^2 + k_n^2) F_n = U_{n0} e^{i\mathbf{k}_0 \cdot \mathbf{r}} \tag{12}$$

and

$$f_n(\theta,\phi) = -\frac{1}{4\pi}\int U_{n0} e^{i(\mathbf{k}_0 - \mathbf{k}_n)\cdot \mathbf{r}_2} d\mathbf{r}_2, \tag{13}$$

with

$$|\mathbf{k}_0 - \mathbf{k}_n| = (k_0^2 + k_n^2 - 2k_0 k_n \cos\theta)^{\frac{1}{2}}.$$

4. TWO-STATE APPROXIMATIONS—THE DISTORTED WAVE (D.W.) METHOD

For slow collisions Born's approximation is no longer useful. The first approach to a suitable approximation in such cases is to make the much less drastic approximation of supposing that, in Eqs. (6), the diagonal matrix elements U_{nn} are much bigger than the non-diagonal, so that all of the latter may be neglected, except those associated with the initial state. This gives the set of equations

$$(\nabla^2 + k_0^2 - U_{00}) F_0 = 0, \tag{14}$$

$$(\nabla^2 + k_n^2 - U_{nn}) F_n = U_{n0} F_0, \quad n \neq 0. \tag{15}$$

This equation for the elastically scattered wave F_0 is the same as that for a particle of wave number k_0 moving under the influence of a static potential $\hbar^2 U_{00}/2m$.

By the use of a generalized Green's function procedure, the equation for F_n may be solved to give,[1]

$$f_n(\theta,\phi) = -\frac{1}{4\pi}\int \mathfrak{F}_n(r_2, \pi - \Theta) U_{n0}(\mathbf{r}_2) F_0(r_2,\theta_2) d\mathbf{r}_2 \tag{16}$$

where

$$\cos\Theta = \cos\theta \cos\theta_2 + \sin\theta \sin\theta_2 \cos(\phi - \phi_2).$$

F_0 is the solution of (13) with the asymptotic form (8) and $\mathfrak{F}_n$ is the corresponding solution of the homogeneous form of (14), i.e.,

$$(\nabla^2 + k_n^2 - U_{nn}) \mathfrak{F}_n = 0, \tag{17}$$

$$\mathfrak{F}_n \sim e^{i\mathbf{k}_n \cdot \mathbf{r}_2} + f_n(\theta_2 \phi_2) r_2^{-1} e^{ik_n r_2}. \tag{18}$$

Comparison with the corresponding first Born approximation (13) shows that allowance has now been made for the distortion of the incident and final electron waves by the mean static fields of the atom in its initial and final states, respectively.

5. THE TWO-STATE APPROXIMATION—CLOSE COUPLING

In the distorted wave method it is assumed that no intermediate state is at all important in the excitation process. Thus to obtain Eqs. (14) and (15), we might have proceeded straight away by approximating to Ψ in (3) by writing

$$\Psi = \psi_0(r_1) F_0(\mathbf{r}_2) + \psi_n(\mathbf{r}_1) F_n(\mathbf{r}_2). \tag{19}$$

We then obtain

$$(\nabla^2 + k_0^2 - U_{00}) F_0 = U_{0n} F_n, \tag{20}$$

$$(\nabla^2 + k_n^2 - U_{nn}) F_n = U_{n0} F_0. \tag{21}$$

If we suppose these equations to be solved by iteration, starting from F_0, the first stage in the iteration gives the distorted wave approximation. It will not be necessary to proceed further in this series of approximations if the coupling $|U_{0n}|$ is small. The distorted wave approximation will only be valid under these circumstances. It is probable, however, that there will be occasions in which intermediate states can be ignored, but $|U_{0n}|$ is not small. The close coupling equations (20), (21) will then provide a satisfactory approximation.

6. ALLOWANCE FOR EXCHANGE

So far we have ignored the indistinguishability of the two electrons. There is no reason why in the approximation (19) we should ignore such terms as $\psi_0(r_2) F_0(\mathbf{r}_1)$ or $\psi_n(\mathbf{r}_2) F_n(\mathbf{r}_1)$ as they correspond to atomic states of the same energies as those already included. These terms arise, in the expansion (3), from atomic states in the continuous spectrum of such high energy that k_n^2, given by (6), is <0. In that sense allowance for exchange involves going beyond a two-state approximation, but we may nevertheless obtain a generalization of Eqs. (20) and (21) which in another sense may be regarded as a two-state approximation allowing for exchange. To obtain this we write

$$\Psi^{\pm} = \psi_0(r_1) F_0^{\pm}(\mathbf{r}_2) \pm \psi_0(r_2) F_0^{\pm}(\mathbf{r}_1) + \psi_n(\mathbf{r}_1) F_n^{\pm}(\mathbf{r}_2) \pm \psi_n(\mathbf{r}_2) F_n^{\pm}(\mathbf{r}_1) \tag{22}$$

i.e., we work with functions which are either symmetrical or antisymmetrical in the space coordinates of the electrons, but consider only two atomic states. On substitution in (1) we now find by following the same procedure as before, the equations

$$(\nabla^2 + k_0^2 - U_{00}) F_0^{\pm}(\mathbf{r}_2) \pm \int K_{00}(r_2, r_2') F_0^{\pm}(r_2') dr_2' = U_{n0} F_n^{\pm} \mp \int K_{0n}(\mathbf{r}_2, \mathbf{r}_2') F_n^{\pm}(\mathbf{r}_2') d\mathbf{r}_2', \tag{23}$$

$$(\nabla^2 + k_n^2 - U_{nn}) F_n^{\pm}(\mathbf{r}_2) \pm \int K_{nn}(r_2, r_2') F_n^{\pm}(r_2') dr_2' = U_{n0} F_0^{\pm} \mp \int K_{n0}(\mathbf{r}_2, \mathbf{r}_2') F_0^{\pm}(\mathbf{r}_2') d\mathbf{r}_2', \tag{24}$$

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[1] N. F. Mott and H. S. W. Massey, *Theory of Atomic Collisions* (Clarendon Press, Oxford, 1949), second edition, p. 113.

where

$$K_{00}=\psi_0^*(r_1)\psi_0(r_2)\left\{k_0^2-\frac{2m}{\hbar^2}\left(\frac{e^2}{r_{12}}+E_0\right)\right\}, \tag{25}$$

$$K_{nn}=\psi_n^*(r_1)\psi_n(r_2)\left\{k_n^2-\frac{2m}{\hbar^2}\left(\frac{e^2}{r_{12}}+E_n\right)\right\}, \tag{26}$$

$$K_{0n}=\psi_n^*(r_1)\psi_0(r_2)\left\{k_n^2-\frac{2m}{\hbar^2}\left(\frac{e^2}{r_{12}}+E_0\right)\right\}=K_{n0}^*. \tag{27}$$

Thus the pair of coupled differential equations [(20), (21)] are now replaced by two coupled integro-differential equations. The kernels K_{00}, K_{nn}, represent additional, velocity dependent, interactions producing distortion of the incident and final electron waves, respectively, while K_{0n} contributes to the coupling which produces transitions between the two states. If the equations can be solved to give solutions of the correct asymptotic form, the differential cross section for excitation of the nth state is

$$I_n(\theta,\phi)d\omega=\{\tfrac{1}{4}|f_n^+(\theta)|^2+\tfrac{3}{4}|f_n^-(\theta)|^2\}d\omega. \tag{28}$$

The fractional weight attached to the space symmetrical and antisymmetrical cases is determined from the chance that the electron spins should be parallel or antiparallel, the over-all wave function, including spin, necessarily being antisymmetric in the two electrons.

The generalized form of the distorted wave approximation, which we shall refer to as the exchange and potential-distorted or E.P.D.W. approximation, is obtained by supposing that in (23), (24), U_{0n} and K_{0n} are small, so that iterative solution from $F_0^\pm$ converges very rapidly and we take, in place of (14) and (15),

$$(\nabla^2+k_0^2-U_{00})F_0^\pm\pm\int K_{00}(\mathbf{r}_2',\mathbf{r}_2)F_0^\pm(\mathbf{r}_2')d\mathbf{r}_2'=0, \tag{29}$$

$$(\nabla^2+k_n^2-U_{nn})F_n^\pm\pm\int K_{nn}(\mathbf{r}_2',\mathbf{r}_2)F_n^\pm(\mathbf{r}_2')d\mathbf{r}_2'$$
$$=U_{n0}F_0^\pm\mp\int K_{n0}(\mathbf{r}_2',\mathbf{r}_2)F_1(\mathbf{r}_2')d\mathbf{r}_2'. \tag{30}$$

The first equation gives the elastic scattering. It differs from (14) in that allowance is made for an exchange interaction.

The symmetrical and antisymmetrical differential cross sections for excitation of the nth state now take the form

$$I_n^\pm(\theta,\phi)d\omega=|f_n^\pm(\theta,\phi)|^2d\omega \tag{31}$$

where

$$f_n^\pm(\theta,\phi)=-\frac{1}{4\pi}\int\mathfrak{F}_n^\pm(r,\pi-\Theta)\left\{U_{n0}F_0^\pm(r_1,\theta)\right.$$
$$\left.\mp\int K_{n0}(r,r^1)F_0^\pm(r^1,\theta^1)dr^1\right\}dr. \tag{32}$$

and $F_0^\pm$ are the solutions of (29) which have the asymptotic form (9) and $\mathfrak{F}_n^\pm$ those of (30) with the right-hand size zero which have the asymptotic form (18).

