PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

The Hartree-Fock Equations for Continuous States with Applications to Electron Excitation of the Ground Configuration Terms of O $_{\text{I}}$

M. J. Seaton

Phil. Trans. R. Soc. Lond. A 1953 **245**, 469-499
doi: 10.1098/rsta.1953.0004

THE HARTREE-FOCK EQUATIONS FOR CONTINUOUS STATES WITH APPLICATIONS TO ELECTRON EXCITATION OF THE GROUND CONFIGURATION TERMS OF O I

By M. J. SEATON
University College, London

(*Communicated by H. S. W. Massey, F.R.S.—Received* 5 *June* 1952—
Revised 28 *August* 1952)

CONTENTS

	PAGE
INTRODUCTION	470
PART I. THE HARTREE-FOCK EQUATIONS FOR CONTINUOUS STATES	471
1. Summary of the Hartree-Fock method for bound states	471
1·1. General formulation	471
1·2. Addition of an electron to an ion	472
1·3. Separation of spin and angular co-ordinates and introduction of angular momentum operators	473
2. Anti-symmetric wave functions for continuous states	474
2·1. Notation	475
2·2. Exact equations using an infinite expansion	475
2·3. Approximate equations: the use of an explicitly anti-symmetric expansion	476
2·4. Discussion of the equations	478
3. The use of Hartree-Fock core functions	478
3·1. Reduction of integrals	479
3·2. Comparison with Hartree-Fock equations for bound states	480
3·3. Separation of spin and angular co-ordinates and introduction of the total angular momenta	480
4. The radial equations for certain nl^qkl configurations	481
4·1. The $nsks$ configuration	481
4·2. np^2kp and np^4kp configurations	482
4·3. The exact resonance approximation	483
4·4. Solution of the coupled equations	484
4·5. Radial equations for $1s^2 2s^2 np^q kp$ configurations	485
PART II. ELECTRON EXCITATION OF THE GROUND CONFIGURATION TERMS OF O I	486
5. Expressions for electron excitation rates	486
5·1. General collision theory	486
5·2. Degenerate systems	486
5·3. Resolution into free-electron orbital angular momentum components	486
5·4. Resolution into total angular momentum interactions	487
5·5. The distorted wave Born-Oppenheimer approximation	488
6. Electron excitation of the ground configuration terms of O I	488
6·1. Wave functions and energies for O I	
6·2. Calculations using a modified D.W.B.O. approximation	489
6·3. The exact resonance approximation: wave functions	491
6·4. The exact resonance approximation: collision parameters	492
6·5. Solution of the coupled equations	495
6·6. Other contributions to the collision parameters	496
6·7. Summary	496
7. Elastic scattering of slow electron by O I	497
7·1. The s-wave	497
7·2. The p-wave, ^2P interaction	498
7·3. The p-wave, other interactions	498
7·4. Summary	499
References	499

Part I is concerned with the general theory of anti-symmetric wave functions for continuous states of atomic systems. For an $(N+1)$-electron system the complete wave function is expressed in terms of an expansion involving products of the N-electron core functions multiplied by free electron orbitals, the equations satisfied by the latter being obtained from the Schrödinger equation. It is shown that the only consistent means of obtaining anti-symmetric wave functions in approximate solutions is to make the expansion explicitly anti-symmetric. This procedure gives equations for the free-electron orbitals which are similar to bound-state Hartree-Fock equations. The further approximation of using Hartree-Fock wave functions for the core states is then discussed.

Certain nl^qkl configurations are analyzed in detail using a total angular momentum representation. It is shown that the equations may be uncoupled if the energy differences between the nl^q terms are neglected (exact resonance approximation), and that approximate solutions of the full coupled equations may be obtained in terms of the exact resonance solutions provided that a suitable normalization condition is used.

Part II is concerned with applications to electron excitation of the ground configuration terms of O I. Distorted wave approximations show that other effects are insignificant compared to the contribution from the p angular momentum component of the free orbitals, but give for this results which are too large by several orders of magnitude. The coupled equations for the p-wave are solved in an exact resonance approximation, with neglect of $1s$, $2s$ exchange interactions. At a check point an exact resonance solution including $1s$, $2s$ exchange terms is obtained, and finally a complete solution of the coupled equations. Inelastic collision cross-sections calculated from the exact resonance solutions are found to be 72 % (without $1s$, $2s$ exchange) and 95 % (with $1s$, $2s$ exchange) of the result from the complete solution. Final curves for the collision parameters, which rise to within 70 % of the limit set by charge conservation, are considered to be of an accuracy approaching that of the Hartree-Fock method for bound-state problems.

A final section is concerned with the contributions of the p-wave to elastic scattering of slow electrons by O I.

INTRODUCTION

Forbidden transitions between the three terms, ^3P, ^1D and ^1S, of the ground configuration of atomic oxygen give rise to some of the most prominent lines in the spectrum of the aurora and of the novae. They are typical of many similar transitions occurring in the aurora, nebulae, novae and solar corona (Bates, Massey & Pearse 1948; Aller & Menzel 1945; Barbier 1948; Woolley & Allen 1948). It is to be expected that electron excitation and deactivation phenomena are important factors in determining the populations of these levels, and it is therefore of considerable astrophysical interest to have reliable data on the rate coefficients involved.

The mechanism of electron excitation of such levels depends largely, if not entirely, on electron exchange effects, which result from taking properly anti-symmetric wave functions for the complete system of atom plus free electron. Previous calculations, which only allowed for exchange by first-order perturbation methods, have recently been shown to give cross-sections which may exceed the limit set by change conservation by as much as several orders of magnitude (Bates, Fundaminsky, Leech & Massey 1950). To make further progress, it is therefore necessary to develop a more complete treatment of electron exchange for continuous states.

The approach adopted is suggested by the Hartree-Fock method for bound states, which is summarized in the first section of the present paper. Although Hartree-Fock wave functions have previously been used in various continuous state problems,† no complete justi-

---

† Morse & Allis 1933; Bates & Massey 1941, 1943, 1947; Bates & Seaton 1949; Seaton 1950, 1951 *a*, *b*; Huang 1945.

fication for the procedure appears to have been given (*T.A.C.* p. 218),† and the equations used, derived largely by analogy with the bound-state equations, have not included the coupling terms required in collision theory. Bound-state Hartree-Fock equations are obtained by adopting an explicitly anti-symmetric expression for the wave functions and using the Ritz variation method to minimize the energy integral. Since this method is not immediately applicable for continuous states, the method used is to express the complete wave function in terms of an explicitly anti-symmetric expansion involving core wave functions and free-electron orbitals, the equations satisfied by the latter being obtained from the Schrödinger equation. This is discussed in part I of the present paper. A somewhat similar approach to nuclear problems is provided by the resonating group-structure method of Wheeler (1937).

For the calculation of the electron excitation parameters of O I (part II) the p-wave is the only angular momentum component for which the full coupled equations are required. The problem of solving these equations is of comparable complexity to the problem of calculating atomic structures by the Hartree-Fock method, for while there is no eigenvalue problem as in the bound case, solutions are required over a range of energy values. In solving the coupled equations by an iteration procedure it is most desirable to have a good first approximation. It is shown that this may be obtained in an exact resonance approximation, for which the equations may be uncoupled. The method used should be applicable to a number of excitation processes of astrophysical interest.‡

Hartree atomic units, for which $h = 2\pi$, $m = 1$ and $e = 1$ (*T.A.S.* p. 428) are used throughout, with the exceptions that cross-sections are given in units of $\pi \mathbf{a}_0^2$ ($8{\cdot}806 \times 10^{-17}\,\mathrm{cm}^2$, or π times the atomic unit of area) and numerical values for energies are given in rydbergs (13·54 eV, or half the atomic unit of energy).

PART I. THE HARTREE-FOCK EQUATIONS FOR CONTINUOUS STATES

1. *Summary of the Hartree-Fock method for bound states*§

1·1. *General formulation*

We consider the Hartree-Fock method for an N-electron atom with nuclear charge Z and Hamiltonian

$$H = \sum_{i=1}^{N}\left(-\tfrac{1}{2}\nabla_i^2 - \frac{Z}{r_i}\right) + \sum_{i>j=1}^{N}\frac{1}{r_{ij}}. \tag{1}$$

Denoting the space and spin co-ordinates by $\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N$, the complete wave function ψ is written as a linear combination of anti-symmetric functions of the form

$$D\{u_1, u_2, \ldots, u_N; \mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N\} = \frac{1}{\surd(N!)}\begin{vmatrix} u_1(1) & u_2(2) & \ldots & u_1(N) \\ u_2(1) & \ldots & \ldots & \ldots \\ \vdots & \vdots & \vdots & \vdots \\ u_N(1) & \ldots & \ldots & u_N(N) \end{vmatrix}. \tag{2}$$

---

† References to Mott & Massey, *Theory of atomic collisions*, Oxford, 1949, will for brevity be given as *T.A.C.* followed by the page number. Similarly, references to Condon & Shortley, *Theory of atomic spectra*, Cambridge, 1935, 1951, will be given as *T.A.S.*

‡ Further calculations on electron excitation of the ground configuration terms of O III, O II, Ne III and N II are being carried out and will be reported elsewhere.

§ For general references to the Hartree-Fock method see Hartree (1946–7), Fock (1930), Lennard-Jones (1930) and Slater (1951).

These will be referred to as D-functions. The one-electrons orbitals $u_i(j) \equiv u_i(\mathbf{x}_j)$ are to be determined using the variation principle. Within a given D-function we may take the u_i to form an orthonormal set,

$$\Delta(ij) \equiv \int u_i^*(\mathbf{x})\, u_j(\mathbf{x})\, \mathrm{d}\mathbf{x} = \delta(i,j), \tag{3}$$

which ensures that the D-functions are normalized to unity. This involves no loss of generality, since any constant multiple of u_i may be added to u_j $(i \neq j)$ without altering D.

The equations satisfied by the u_i may readily be obtained when ψ is represented by a single D-function. The energy integral $E = \int D^* H D \,\mathrm{d}\mathbf{x}_1 \dots \mathrm{d}\mathbf{x}_N$ reduces to

$$E = \sum_{i=1}^{N} \left\{ H_1(ii) + \frac{1}{2} \sum_{j=1}^{N} [(ij\,|\,ij) - (ij\,|\,ji)] \right\}, \tag{4}$$

where

$$H_1(ab) = \int u_a^*(1)\, H_1\, u_b(1)\, \mathrm{d}\mathbf{x}_1, \tag{5}$$

$$H_1 = -\tfrac{1}{2}\nabla_1^2 - \frac{Z}{r_1} \tag{6}$$

and

$$(ab\,|\,cd) = \int\!\!\int u_a^*(1)\, u_b^*(2)\, \frac{1}{r_{12}}\, u_c(1)\, u_d(2)\, \mathrm{d}\mathbf{x}_1 \mathrm{d}\mathbf{x}_2. \tag{7}$$

To ensure that (3) is satisfied the u_i are varied so as to minimize

$$E' = E - \sum_{i,j=1}^{N} \lambda_{ij}\, \Delta(ij), \tag{8}$$

the λ_{ij} being Lagrange multipliers. This gives the Hartree-Fock equations†

$$H_1 u_i(1) + \sum_{j=1}^{N} \{v_{jj}(1)\, u_i(1) - v_{ji}(1)\, u_j(1) - \lambda_{ij} u_j(1)\} = 0, \tag{9}$$

where

$$v_{ab}(1) = \int u_a^*(2)\, \frac{1}{r_{12}}\, u_b(2)\, \mathrm{d}\mathbf{x}_2. \tag{10}$$

Multiplying (9) by $u_k^*(1)$ and integrating over $\mathbf{x}_1$ using (3) gives

$$\lambda_{ik} = H_1(ik) + \sum_j [(kj\,|\,ij) - (kj\,|\,ji)]. \tag{11}$$

The energy reduces to

$$E = \sum_{i=1}^{N} \{\lambda_{ii} - \tfrac{1}{2} \sum_j [(ij\,|\,ij) - (ij\,|\,ji)]\}. \tag{12}$$

1·2. *Addition of an electron to an ion*

We consider the addition of a valence electron to an N-electron core *in the approximation of neglecting the perturbation of the core wave function.* When both the core and the complete system may be expressed as single D-function the energy is

$$E = E^c + H_1(N+1, N+1) + \sum_{i=1}^{N} [(i, N+1\,|\,i, N+1) - (i, N+N+1\,|\,1, i)], \tag{13}$$

---

† Omission of the v_{ji} and λ_{ji} for $j \neq i$ gives the Hartree self-consistent field equations.

E^c being the core energy (4) or (12). Variation of u_{N+1} gives

$$[H_1 - \lambda_{N+1,N+1}]\,u_{N+1} + \sum_{i=1}^{N} \{v_{ii}u_{N+1} - v_{i,N+1}u_i - \lambda_{N+1,i}u_i\} = 0, \tag{14}$$

with $$\lambda_{N+1,k} = H(k, N+1) + \sum_{j=1}^{N} [(kj\,|\,N+1, j) - (kj\,|\,j, N+1)] \quad (k = 1 \text{ to } N+1). \tag{15}$$

The energy reduces to $E = E^c + \lambda_{N+1,N+1}$; $\lambda_{N+1,N+1}$ may therefore be interpreted as the energy of the valence electron.

1·3. *Separation of spin and angular co-ordinates and introduction of angular momentum operators*

The equations derived in the previous two sections involved equating ψ to a single D-function. To proceed further it is necessary to consider the symmetry properties of the wave functions, which requires the adoption of a more explicit functional form for the u_i. In the present section we summarize the method used by Hartree as a basis for detailed numerical calculations (Hartree 1946–7).

The functions u_i are taken in the form

$$u_i(\mathbf{x}) = \delta(m_i^s, s)\,\Theta_{l_i}^{m_i^l}(\theta)\,\Phi^{m_i^l}(\phi)\,\frac{1}{r}\,P_i(n_i l_i\,|\,r), \tag{16}$$

where m_i^s is the spin quantum number $(\pm\frac{1}{2})$, s the spin co-ordinate, and $\Theta_{l_i}^{m_i^l}$, $\Phi^{m_i^l}$ are normalized spherical harmonics (*T.A.S.* p. 52). The radial functions $P_i(n_i l_i\,|\,r)$ remain to be determined from the variation principle. The quantum number n_i is defined so that there are $(n_i - l_i - 1)$ nodes in P_i, excluding the origin and infinity, and, for a given state, $P_i(n_i l_i\,|\,r)$ is taken to depend only on $n_i l_i$. The set of $n_i l_i$ is referred to as the configuration.

For a central field model the energy depends only on the configuration; it is therefore assumed to be a good approximation to take ψ as a linear combination of D-functions all belonging to the same configuration.† It is desirable to choose the linear combinations so as to diagonalize the energy matrix within the configuration. This is facilitated by the introduction of the angular momentum operators $\mathbf{L}^2$, M_L, $\mathbf{S}^2$, M_S for the total and component orbital and spin angular momenta. Using vector coupling formulae (*T.A.S.* chaps. III, VIII) the linear combinations may be chosen so as to make ψ an eigenfunction of these operators. When the configuration and angular momentum quantum numbers give a unique specification of states this representation results in a complete diagonalization of the energy matrix within the configuration. When the configuration and angular momenta do not give a complete specification of states it is necessary to introduce other quantum numbers, the usual choice being the angular momentum of a part of the configuration, referred to as a *parent term*. In this case the energy matrix contains non-diagonal elements connecting states of the same total angular momenta but different parent terms. Such elements are usually neglected for bound states.

In general, unlike orbitals occurring in different D-functions cannot be made orthogonal without imposing additional restrictions on the wave functions. The simplest case where such a situation arises is the ${}^1S$ term of the $nsn's$ configuration, for which

$$\psi = \surd(\tfrac{1}{2})\,[D\{u^+(n)\,u^-(n')\} - D\{u^-(n)\,u^+(n')\}],$$

the ± superscript giving the sign of m^s. In this case $\Delta(u^+(n), u^+(n'))$ and $\Delta(u^-(n), u^-(n'))$ are not zero unless $\int_0^\infty P(ns)\,P(n's)\,\mathrm{d}r = 0$, but with anti-parallel spins this condition cannot

---

† A more complicated case has been treated in detail by Hartree, Hartree & Swirles 1939.

be imposed without altering the D-functions. In general, unlike orbitals may always be made orthogonal by imposing the condition

$$\int_0^\infty P(n_i l\,|\,r)\,P(n_j l\,|\,r)\,\mathrm{d}r = \delta(i,j), \tag{17}$$

but it should be realized that this may involve additional restrictions on the wave functions.

The evaluation of the matrix elements, assuming unlike orbitals to be orthogonal, is discussed by Condon & Shortley (*T.A.S.* chap. VI) and by Hartree (1946–7). It is convenient to summarize the formulae used in reducing (5) and (7) to radial integrals. Writing for brevity $P(n_i l_i\,|\,r) = P_i(r)$ these are:

$$H_1(a,b) = \delta(m_a^s, m_b^s)\,\delta(l_a, l_b)\,\delta(m_a^l, m_b^l)\,\mathscr{H}_1^l(a,b), \tag{18}$$

with $l = l_a$ or l_b, and

$$\mathscr{H}_1^l(a,b) = \int_0^\infty P_a(1)\,\mathscr{H}_1^l P_b(1)\,\mathrm{d}r_1, \tag{19}$$

$$\mathscr{H}_1^l = -\frac{1}{2}\left(\frac{\mathrm{d}^2}{\mathrm{d}r_1^2} - \frac{l(l+1)}{r_1^2}\right) - \frac{Z}{r_1}, \tag{20}$$

$$(ab\,|\,cd) = \delta(m_a^s, m_c^s)\,\delta(m_b^s, m_d^s)\,\delta(m_a^l+m_b^l, m_c^l+m_d^l)\sum_t c_t(l_a, m_a^l;\, l_c, m_c^l)\,c_t(l_d m_d^l;\, l_b m_b^l)\,R_t(abcd) \tag{21}$$

with

$$\begin{aligned} R_t(abcd) &= \int_0^\infty P_a(1)\,P_c(1)\,y_t(P_b P_d\,|\,1)\,\mathrm{d}r_1 \\ &= \int_0^\infty P_b(1)\,P_d(1)\,y_t(P_a P_c\,|\,1)\,\mathrm{d}r_1, \end{aligned} \tag{22}$$

$$y_t(P_b P_d\,|\,1) = \frac{1}{r_1^{t+1}}\int_0^{r_1} P_b(2)\,P_d(2)\,r_2^t\,\mathrm{d}r_2 + r_1^t\int_{r_1}^\infty P_b(2)\,P_d(2)\,\frac{1}{r_2^{t+1}}\,\mathrm{d}r_2. \tag{23}$$

The energy having been expressed in terms of radial integrals the equations satisfied by the radial functions may be determined (Hartree & Hartree 1936). The equations for $P(2p)$ in $1s^2\,2s^2\,2p^q$ configurations ($q = 2$ or 4) are quoted for the benefit of future reference. In the foregoing notation† these are

$$\begin{aligned} \{\mathscr{H}^p + 2y_0(1s,1s) + 2y_0(2s,2s) + (q-1)\,y_0(2p,2p) + \nu y_2(2p,2p) + \tfrac{1}{2}\epsilon_{2p\,2p}\}\,P(2p) \\ -\tfrac{1}{3}y_1(1s,2p)\,P(1s) - \tfrac{1}{3}y_1(2s,2p)\,P(2s) = 0 \end{aligned} \tag{24}$$

(Hartree, Hartree & Swirles 1939). The coefficient ν depends on q and on the term value. Numerical values are given in table 1.

TABLE 1. THE COEFFICIENT ν

	^3P	^1D	^1S
$q=2$	$-0{\cdot}20$	$+0{\cdot}04$	$+0{\cdot}40$
$q=4$	$-0{\cdot}30$	$-0{\cdot}18$	$0{\cdot}00$

2. *Anti-symmetric wave functions for continuous states*

We consider the problem of determining the wave functions for an $(N+1)$-electron system given the exact wave functions for the corresponding N-electron core.

---

† The function y_t used here is Y_t/r, where Y_t is the function used by Hartree. ϵ_{2p2p} $(=-2\lambda_{2p2p})$ is as used by Hartree.

2·1. *Notation*

For any co-ordinate $\mathbf{x}_i$ the complete $(N+1)$-electron Hamiltonian may be written

$$H = H_i + H(i^{-1}) + \sum_{\substack{j=1\\(j\neq i)}}^{N+1} \frac{1}{r_{ij}}, \tag{25}$$

where

$$H_i = -\tfrac{1}{2}\nabla_i^2 - \frac{Z}{r_i} \tag{26}$$

contains $\mathbf{x}_i$ alone and

$$H(i^{-1}) = \sum_{\substack{j=1\\(j\neq i)}}^{N+1} \left[H_j + \sum_{\substack{k>j\\(k\neq i)}}^{N+1} \frac{1}{r_{jk}} \right] \tag{27}$$

contains no $\mathbf{x}_i$ terms. The core wave functions, denoted† by

$$\psi_n(i^{-1}) = \psi_n(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_{i-1}, \mathbf{x}_{i+1}, \ldots, \mathbf{x}_{N+1})$$

are solutions of

$$H(i^{-1})\,\psi_n(i^{-1}) = E_n \psi_n(i^{-1}). \tag{28}$$

They are anti-symmetric and may be taken to form an orthonormal set.

$(N+1)$-electron functions which may not be anti-symmetric for interchange of co-ordinate $\mathbf{x}_i$ with any other co-ordinate are denoted by $\mathrm{X}_{(i)}$. Completely anti-symmetric functions are denoted by Ψ.

Integration over all co-ordinates except $\mathbf{x}_i$ is conveniently denoted by $\int \ldots \mathrm{d}\mathbf{x}_i^{-1}$.

2·2. *Exact equations using an infinite expansion*

It follows from the completeness of the ψ_n that the complete wave function may be expanded in the form

$$\mathrm{X}_{(i)} = \sum_{n=1}^{\infty} \psi_n(i^{-1})\,\theta_n(i), \tag{29}$$

where the summation is over all core states, and is understood to include an integration over states in the continuum. For a given $\mathrm{X}_{(i)}$ this determines the θ_n uniquely;

$$\theta_n(i) = \int \psi_n^*(i^{-1})\,\mathrm{X}_{(i)}\,\mathrm{d}\mathbf{x}_i^{-1}.$$

The equations satisfied by the θ_n are obtained on writing the Schrödinger equation

$$[H-E]\,\mathrm{X}_{(i)} = 0 \tag{30}$$

in the form

$$\int \psi_m^*(1^{-1})\,[H-E]\,\mathrm{X}_{(1)}\,\mathrm{d}\mathbf{x}_1^{-1} = 0 \quad (\text{all } m). \tag{31}$$

Using (28) and the orthonormality of the ψ_n this gives

$$[H_1 - \tfrac{1}{2}k_m^2]\,\theta_m(1) + \sum_{n=1}^{\infty} V_{mn}(1)\,\theta_n(1) = 0 \quad (\text{all } m), \tag{32}$$

where $\tfrac{1}{2}k_m^2 = (E - E_m)$ and

$$V_{mn}(1) = \int \psi_m^*(1^{-1}) \sum_{j\neq 1} \frac{1}{r_{1j}} \psi_n(1^{-1})\,\mathrm{d}\mathbf{x}_1^{-1}. \tag{33}$$

---

† This notation is similar to that of Yamanouchi & Kotani (1940).

For results of physical significance we require the complete wave function to be anti-symmetric. This requirement may be included in the boundary conditions on $X_{(i)}$, or we may solve without this condition and then form the anti-symmetric function $\Psi = \mathscr{A} X_{(i)}$, where $\mathscr{A}$ is the operator

$$\mathscr{A} = \frac{-1}{\sqrt{(N+1)}} \sum_{i=1}^{N+1} (-1)^i.$$

This procedure is always possible so long as we have an exact solution of the Schrödinger equation.

2·3. *Approximate equations: the use of an explicitly anti-symmetric expansion*

In practical calculations the approximation is invariably made of neglecting part of the summation over n in the expansion (29); an exact solution of the Schrödinger equation can then no longer be obtained. The function†

$$X_{(i)} = \sum_{n=1}^{n_0} \psi_n(i^{-1})\, \theta_n(i) \quad (n_0 \neq \infty) \tag{34}$$

may be made to satisfy the equations

$$\int \psi_m^*(1^{-1})\, [H-E]\, X_{(1)}\, \mathrm{d}\mathbf{x}_1^{-1} = 0 \quad (\text{all } m \leqslant n_0) \tag{35}$$

which are equivalent to the Schrödinger equation (30) in the limit $n_0 \to \infty$. It gives equations for the θ_m of the form (32) with $n, m \leqslant n_0$.

An unsatisfactory feature of the restricted expansion (34) is that it gives no consistent means of obtaining anti-symmetric wave functions. When $n_0 \neq \infty$ it is in general no longer possible to impose anti-symmetry as a boundary condition on $X_{(i)}$, as is immediately obvious for the important case where $X_{(i)}$ represents a continuous state and the ψ_n are restricted to bound states. The anti-symmetrized function $\mathscr{A} X_{(i)}$ may be formed, but this will not be a solution of

$$\int \psi_m^*(1^{-1})\, [H-E] \mathscr{A} X_{(i)}\, \mathrm{d}\mathbf{x}_1^{-1} = 0 \quad (\text{all } m \leqslant n_0),$$

since (35) does not ensure that

$$\int \psi_m^*(1^{-1})\, [H-E]\, X_{(i)}\, \mathrm{d}\mathbf{x}_1^{-1} = 0 \quad (i \neq 1, \text{ all } m \leqslant n_0). \tag{36}$$

For scattering problems nothing would be gained by this procedure if ψ_n is restricted to bound states (cf. (83), (84)).

An alternative approach is provided by substituting the explicitly anti-symmetric expansion

$$\Psi = \sum_{n=1}^{n_0} \mathscr{A} \psi_n(i^{-1})\, \phi_n(i) \tag{37}$$

in the equations

$$\int \psi_m^*(1^{-1})\, [H-E]\, \Psi\, \mathrm{d}\mathbf{x}_1^{-1} = 0 \quad (\text{all } m \leqslant n_0). \tag{38}$$

Using the anti-symmetric property of the ψ_n these may be written

$$\int \psi_m^*(1^{-1})\, [H-E] \sum_{n=1}^{n_0} (\psi_n(1^{-1})\, \phi_n(1) - N\psi_n(2^{-1})\, \phi_n(2))\, \mathrm{d}\mathbf{x}_1^{-1} = 0, \tag{39}$$

---

† n is not necessarily in order of increasing E.

MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES
PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A

which, using (28) and the orthonormality of the ψ_n, give

$$[H_1-\tfrac{1}{2}k_m^2]\,\phi_m(1)+\sum_{n=1}^{n_0}\{V_{mn}(1)\,\phi_n(1)-W_{mn}(1)\}=0, \tag{40}$$

where V_{mn} is defined by (33) and

$$W_{mn}(1)=N\int\psi_m^*(1^{-1})\,[H-E]\,\psi_n(2^{-1})\,\phi_n(2)\,\mathrm{d}\mathbf{x}_1^{-1} \tag{41a}$$

$$=N\int\psi_m^*(1^{-1})\left[H_2-\tfrac{1}{2}k_n^2+\sum_{j\neq 2}\frac{1}{r_{j2}}\right]\psi_n(2^{-1})\,\phi_n(2)\,\mathrm{d}\mathbf{x}_1^{-1} \tag{41b}$$

$$=N\int\psi_m^*(1^{-1})\left[H_1-\tfrac{1}{2}k_m^2+\sum_{j\neq 1}\frac{1}{r_{j1}}\right]\psi_n(2^{-1})\,\phi_n(2)\,\mathrm{d}\mathbf{x}_1^{-1}. \tag{41c}$$

The expression (41 *c*) for W_{mn} is obtained using the Hermitian property of $H(1^{-1})$. This requires that $\psi_m(1^{-1})$ and $\psi_n(2^{-1})\,\phi_n(2)$ should be sufficiently convergent. It is always justified if ψ_m is a bound state and is probably justified in all cases of practical interest.