Allowance for exchange thus has the twofold effect of modifying the distortion of the incident and final electron waves as well as the coupling which leads to the transition.

Two further approximations suggest themselves at this stage. The first is to ignore the influence of exchange on the distortion, i.e., K_{00} and K_{nn} are neglected in (29) and (30). This will not usually be very effective unless K_{0n} is also negligible.

A further, more drastic, approximation is to ignore distortion altogether so that F_0 and $\mathfrak{F}_n$ in (32) are replaced by plane waves and we obtain the modification of Born's first approximation first suggested by Oppenheimer[2] namely

$$f_n^\pm(\theta,\phi)=-\frac{1}{4\pi}\left[\int U_{n0}e^{i(\mathbf{k}_0-\mathbf{k}_n)\cdot\mathbf{r}}d\mathbf{r}\right.$$
$$\mp\int\int e^{i(\mathbf{k}_0\cdot\mathbf{r}_1-\mathbf{k}_n\cdot\mathbf{r}_2)}$$
$$\times\left\{k_n^2-\frac{2m}{\hbar^2}\left(\frac{e^2}{r_{12}}+E_0\right)\right\}$$
$$\left.\times\psi_0(r_2)\psi_n^*(\mathbf{r}_1)d\mathbf{r}_1d\mathbf{r}_2\right]. \tag{33}$$

This approximation appears to be of little value in practice unless U_{n0} vanishes. Thus it is only valid for high electron energies for which the second, exchange, integral is negligibly small compared with the first, unless U_{n0} is itself negligible.

To summarize the various two-state approximations and introduce a short title for each it is best to proceed from Eqs. (23) and (24). We then have Table I.

7. ALLOWANCE FOR INTERMEDIATE STATES

There are certain circumstances in which it is necessary to take into account the interactions of more than two states, but still only a small number. An example of this is the excitation of transitions between states of the same configuration. Thus there are three terms arising from the ground $2p^4$ configuration of OI, namely in order of increasing energy ^3P, ^1D, and ^1S. It has been shown[3,4] that it is necessary to allow for close coupling between these three terms in order to obtain reasonably accurate values for the differential cross sections for collisions of slow electrons with atomic oxygen. This is particularly true for collisions in which transitions between the terms are excited, but it applies also to the

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[2] J. R. Oppenheimer, Phys. Rev. **32**, 361 (1928).

[3] Bates, Fundaminsky, Leech, and Massey, Phil. Trans. Roy. Soc. **A243**, 93 (1950).

[4] M. J. Seaton, Phil. Trans. Roy. Soc. **A245**, 469 (1953).

Table I.

Approximation in Eqs. (23) (24)	Title	Short title
$K_{00}=K_{nn}=K_{0n}=U_{00}=U_{nn}=0$, U_{0n} small	First Born approximation	B.
$K_{00}=K_{nn}=U_{00}=U_{nn}=0$, U_{0n}, K_{0n} small	Born-Oppenheimer approximation	B.O.
$K_{00}=K_{nn}=K_{0n}=0$, U_{0n} small	Distorted wave approximation	D.W.
$K_{00}=K_{nn}=0$, K_{0n}, U_{0n} small	Potential distorted exchange approximation	P.D.E.
K_{0n}, U_{0n} small	Exchange and potential distorted exchange approx.	E.P.D.E.
$K_{00}=K_{nn}=K_{0n}=0$	Close coupling without exchange	C.C.
None	Close coupling with exchange	E.C.C.

excitation of other transitions. It may well be a general feature that, in calculating cross sections for excitation of a transition between two states, it is necessary to allow for close coupling of either or both with states with the same configurations. In such cases the difficulties of numerical determination of the cross sections are enhanced but still remain possible when allowance is made for the availability of electronic computing techniques.

As pointed out and utilized by Seaton,[4] it may often be a good first approximation in these cases to neglect consistently the energy differences between the states arising from the same configuration. If this is done, it often happens that the resulting equations may be handled with comparative ease. This will be illustrated in more detail later (Sec. 10.2).

It is more difficult to allow for the influence of all possible intermediate states each of which may contribute only a small amount. An important example of this is the effect of polarization on the elastic scattering. If it is quite small and we are concerned with encounters at not too low velocities, Born's second approximation is likely to give a satisfactory correction. Once this approximation has been calculated, it is possible to obtain a still further improvement by using the Schwinger[5] variational method. The evaluation of the second approximation is a difficult and lengthy task, however. In low-energy impacts, and especially for elastic scattering, a simpler variational procedure, based on the Hulthèn[6] variational method, can be used. Examples of these methods will be discussed in Sec. 11.

8. RANGE OF VALIDITY OF APPROXIMATE METHODS

The range of validity of Born's first approximation is fairly well known and understood. This is particularly true for elastic scattering.[7] Much less information is available at the present time about the approximate methods discussed above for slow collisions. Considerable new experience has been gained in this direction during the last few years and the indications provided from this will be discussed in Sec. 12.

We shall now discuss the detailed application of the different methods.

9. APPLICATION OF THE DISTORTED WAVE METHOD

9.1 Collisions with Atomic Hydrogen —Elastic Scattering

With the distorted wave method, it is possible to consider the elastic scattering as quite distinct from the inelastic. We shall therefore discuss it first.

The integro-differential equation for the elastically scattered wave F_0 is given in (29). If we expand F_0 in the form

$$F_0(\mathbf{r})=r^{-1}\Sigma_l f_l(r)P_l(\cos\theta) \tag{34}$$

the functions f_l must satisfy the equation

$$\left[\frac{d^2}{dr^2}+k_0^2-U_{00}-\frac{l(l+1)}{r^2}\right]f_l^{\pm} \pm\int \kappa_l(r,r')f_l^{\pm}(r')dr'=0 \tag{35}$$

where

$$\kappa_l=4\pi rr'\left[k_0^2\delta_{0l}-\frac{2m}{\hbar^2}\{E_0\delta_{0l}+e^2\gamma_l(r,r')\}\right]\Big/(2l+1), \tag{36}$$

$$\gamma_l(r,r')=r'^l/r'^{l+1},\quad r>r';\quad =r'^l/r'^{l+1},\quad r<r'.$$

A well-behaved solution of this equation can be found, in principle, which has the asymptotic form

$$f_l^{\pm}\sim\sin(k_0r-\tfrac{1}{2}l\pi+\eta_l^{\pm}). \tag{37}$$

The differential elastic scattering cross section then takes the form

$$I_0^{\pm}(\theta)=\frac{1}{4k^2}|\Sigma(2l+1)[\exp(2i\eta_l^{\pm})-1]P_l(\cos\theta)|^2 \tag{38}$$

so that the problem reduces to that of determining the $\eta_l^{\pm}$.

For low velocities of impact the only important phase shift is $\eta_0^{\pm}$ and in fact, for collisions with atomic hydrogen, this is the only phase shift which ever approaches or exceeds $\pi/2$. All the higher order phases are small enough to be calculated by the perturbation

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[5] J. Schwinger, unpublished lectures (1947).

[6] L. Hulthèn, Kgl. Fysiograf. Sällskap. Lund. Förh. **14**, 1 (1944).

[7] W. Kohn, Revs. Modern Phys. **26**, 292 (1954).

formula

$$\eta_l^{\pm}=-k_0\left[\int_0^{\infty} rj_l(k_0r)\left\{rU(r)j_l(kr)\pm\int_0^{\infty}\kappa_l(r,r')j_l(k_0r')r'dr'\right\}dr\right]=\eta_{lB}^{\pm}, \quad (39)$$

where $j_l(x)=(\pi/2x)^{\frac{1}{2}}J_{l+\frac{1}{2}}(r)$ and $I_0(\theta)$ can be written quite closely in the form

$$I_0(\theta)=I_0{}^B(\theta)+\{I_0{}^B(\theta)\}^{\frac{1}{2}}k^{-1}[\sin 2\eta_0-2\eta_{0B}]+\frac{1}{4k^2}[(\sin 2\eta_0-2\eta_{0B})^2+(\cos 2\eta_0-1)^2], \quad (40)$$

where $I_0{}^B(\theta)$ is as given by Born's first approximation.

The integro-differential equations (35) may be solved directly by a numerical iterative procedure as was first done by Morse and Allis.[8] The zero-order phase shifts which they obtained are illustrated in Fig. 1, together with these obtained when exchange is neglected. A recent recalculation of $\lim_{k_0\to 0}\eta_0{}^{\pm}/k_0$ by Seaton[9] shows that this limit for $\eta_0{}^{+}$ as given by Morse and Allis is incorrect, and this correction has been indicated in Fig. 1.

An alternative procedure which can be carried out with somewhat less labor and which may be generalized to more complicated conditions, such as the inclusion of polarization, is to use a variational method.

A number of variational methods have been proposed, but the ones most extensively employed up to the present are those due to Hulthèn[6] and to Kohn.[10]

These depend on the evaluation of an integral I^t which has the form

$$I^t=\int_0^{\infty} f_l{}^t(r)Lf_l{}^t(r)dr \quad (41)$$

where Eq. (35) may be written $Lf_l(r)=0$ so that L is the operator

$$\left[\frac{d^2}{dr^2}+k_0{}^2-U_{00}-\frac{l(l+1)}{r^2}\pm\int\kappa_l(r,r')\cdot dr'\right]. \quad (42)$$

If $f_l{}^t$ is an exact solution of (35) I^t must vanish. Even if it is not exact but is a well-behaved function with asymptotic form

$$f_l{}^t\sim\sin(k_0r-\tfrac{1}{2}l\pi)+a\cos(k_0r-\tfrac{1}{2}l\pi) \quad (43)$$

it may be shown that I^t satisfies a variational condition. Thus if the function $f_l{}^t$ is varied, while still remaining a well-behaved function of asymptotic form (43) but with a different value of a, it may be shown that

$$\delta(I^t+a/k)=0. \quad (44)$$

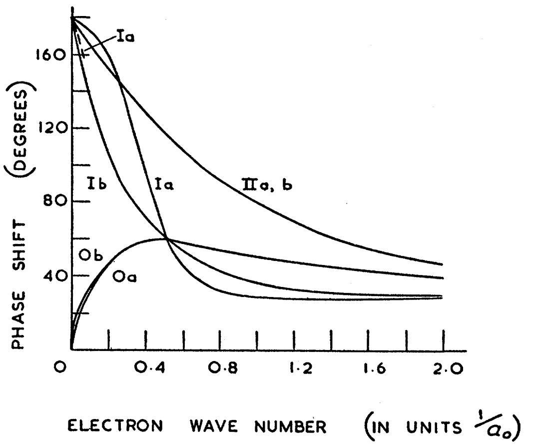

FIG. 1. Phase shifts $\eta_0{}^{\pm}$ for scattering of electrons by atomic hydrogen. Curves O—calculated neglecting exchange (a) by accurate numerical integration (b) by Hulthèn variational method. Curves I—exchange included (symmetrical case) (a) by accurate numerical integration—(Morse and Allis)- - -(Seaton) (b) by Hulthèn variational method. Curves II—exchange included (antisymmetrical case) (a) by accurate numerical integration (b) by Hulthèn variational method.

To make use of this result, a trial function $f_l{}^t$ is introduced, which includes a number of arbitrary parameters $c_1, \cdots, c_n$ as well as a. I^t is calculated with this function giving $I^t(c_1, \cdots c_n, a)$. The parameters $c_1, c_2, \cdots, c_n, a$, are then determined from the equation

$$\partial I^t/\partial c_r=0,\ r=1,\cdots,n;\ \partial I^t/\partial a=1/k. \quad (45)$$

The correct value of a is $\tan\eta_l$ so that from the condition (43) we have

$$\tan\eta_l=I^t+a/k. \quad (46)$$

This is the technique of Kohn's method. Hulthèn's method differs in that, in place of the last of Eqs. (44) the condition

$$I^t=0 \quad (47)$$

is imposed, so

$$\tan\eta_l=a. \quad (48)$$

The practical disadvantage of this method is that Eq. (47) is quadratic, so that two solutions are found for a. To remove the ambiguity, recourse is had, for discrimination, to some further condition, as for example the integral equation

$$\sin\eta_l=-k\left[\int_0^{\infty} rj_l(kr)\left\{rU(r)f_l(kr)\pm\int_0^{\infty}\kappa_l(r,r')f_l(kr')r'dr'\right\}dr\right]. \quad (49)$$

These methods have been applied to the calculation of $\eta_0{}^{\pm}$ from (46) and (48) by Massey and Moiseiwitsch[11] using trial functions of the form first suggested by

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[8] P. M. Morse and W. P. Allis, Phys. Rev. 44, 269 (1933).

[9] M. J. Seaton, Proc. Phys. Soc. (London) (to be published).

[10] W. Kohn, Phys. Rev. 74, 1763 (1948).

[11] H. S. W. Massey and B. L. Moiseiwitsch, Proc. Roy. Soc. (London) **A205**, 483 (1951).

Huang,[12] namely,

$$f_0{}^t=\sin k_0r+(a+be^{-r/a_0})(1-e^{-r/a_0})\cos k_0r, \qquad (50)$$

involving one parameter in addition to a. Figure 1 illustrates the comparison between the phase shifts they obtained, using Hulthèn's method, with those calculated by numerical solution of Eqs. (35) by Morse and Allis.[8] The agreement is seen to be reasonably close, particularly for $\eta_0{}^-$. For this phase, both variational methods gave very nearly the same results, but for $\eta_0{}^+$ Kohn's method gave appreciably different results. It is significant that in this case the agreement with the exact calculations is less satisfactory. A useful guide to the accuracy of the variational results seems to be the comparison between the results given by the two methods. When they agree, both are probably nearly correct. When they disagree appreciably, available evidence indicates that the Hulthèn method is to be preferred, but much more evidence is required to confirm this.

Although the phase shifts given by the variational methods are correct to the second order, this is not necessarily true of the trial wave functions themselves. Nevertheless, for applications such as those described in the next section, they probably represent a good approximation. Table I gives a comparison of some trial functions for the case when exchange is neglected with exact numerical solutions. The agreement is encouraging.

Hardly any experimental data is available as yet about elastic scattering by atomic hydrogen (see, however, Sec. 11). Corresponding calculations for helium which may be subjected to test by comparison with experiment are described in Sec. 9.6. Inclusion of polarization effects in calculating elastic scattering cross sections is discussed in Sec. 11.

9.2 Collisions with Atomic Hydrogen—Excitation of the 2s Level

The application of the E.P.D.E. approximation to the excitation of the $2s$ level of atomic hydrogen involves the determination not only of the functions F_0 for motion of the incident electron in the exchange and potential field of the normal atom, but also those $\mathfrak{F}_n$ for motion of the scattered electron in the corresponding field of an atom in a $2s$ state. In view of the evidence that the Hulthèn and Kohn variational methods give good approximations to the functions F_0, Erskine and Massey[13] followed a similar procedure for the functions $\mathfrak{F}_n$. As for F_0 we may consider $\mathfrak{F}_n$ expanded in the form

$$\mathfrak{F}_n=r^{-1}\Sigma f_{n,l}(r)P_l(\cos\theta). \qquad (51)$$

The only functions $F_{n,l}$ which are appreciably distorted by the field of the excited atom are those with $l=0$ and 1, and of these the effect is much more pronounced for $l=0$. Erskine and Massey[13] therefore considered only the contribution to the inelastic cross section which arises from incident electrons of zero angular momentum. By checking against the exact numerical solutions for the functions $F_{n,0}$ when exchange distortion is neglected [K_{nn} just equal to 0 in (30)], they found that a trial function of the form (50) was not satisfactory for this case and was replaced by

$$f_{n,0}{}^t=(1+ce^{-r/a_0})\sin k_nr+a(1-e^{-r/a_0})\cos k_nr. \qquad (52)$$

The reason for the change from (50) to (52) is that the field of the excited atom has a much greater range than that of the normal atom and the phase shift ζ_0 which it produces in $f_{n,0}$ exceeds π within an energy range of importance in the calculation. The phase shift η_0 in the incident wave is always less than π.

The zero-order partial cross sections for excitation of the $2s$ level obtained in this way are given in Table II. As before, it is necessary, when exchange is allowed for, to calculate both symmetric and antisymmetric cross sections and take the weighted mean for excitation by an unpolarized electron beam.

Table III, Sec. 10.3 includes values calculated by various approximations (referred to in Table I as B, B.O., D.W., and E.P.D.E.). Comparison of the B. and D.W. results in which exchange is neglected, would suggest at first sight that potential distortion is not very important, but the similarity of the values given in columns 2 and 3 of the table is illusory. The corresponding amplitudes are actually of opposite sign. This is reflected in the fact that whereas the B.O. approximation gives much larger symmetrical than antisymmetrical cross sections, the E.P.D.E. gives exactly the opposite result.

Comparison with the maximum possible cross section $\pi/k_0{}^2$ allowed by the conservation limit shows that the B.O. antisymmetrical cross section actually exceeds this limit for $k_0a_0=1$, but the E.P.D.E. values always

TABLE II. Comparison of wave functions $f_0(kr)$ for scattering of electrons by hydrogen atoms, as calculated by accurate numerical integration and by Hulthèn variational method (exchange has been neglected throughout).

	$ka_0=0.2$		$ka_0=1.0$	
r/a_0	Numerical integration	Variational method	Numerical integration	Variational method
0.2	+0.309	0.309	+0.425	+0.421
0.4	+0.517	0.519	+0.695	+0.701
0.6	+0.658	0.664	+0.849	+0.864
0.8	+0.755	0.764	+0.913	+0.933
1.0	+0.823	0.834	+0.908	+0.926
2	+0.968	0.977	+0.238	+0.227
3	+0.998	1.000	−0.691	−0.703
4	+0.979	0.981	−0.981	−0.985
5	+0.920	0.921	−0.369	−0.370
6	+0.824	0.825	+0.583	−0.582
7	+0.695	0.696	+0.999	−0.999
8	+0.538	0.539	+0.496	+0.498
9	+0.360	0.361	−0.463	−0.461
10	+0.168	0.169	−0.996	−0.996

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[12] S. S. Huang, Phys. Rev. **76**, 1878 (1949).