While equations (37) and (38), together with a specification of boundary conditions, define Ψ uniquely it is readily verified that the ϕ_n are not uniquely defined. In solving the equations (40) it is therefore necessary to adopt a convention which makes the ϕ_n unique without altering the value of Ψ. Expansion (37) gives

$$\surd(N+1)\int\psi_m^*(1^{-1})\,\Psi\,\mathrm{d}\mathbf{x}_1^{-1}=\phi_m(1)-N\sum_n\int\psi_m(1^{-1})\,\psi_n(2^{-1})\,\phi_n(2)\,\mathrm{d}\mathbf{x}_1^{-1},$$

where the left-hand side is uniquely defined. One possible convention consistent with this would be to take

$$\int\psi_m^*(1^{-1})\,\phi_n(2)\,\mathrm{d}\mathbf{x}_2=0\quad\text{when}\quad m\leqslant n\leqslant n_0, \tag{42}$$

giving

$$\left.\begin{aligned}\phi_1(1)&=\surd(N+1)\int\psi_1^*(1^{-1})\,\Psi\,\mathrm{d}\mathbf{x}_1^{-1},\\ \phi_2(1)&=\surd(N+1)\int\psi_2^*(1^{-1})\,\Psi\,\mathrm{d}\mathbf{x}_1^{-1}+N\int\psi_2^*(1^{-1})\psi_1(2^{-1})\,\phi_1(2)\,\mathrm{d}\mathbf{x}_1^{-1},\end{aligned}\right\} \tag{43}$$

etc.

It is obvious that when the complete expansions are used ($n_0=\infty$) both (34) and (37) give exact solutions of the Schrödinger equation and that $\phi_n=\theta_n$ provides a solution of the equations (40). When $n_0\neq\infty$, $X_{(i)}$ is in general not a solution of (36), while with the explicitly anti-symmetric expansion no such difficulty arises. It may therefore be expected that Ψ will provide a better approximation to a solution of the Schrödinger equation than does $X_{(i)}$. We may gain some further idea of the relative accuracy of the two expansions by evaluating $[H-E]\,X_{(1)}$ and $[H-E]\,\Psi$, which are zero for exact wave functions, for the simple case of $N=1$. We obtain

$$\left.\begin{aligned}[H-E]\,X_{(1)}&=\sum_{s=1}^{\infty}\sum_{t=n_0+1}^{\infty}\psi_s(1)\,\psi_t(2)\int\psi_s^*(1)\,\psi_t(2)\,\frac{1}{r_{12}}\,X_{(1)}\,\mathrm{d}\mathbf{x}_1\,\mathrm{d}\mathbf{x}_2,\\ [H-E]\,\Psi&=\sum_{s=n_0+1}^{\infty}\sum_{t=n_0+1}^{\infty}\psi_s(1)\,\psi_t(2)\int\psi_s^*(1)\,\psi_t^*(2)\,\frac{1}{r_{12}}\,\Psi\,\mathrm{d}\mathbf{x}_1\,\mathrm{d}\mathbf{x}_2.\end{aligned}\right\} \tag{44}$$

It is seen that the second of these expressions will in general be the smaller owing to the more restricted range of s (note also that the diagonal terms $s=t$ are zero for Ψ but not for $X_{(1)}$).

2·4. *Discussion of the equations*

The equations (40) resemble bound state Hartree-Fock equations, the W_{mn} being typical exchange terms, while the equations (32) resemble the Hartree self-consistent field equations. The interpretation of the equations may be further discussed by considering the case where Ψ represents an ion together with an unbound electron such that the total energy E is less than the ionization potential of the ion. For large $\mathbf{x}_1$ (40) becomes

$$\left[-\tfrac{1}{2}\nabla_1^2-\frac{(Z-N)}{r_1}-\tfrac{1}{2}k_m^2\right]\phi_m(1)=0, \tag{45}$$

which gives the equation of motion in the asymptotic field of the ion with kinetic energy $\frac{1}{2}k_m^2$ at infinite separation. There are in general a number of states ψ_m for which $\frac{1}{2}k_m^2=(E-E_m)$ is positive. The V_{mm} and W_{mm} give the mean unperturbed exchange fields of these states, and the V_{mn} and W_{mn} are coupling terms which allow for the electron-inducing transitions. The terms involving energetically inaccessible states ($\frac{1}{2}k_m^2$ negative) may be interpreted as giving a polarization correction.† (An alternative treatment of polarization has recently been given by Kolodziejski (1951), but this does not allow for exchange.)

When all energetically accessible states are included the anti-symmetric expansion may be expected to give results of an accuracy comparable to that of the Hartree-Fock method for valence electron states (with neglect of core perturbation). Results obtained by the solution of (40) in this approximation have been compared with experiment for elastic scattering of slow electrons by He (Morse & Allis 1933) and for photo-ionization of Na (Seaton 1951 *b*). Good general agreement with experiment was obtained in both cases, a considerable improvement resulting from the inclusion of the exchange terms.

3. *The use of Hartree-Fock core functions*

The present section deals with the approximate form of the equations (40) which is obtained when Hartree-Fock wave functions are used for the core states. We consider first the derivation of (40) from (37) and (38) when Hartree-Fock functions are used.

In deriving (40) the ψ_n were assumed to be (i) anti-symmetric, (ii) orthonormal and (iii) solutions of the Schrödinger equation (28). Hartree-Fock functions satisfy (i), giving equation (39), but are frequently calculated without imposing (ii) (Hartree 1946–7) and only satisfy (iii) in the trivial case of $N=1$. The lack of orthogonality of the ψ_n may be overcome by forming linear combinations, but this may result in a considerable loss of accuracy in the wave functions. It may be a better approximation simply to ignore terms arising from non-orthogonality.‡ Either procedure leads to the equations (40), provided that E_m is now defined as $\int\psi_m^*(1^{-1})\,H(1^{-1})\,\psi_m(1^{-1})\,d\mathbf{x}_1^{-1}$. A further difficulty arises with the W_{mn} terms, for which the expressions (41 *a*), (41 *b*) and (41 *c*) are not equal using approximate wave functions. In principle we may always evaluate (41 *a*) and simplify the resulting

---

† This interpretation is only valid for the anti-symmetric expansion (37). Using the expansion (34) coupling terms between states of different spin quantum numbers can only be obtained by including continuous ψ_n states.

‡ No orthogonality difficulty arises for states belonging to different terms, such as are considered in §4 and part II.

expression using the equations satisfied by the core functions, but in practice this procedure is very tedious, and it is frequently convenient to use one of the approximate expressions (41 *b*) or (41 *c*). The expression (41 *b*) corresponds to the 'prior' interaction, and (41 *c*) to the 'post' interaction in the Born-Oppenheimer approximation (Bates *et al.* 1950).

3·1. *Reduction of integrals*

With Hartree-Fock core functions the V_{mn} and W_{mn} may be expressed in terms of integrals over D-functions of the type

$$\left.\begin{aligned} V_{a,b}(1) &= \int D_a^*(1^{-1}) \sum_{i=2}^{N+1} \frac{1}{r_{i1}} D_b(1^{-1})\,\mathrm{d}\mathbf{x}_1^{-1}, \\ W_{a,b,n}(1) &= N\int D_a^*(1^{-1})\,[H-E]\,D_b(2^{-1})\,\phi_n(2)\,\mathrm{d}\mathbf{x}_1^{-1}, \end{aligned}\right\} \tag{46}$$

where
$$D_a(1^{-1}) = D\{a_1, a_2, \ldots, a_N; \mathbf{x}_2, \mathbf{x}_3, \ldots, \mathbf{x}_{N+1}\},$$
$$D_b(2^{-1}) = D\{b_1, b_2, \ldots, b_N; \mathbf{x}_1, \mathbf{x}_3, \ldots, \mathbf{x}_{N+1}\}.$$

The $V_{a,b}$ integrals are of a standard type (*T.A.S.* chap. VI) and need not be considered further. The $W_{a,b,n}$ integrals may be evaluated as follows. The D-functions are expanded in the form

$$\left.\begin{aligned} D_a(1^{-1}) &= -\frac{1}{\sqrt{N}} \sum_{j=1}^{N} (-1)^j a_j(2)\,\Delta(a_j), \\ D_b(2^{-1}) &= -\frac{1}{\sqrt{N}} \sum_{k=1}^{N} (-1)^k b_k(1)\,\Delta(b_k), \end{aligned}\right\} \tag{47}$$

where $\sqrt{\{(N-1)!\}}\,\Delta(a_j)$, $\sqrt{\{(N-1)!\}}\,\Delta(b_k)$ are the minors of $a_j(2)$, $b_k(1)$ in the determinants for $D_a(1^{-1})$ and $D_b(2^{-1})$ respectively. It should be noted that both $\Delta(a_j)$ and $\Delta(b_k)$ are functions of $\mathbf{x}_3, \mathbf{x}_4, \ldots, \mathbf{x}_{N+1}$. These expansions give

$$W_{a,b,n}(1) = \sum_{j,k=1}^{N} (-1)^{j+k} \int a_j^*(2) \left\{ \int \Delta^*(a_j)\,[H-E]\,\Delta(b_k)\,\mathrm{d}\mathbf{x}_3 \ldots \mathrm{d}\mathbf{x}_{N+1} \right\} \phi_n(2)\,\mathrm{d}\mathbf{x}_2 \,.\, b_k(1), \tag{48}$$

which involves only integrals of a standard type (*T.A.S.* chap. VI). We consider the further evaluation of $W_{a,b,n}(\text{prior})$, (41 *b*), and $W_{a,b,n}(\text{post})$, (41 *c*), making the additional assumption that any two orbitals a_j, b_k are either identical or orthogonal. While this assumption is not always justified it is a useful approximation in a number of cases of interest. With this assumption $W_{a,b,n}(\text{prior or post})$ is zero if more than two of the a_j differ from all the b_k. All other cases may be reduced to the following three by suitable permutation of the order of the a_j, b_k (a + or − sign being introduced according to the parity of the permutation):

Case A. $a_j = b_j$ for $j = 1$ to $N-2$, neither of a_{N-1}, a_N are equal to b_{N-1} or b_N:

$$\begin{aligned} W_{a,b,n}(\text{prior}) = {} & [(a_N a_{N-1} \mid b_N \phi_n) - (a_{N-1} a_N \mid b_N \phi_n)]\, b_{N-1} \\ & - [(a_N a_{N-1} \mid b_{N-1} \phi_n) - (a_{N-1} a_N \mid b_{N-1} \phi_n)]\, b_N. \end{aligned} \tag{49}$$

Case B. $a_j = b_j$ for $j = 1$ to $N-1$, $a_N \neq b_N$:

$$\begin{aligned} W_{a,b,n}(\text{prior}) = {} & \sum_{j=1}^{N-1} \{ [(a_N a_j \mid b_N \phi_n) - (a_j a_N \mid b_N \phi_n)]\, b_j \\ & - [(a_N a_j \mid b_j \phi_n) - (a_j a_N \mid b_j \phi_n)]\, b_N \} \\ & + [H_2(a_N \phi_n) - \tfrac{1}{2} k_n^2 \Delta(a_N \phi_n) + v(a_N \phi_n)]\, b_N. \end{aligned} \tag{50}$$

Case C. $a_j = b_j$ for all j, i.e. $D_a \equiv D_b$:

$$W_{a,b,n}(\text{prior}) = \sum_{j,k=1}^{N} \{[(a_k a_j \mid b_k \phi_n) - (a_j a_k \mid b_k \phi_n)] + [H_2(a_j \phi_n) - \tfrac{1}{2}k_n^2 (a_j \phi_n) + v(a_j \phi_n)]\}\, b_j. \qquad (51)$$

$W_{a,b,n}(\text{post})$ is obtained from the above formulae on replacing

$$(a_p a_q \mid b_r \phi_n) \quad \text{by} \quad v(a_p b_r)\, \Delta(a_q \phi_n)$$

and

$$H_2(a_p \phi_n) - \tfrac{1}{2}k_n^2 \Delta(a_p \phi_n) \quad \text{by} \quad \Delta(a_p \phi_n)\, [H_1 - \tfrac{1}{2}k_m^2].$$

3·2. *Comparison with Hartree-Fock equations for bound states*

Neglecting all V_{mn} and W_{mn} with $n \neq m$ and taking ψ_m to be the single D-function $D\{u_1 \ldots u_N\}$, the equations (40) reduce to

$$[H_1 - \tfrac{1}{2}k_m^2]\, \phi_m + \sum_{i=1}^{\infty} \{v_{ii} \phi_m - v_{im} u_i - \lambda_{mi} u_i\} = 0, \qquad (52)$$

with

$$\lambda_{mi} = H_2(im) - \tfrac{1}{2}k_m^2 \Delta(im) + \sum_{j=1}^{N} [(ji \mid jm) - (ij \mid jm)]. \qquad (53)$$

This form is obtained directly using the prior interaction, but using the equations (9) satisfied by the u_j it may be shown that both the post-interaction and the 'exact' interaction (41 *a*) give the same equations.

Since for this case Ψ is itself a D-function it is obvious that Ψ is unaltered if constant multiples of the u_j are added to ϕ_m. It is of interest to see how this result follows directly from the equations (9), (11) and (52), (53). If (52) be multiplied by $u_i^*(1)$ and integrated over $\mathbf{x}_1$ an expression is obtained for λ_{mi} which is identical with (53). It follows that if (52) is solved with any arbitrary parameters λ_{mi}, (53) remains valid; the λ_{mi} are therefore indeterminate. It may then be shown that the solution ϕ_m^0 obtained with $\lambda_{mi} = 0$ (all i) gives $\Delta(u_i \phi_m) = 0$ (all i), and that the function

$$\phi_m = \phi_m^0 + \sum_j \mu_{mj} u_j,$$

where the μ_{mj} are arbitrary constants, is a solution of (53) when the λ_{mi} are given by

$$\lambda_{mi} = -\tfrac{1}{2}k_m^2 \mu_{mi} + \sum_j \mu_{mj} \lambda_{ji}.$$

It is seen that the equation (52) is identical with the Hartree-Fock 'valence-electron' equation considered in § 1·2.

3·3. *Separation of spin and angular co-ordinates and introduction of the total angular momenta*

The functions ϕ_m may always be expanded in the form

$$\phi_m(\mathbf{x}) = \sum_{m^s, m^l, l} \delta(m^s, s)\, \Theta_l^{m^l}(\theta)\, \Phi^{m^l}(\phi)\, \frac{1}{r} F_m(m^l m^s kl \mid r). \qquad (54)$$

For many purposes it is a useful approximation to retain only a single term in the summation over l. The present section is devoted to a general discussion of the states arising from a given configuration of the core, denoted by γ^c, together with a free electron of configuration kl. For simplicity γ^c is taken to be a configuration for which the core angular momenta, denoted by $L^c S^c M_L^c M_S^c$, give a complete specification of states. Retaining only those terms within the $\gamma^c kl$ configuration, the expansion (37) will include all products of the form

$$\psi_n(\gamma^c L^c S^c M_L^c M_S^c \,|\, i^{-1})\, \phi_n(kl\, m^l m^s \,|\, i). \tag{55}$$

An expansion of this form would in general lead to equations for the ϕ_m's involving coupling terms connecting degenerate states of the core levels. These may be eliminated by a method analogous to that used to diagonalize the energy matrix in the bound case (§ 1·3).

So long as only electrostatic interactions are considered the angular momenta of the whole system are rigorously conserved. These will be denoted by $L^T S^T M_L^T M_S^T$. If the states of the system be taken in a representation labelled by these quantum numbers, it follows that there will be no coupling terms connecting states of different total angular momenta, and hence no coupling terms connecting the degenerate core states. Each set of $L^T S^T M_L^T M_S^T$ gives a set of coupled equations for the radial functions, but as in the bound case (*T.A.S.* p. 49) these are independent of $M_L^T M_S^T$ for a given $L^T S^T$. Consistent with the usual bound-state procedure the radial equations for the functions F may be taken to depend only on $\gamma^c kl$, $L^c S^c$, $L^T S^T$; these quantum numbers are conveniently denoted by the single subscript n. The angular momentum eigenfunctions

$$X_{(i),\,n} \equiv X_{(i)}(\gamma^c kl, L^c S^c, L^T S^T M_L^T M_S^T) \tag{56}$$

may be obtained in the form

$$X_{(i),\,n} = \sum_{\nu} B_\nu\, \psi(\gamma^c, L^c S^c, M^c_{L_\nu} M^c_{S_\nu} \,|\, i^{-1})\, \phi(kl\, m^l_\nu m^s_\nu \,|\, i), \tag{57}$$

the B_ν being determined from vector-coupling formulae (*T.A.S.* p. 228). The radial equations satisfied by the F_m are then obtained on simplifying (cf. (39))

$$\int \left\{\frac{X_{(1),\,m}}{F_m(r_1)}\right\}^* [H-E] \sum_n (X_{(1),\,n} - N X_{(2),\,n})\, \mathrm{d}r_1^{-1} = 0, \tag{58}$$

the integration being over all co-ordinates except r_1. The evaluation of the integrals has been discussed in §§ 3·1 and 1·3.

4. *The radial equations for certain $nl^q kl$ configurations*

In the present section we discuss the radial equations and the uniqueness of radial functions for certain configurations of the form $nl^q kl$. It will be seen that a definite choice of the spin and angle factors in the wave functions may remove, in part or completely, the lack of uniqueness in the ϕ_n.

The notation for radial functions and operators introduced in § 1·3 will be used.

4·1. *The nsks configuration*

The two core D-functions may be denoted by u^+ and u^-, the ± sign giving the sign of m^s. The core term is ^2S and the complete system is either ^3S or ^1S, the former giving

$$^3S,\ M_S^T = 1, \quad X_{(1)} = u^+(2)\, \phi^+(1), \tag{59}$$

and the latter

$$^1S,\ M_S^T = 0, \quad X_1 = \frac{1}{\sqrt{2}}[u^+(2)\, \phi^-(1) - u^-(2)\, \phi^+(1)]. \tag{60}$$

The radial equations are

$$[\mathscr{H}^s + y_0(PP) - \tfrac{1}{2}k^2]\,F = \tau[y_0(PF) + \lambda(PF)]\,P, \tag{61}$$

where $\tau = +1$ for ^3S and -1 for ^1S. In both cases

$$\lambda(PF) = \mathscr{H}^s(PF) - \tfrac{1}{2}k^2\Delta(PF). \tag{62}$$

The bound function $P = P(ns)$ satisfies the exact hydrogenic equation

$$[\mathscr{H}^s + \tfrac{1}{2}\epsilon]\,P = 0, \tag{63}$$

and hence there is no post-prior discrepancy. Multiplying this by F and integrating gives

$$\mathscr{H}^s(PF) + \tfrac{1}{2}\epsilon\Delta(PF) = 0, \tag{64}$$

while multiplying (61) by P and integrating gives

$$\tau\lambda(PF) = \mathscr{H}^s(PF) + (1-\tau)\,R_0(PPPF) - \tfrac{1}{2}k^2\Delta(PF). \tag{65}$$

From (62) and (64), $\lambda(PF) = -\tfrac{1}{2}(k^2+\epsilon)\,\Delta(PF).$

For $\tau = +1$ (^3S), (62) and (65) are identical and λ indeterminate. As in § 3·2 we may choose the orthogonal solution giving $\lambda(PF) = 0$. For $\tau = -1$ (^1S), (62), (64) and (65) give

$$\lambda(PF) = -\tfrac{1}{2}(k^2+\epsilon)\,\Delta(PF) = -R_0(PPPF).$$

In this case F is uniquely defined (see § 1·3). We cannot impose the orthogonality condition (17) without modifying the equations and wave functions.

4·2. *np^2kp and np^4kp configurations*

The np^q configuration with $q = 2$ or 4 gives the core terms ^3P, ^1D and ^1S. These will be denoted by subscripts 1, 2 and 3, and the corresponding $P(np)$ radial functions will be denoted by P_1, P_2 and P_3. The angular momentum states of np^qkp are

(1)	$np^q(^3P)\,kp$:	^2S	^2P	^2D		$^4S, P, D$
(2)	$np^q(^1D)\,kp$:		^2P	^2D	^2F	
(3)	$np^q(^1S)\,kp$:		^2P			

^2P and ^2D are the only angular momentum interactions common to more than one of the core terms, and will be the only cases to be considered in detail. The radial equations for $F_1(kp)$, $F_2(kp)$ and $F_3(kp)$ take the form†

$$[\mathscr{H}^p - \tfrac{1}{2}k_m^2]\,F_m + \sum_{n=1}^{3}\{V_{mn}F_n - W_{mn}\} = 0, \tag{66}$$

where

$$V_{mn} = \rho_{mn}y_0(P_mP_n) + \sigma_{mn}y_2(P_mP_n), \tag{67}$$

$$W_{mn} = \alpha_{mn}\{\beta_{mn}y_0(P_mF_n) + \gamma_{mn}y_2(P_mF_n) + \lambda_{mn}\}\,P_n, \tag{68}$$

$$\lambda_{mn}(\text{prior}) = \beta_{mn}\{(q-1)\,R_0(P_mP_mP_nF_n) + \mathscr{H}^p(P_mF_n) - \tfrac{1}{2}k_n^2\Delta(P_mF_n)\} + \delta_{mn}R_2(P_mP_mP_nF_n), \tag{69}$$

$$\lambda_{mn}(\text{post}) = \Delta(P_mF_n)\,\beta_{mn}\{(q-1)\,y_0(P_mP_n) + \mathscr{H}^p - \tfrac{1}{2}k_m^2\} + \Delta(P_mF_n)\,\delta_{nm}y_2(P_mP_n). \tag{70}$$

---

† We neglect terms arising from $\Delta(P_mP_n)$ not being exactly unity when $n \neq m$, since these involve only second-order effects in the small differences between the P's.

The constants ρ, σ, α, β and γ are given in table 2, and the equations for the core radial functions are given by (24) (omitting the 1*s* and 2*s* terms). It should be noted that the coefficient of $y_2(P_m P_n)$ in λ_{mn}(post) is δ_{nm} and *not* δ_{mn}.

TABLE 2. MATRIX ELEMENTS FOR $np^q kp$ CONFIGURATIONS ($q = 2$ OR 4)

q	L^T, S^T	m, n	ρ	σ	α	β	γ	δ
2	^2P	1, 1	2	$+0{\cdot}20$	$-\frac{1}{2}$	1	$+0{\cdot}40$	$-0{\cdot}20$
		1, 2	0	0	$+\frac{1}{2}\sqrt{5}$	1	$+0{\cdot}16$	$-0{\cdot}20$
		1, 3	0	0	$+1$	1	$-0{\cdot}20$	$-0{\cdot}20$
		2, 1	0	0	$+\frac{1}{2}\sqrt{5}$	1	$+0{\cdot}16$	$+0{\cdot}04$
		2, 2	2	$+0{\cdot}28$	$+\frac{1}{6}$	1	$+1{\cdot}84$	$+0{\cdot}04$
		2, 3	0	$-0{\cdot}16\sqrt{5}$	$-\frac{1}{3}\sqrt{5}$	1	$+0{\cdot}04$	$+0{\cdot}04$
		3, 1	0	0	$+1$	1	$-0{\cdot}20$	$+0{\cdot}40$
		3, 2	0	$-0{\cdot}16\sqrt{5}$	$-\frac{1}{3}\sqrt{5}$	1	$+0{\cdot}04$	$+0{\cdot}40$
		3, 3	2	0	$+\frac{1}{3}$	1	$+0{\cdot}40$	$+0{\cdot}40$
2	^2D	1, 1	2	$-0{\cdot}04$	$-\frac{1}{2}$	1	$+0{\cdot}16$	$-0{\cdot}20$
		1, 2	0	0	$-\frac{3}{2}$	1	$-0{\cdot}08$	$-0{\cdot}20$
		2, 1	0	0	$-\frac{3}{2}$	1	$-0{\cdot}08$	$+0{\cdot}04$
		2, 2	2	$-0{\cdot}28$	$-\frac{1}{2}$	1	$-0{\cdot}32$	$+0{\cdot}04$
4	^2P	1, 1	4	$-0{\cdot}20$	-2	1	$-0{\cdot}05$	$-0{\cdot}15$
		1, 2	0	0	$-\sqrt{5}$	1	$-0{\cdot}02$	$-0{\cdot}42$
		1, 3	0	0	$+1$	1	$-0{\cdot}20$	$-0{\cdot}60$
		2, 1	0	0	$-\sqrt{5}$	1	$-0{\cdot}02$	$-0{\cdot}18$
		2, 2	4	$-0{\cdot}28$	$-\frac{2}{3}$	1	$-0{\cdot}59$	$-0{\cdot}09$
		2, 3	0	$+0{\cdot}16\sqrt{5}$	$+\frac{1}{3}\sqrt{5}$	1	$+0{\cdot}04$	$-0{\cdot}36$
		3, 1	0	0	$+1$	1	$-0{\cdot}20$	0
		3, 2	0	$+0{\cdot}16\sqrt{5}$	$+\frac{1}{3}\sqrt{5}$	1	$+0{\cdot}04$	0
		3, 3	4	0	$+\frac{2}{3}$	1	$+0{\cdot}40$	0
4	^2D	1, 1	4	$+0{\cdot}04$	1	1	$-0{\cdot}14$	$+0{\cdot}18$
		1, 2	0	0	1	0	$+0{\cdot}18$	$-0{\cdot}18$
		2, 1	0	0	1	0	$+0{\cdot}18$	$-0{\cdot}18$
		2, 2	4	$+0{\cdot}28$	1	1	$+0{\cdot}34$	$-0{\cdot}06$

4·3. *The exact resonance approximation*

Certain essential features of the solutions of these equations may be obtained by considering an approximation in which the y_2 and R_2 terms are consistently neglected. For the core states this gives equal energies and identical radial functions for the three terms; the subscripts 1, 2 and 3 on $P(np)$ and k^2 may therefore be omitted. This will be referred to as the exact resonance, or E.R., approximation.

Denoting the core potential by

$$V = qy_0(PP) \tag{71}$$

and introducing the function

$$\mathscr{I}(F) = [y_0(PF) + \lambda(PF)]\,P, \tag{72}$$

with†

$$\lambda(PF) = \mathscr{H}^p(PF) + (q-1)\,R_0(PPPF) - \tfrac{1}{2}k^2\Delta(PF), \tag{73}$$

the equations for the functions F_n reduce to

$$[\mathscr{H}^p + V - \tfrac{1}{2}k^2]\,F_m = \sum_n \mathscr{I}(\alpha_{mn}\beta_{mn}F_n). \tag{74}$$

† Using the equation for P it may be shown that λ(post) takes this form in the E.R. approximation.

They may always be uncoupled by taking suitable linear combinations, and the solutions may then be expressed in terms of two functions $\mathscr{F}$ and $\mathscr{G}$ satisfying

$$[\mathscr{H}^p + V - \tfrac{1}{2}k^2]\,\mathscr{F} = \mathscr{I}(\mathscr{F}), \tag{75}$$

$$[\mathscr{H}^p + V - \tfrac{1}{2}k^2]\,\mathscr{G} = -q\mathscr{I}(\mathscr{G}). \tag{76}$$

By the argument of §§ 3·2 and 4·1 it may be shown that $\mathscr{F}$ may be chosen orthogonal to P, giving

$$\lambda(P\mathscr{F}) = -\tfrac{1}{2}(k^2+\epsilon)\,\Delta(P\mathscr{F}) = 0, \tag{77}$$

but that $\mathscr{G}$ is uniquely defined and that

$$\lambda(P\mathscr{G}) = -\tfrac{1}{2}(k^2+\epsilon)\,\Delta(P\mathscr{G}) = -R_0(PPP\mathscr{G}). \tag{78}$$

Table 3 gives the linearly independent sets of solutions for the F's in terms of $\mathscr{F}$ and $\mathscr{G}$. It will be seen that in this approximation there are no coupling terms between F_1 and F_2 for $np^4kp\,{}^2D$, and that both functions are constant multiples of $\mathscr{F}$.