[13] G. A. Erskine and H. S. W. Massey, Proc. Roy. Soc. (London) **212**, 521 (1952).

remain below the limit. However, even the E.P.D.E. symmetrical value is as large as 0.7 of the maximum for $k_0a_0=1$, suggesting that the coupling is not really weak under these conditions.

Bransden and McKie[14] have calculated the C.C. approximation for this case by numerical solution of the coupled differential equations. These results are also included in Table II. It will be seen that they agree quite well with the D.W. results which shows that at any rate the potential coupling U_{0n} can be treated as weak. The E.C.C. approximation has not yet been worked out, but would be of much interest (see, however, Sec. 9.6). Again there is no experimental evidence against which to check the calculations.

9.3 Collisions with Atomic Hydrogen—Excitation of the 2*p* States

The calculation of the distorted wave approximations for excitation of the $2p$ state is rendered difficult by the angular dependence of the p wave functions. The problem has been formulated by Khashaba and Massey.[15] The wave function representing the motion of the scattered electron in the field of an atom in a $2p$ state may be expanded in harmonics (which are no longer exclusively zonal), but the radial functions in this expansion are now solutions of coupled integro-differential equations. By making certain approximations about the coupling terms, preliminary numerical results have been obtained which reveal the great importance of distortion in reducing very much the contribution to the cross section from incident electrons of zero angular momentum. This is important in determining the polarization of the radiation emitted by $2p$ hydrogen atoms excited by electron impact at energies near the threshold.

9.4 Possible Close Coupling between Orbitally Degenerate States

The available evidence seems to indicate that the excitation of the $2s$ and $2p$ states of hydrogen can be treated with reasonable adequacy by the distorted wave method, but there is one further aspect which must be considered. The $2s$ and $2p$ states have been treated independently, but they have the same energy and therefore may be closely coupled in the following sense. Referring to the distorted wave formula (32) it has been assumed in the calculations reported above that the function $\mathfrak{F}_n$ refers to the motion of the scattered electron in the field of a $2s$ or $2p$ atom, respectively. The orbital degeneracy suggests that it must be replaced essentially by more complicated functions which are the solutions of coupled equations involving the $2s$ and $2p$ but not the $1s$ states. Calculations are at present in progress to check this point. A rather similar situation arises in the excitation of atomic oxygen, but here the coupling is essentially between the three terms of the ground configuration, so that the complication refers to the function equivalent to F_0 in (32) (see Sec. 10.3).

9.5 Excitation of the 2*s* State of He$^+$

Bransden and Dalgarno[16] have calculated cross sections for excitation of the $2s$ level of He$^+$ by a method essentially similar to that used by Erskine and Massey for H. The additional complication is the Coulomb field of the ion which complicates the choice of trial functions corresponding to (50), (52).

They find that the coupling is considerably weaker in this case than for hydrogen so that the distorted wave method is almost certainly reliable, apart from any complication due to orbital degeneracy.

9.6 Collisions with Helium

The distorted wave method has been applied by Moiseiwitsch[17] to the elastic scattering and by Massey and Moiseiwitsch[18] to inelastic collisions involving the excitation of the 2^1S and 2^3S levels. Further work is in progress on the excitation of the corresponding P levels. In addition, Marriott[19] has carried out an extensive investigation of the superelastic collisions with 2^1S helium atoms leading to deactivation to the 2^3S level. The evidence obtained from the results is that for collisions in which the helium atom is initially in its ground state, the distorted wave method appears adequate, but there is a possibility that close coupling, through exchange, between the 2^1S and 2^3S levels may have to be taken into account in obtaining the distorted wave functions for substitution in the appropriate extension of (32).

For this three electron problem the appropriate form of the collision wave function Ψ is a little different from (22). Distinguishing the three electrons by the suffices 1, 2, 3, and considering the case of the elastic scattering and excitation of the $2S$ levels, we begin from the function

$$\begin{aligned}\Psi(1,2;3)= \textstyle\sum_{\text{cyclic}} \{&\psi_0(r_1,r_2)F_0(\mathbf{r}_3)\chi^-(12;3)\\ &+\psi_1(r_1,r_2)F_1(\mathbf{r}_3)\chi^-(1,2;3)\\ &+\psi_3(r_1,r_2)F_3(\mathbf{r}_3)\chi^+(12;3)],\end{aligned} \tag{53}$$

where ψ_0, ψ_1, and ψ_3 are, respectively, the wave functions for the 1^1S, 2^1S, and 2^3S states of helium. χ^- and χ^+ are doublet spin wave functions given by

$$\begin{aligned}\chi^-(1,2;3)&=\frac{1}{\sqrt{2}}(\alpha_1\beta_2-\alpha_2\beta_1)\alpha_3,\\ \chi^+(1,2;3)&=\frac{1}{\sqrt{6}}\{(\alpha_1\beta_2+\alpha_2\beta_1)\alpha_1-2\alpha_1\alpha_2\beta_3\},\end{aligned} \tag{54}$$

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[14] B. H. Bransden and A. McKie, Proc. Phys. Soc. (London) (to be published).

[15] S. Khashaba and H. S. W. Massey, Proc. Roy. Soc. (London) (to be published).

[16] B. H. Bransden and A. Dalgarno, Proc. Phys. Soc. (London) (to be published).

[17] B. L. Moiseiwitsch, Proc. Roy. Soc. (London) **A219**, 102 (1953).

[18] H. S. W. Massey and B. L. Moiseiwitsch, Proc. Roy. Soc. (London) **A227**, 38 (1954).

[19] R. Marriott, Proc. Phys. Soc. (London) (to be published).

where α and β are the usual one-electron spin functions. The function (53) represents a doublet state and satisfies the Pauli principle. It is similar to the resonating group structure wave functions used in nuclear physics.

On substitution in the wave function and use of the properties of the functions ψ_0, ψ_1, and ψ_3, we obtain coupled integro-differential equations for F_0, F_1, and F_3. Some extra care is needed in obtaining meaningful results, because ψ_0, ψ_1, and ψ_3 are only known approximately. Massey and Moiseiwitsch obtained the equations

$$\begin{aligned}[\nabla_3^2+k_i^2-U_{ii}]F_i(\mathbf{r}_3) &- \int\int F_i(\mathbf{r}_1)K_{ii}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)d\mathbf{r}_1d\mathbf{r}_2 \\ &= \sum_{j,k}\left\{\alpha_{ij}\int\int F_j(\mathbf{r}_1)K_{ij}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)d\mathbf{r}_1d\mathbf{r}_2 + U_{ij}F_j(\mathbf{r}_3)\right\}, \quad i, j, k=0, 1, 3 \end{aligned} \tag{55}$$

where

$$U_{ij}=\frac{2me^2}{\hbar^2}\int\int\psi_i^*(r_1,r_2)\left(-\frac{2}{r_3}+\frac{1}{r_{13}}+\frac{1}{r_{23}}\right)\psi_j(r_1,r_2)d\mathbf{r}_{,1}d\mathbf{r}_2$$

$$\begin{aligned}K_{ij}=\Bigg[&\psi_j(r_2,r_3)\nabla_1^2\psi_i^*(r_1,r_2) \\ &+\psi_i^*(r_1,r_2)\nabla_2^2\psi_j(r_1,r_2)+\psi_i^*(r_1,r_2)\nabla_3^2\psi_j(r_2,r_3) \\ &+\frac{2me^2}{\hbar^2}\left(\frac{2}{r_1}+\frac{2}{r_2}+\frac{2}{r_3}-\frac{1}{r_{12}}-\frac{1}{r_{13}}-\frac{1}{r_{23}}+E\right) \\ &\times\psi_i^*(r_1,r_2)\psi_j(r_2,r_3)\Bigg].\end{aligned} \tag{56}$$

k_0, k_1, and k_2 are the wave numbers of the incident electron and of the electron scattered after exciting the 2^1S and 2^3S states, respectively. $\alpha_{01}=1$, $\alpha_{03}=\alpha_{13}=-\sqrt{3}$. From symmetry considerations it is clear that $U_{03}=U_{13}=0$.