Table 3. Exact resonance solutions for F_1, F_2 and F_3

q	L^T, S^T		solution (1)	solution (2)	solution (3)
2	${}^2P$	$F_1 =$	$+2\mathscr{F}$	0	$+3\mathscr{G}$
		$F_2 =$	0	$+2\mathscr{F}$	$-\sqrt{5}\mathscr{G}$
		$F_3 =$	$+3\mathscr{F}$	$-\sqrt{5}\mathscr{F}$	$-2\mathscr{G}$
2	${}^2D$	$F_1 =$	$-\mathscr{F}$	$+\mathscr{G}$	—
		$F_2 =$	$+\mathscr{F}$	$+\mathscr{G}$	—
4	${}^2P$	$F_1 =$	$+\mathscr{F}$	0	$+3\mathscr{G}$
		$F_2 =$	0	$+\mathscr{F}$	$+\sqrt{5}\mathscr{G}$
		$F_3 =$	$+3\mathscr{F}$	$+\sqrt{5}\mathscr{F}$	$-\mathscr{G}$
4	${}^2D$	$F_1 =$	$+\mathscr{F}$	0	—
		$F_2 =$	0	$+\mathscr{F}$	—

We may now give the E.R. approximation for those states (${}^4S, P, D$ and ${}^2S$) which give no coupling between the core terms. All of these are constant multiples of $\mathscr{F}$, with the single exception of $np^2kp\,{}^4S$, for which the radial function is a constant multiple of $\mathscr{G}$.

It is seen that the non-orthogonal function $\mathscr{G}$ occurs in those states of the np^qkp configuration which are also allowed states of np^{q+1} (i.e. $np^3\,{}^4S$, ${}^2P$, ${}^2D$ and $np^5\,{}^2P$). These are the states for which, in any of the D-functions composing the complete wave function Ψ, the functions u_i occur with spin and angle factors which are always different from those of ϕ.

4·4. *Solution of the coupled equations*

The E.R. approximation consists in making the following approximations in the equations for F_1, F_2 and F_3:

(i) Neglecting the y_2 and R_2 terms and the differences between P_1, P_2 and P_3, and

(ii) putting $k_1^2 = k_2^2 = k_3^2 = k^2$.

Experience in bound-state calculations indicates that (i) is unlikely to lead to serious error, but the significance of (ii) requires further examination. We consider as an example the simplest case, $np^2kp\,{}^2D$. For this the E.R. solution (1) (table 3) is $-F_1 = +F_2 = +\mathscr{F}(k)$.

If approximation (i) is made without approximation (ii) the equations for F_1 and F_2 are

$$\left.\begin{aligned}[\mathscr{H}^p+V-\tfrac{1}{2}k_1^2]\,F_1 &= \mathscr{I}(-\tfrac{1}{2}F_1-\tfrac{3}{2}F_2),\\ [\mathscr{H}^p+V-\tfrac{1}{2}k_2^2]\,F_2 &= \mathscr{I}(-\tfrac{3}{2}F_1-\tfrac{1}{2}F_2).\end{aligned}\right\} \tag{79}$$

It is readily verified that a solution of these equations would be given by

$$F_1=-\mathscr{F}(k_1),\quad F_2=+\mathscr{F}(k_2), \tag{80}$$

if $\mathscr{I}(\mathscr{F}(k_1))$ *was equal to* $\mathscr{I}(\mathscr{F}(k_2))$. If this condition is nearly satisfied we may expect (80) to provide a good approximation to the solution of (79).

This condition cannot be discussed further until the normalization of $\mathscr{F}(k)$ has been defined. The exchange integrals in $\mathscr{I}$ depend on the form of the functions for small to moderate radial distances, and it is therefore convenient to normalize in terms of the behaviour at the origin. For any function $F(kl\,|\,r)$ this may be measured in terms of

$$K[F]\equiv[F/r^{l+1}]_{r=0}. \tag{81}$$

If we normalize $\mathscr{F}(k)$ so that $K[\mathscr{F}(k)]$ is independent of k^2, then it is to be expected that the condition $\mathscr{I}(\mathscr{F}(k_1))\doteq\mathscr{I}(\mathscr{F}(k_2))$ will be satisfied to a good approximation.

The functions (80) may be taken as an initial approximation for the iterative solution of the coupled equations (79) or of the exact radial equations, the normalization condition $\mathrm{K}[F_1]=-\mathrm{K}[F_2]$ being maintained throughout. A second solution may be obtained, starting with E.R. solution (2), and maintaining $\mathrm{K}[F_1]=+\mathrm{K}[F_2]$ throughout. In obtaining solutions of the coupled equations it is necessary to adopt a uniqueness convention for both sets of solutions. A suitable convention, consistent with (77) and (78) in the E.R. approximation, would be to take

$$\lambda_{11}+3\lambda_{12}=3\lambda_{21}+\lambda_{22} \tag{82}$$

for both sets of solutions. A convenient means of satisfying such conditions at all stages of an iterative solution has been given by Seaton (1951 *a*).

4·5. *Radial equations for* $1s^2\,2s^2\,2p^q\,kp$ *configurations*

Denoting $P(1s)$, $P(2s)$ by S^1, S^2, the radial equations for $1s^2\,2s^2\,2p^q\,kp$ may be obtained on adding the following terms to the equations given in § 4·3:

(i) the term

$$\sum_{\kappa=1,\,2}2y_0(S^\kappa_m S^\kappa_m)$$

is added to all V_{mm},

(ii) the term

$$\sum_{\kappa=1,\,2}\tfrac{1}{3}y_1(S^\kappa_m F_m)\,S^\kappa_m$$

is added to all W_{mm},

(iii) the term

$$\sum_{\kappa=1,\,2}\beta_{mn}\{2R_0(S^\kappa_m P_m S^\kappa_n F_n)-\tfrac{1}{3}R_1(P_m S^\kappa_m S^\kappa_n F_n)\}\,P_n$$

is added to all W_{mn}(prior), and the term

$$\sum_{\kappa=1,\,2}\beta_{mn}\,\Delta(P_m F_n)\,\{2y_0(S^\kappa_m S^\kappa_n)\,P_n-\tfrac{1}{3}y_1(S^\kappa_m P_n)\,S^\kappa_n\}$$

is added to all W_{mn}(post).

In the E.R. approximation the relations (77), (78) remain valid if the y_1 and R_1 terms are included in the equations for the F_m and the bound-state equations (24), or if they are omitted in all of these equations.

PART II. ELECTRON EXCITATION OF THE GROUND CONFIGURATION TERMS OF O I

5. *Expressions for electron excitation rates*

5·1. *General collision theory*

Using the expansion $\Psi = \sum_n \mathscr{A} \psi_n(i^{-1})\, \phi_n(i)$ for the wave function of a system consisting of an ion plus a free electron, and neglecting continuous ψ_n states, the usual quantum-mechanical expression for the current gives for large radial distances,

$$\mathbf{j} = \sum_n \mathbf{j}_n, \tag{83}$$

with

$$\mathbf{j}_n = \frac{1}{2i}\{\phi_n^* \nabla \phi_n - \phi_n \nabla \phi_n^*\}. \tag{84}$$

To determine the rate of transitions between two non-degenerate states n and n', the wave functions must be determined with asymptotic form

$$\phi_n \sim \mathrm{e}^{\mathrm{i}k_n z} + f_{nn}(\theta)\frac{\mathrm{e}^{\mathrm{i}k_n r}}{r}, \tag{85}$$

$$\phi_{n'} \sim f_{nn'}(\theta, \phi)\frac{\mathrm{e}^{\mathrm{i}k_{n'} r}}{r}. \tag{86}$$

The inelastic collision cross-section is then given, in units $\pi \mathbf{a}_0^2$, by

$$Q(n \to n') = \frac{1}{\pi}\frac{k_{n'}}{k_n}\int |f_{nn'}|^2 \sin\theta \,\mathrm{d}\theta\, \mathrm{d}\phi, \tag{87}$$

all other quantities being in atomic units.

For many purposes a more convenient quantity than $Q(n \to n')$ is the collision parameter, $\Omega(n, n') = k_n^2 Q(n \to n')$, introduced by Hebb & Menzel (1940). Detailed balancing requires that $\Omega(n, n') = \Omega(n', n)$.

5·2. *Degenerate systems*

The collision parameter connecting two degenerate levels n and n', with wave functions ψ_{n_s} $(s = 1$ to $\omega_n)$ and $\psi_{n'_t}$ $(t = 1$ to $\omega_{n'})$, is defined by

$$\Omega(n, n') = \sum_{s,t} \Omega(n_s, n'_t). \tag{88}$$

The cross-section for the transition $n \to n'$ is then given by

$$Q(n \to n') = \Omega(n, n')/k_n^2 \omega_n.$$

Spin factors have been omitted in (85) to (87). These may be allowed for by taking the incident wave to be plane polarized. $\Omega(n, n')$ is, of course, independent of the choice of directions of incidence and spin polarization.

5·3. *Resolution into free-electron orbital angular momentum components*

The plane wave e^{ikz} may be expanded in the form

$$\mathrm{e}^{ikz} = \frac{1}{k}\sum_l [4\pi(2l+1)]^{\frac{1}{2}}\, i^l \Theta_l^0 \Phi^0 \frac{1}{r} G(kl \mid r) \tag{89}$$

(*T.A.C.* p. 22), where $G(kl \mid r) = (\pi k r/2)^{\frac{1}{2}} J_{l+\frac{1}{2}}(kr)$ has asymptotic form

$$G(kl \mid r) \sim \sin(kr - \tfrac{1}{2}l\pi). \tag{90}$$

The incident wave may therefore be written as

$$\phi_{n_s} = \frac{1}{k_n}\sum_{l}\delta(+\tfrac{1}{2},s)\,[4\pi(2l+1)]^{\frac{1}{2}}\,i^l\Theta_l^0\,\Phi^0\frac{1}{r}F_{n_s}(k_n l\,|\,r), \tag{91}$$

where
$$F_{n_s}(k_n l\,|\,r) \sim \sin(k_n r-\tfrac{1}{2}l\pi)+C^l(n_s,n_s)\,\mathrm{e}^{\mathrm{i}(k_n r-\frac{1}{2}l\pi)}, \tag{92}$$

and the scattered wave as

$$\phi_{n'_t} = \frac{1}{k_n}\sum_{l'}\delta(m'_s,s)\,[4\pi(2l+1)]^{\frac{1}{2}}\,i^l\Theta_{l'}^{m^{l'}}\Phi^{m^{l'}}\frac{1}{r}F_{n'_t}(k_{n'}l'\,|\,r), \tag{93}$$

where
$$F_{n'_t}(k_{n'}l'\,|\,r) \sim C^{l'}(n_s,n'_t)\,\mathrm{e}^{\mathrm{i}(k_{n'}r-\frac{1}{2}l'\pi)}. \tag{94}$$

The conservation of component angular momenta for the whole system gives

$$m^{s'} = M_S^C+\tfrac{1}{2}-M_S^{C'} \quad\text{and}\quad m^{l'} = M_L^C-M_L^{C'},$$

where M_S^C, M_L^C and $M_S^{C'}$, $M_L^{C'}$ are the component angular momenta of ψ_{n_s} and $\psi_{n'_t}$.

Using the orthogonal properties of the spherical harmonics the collision parameter may be written

$$\Omega(n,n') = 4\frac{k_{n'}}{k_n}\sum_{l'}(2l'+1)\sum_{s,t}|\,C^{l'}(n_s,n'_t)\,|^2. \tag{95}$$

It may therefore be expressed as the sum of terms arising from the orbital angular momentum components l' of the scattered wave. The amplitudes $C^{l'}(n_s,n'_t)$ may be further analyzed into terms arising from the orbital angular momentum components l of the incident wave. In many cases the contributions from $l=l'$ are much greater than the contributions from $l\neq l'$.† If the latter be neglected we may write

$$\Omega(n,n') = \sum_{l}\Omega^l(n,n'), \tag{96}$$

where $\Omega^l(n,n')$ involves only the l components of both incident and scattered waves.

The conservation theorem of Mott (1931) and of Bohr, Peierls & Placzek (unpublished; see *T.A.C.* p. 133) states that for any non-degenerate state q,

$$\sum_{p\neq q}\Omega^l(q,p)\leqslant(2l+1), \tag{97}$$

from which it follows that
$$\Omega^l(n,n')\leqslant(2l+1)\,\omega_<, \tag{98}$$

where $\omega_<$ is the smaller of ω_n, $\omega_{n'}$.

5·4. *Resolution into total angular momentum interactions*

In § 3·3 it was shown that the states of an ion plus a free l-electron could most conveniently be represented using the total angular momenta. For a given angular momentum interaction, $L_i^T S_i^T M_{L_i}^T M_{S_i}^T$, the amplitudes $C^{l,i}(n,n')$ are independent of $M_{L_i}^T M_{S_i}^T$, giving

$$\sum_{s,t}|\,C^l(n_s,n'_t)\,|^2 = \sum_{i}\frac{\omega^i}{2(2l+1)}|\,C^{l,i}(n,n')\,|^2, \tag{99}$$

---

† This only applies to transitions for which n and n' have the same parity. In general the conservation of parity requires that the only non-zero contributions arise from $(l-l')$ even if n, n' have the same parity, and from $(l-l')$ odd if n, n' have opposite parity.

the summation being over all interactions with different $L_i^T S_i^T$. ω^i is the interaction statistical weight, $(2L_i^T+1)(2S_i^T+1)$, and $2(2l+1)$ is the free electron statistical weight. It follows that $\Omega^l(n,n') = \sum_i \Omega^{l,i}(n,n')$ with

$$\Omega^{l,i}(n,n') = 2\omega^i \frac{k_{n'}}{k_n} |C^{l,i}(n,n')|^2. \tag{100}$$

The conservation theorem limit takes the form

$$\sum_{n \neq n'} \Omega^{l,i}(n,n') \leqslant \tfrac{1}{2}\omega^i. \tag{101}$$

The use of total-spin interactions is common in collision theory, but total orbital angular momentum interactions do not appear to have been used previously. The justification for this procedure is that the complete wave function may always be expressed as a linear combination of total angular momentum wave functions, and that physical results, summed over degenerate states, are independent of the representation chosen (see, for example, Schiff 1949).

5·5. *The distorted wave Born-Oppenheimer approximation*

The D.W.B.O. approximation (Massey & Mohr 1952; Erskine & Massey 1952) is based on the assumption that all coupling terms are small. The wave incident on state n is calculated with the neglect of all coupling terms and the wave scattered from state n' is calculated with the inclusion of only those coupling terms directly connecting n and n'. The cross-section is given by (87) with

$$f_{n,n'}(\theta,\phi) = -\frac{1}{2\pi}\int \phi^*_{n'}(1)\,[V_{n'n}(1)\,\phi_n(1) - W_{n'n}(1)]\,\mathrm{d}\mathbf{x}_1 \tag{102}$$

(*T.A.C.* pp. 113, 146; see also Erskine & Seaton 1953), where ϕ_n, $\phi_{n'}$ are solutions of

$$\left.\begin{aligned} [H_1 - \tfrac{1}{2}k_n^2]\,\phi_n + V_{nn}\phi_n - W_{nn} &= 0,\\ [H_1 - \tfrac{1}{2}k_{n'}^2]\,\phi_{n'} + V_{n'n'}\phi_{n'} - W_{n'n'} &= 0. \end{aligned}\right\} \tag{103}$$

ϕ_n is taken to have asymptotic form (85) and

$$\phi_{n'}(1) \sim \mathrm{e}^{\mathrm{i}\mathbf{k}_{n'}\cdot\mathbf{r}_1} + f_{n'n'}(\theta_1,\phi_1)\,\frac{\mathrm{e}^{\mathrm{i}k_{n'}r_1}}{r_1}, \tag{104}$$

where $\mathbf{k}_{n'}$ is a vector of modulus $k_{n'}$ in the (θ,ϕ) direction.

When approximate wave functions are used for ψ_n, $\psi_{n'}$, the detailed balanced condition $\Omega(n,n') = \Omega(n',n)$ is always satisfied using (41 *a*), but may not be satisfied using either (41 *b*) (prior interaction) or (41 *c*) (post interaction); in all cases $\Omega_{\text{prior}}(n,n') = \Omega_{\text{post}}(n',n)$.

6. *Electron excitation of the ground configuration terms of* O I

6·1. *Wave functions and energies for* O I

Hartree *et al.* (1939) have calculated Hartree-Fock wave functions for the three terms, ^3P, ^1D and ^1S, of the ground configuration $1s^2\,2s^2\,2p^4$ of O I. The observed and Hartree-Fock energies, the ϵ_{2p2p} parameters and the statistical weights are quoted in table 4. As before, the three terms are denoted by subscripts 1, 2 and 3.

TABLE 4

term	n	ω_n	excitation energy in rydbergs		ϵ_n
			observed	Hartree-Fock	
^3P	1	9	0	0	$1{\cdot}26_2$
^1D	2	5	0·145	0·152	$1{\cdot}20_2$
^1S	3	1	0·308	0·378	$1{\cdot}11_1$

6·2. *Calculations using a modified D.W.B.O. approximation*

Excitation functions for the $1 \rightarrow 2$ and $1 \rightarrow 3$ transitions have been calculated by Yamanouchi, Inui & Amemiya (1940) using a *modified* D.W.B.O. approximation. The following approximations were made in addition to those essential to the D.W.B.O. method:

(i) The exchange distortion terms, W_{nn}, were omitted.

(ii) The free orbitals were assumed orthogonal to the bound orbitals.

(iii) The y_2 terms in the potentials were omitted.

These calculations gave curves for $\Omega(1,2)$ and $\Omega(1,3)$ with maxima of $\Omega(1,2) = 1350$ at $k_1^2 = 0{\cdot}64\,\mathrm{Ry}$, and $\Omega(1,3) = 197$ at $k_1^2 = 0{\cdot}81\,\mathrm{Ry}$. It was found that, *compared to the contribution from the p waves, all other contributions were utterly negligible*. Using the conservation limit (98), Bates *et al.* (1950) were therefore able to show that these results were too great by factors of at least 89 and 66 respectively.

The configuration np^4kp has been discussed in § 4, where it was shown that ^2P and ^2D were the only angular momentum interactions leading to transitions. According to (100) the collision parameters are given by

$$\left.\begin{aligned}\Omega^p(1,2) &= 2\frac{k_2}{k_1}\{6\,|\,C^{p,{}^2P}(1,2)\,|^2+10\,|\,C^{p,{}^2D}(1,2)\,|^2\},\\ \Omega^p(1,3) &= 2\frac{k_3}{k_1}\{6\,|\,C^{p,{}^2P}(1,3)\,|^2\}.\end{aligned}\right\} \qquad (105)$$

Since V_{12} and V_{13} are identically zero, the *complete* D.W.B.O. approximation gives

$$|\,C^{p,i}(n,m)\,| = \frac{2}{k_m}\int_0^\infty F_m\,W^{p,i}_{mn}\,\mathrm{d}r, \qquad (106)$$

where the $W^{p,i}_{mn}$ are given by (68) and table 2, and the F_m are solutions of

$$[\mathscr{H}^p + V_{mm} - \tfrac{1}{2}k_m^2]\,F_m - W_{mm} = 0, \qquad (107)$$

bounded at the origin and normalized to $F_m \sim \sin(k_m r - \frac{1}{2}\pi + \eta_m)$.

The modified D.W.B.O. calculations were checked for $\Omega(1,2)$ at $k_1^2 = 0{\cdot}64\,\mathrm{Ry}$, making approximations (i) to (iii) and in addition.

(iv) The y_2 terms in the exchange integrals were omitted. In this approximation

$$\Omega^p(1,2) = \frac{240}{k_1k_2}\,|\,R_0(P_1P_2F_2F_1)\,|^2. \qquad (108)$$

The value $\Omega(1,2) = 1240$ was obtained, in good agreement with the previous calculation and showing that the further approximation (iv) is of little consequence.† In this approxi-

---

† There are also other minor differences. We used calculated energies and the same radial function (P_1) for both potentials, while Yamanouchi *et al.* used observed energies and allowed for the differences of the radial functions in the potentials.

mation the ${}^2D$ interaction gives no contribution so that the conservation limit (101) is $\Omega^p(1,2)+\Omega^p(1,3)\leqslant 3$; the modified D.W.B.O. results are seen to be too large by a factor of order at least 500.

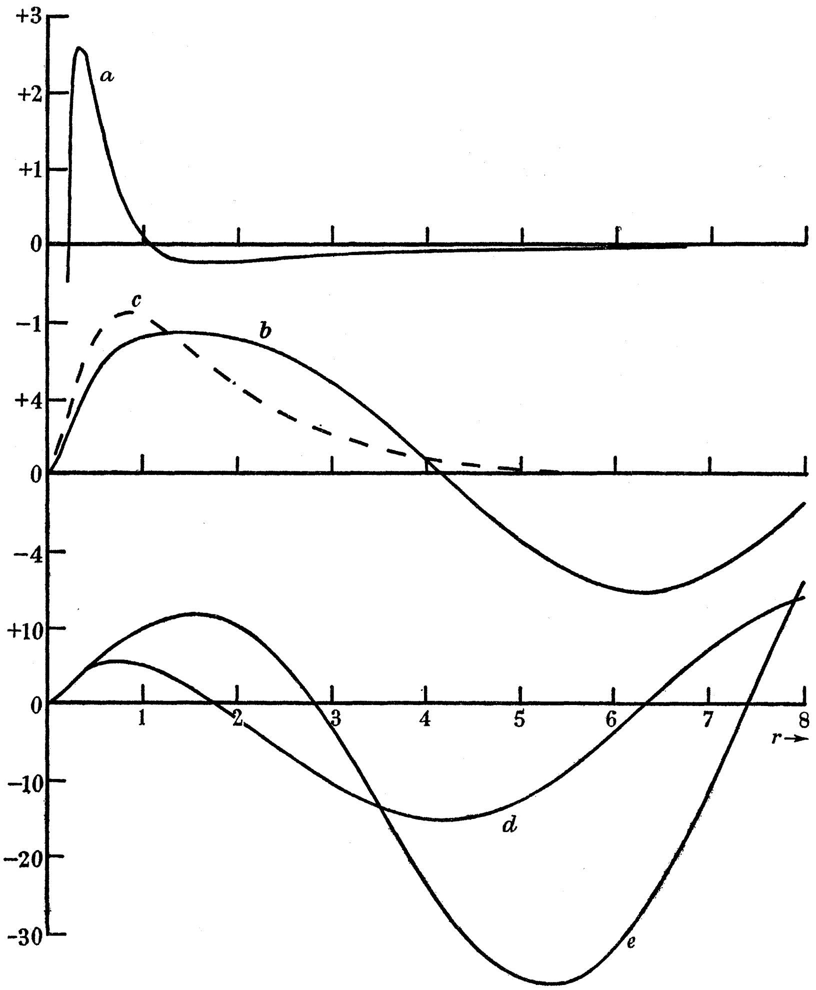

Figure 1. Examples of wave functions. Curve a, the effective potential $\mathfrak{f}_{11}$. Curve b, the non-exchange radial function F_1 for $k_1^2=0{\cdot}64\,\mathrm{Ry}$. Curve c, $10\times P(2p)$. Curve d, the E.R. radial function $\mathscr{F}$ for $k^2=0{\cdot}64\,\mathrm{Ry}$. Curve e, the E.R. radial function $\mathscr{G}$ for $k^2=0{\cdot}64\,\mathrm{Ry}$.

The reason for the failure of this approximation may be seen by referring to figure 1. Curve a gives the effective potential, $\mathfrak{f}_{11}=\dfrac{Z}{r}-V_{11}-\dfrac{1}{2}\left(\dfrac{2}{r^2}\right)$, which is seen to have a minimum for $r\simeq 1{\cdot}6$. As emphasized by Yamanouchi *et al.* this minimum, augmented by polarization effects, makes possible the bound $2p^5$ state of O^-. It follows that, for $k_1^2\simeq 0{\cdot}5$, $\mathfrak{f}_{11}+k_1^2/2$ is close to zero between $r=1$ and $r=2$, giving a small curvature to F_1. This is illustrated in curve b. In consequence the first node of F_1 is far out, and there is a large overlap between F_1 and P (curve c). This accounts for the large modified D.W.B.O. results. Under these conditions the exchange distortion and coupling terms, far from being small, will tend to dominate the radial equations.†

---

† No calculations have been made using the complete D.W.B.O. method, with which more reasonable results might be obtained (cf. Massey & Mohr 1952).

It is also clear from figure 1 that the bound and free radial functions are certainly not orthogonal. If approximation (ii) is not made we have

$$\Omega^{p}(1,2) = \frac{240}{k_1k_2}\left|R_0(P_1P_2F_2F_1) - \tfrac{1}{2}(k_1^2+\epsilon_2)\,\Delta(P_2F_1)\,\Delta(P_1F_2)\right|^2,$$

$$\Omega^{p}(2,1) = \frac{240}{k_1k_2}\left|R_0(P_2P_1F_1F_2) - \tfrac{1}{2}(k_2^2+\epsilon_1)\,\Delta(P_1F_2)\,\Delta(P_2F_1)\right|^2,$$

where use has been made of the equations satisfied by the $P(2p)$'s. Numerical calculations for $k_1^2 = 0{\cdot}64$ Ry gave

$$R_0(P_1P_2F_2F_1) = 1{\cdot}70,$$

$$\tfrac{1}{2}(k_1^2+\epsilon_2)\,\Delta(P_2F_1)\,\Delta(P_1F_2) = 2{\cdot}59, \quad \tfrac{1}{2}(k_2^2+\epsilon_1)\,\Delta(P_1F_2)\,\Delta(P_2F_1) = 2{\cdot}46,$$

$$\Omega(1,2) = 334, \quad \Omega(2,1) = 244.$$

It is seen that the omitted orthogonality terms give contributions larger than, and of opposite sign to, the terms included by Yamanouchi *et al.* They also lead to a departure from the detailed balance condition.

6·3. *The exact resonance approximation: wave functions*

The equations (75), (76) for the E.R. radial functions $\mathscr{F}$ and $\mathscr{G}$ were solved for O I + p-electron, making the approximation of neglecting the $1skp$ and $2skp$ exchange interactions (§ 4·5). Since the $1s2p$ and $2s2p$ exchange interactions were included in the calculation of the bound wave functions the complete relations (77), (78) could not be satisfied. The λ parameters were therefore adjusted to make $\mathscr{F}$ and $\mathscr{G}$ satisfy

$$\Delta(P\mathscr{F}) = 0, \tag{109}$$

$$\tfrac{1}{2}(k^2+\epsilon)\,\Delta(P\mathscr{G}) = R_0(PPP\mathscr{G}). \tag{110}$$

It was found that a fairly rapid convergence was obtained by satisfying these relations at all stages of the iterative solutions (Seaton 1951 *a*). The $2p$ function used was $P = P_2$.†

The asymptotic form of the E.R. functions was obtained by fitting to the Bessel function solutions for large radial distances:

$$\left.\begin{aligned}\mathscr{F} &= \sqrt{\left(\frac{\pi kr}{2}\right)}\,[\alpha J_{\frac{3}{2}}(kr)+\beta J_{-\frac{3}{2}}(kr)],\\ \mathscr{G} &= \sqrt{\left(\frac{\pi kr}{2}\right)}\,[\gamma J_{\frac{3}{2}}(kr)+\delta J_{-\frac{3}{2}}(kr)],\end{aligned}\right\} \tag{111}$$

the asymptotic forms being then given by

$$\left.\begin{aligned}\mathscr{F} &\sim \alpha\sin x - \beta\cos x,\\ \mathscr{G} &\sim \gamma\sin x - \delta\cos x,\end{aligned}\right\} \tag{112}$$

with $x = kr - \frac{1}{2}\pi$. Table 5 gives the calculated values of $k^2\alpha$, β/k, $k^2\gamma$ and δ/k, which remain finite as $k^2 \to 0$. $\mathscr{F}$ and $\mathscr{G}$ were normalized for all k^2 so that $K[\mathscr{F}] = K[\mathscr{G}] = 100$ (§ 4·4). Figure 1 *d* and *e* gives graphs of $\mathscr{F}$ and $\mathscr{G}$ for $k^2 = 0{\cdot}64$ Ry, which may be compared with the non-exchange function of curve *b*.