The distorted wave approximation now proceeds as before. If U_{01}, K_{01}, K_{03}, and K_{13} are all treated as small, but not U_{00}, U_{11}, U_{33}, K_{00}, K_{11}, and K_{33}, the scattered amplitudes $f_1(\theta)$ and $f_3(\theta)$ for excitation to the 2^1S and 2^3S states, corresponding to (32) are given by

$$\begin{aligned}f_j(\theta)=-\frac{1}{4\pi}\int\mathfrak{F}_j(r,\pi-\Theta)\Bigg[&U_{ji}F_i(r,\theta) \\ &+\alpha_{ji}\int\int K_{ji}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r})F_i(r_1,\theta_1)d\mathbf{r}_1d\mathbf{r}_2\Bigg]d\mathbf{r}, \\ &\qquad i=0 \\ &\qquad j=1 \text{ or } 3\end{aligned} \tag{57}$$

where $\mathfrak{F}_j$ is the solution, normalized as (18), of (55) in which $i=1$ or 3 is appropriate and the right-hand side is taken as zero. F_0 is the similar solution with $i=0$. Before describing the results of the calculation it is important to note that the most serious neglect is probably that of K_{13}, because this is a coupling between states of nearly equal energy. This is a similar situation to that arising from orbital degeneracy in hydrogen (see Sec. 9.4). Evidence that the coupling between the 2^1S and 2^3S is quite strong is provided by the calculations referred to below of the cross sections for excitation of the 2^1S–2^3S transition. To take it into account, the functions $\mathfrak{F}_1$ and $\mathfrak{F}_3$ should be obtained from the appropriate form of (55) with all terms neglected on the right-hand side except that involving K_{13}. The increased complication is obvious, but it may eventually have to be included.

The only large contribution to the elastic scattering of electrons with energy less than 20 ev comes from incident electrons of zero angular momentum. The elastic scattering of these electrons was calculated by Moiseiwitsch using the same variational methods and a trial wave function of the same form as (50). His results agree quite well with those obtained by Allis and Morse[8] who solved the integro-differential equation for F_0 by numerical methods. Comparison with experiment reveals quite good agreement, as far as the total elastic cross section is concerned, down to quite low electron energies. Even for thermal electrons, it is not too unsatisfactory. The calculated low-energy limit of the cross section is 8.6 πa_0^2, while that observed[20] for thermal electrons is 6.1 πa_0^2. To indicate the importance of exchange distortion at low energies it is to be noted that if K_{00} is neglected, the calculated values rise to 79 πa_0^2, far above the observed value.

The detailed calculations for excitation of the 2^1S and 2^3S states employed these variationally determined functions F_0. $\mathfrak{F}_1$ and $\mathfrak{F}_2$ were determined in a similar manner to the corresponding functions $\mathfrak{F}_1^{\pm}$ for hydrogen. In particular, distortion of the partial waves in the expansion (51) was neglected except for the s wave ($l=0$). This neglect is a little more serious than for hydrogen as there is appreciable distortion also of the final waves with $l=1$. It is still true, however, that the effect of distortion is very much more important for the s scattering.

Figure 2 illustrates the results obtained for excitation of the 2^3S level. The great reduction in the cross section due to incident waves with $l=0$ below that given by the Born-Oppenheimer approximation is obvious. Available experimental evidence[21] indicates that the absolute magnitude of the calculated E.P.D.E. approximation is not far from correct. Except near the threshold, this approximation gives results which differ very little from the P.D.E. A remarkable effect

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[20] Phelps, Fundingsland, and Brown, Phys. Rev. **84**, 559 (1951).

[21] R. Dorrestein, Physica **9**, 447 (1942); H. Maier-Leibniz, Z. Physik **95**, 499 (1935).

is noted, however, near the threshold in that the E.P.D.E. curve exhibits a very sharp peak there, absent from the P.D.E. results. This peak arises because of a near resonance effect in the distortion of the $\mathfrak{F}_3$ wave. When exchange as well as potential distortion is allowed for, the phase shift $\zeta_0{}^3$ produced in the $l=0$ component of $\mathfrak{F}_3$, although tending to π in the limit $k_3 \to 0$, remains close to $3\pi/2$ until k_3 becomes very small indeed, i.e.

$$\lim_{k_3\to 0} \zeta_0{}^3/k_3$$

is large (see Fig. 3). The resonance case arises when the limit tends actually to ∞, $\zeta_0{}^3 \to 3\pi/2$, and in this case the cross section would tend to a finite limit at the threshold, instead of vanishing as k_3. The sharp peak is an indication of an approach to these conditions. In the P.D.E. case

$$\lim_{k_3\to 0} \zeta_0{}^3/k$$

is much smaller and there is no appearance of near-resonance effects.

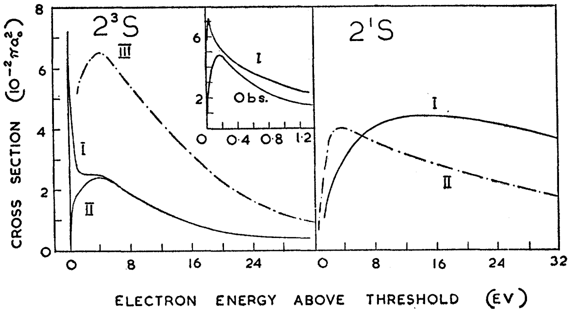

FIG. 2. Cross sections for excitation of the 2^3S and 2^1S states of helium by electron impact. I. E.P.D.E. approximation. II. P.D.E. approximation. III. B.O. approximation $\times 1/20$. *Inset* (I) E.P.D.E. approximation (2^3S) (b) Observed—Maier-Leibniz (2^3S).

It is hardly to be expected that the theory is of such accuracy as to be able to predict correctly the distortion for very small k_3. In this case, however, there is some evidence from the experiments of Maier-Leibniz[21] that a sharp peak near the threshold does occur (see insert of Fig. 2). Whether or not this is confirmed by further experiment, there seems little doubt that, for the excitation of some states of some atoms, near-resonance effects will arise near the threshold.

The results obtained for excitation of the 2^1S level are illustrated in Fig. 2. In this case even the E.P.D.E. approximation gives no approach to resonance near the threshold,[22] the behavior of the phase shift for the $l=0$ component of $\mathfrak{F}_1$ being as illustrated in Fig. 3.

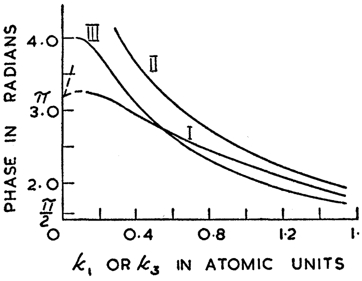

FIG. 3. Zero-order phase shifts for motion of electrons in the field of an excited helium atom as calculated by variational methods. I. Atom in either a 2^1S or 2^3S state (exchange neglected). II. Atom in a 2^1S state (exchange included). III. Atom in a 2^3S state (exchange included). ---- behavior near zero energy limit.

Mariott[19] has calculated the cross section for the superelastic collision 2^1S-2^3S by using Eq. (55) with all terms involving F_0 absent.[3] He finds that the coupling in this case is strong—for incident energies <2 ev the distorted wave method gives results for deactivation by s electrons which are substantially greater than the allowed minimum $\pi/k_1{}^2$. Because of this Marriott undertook the lengthy task of solving numerically the coupled integro-differential equations for F_1 and F_3. The results he obtained will be discussed in Sec. 10.3.

9.7 Collisions with Other Atoms

For complex atoms the distortion effects will be very complicated, and it is to be expected that the cross sections for excitation of different levels will exhibit very irregular variation with electron energy near the threshold. This has been found by Jongerius and Smit[23] in their recent experiments on the excitation of mercury. Thus Fig. 4 illustrates some of their results. In terms of phase shifts, whereas for excitation of the lower states of hydrogen and helium the phase shifts which measure the degree of distortion do not exceed π appreciably and then only for the s waves, for complex atoms the phase shifts even for p and d waves may be much greater, so that the matrix elements appearing in the distorted wave formula corresponding to (32) will vary rapidly with the final electron wave number.

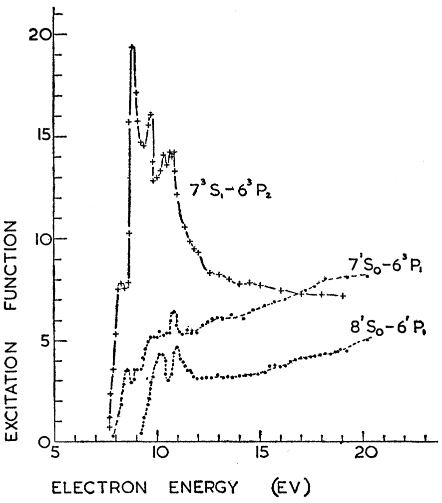

FIG. 4. Cross sections for electron impact excitation of certain mercury lines as observed by Jongerius and Smit.

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[22] The close coupling between the 2^1S and 2^3S states, which is not allowed for in the E.P.D.E. approximation may, however, lead to a near resonance situation for 2^1S also.

[23] H. Jongerius and A. Smit, Physica (to be published).

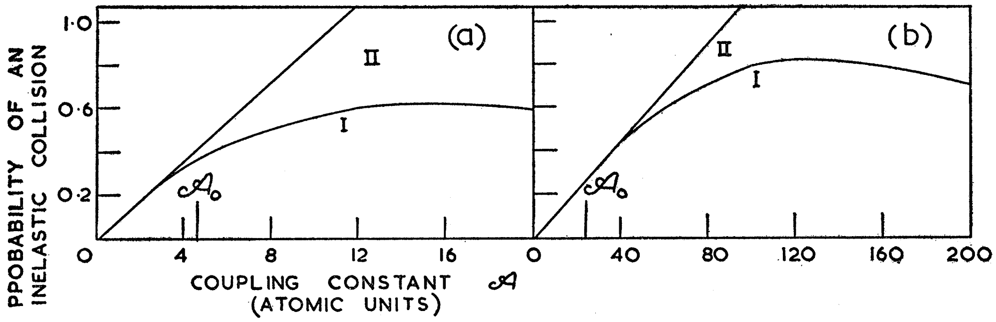

FIG. 5. Probability of excitation in the schematic model as a function of $\mathcal{A}=9A^2/(r_0r_1)^3$. Curves I—exact calculation. Curves II—E.P.D.E. approximation. (a) Distortion approximately as in hydrogen. (b) Distortion approximately as in helium. In each case $\mathcal{A}_i$ indicates approximately the order of the actual coupling.