---

† For strict consistency $P = P_3$ should be used, since this is calculated without y_2 terms, but it was considered that P_2 might give a slightly better approximation.

TABLE 5. THE ASYMPTOTIC FORM OF E.R. WAVE FUNCTIONS

k^2	$-k^2\alpha$	$-\beta/k$	$-k^2\gamma$	$-\delta/k$
0	4·12	$15{\cdot}9_0$	2·81	$141{\cdot}_4$
0·08	4·90	$14{\cdot}7_5$	6·93	$119{\cdot}_7$
0·148	5·45	$13{\cdot}8_5$	8·57	$104{\cdot}_6$
0·30	6·56	12·10	9·16	77·3
0·64	7·94	9·28	+4·65	43·7
0·98	8·54	7·35	−0·42	27·2

6·4. *The exact resonance approximation: collision parameters*

If the energy differences are neglected the collision parameters are given by the exact resonance expressions (cf. *T.A.C.* p. 148)

$$\left.\begin{aligned}\Omega(1,2)&=\Omega(2,1)=\tfrac{12}{5}\sin^2(\zeta-\xi),\\ \Omega(1,3)&=\Omega(3,1)=\tfrac{12}{25}\sin^2(\zeta-\xi),\\ \Omega(2,3)&=\Omega(3,2)=\tfrac{4}{15}\sin^2(\zeta-\xi),\end{aligned}\right\}\tag{113}$$

where ζ and ξ are the phases of $\mathscr{F}$ and $\mathscr{G}$ (i.e. $\zeta=\tan^{-1}(\beta/\alpha)$ and $\xi=\tan^{-1}(\gamma/\delta)$). This will be referred to as approximation I. While these expressions may be expected to give the general features correctly, they will be considerably in error for small values of k^2. A better approximation is obtained when energy differences are allowed for in calculating the Ω's. In § 4·4 it was shown that approximate wave functions, allowing for energy differences, could be obtained from the E.R. functions when the latter were suitably normalized (approximation II).

It is necessary to consider the calculation of the amplitudes $C^l(n,m)$ given the general mathematical solutions of the radial equations. In general, there will be three linearly independent sets of solutions, convergent at the origin, for F_1, F_2 and F_3, and without loss of generality these may be taken to be real. We denote them by $F_n^{(1)}$, $F_n^{(2)}$, $F_n^{(3)}$ $(n=1,2,3)$, and express their asymptotic forms as

$$F_n^{(1)}\sim a_n\sin(x_n+\lambda_n),\quad F_n^{(2)}\sim b_n\sin(x_n+\mu_n),\quad F_n^{(3)}\sim c_n\sin(x_n+\nu_n),\tag{114}$$

where $x_n=k_nr-\frac{1}{2}l\pi$. The general mathematical solutions are then

$$F_n=uF_n^{(1)}+vF_n^{(2)}+wF_n^{(3)},\tag{115}$$

u, v and w being arbitrary constants. We consider the determination of the amplitudes in the solutions which have asymptotic form

$$\left.\begin{aligned}F_1&\sim\sin x_1+C(1,1)\,\mathrm{e}^{\mathrm{i}x_1},\\ F_2&\sim C(1,2)\,\mathrm{e}^{\mathrm{i}x_2},\\ F_3&\sim C(1,3)\,\mathrm{e}^{\mathrm{i}x_3}.\end{aligned}\right\}\tag{116}$$

Substituting (115) in (116) and equating coefficients of $\mathrm{e}^{\mathrm{i}x_n}$ and $\mathrm{e}^{-\mathrm{i}x_n}$ gives

$$\left.\begin{aligned}uA_1+vB_1+wC_1&=1,\\ uA_2+vB_2+wC_2&=0,\\ uA_3+vB_3+wC_3&=0,\end{aligned}\right\}\tag{117}$$

and
$$\left.\begin{aligned} uA_1^*+vB_1^*+wC_1^* &= 1+2iC(1,1),\\ uA_2^*+vB_2^*+wC_2^* &= 2iC(1,2),\\ uA_3^*+vB_3^*+wC_3^* &= 2iC(1,3),\end{aligned}\right\} \tag{118}$$

where $A_n = a_n\,\mathrm{e}^{-\mathrm{i}\lambda_n}$, $B_n = b_n\,\mathrm{e}^{-\mathrm{i}\mu_n}$, $C_n = c_n\,\mathrm{e}^{-\mathrm{i}\nu_n}$. Solving (117) for u, v, w and substituting in (118) gives finally

$$D(1+2iC(1,1)) = \begin{vmatrix} A_1^* & B_1^* & C_1^* \\ A_2 & B_2 & C_2 \\ A_3 & B_3 & C_3 \end{vmatrix}, \tag{119}$$

$$D2iC(1,2) = \begin{vmatrix} A_2^* & B_2^* & C_2^* \\ A_2 & B_2 & C_2 \\ A_3 & B_3 & C_3 \end{vmatrix}, \tag{120}$$

$$D2iC(1,3) = \begin{vmatrix} A_3^* & B_3^* & C_3^* \\ A_2 & B_2 & C_2 \\ A_3 & B_3 & C_3 \end{vmatrix}, \tag{121}$$

with
$$D = \begin{vmatrix} A_1 & B_1 & C_1 \\ A_2 & B_2 & C_2 \\ A_3 & B_3 & C_3 \end{vmatrix}. \tag{122}$$

In approximation II we take (cf. table 3),

$$\left.\begin{aligned} &A_1 = (\alpha_1+i\beta_1), && B_1 = 0, && C_1 = 3(\gamma_1+i\delta_1),\\ &A_2 = 0, && B_2 = (\alpha_2+i\beta_2), && C_2 = \surd 5\,(\gamma_2+i\delta_2),\\ &A_3 = 3(\alpha_3+i\beta_3), && B_3 = \surd 5\,(\alpha_3+i\beta_3), && C_3 = -(\gamma_3+i\delta_3),\end{aligned}\right\} \tag{123}$$

where α_n, β_n and γ_n, δ_n are the constants for $\mathscr{F}(k_n)$ and $\mathscr{G}(k_n)$ in (111).

It is necessary to consider separately those energies for which $\frac{1}{2}k_1^2$ is less than the excitation energy of state $3(^1S)$. Considering the coupled equations for F_1, F_2 alone, the E.R. approximation gives as before two functions $\mathscr{F}$ and $\mathscr{G}$, the former satisfying (75) and the latter satisfying
$$[\mathscr{H}^p+V-\tfrac{1}{2}k^2]\,\mathscr{G} = \tau\mathscr{I}(\mathscr{G}), \tag{124}$$
with $\tau = -\frac{11}{3}$. It was not considered that this would differ sufficiently from the function $\mathscr{G}$ previously computed (satisfying (124) with $\tau = -4$) to justify the labour of a separate calculation. In place of (123) we have for this case

$$\left.\begin{aligned} &A_1 = -\surd 5\,(\alpha_1+i\beta_1), && B_1 = 3(\gamma_1+i\delta_1),\\ &A_2 = 3(\alpha_2+i\beta_2), && B_2 = \surd 5\,(\gamma_2+i\delta_2),\end{aligned}\right\} \tag{125}$$

and $C(1,2)$ is given by an obvious modification of (120).

Graphs of the Ω's in approximation II are given in figure 2, obtained from interpolating the constants in table 5. Since the detailed balance condition is not satisfied $\Omega(n,m)$ and $\Omega(m,n)$ have been computed separately. The conservation theorem limit (101) is seen to be satisfied. (The satisfaction of these conditions is not necessarily a guide to the accuracy of the result; *both* are satisfied in approximation I.) It is seen that there is a discontinuity of slope† in $\Omega(1,2)$ and $\Omega(2,1)$ at the threshold energy ($k_1^2 = 0{\cdot}378$ Ry) for excitation of state 3. This provides an interesting confirmation of the idea (see, for example, Bates *et al.* 1950) that, for strong coupling, the neglect of energetically possible transitions will tend to result in Ω being over-estimated.

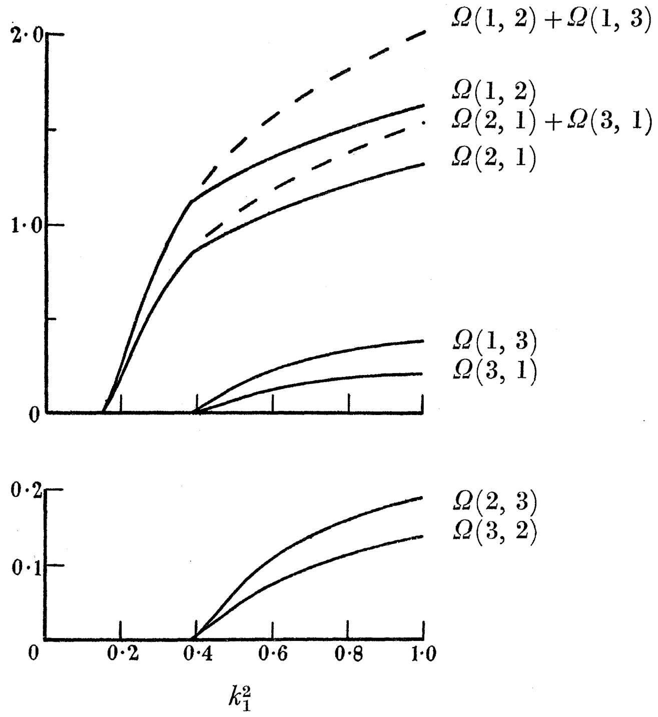

FIGURE 2. Collision parameters $\Omega(n, m)$ and $\Omega(m, n)$ in approximation II.

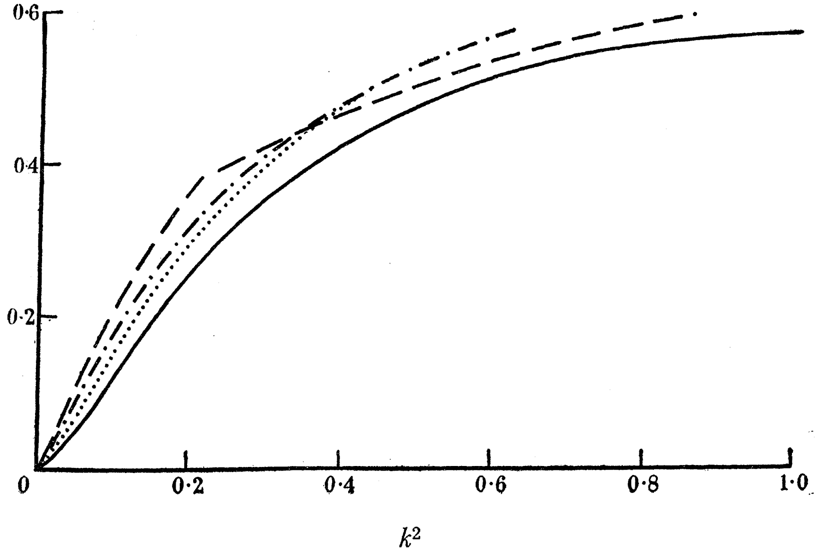

FIGURE 3. $\dfrac{75\bar{\Omega}(n, m)}{4\omega_n\omega_m}$. —— approx. I, $\sin^2(\zeta-\xi)$; - - - approx. II, $n=1$, $m=2$; ·–·– approx. II, $n=1$, $m=3$; .... approx. II, $n=2$, $m=3$.

---

† There is also a jump discontinuity in $\Omega(1, 2)$, but this is so small that it cannot be shown to the scale of figure 2.

Figure 3 gives a comparison of approximations I and II. In approximation I

$$75\Omega(n,m)/4\omega_n\omega_m = \sin^2(\zeta-\xi)$$

for all n, m. We compare this with $75\bar{\Omega}(n,m)/4\omega_n\omega_m$, where $\bar{\Omega}(n,m) = \surd\{\Omega(n,m)\,\Omega(m,n)\}$ is calculated on approximation II.

6·5. *Solution of the coupled equations*

The coupled equations for F_1 and F_2 were solved for $k_1^2 = 0{\cdot}30\,\mathrm{Ry}$, for which state 3 is energetically inaccessible (F_3 was put equal to zero). λ_{mn}(prior) was used, since this is not a function of r and is therefore much simpler than λ_{mn}(post). The only other approximation was to use the mean $2p$ function, $\bar{P} = (P_1+P_2)/2$, in the exchange integrals. This is unlikely to lead to any significant error. The two linearly independent sets of solutions were first written as

$$F_1^{(1)} = -\surd 5\,\mathscr{F}_1^\dagger, \quad F_1^{(2)} = 3\mathscr{G}_1^\dagger,$$

$$F_2^{(1)} = +3\mathscr{F}_2^\dagger, \quad F_2^{(2)} = \surd 5\,\mathscr{G}_2^\dagger,$$

and taken to be normalized so that $K[\mathscr{F}_1^\dagger] = K[\mathscr{F}_2^\dagger] = 100$ and $K[\mathscr{G}_1^\dagger] = K[\mathscr{G}_2^\dagger] = 100$. The uniqueness convention used was to put

$$2\surd 5\,\lambda_{11}(\bar{P}F_1) + 5\lambda_{12}(\bar{P}F_2) = 3\surd 5\,\lambda_{21}(\bar{P}F_1) + 2\lambda_{22}(\bar{P}F_2),$$

which ensures that $\mathscr{F}^\dagger$ and $\mathscr{G}^\dagger$ reduce in the E.R. approximation to the previously computed $\mathscr{F}$ and $\mathscr{G}$.