The effect of distortion in inelastic collisions with complex atoms is also manifest from the complicated oscillations observed in the angular distribution[24] at large angles of electrons scattered after exciting the resonance levels of atoms such as argon and mercury. It was confirmed some years ago by detailed calculations for neon and argon[25] that this was indeed a consequence of the distorted wave formula.

Detailed calculations by the distorted wave method have been carried out mainly for excitation of the transitions between the terms of the lowest configurations, including particularly O^{++}, O^{+}, and O. As in these cases close coupling occurs for excitation by p electrons, we shall consider them in the next section.

10. CALCULATIONS INVOLVING CLOSE COUPLING

10.1 Schematic Model

It is possible to obtain information about the way the distorted wave method breaks down when close coupling, through exchange, prevails, by considering a schematic model similar to one introduced by Morse and Allis[26] for studying the effect of exchange on elastic scattering. Thus Massey and Mohr[27] studied the schematic equations

$$\begin{aligned} f_0''+(k_0^2-U_{00})f_0&=\int K(r,r^1)f_1(r^1)dr^1,\\ f_1''+(k_1^2-U_{11})f_1&=\int K(r,r^1)f_0(r^1)dr^1, \end{aligned} \tag{58}$$

where

$$\begin{aligned} U_{00}&=-C_0, \quad r<r_0, \qquad U_{11}=-C_1, \quad r<r_1,\\ &=0, \qquad r>r_0, \qquad\quad =0, \qquad r>r_1, \end{aligned} \tag{59}$$

$$K=\frac{6me^2}{\hbar^2}\frac{Arr^1}{(r_0^3r_1^3)^{\frac{1}{2}}}\,r<r_0,\ r^1<r_1;\ =0 \text{ otherwise.} \tag{60}$$

The kernel K can be regarded as arising from a three-dimensional kernel proportional to $Ae^2/|\mathbf{r}-\mathbf{r}^1|$. There is no difficulty in solving these equations so that the probability of an elastic collision involving a change of electron wave number from k_0 to k_1 may be calculated as a function of the coupling constant A for any given k_0.

The probability may be defined as the ratio of the cross section to the maximum possible, π/k_0^2. The distorted wave approximation naturally gives a probability proportional to A^2. Figure 5 shows how the exact probability, in this schematic model, behaves when the distorted wave approximation gives results which are too great. It seems that when this is so, the trial cross section remains quite close to the maximum even for very strong coupling. This is a useful guide, but not to be relied upon to represent all possible situations which may arise.

10.2 Methods for Dealing with Close Coupling Situations

The methods at present available may be summarized as follows: (a) direct numerical solution of coupled integral-differential equations; (b) variational methods; (c) approximations based on the assumption of exact resonance.

Little need be said about the first method. The solution by hand computation of such complicated equations is only just within the bounds of practical possibility, but the availability of electronic computers offers opportunities of carrying out many calculations of this kind.

Variational methods for dealing with two coupled equations may be obtained by fairly obvious extensions of the methods used for dealing with elastic scattering. The coupled equations involved may be written in the form

$$L_{00}f_0=L_{01}f_1, \tag{61}$$

$$L_{11}f_1=L_{10}f_0, \tag{62}$$

where

$$\begin{aligned} L_{00}f_0&=f_0''+(k_0^2-U_{00})f_0+\int K_{00}(r',r)f_0(r')dr',\\ L_{11}f_1&=f_1''+(k_1^2-U_{11})f_1+\int K_{11}(r',r)f_1(r')dr', \qquad (63)\\ L_{01}f_1&=U_{01}f_1+\int K_{01}(r',r)f_1(r')dr'. \end{aligned}$$

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[24] C. B. O. Mohr and F. H. Nicoll, Proc. Roy. Soc. (London) **A138**, 229, 469 (1932); **A142**, 360, 647 (1933).

[25] H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. (London) **A146**, 880 (1933).

[26] P. M. Morse and W. P. Allis, Phys. Rev. 44, 269 (1933).

[27] H. S. W. Massey and C. B. O. Mohr, Proc. Phys. Soc. (London) **A65**, 845 (1952).

In general, $U_{01}=U_{10}^*$, $K_{01}=K_{10}^*$, but for simplicity we shall take all the interaction operators as real. We require solutions which have the asymptotic forms for large r

$$\begin{aligned} f_0 &\sim \sin k_0 r+\alpha e^{ik_0 r}, \\ f_1 &\sim \beta e^{ik_1 r} \end{aligned} \tag{64}$$

so that the partial cross section for excitation is $4\pi(k_1/k_0)|\beta|^2/|1-i\alpha|^2$. Moiseiwitsch[28] bases his variational method on the integral

$$I=\int_0^\infty [f_1^*(L_{00}f_0-L_{01}f_1)+f_0^*(L_{11}f_1-L_{10}f_0)]dr. \tag{65}$$

Trial functions f_0^t, f_1^t are now introduced which vanish at $r=0$, have the asymptotic forms (64) but with α_t and β_t not necessarily equal to the correct α and β. These functions will also normally include n adjustable parameters $c_1, \cdots, c_n$. Optimized values for α_t, β_t, $c_1, \cdots, c_n$ are then obtained from the equations

$$I^t=0, \quad \frac{\partial I^t}{\partial\beta_t}+2i\frac{k_1}{k_0}\beta_t^*\frac{\partial I^t}{\partial\alpha_t}=0, \quad \frac{\partial I^t}{\partial c_r}=0, \quad r=1, \cdots n. \tag{66}$$

The values of α_t, β_t obtained in this way may be improved as approximations to the true α and β by imposing a further condition which would be exactly satisfied by the time solutions. Moiseiwitsch does this by introducing the further integral

$$I'=\int_0^\infty [f_1(L_{00}f_0-L_{01}f_1)+f_0(L_{11}f_1-L_{10}f_0)]dr. \tag{67}$$

from which the improved value β_t' for β becomes

$$\beta_t'=\beta_t-I^{t\prime}/k_0. \tag{68}$$

This method has the advantage that it automatically ensures that the results obtained for α and β satisfy the conservation requirements, namely,

$$\operatorname{Im}\alpha=|\beta|^2 k_1/k_0. \tag{69}$$

In practice it is rather tedious to apply, as it involves operations with complex numbers. Alternative methods may be developed which work in terms of real numbers only. These depend essentially on the fact that the asymptotic behavior of the solutions of (61, 62) which vanish at the origin may be expressed in terms of two phase shifts η and ζ and a mixing parameter λ so that

$$\begin{aligned} f_0 &\sim A\sin(k_0r+\eta)+B\sin(k_0r+\zeta), \\ f_1 &\sim \frac{k_0}{k_1}\left\{A\lambda\sin(k_1r+\eta)-B\lambda^{-1}\frac{k_1}{k_0}\sin(k_1r+\zeta)\right\} \end{aligned} \tag{70}$$

and the partial cross section for excitation is given by

$$4\pi\frac{k_1}{k_0}\left(\frac{\lambda}{k_1+k_0\lambda^2}\right)^2\sin^2(\eta-\zeta). \tag{71}$$

A variational principle for determining η, ζ, and λ in any given case has been given by Rubinow[29] and by Blatt and Biedenharn.[30] Although these avoid operations with complex numbers, they are complicated to use in practice. Kohn has given a relatively simple principle for determining the proper phases η and ζ, but this method does not provide a corresponding principle from which to obtain λ.

The Schwinger variational principle may also be employed, but it is rather inflexible as to choice of trial function and even with the simplest functions is complicated to work out. It will be considered in more detail in its more general form in Sec. 11 in connection with allowance for intermediate states for which it is much more suitable.

The third method has been employed very successfully by Seaton[4] for the calculation of cross sections for excitation of transitions within the ground p^2, p^3, or p^4 configurations of ions and atoms. It is based on the fact that if $k_0^2=k_1^2$, $U_{00}=U_{11}$, and $K_{00}=K_{11}$ Eqs. (61) and (62) may be uncoupled by the substitution $g^+=f_0+f_1$, $g^-=f_0-f_1$, so that

$$(L_{00}\pm L_{01})g^\pm=0. \tag{72}$$

If solutions of these uncoupled equations are obtained which have asymptotic form

$$g^\pm\sim\sin(k_0r+\eta^\pm) \tag{73}$$

then the partial cross sections q_{00}, q_{01}, for elastic scattering and for excitation, respectively, are given by

$$q_{00}=\frac{\pi}{k_0^2}\{2\sin^2\eta^++2\sin^2\eta^--\sin^2(\eta^+-\eta^-)\}, \tag{74}$$

$$q_{01}=\frac{\pi}{k_0^2}\sin^2(\eta^+-\eta^-). \tag{75}$$

This may be generalized to cases in which three or more coupled equations are involved. Seaton found that, in formulating the problem of the collisions of electrons with the ions or atoms concerned, the three coupled equations for the functions F_0, F_1, F_2 of the colliding electron associated with the ion or atom in each of the respective terms arising from the ground configuration, could be uncoupled if certain relatively small exchange terms were consistently neglected, so that the energy differences between the terms vanished. The solutions of these uncoupled equations could then be used to oftain very good first approximations on which to base

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[28] B. L. Moiseiwitsch, Phys. Rev. **82**, 753 (1951).

[29] S. I. Rubinow, Phys. Rev. **98**, 183 (1955).

[30] J. Blatt and S. Biedenharn, Revs. Modern Phys. **24**, 258 (1952).

TABLE III. Comparison of cross sections for excitation of the 2*s* state of hydrogen by electrons of zero angular momentum, calculated by different approximations.[a]

Wave number of incident electrons (k_0) (atomic units)	Energy of incident electrons (ev)	Theoretical maximum ($1/k_0^2$)	Cross sections in units πa_0^2									
			Exchange neglected			Exchange included						
						Sym.		Antisym.		Mean	
			Born	D.W.	C.C.	B.O.	E.P.D.E.	B.O.	E.P.D.E.	B.O.	E.P.D.E.
0.866	10.2	···	0	0	0	0	0	0	0	0	0
1.0	13.5	1.00	0.198	0.239	0.204	0.287	0.711	2.02	0.0316	1.59	0.178
1.2	19.4	0.694	0.127	0.118	0.102	0.011	0.344	0.668	0.010	0.503	0.094
1.5	30.4	0.444	0.0585	0.045	0.045	0.014	0.127	0.134	0.010	0.104	0.035
2.0	54	0.250	0.0194	0.014	0.0155	0.018	0.0255	0.0205	0.006	0.020	0.011

[a] Column E refers to results obtained by an accurate numerical integration for the case when exchange is neglected.

a rapidly convergent series of approximations to the exact solution of the coupled equations.

10.3 Close Coupling Problems Which have been Investigated

The only case at present involving exchange coupling which has been dealt with by direct numerical solution is that of the transition 2^1S-2^3S in helium already referred to in Sec. 9.6 above. The final results for the cross section, obtained by Marriott,[19] do not differ by much more than the experimental error from the mean values for electrons of nearly thermal energies obtained by Phelps and Molnar[31] from an experimental study of the decay of 2^1S metastable helium concentration in a discharge afterglow. Bransden and McKie[14] have solved the equations for the 1*s*–2*s* excitation in hydrogen, neglecting exchange coupling. Their results are given in Table III and have been discussed in Sec. 9.2. The extension of this work to include exchange coupling is in progress.

Very few calculations involving variational methods have yet been carried out. Massey and Moiseiwitsch[32] have applied the method proposed by Moiseiwitsch[33] to the excitation of the 1*s*–2*s* transition in hydrogen. Because of the complexity of the calculation they used very simple trial functions

$$\begin{aligned} f_0{}^t &= \sin k_0r + (\alpha + be^{-r/a_0})(1-e^{-r/a_0})\cos k_0r, \\ f_1{}^t &= (1-e^{-r/a_0})\beta e^{ik_1r}. \end{aligned} \tag{76}$$

These functions are not very satisfactory as they do not allow for any mixing of the incident and final waves, a neglect which is likely to be serious in close coupling situations. Their final results differ appreciably from those given by the E.P.D.E. method, but are probably unreliable for the reasons stated. This is supported by the fact that when exchange is neglected the exact numerical solutions by Bransden and McKie[14] agree with the distorted wave and not with the variational method. It is clearly necessary to carry out exploratory calculations for simplified equations which may be solved exactly in order to determine which variational methods give the best results and what forms are most suitable to assume for the trial functions. Calculations on these lines are being carried out by Huck.

The third method based on the exact resonance equations has been applied by Seaton[4] in an extensive investigation directed towards obtaining cross-section data for astrophysical and geophysical applications. The coupling is very strong for transitions between levels within the ground configuration when the continuum transition is one of the *p*-*p* type. Thus calculations[34] carried out for the excitation of the $^3P-^1S$ and $^3P-^1D$ transitions in atomic oxygen, using the P.D.E. method give results exceeding the maximum possible by factors of 66 and 89, respectively! This factor decreases rapidly in proceeding[35,36] to O^+ and O^{++}, but even for the latter the factor is about 2. Seaton calculated the cross sections for excitation by *p* electrons using Hartree-Fock self-consistent field wave functions for the atoms and ions and a resonating group formulation for the collision wave functions which amounts essentially to extension of the Hartree-Fock method to include continuum states. Some check on the accuracy of the continuum wave functions which he uses is afforded by a relation between the low velocity limit of the phase shift to the high series limit of the quantum defect for the corresponding series of bound states. This check, which is far from complete, and has only been carried out for O^{++}, nevertheless suggests that the continuum wave functions are not seriously in error.

Contributions[37] from incident electrons with angular momentum quantum numbers different from 1 could be calculated by the E.P.D.E., or often simply by the P.D.E. method, the coupling being no longer strong and exchange effects relatively weak.

Seaton[38] has applied the results of his calculations, particularly for O^+, O^{++}, N^+, and N^{++}, to the determination of the temperatures and electron concentrations in gaseous nebulae. He has also used the results for O

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[31] A. V. Phelps, Phys. Rev. **99**, 1307 (1955).

[32] H. S. W. Massey and B. L. Moiseiwitsch, Proc. Phys. Soc. (London) **A66**, 406 (1953).

[33] B. L. Moiseiwitsch, Phys. Rev. **82**, 753 (1951).

[34] Yamanouchi, Inui, and Amemiya, Proc. Phys. Math. Soc. Japan **22**, 847 (1940).

[35] L. H. Aller (private communication).

[36] M. H. Held and D. H. Menzel, Astrophys. J. **92**, 408 (1940).

[37] M. J. Seaton, Proc. Roy. Soc. (London) **A218**, 400 (1953); **231**, 37 (1955).

[38] M. J. Seaton, Monthly Notices Roy. Astron. Soc. **114**, 154 (1954).

in a discussion of airglow and auroral excitation. Percival and Seaton[39] have also considered certain aspects of the latter which depend on the cross sections for excitation of the $(2p)^3 3p^5P$ and $(2p)^3 3p^3P$ states of O from the ground state. The E.P.D.E. method is suitable for calculating these provided the distortion of the incident p wave allows for the close coupling between the terms of the ground configuration. Percival[40] included this by using the appropriate exact resonance solution of the coupled equations. To the accuracy of the remainder of the calculation this was adequate. The main uncertainty arises from the difficulty of obtaining accurate p orbitals for the excited ^3P terms which are orthogonal to those of the ground ^3P term.

10.4 Close Coupling in Optically Allowed Transitions

The close coupling situations already discussed arise from transitions within a configuration, which are therefore optically forbidden. Although the corresponding cross sections are often large near the threshold, optically allowed transitions are usually the strongest at higher energies. There is evidence from comparison of observed data for these transitions with results obtained by Born's approximation that, while the latter begins to overestimate the cross section at electron energies several times the threshold, it is not grossly in error even quite close to the threshold. In most cases it seems likely that the error arises from the neglect of small contributions from many intermediate states rather than from close coupling in the sense in which we are using the term. However, Seaton[41] has found that there are some cases in which close coupling is important.

In optically allowed transitions, major contributions to interaction between the atom and incident electron come from such large distances that distortion is unimportant, and the closeness of the coupling may be tested by calculating the partial cross sections for incident electrons of given angular momentum using Born's approximation. If the resulting values exceed the maximum allowed for that angular momentum, close coupling certainly prevails. For the excitation of the upper states of the sodium D lines (requiring 2.10 ev), close coupling occurs for electrons with quite high angular momentum. Thus for 30-volt electrons it occurs for $l \leq 6$ and for 3 volt electrons for $l \leq 3$. Seaton has made a rough correction to the excitation cross sections calculated for Born's approximation by replacing all the partial cross sections in this approximation, which are greater than the allowed maximum, by a mean value equal to half the appropriate maximum, leaving the others unaltered. As seen in Fig. 6, this already effects quite a marked improvement in comparison with observation.

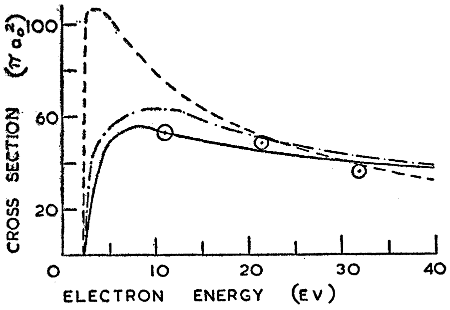

FIG. 6. Comparison of observed and calculated cross sections for excitation of the D lines of sodium by electron impact. ——— Observed [W. Christoph, Ann. Physik **23**, 51 (1935); G. Haft, Z. Physik **82**, 73 (1933)]. — — — Calculated by Born's approximation. —·—·— Calculated by Seaton by making approximate allowance for close coupling for small incident angular momenta.

Another case in which strong coupling occurs, though to a less marked extent, is in the excitation of the $2s$-$2p$ transition in atomic hydrogen. For the $1s$–$2p$ excitation it does not seem to be important and the main errors arise from neglect of intermediate state effects.

11. CALCULATIONS ALLOWING FOR INTERMEDIATE STATES

The first calculations[42] which take into account contributions from intermediate states were carried out for the elastic scattering of electrons by hydrogen and helium atoms. In this work, Born's second approximation was evaluated by a method which neglected the excitation energy of the most significant excited states contributing to the polarization, in comparison with the incident energy. The results obtained were encouraging in that the calculated angular distribution of scattered electrons became steeper at small angles, in agreement with observation. Quite good agreement was in fact obtained for electron energies ranging from 200 ev down to 50 ev, for which the approximations involved were becoming serious.

A similar calculation has recently been carried out by Rothenstein[43] for the excitation of the $2p$ level of hydrogen and the 2^1P level of helium. Again he finds improved agreement with observation, the calculated cross section being reduced to an extent which increases as the electron energy decreases and which is of about the right magnitude for electron energies down to the limit for which the method is likely to give good results.

The Schwinger variation method may be used to extend the effectiveness of calculations based on Born's second approximation. If f_{B1}, f_{B2} are the scattered amplitudes according to the respective first and second Born approximations, Schwinger's method shows that

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[39] I. C. Percival and M. J. Seaton, J. Atmos. and Terrest. Phys. (to be published).

[40] I. C. Percival, Proc. Phys. Soc. (London) (to be published).

[41] M. J. Seaton, Proc. Phys. Soc. (London) **A68**, 457 (1955).

[42] H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. (London) **A146**, 880 (1930).

[43] M. Rothenstein, Proc. Phys. Soc. (London) **A68**, 173 (1955).

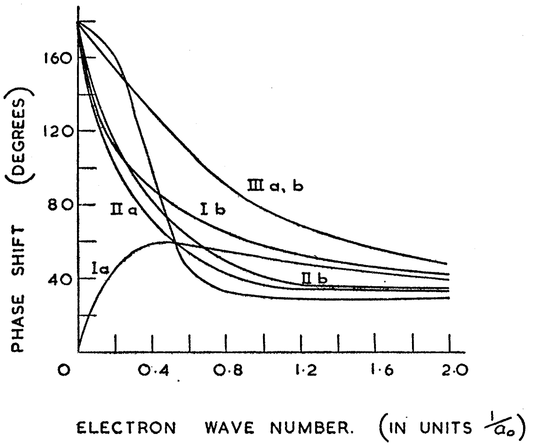

FIG. 7. Illustrating the effect of inclusion of a term depending on interelectronic separation on the zero-order phase shifts η_0 for elastic scattering of electrons by atomic hydrogen, as calculated by the Hulthèn variational method. Ia Exchange and polarization neglected. Ib Polarization included, exchange neglected. IIa Exchange included, polarization neglected (symmetrical case). IIb Exchange and polarization included (symmetrical case) IIIa Exchange included, polarization neglected (antisymmetrical case). IIIb Exchange and polarization included (antisymmetrical case).

the best approximation for the true scattered amplitude which may be obtained from f_{B1} and f_{B2} is

$$f=f_{B1}^2/(f_{B1}-f_{B2}),$$

exchange effects being neglected. Thus, for collisions of electrons of wave number k with hydrogen atoms, in which the direction of the electron motion is changed from that of the unit vector $\mathbf{n}_0$ to $\mathbf{n}$,

$$f_{B1}=-\frac{2me^2}{\hbar^2}\int\int|\psi_0(r_2)|^2\left(\frac{1}{r_{12}}-\frac{1}{r_1}\right)\times\exp[ik(\mathbf{n}_0-\mathbf{n})\cdot\mathbf{r}]d\mathbf{r}_1d\mathbf{r}_2,$$

$$f_{B2}=\frac{16m^2e^4}{\hbar^4}\int\int\int\int\exp(ik\mathbf{n}_0\cdot\mathbf{r}_1)\psi_0(r_2)\times\left(\frac{1}{r_{12}}-\frac{1}{r_1}\right)\left(\Sigma_n+\int\right)\left\{\frac{\exp[ik_r|\mathbf{r}_1-\mathbf{r}_1{}^1|]}{|\mathbf{r}_1-\mathbf{r}_1{}^1|}\times\psi_n(\mathbf{r}_2)\psi_n{}^*(\mathbf{r}_2{}^1)\right\}\left(\frac{1}{r_{12}{}^1}-\frac{1}{r_1{}^1}\right)\exp(ik_0\mathbf{n}_0\cdot\mathbf{r}_1{}^1)\times\psi_0(r_2{}^1)d\mathbf{r}_1d\mathbf{r}_2d\mathbf{r}_1{}^1d\mathbf{r}_2{}^1.$$

ψ_0, ψ_n are wave functions for the ground and nth excited states, respectively. Exchange may be allowed for by calculating an exchange amplitude in a similar way.

Newstein[44] has applied this method to the elastic scattering of electrons with energy less than 10 ev by atomic hydrogen. The angular distributions which he obtains are far from isotropic even for 3 ev electrons, but the total cross section is not very different from that calculated neglecting polarization.

An alternative approach to the problem is to use a slight extension of the Hulthèn and Kohn methods. Thus, as suggested by Huang,[12] it is possible to allow explicitly for dependence of the wave function describing the collision on the interelectronic separation in the trial function assumed. Thus, for discussing the collisions of slow electrons with hydrogen atoms, the trial function (50) is modified to

$$f_0{}^t=\sin k_0r_1+\{a+(b+cr_{12})e^{-r_1/a_0}\}(1-e^{-r_1/a_0})\cos k_0r_1$$

so that it depends on the interelectronic separation r_{12}.

Detailed calculations using this trial function have been carried out by Massey and Moiseiwitsch[45] and their results are given in Fig. 7 and Table IV. It will be seen from Fig. 7 that the presence of the r_{12} term has little effect on the antisymmetric phase $\eta_0{}^-$. This would be expected, for the antisymmetry of the wave function in this case reduces the importance of interelectronic repulsion. The effect on the symmetric phase $\eta_0{}^+$ is considerably greater.

Reference to Table IV shows that the effect of the polarization on the cross section is quite small except at electron energies below about 2 ev. This agrees with Newstein's results, except that the angular distribution is assumed to remain isotropic. There is unfortunately very little evidence about the actual magnitude of the elastic cross section for low-energy electrons. All that is available has been derived[46] by somewhat indirect methods from a study of arc discharges in hydrogen. This suggests that the true cross section is 2–3 times larger than calculated with allowance for exchange and polarization, but the position is still far from clear.

No calculations of polarization effects by variational methods have yet been carried out for elastic scattering by atoms other than hydrogen or for any inelastic

TABLE IV. Comparison of elastic cross sections for collisions of electrons with atomic hydrogen as calculated by different approximations.

	Cross sections in units $a_0{}^2$			
Electron wave number (in units $a_0{}^{-1}$)	Exchange and polarization neglected	Exchange neglected, polarization included	Exchange included, polarization neglected	Exchange and polarization included
0.1	548	592	193	168
0.15	334	396	160	138
0.2	214	268	121	112
0.3	106	137	75.9	77.6
0.4	59.6	78.5	53.0	55.0
0.5	37.6	49.0	38.9	41.3
0.6	25.4	32.5	29.1	30.2
0.8	13.2	16.3	17.0	17.5
1.0	7.76	9.20	10.3	10.5
1.2	4.93	5.67	6.42	6.55
1.5	2.78	3.10	3.44	3.54
2.0	1.29	1.39	1.48	1.55

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[44] M. C. Newstein, M.I.T. Technical Report 67, 763 (1954).

[45] H. S. W. Massey and B. L. Moiseiwitsch, Proc. Roy. Soc. (London) **A205**, 483 (1951).

[46] Maerler, Peters, and Schenk, Z. Physik **140**, 115 (1955).

collisions. Much remains to be done before the importance of polarization can be estimated with confidence.

12. SUMMARIZING REMARKS

Although there is insufficient evidence on which to base any very definite rules, it seems that for atomic collisions the two state approximation in which weak coupling is assumed is often quite satisfactory. In using it, however, full allowance must be made for distortion of the incident and final electron waves, not only by the mean potential field of the atom, but also by the exchange interaction. Otherwise, quite incorrect results may be obtained.

In some cases the coupling cannot be treated as weak. This often occurs for transitions between states of nearly the same energy such as terms arising from the same configuration. If there are more than two states of nearly equal energy, it will usually be necessary to regard them as all coupled together.

The importance of intermediate states is still not clear. Their effects seem to be mainly apparent in elastic scattering at small angles and in inelastic collisions involving optically allowed transitions. In the latter cases it seems that the effects, though apparent, are not very large and actually not as important as those due to distortion and exchange in low-energy encounters.

There is scope for much more examination of the range of usefulness of different approximations. With the steady development of techniques of calculation much progress should be achieved in this direction before too long.