The asymptotic forms of $\mathscr{F}_1^\dagger$, $\mathscr{F}_2^\dagger$, $\mathscr{G}_1^\dagger$ and $\mathscr{G}_2^\dagger$ were determined in accordance with (111). The final results are summarized in table 6. Approximation III was obtained as an intermediate stage, using the full E.R. equations, including $1skp$ and $2skp$ exchange interactions and the correct fields including y_2 terms. It was not carried to quite the same degree of self-consistency as the other solutions. Approximation IV is the solution of the complete coupled equations.

Table 6. Summary of solutions for $k_1^2=0{\cdot}30\,\mathrm{Ry}$, $k_2^2=0{\cdot}148\,\mathrm{Ry}$

approx.	$-\alpha_1$	$-\beta_1$	$-\gamma_1$	$-\delta_1$	$-\alpha_2$	$-\beta_2$	$-\gamma_2$	$-\delta_2$	$\Omega(1,2)$	$\Omega(2,1)$	$\bar{\Omega}(1,2)$
I	36·8	5·33	57·9	40·2	36·8	5·33	57·9	40·2	0·48	0·48	0·48
II	21·9	6·6	30·6	42·3	36·8	5·33	57·9	40·2	0·81	0·62	0·71
III	17·8	2·7	30·0	37·1	26·4	0·24	55·8	33·6	0·98	0·88	0·93
IV	17·9	3·0	21·5	31·8	28·8	−0·06	46·7	26·8	1·06	0·90	0·98

Approx. I: E.R. wave functions, no $1s$, $2s$ exchange, no energy differences ($k^2=k_2^2$).
Approx. II: As I, with allowance for energy differences.
Approx. III: As II, with $1s$, $2s$ exchange.
Approx. IV: Solution of coupled equations.

Putting F_3 equal to zero when state 3 is energetically inaccessible is equivalent to neglecting a polarization correction, which should be allowed for by taking F_3 tending to zero exponentially as $r\to\infty$. That this correction is small is suggested by the smallness of the jump discontinuity in $\Omega(1,2)$ at the ^1S threshold. It is in any case unlikely to affect the relative accuracy of the various approximations compared in table 6. The agreement between the

E.R. and exact solutions of the two coupled equations is seen to be good, especially when $1s$, $2s$ exchange terms are included. It will be seen that $\mathscr{F}$ (α and β) gives better agreement between approximations III and IV than does $\mathscr{G}$ (γ and δ). This is due to the use of $\tau = -4$ in (124) for approximation III in place of the correct value of $\tau = -\frac{11}{3}$. When state 3 is excited it is therefore to be expected that approximations III and IV will give even better agreement for $\Omega(1, 2)$ than is shown in table 6.

The 16% difference between $\Omega(1, 2)$ and $\Omega(2, 1)$ in approximation IV is probably a consequence of the post-prior discrepancy (cf. § 5·5). In the absence of any further criterion as to which is most reliable, it appears reasonable to use the geometric mean, $\bar{\Omega}(1, 2)$.

6·6. *Other contributions to the collision parameters*

Having improved the accuracy of the p-wave ^2P interaction it is necessary to reconsider the importance of the other contributions. The p-wave ^2D interaction may be calculated using the D.W.B.O. method, which gives

$$\Omega^{p,\,^2D}(1, 2) = \frac{20}{k_1 k_2} | 0{\cdot}36 R_2(P_1 P_2 \mathscr{F}_2 \mathscr{F}_1) |^2,$$

where the $\mathscr{F}$'s are now normalized to asymptotic amplitude unity. This was calculated for $k_1^2 = 0{\cdot}30$ Ry using the approximation III wave functions, with the result $\Omega^{p,\,^2D}(1, 2) = 0{\cdot}007$. This is less than 1% of the ^2P contribution and is almost certainly given sufficiently accurately by this method.

Yamanouchi *et al.* found that the incident and scattered d-wave was next in importance to the p-wave. For this the bound and free orbitals are automatically orthogonal, and the other approximations of Yamanouchi *et al.* are unlikely to lead to serious error. Their calculations gave $\Omega^d(1, 2)$ rising slowly from the threshold, having the value 0·077 at $k_1^2 = 1{\cdot}0$ Ry, and a maximum of 0·95 at $k_1^2 = 4{\cdot}0$ Ry. Within the range of the present calculations we may conclude that Ω^d is barely significant.

6·7. *Summary*

At the check point it was found that the most important correction to approximation II was the inclusion of $1s$, $2s$ exchange terms. Since these terms have the same form in the equations for $\mathscr{F}$ and $\mathscr{G}$, the correction to the phase difference $(\zeta - \xi)$ increases as the difference between $\mathscr{F}$ and $\mathscr{G}$ increases. It therefore appears reasonable to assume a constant percentage correction to Ω at all energies. Final curves for $\Omega(1, 2)$, $\Omega(1, 3)$ and $\Omega(2, 3)$ are given in figure 4. These have been obtained by multiplying the approximation II values of $\bar{\Omega}$ by a factor of 1·31 to give agreement with approximation III at the check point (see § 6·5), and making some adjustment in the energy scales in order to give figure 4 in terms of observed energies. The parameters cannot be much larger than the values given, since the latter rise to within about 70% of the conservation limit. It also appears improbable that they have been over-estimated to any great extent. A tentative estimate of the probable error in $\Omega(1, 2)$ might be given as ±30%. The uncertainty in $\Omega(1, 3)$ is somewhat greater owing to the larger value of the coefficient γ_{13} ((68) and table 2), and an additional uncertainty in $\Omega(2, 3)$ is introduced by the potential coupling terms. Fortunately, $\Omega(2, 3)$ is of little importance in astrophysical problems. The accuracy of the present calculation should be adequate for most astrophysical applications.†

For higher energies, transitions to excited configurations must be taken into account (for $k_1^2 \geqslant 0{\cdot}809$ the ^2P interaction gives transitions to $3p\,^3P$). The p-wave contributions cannot increase much beyond the values given in figure 4, and must eventually decrease. This will be compensated to some extent by the contributions from higher angular momentum components. The best simple approximation for higher energies is probably to take the Ω's as constant at the maximum values given in figure 4. For sufficiently high energies they must eventually tend to zero, but this is unimportant in most applications.

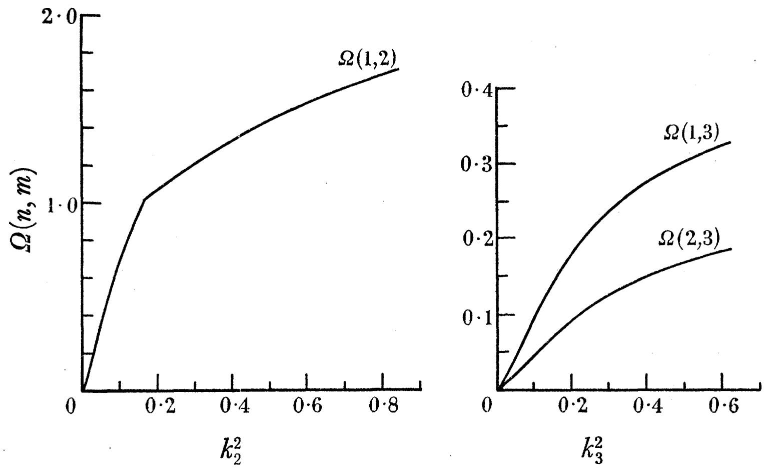

FIGURE 4. Final collision parameters for excitation of the O I ground configuration terms ($1 = {}^3P$, $2 = {}^1D$, $3 = {}^1S$). $\Omega(n, m) = Q(n \rightarrow m) \times k_n^2 \omega_n = Q(m \rightarrow n) \times k_m^2 \omega_m$, with Q in units $\pi \mathbf{a}_0$ and k_n^2 the electron energy in rydbergs (13·54 eV).

7. *Elastic scattering of slow electron by* O I

The elastic scattering of slow electron by O I is of importance in determining the collision frequency in the ionized layers of the Earth's atmosphere. The elastic collision cross-section, $Q_E = \Omega(1,1)/9k_1^2$, remains finite as $k_1^2 \rightarrow 0$, and is therefore a more convenient quantity than the collision parameter $\Omega(1,1)$. We consider separately the various contributions to Q_E.

7·1. *The s-wave*

The contribution of s electrons has been discussed in detail by Bates & Massey (1947). The situation is complicated by the possibility of resonance due to the existence of a $2p^4\,3s$ excited state of O$^-$ with near zero binding energy. In solving the Hartree-Fock equations for free s-electrons, Bates & Massey allowed for this possibility by including a variable polarizability term in the potential. Figure 5 curve *a* gives Q_E^s calculated with the experimental polarizability (case A), which does not give the resonance effect. This is near to the

---

† Barbier (1948) has attempted to deduce the excitation rates for O I from astrophysical data (together with the Hebb & Menzel (1940) parameters for O III). His equations are only strictly valid when Ω is independent of energy, which is not a good approximation for a neutral atom. The result obtained, $\Omega(1, 2) \simeq 0{\cdot}002$, is too small by a factor of order 10^{-3}.

smallest Q_E^s obtained for any value of polarizability. When resonance does occur, Q_E^s is much larger (case B).†

7·2. *The p-wave, ${}^2P$ interaction*

(i) For energies greater than the ${}^1D$ threshold, $Q_E^{p,{}^2P}$ may be calculated using the E.R. wave functions of § 6·3, together with the formulae given in § 6·4. This gives the full line part of curve *b*, figure 5.

(ii) For energies less than the ${}^1D$ threshold,

$$Q_E^{p,{}^2P} = \frac{4}{3}\frac{1}{k_1^2}\sin^2\chi,$$

where χ is the phase of the function F satisfying

$$[\mathscr{H}^p + V - \tfrac{1}{2}k_1^2]\,F = -2\mathscr{I}(F).$$

In view of the uncertainty in Q_E^s the labour of calculating this function did not appear justified. If we replace χ by ξ, the phase of $\mathscr{G}$, we obtain at the ${}^1D$ threshold $Q_E^{p,{}^2P} = 2{\cdot}93\pi\mathbf{a}_0^2$.

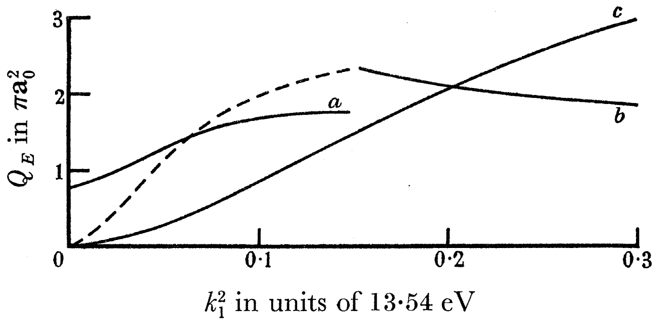

FIGURE 5. Partial cross-sections for elastic scattering of electrons by O I. Curve *a*, Q_E^s calculated by Bates & Massey (1947), assuming a polarizability of 5·7 A.U. (case *A*). Curve *b*, contribution of the ${}^2P$ interaction to Q_E^p. Curve *c*, sum of other contributions to Q_E^p.

The limiting value obtained in (i) above was $2{\cdot}34\pi\mathbf{a}_0^2$. The dashed part of curve *b* was therefore obtained by putting

$$Q_E^{p,{}^2P} = \left(\frac{2{\cdot}34}{2{\cdot}93}\right)\frac{4}{3}\frac{1}{k_1^2}\sin^2\xi.$$

Using the phase of the non-exchange function F gave $Q_E^{p,{}^2P} = 0{\cdot}08\pi\mathbf{a}_0^2$ at the ${}^1D$ threshold, which is much too small.

7·3. *The p-wave, other interactions*

Neglecting y_2 and R_2 terms the sum of all other *p*-wave interactions (${}^2S, D$ and ${}^4S, P, D$) gives

$$Q_E^p = \frac{32}{3}\frac{1}{k_1^2}\sin^2\zeta,$$

where ζ is the phase of $\mathscr{F}$. This is given in figure 5, curve *c*.

---

† The uncertainty introduced by the possiblity of resonance only arises for the *s*-wave. There is no uncertainty of this sort for the collision parameters connecting the ground configuration terms, since Ω^s is identically zero for inelastic collisions involving a change in orbital angular momentum.

7·4. *Summary*

There is strong experimental evidence for the existence of a stable excited state of O^- (Massey 1950). If this state is in the $2p^43s$ configuration with a binding energy which is not too small, or if it is in a configuration other than $2p^43s$, then resonance will not occur and case A may give a good approximation to Q_E^s. The p-wave is then important in determining the exact value of the cross-section. If, on the other hand, the resonance phenomena does occur for the s-wave, then the p-wave contribution to Q_E is utterly negligible.

The author is indebted to Professor H. S. W. Massey, F.R.S., for suggesting the present investigation, and to Professor Massey and Professor D. R. Bates for much helpful advice.

References

Aller, L. H. & Menzel, D. H. 1945 *Astrophys. J.* **102**, 239.
Barbier, D. 1948 *Ann. Astrophys.* **11**, 193.
Bates, D. R., Fundaminsky, A., Leech, J. W. & Massey, H. S. W. 1950 *Phil. Trans.* A, **243**, 93.
Bates, D. R. & Massey, H. S. W. 1941 *Proc. Roy. Soc.* A, **177**, 329.
Bates, D. R. & Massey, H. S. W. 1943 *Phil. Trans.* A, **239**, 269.
Bates, D. R. & Massey, H. S. W. 1947 *Proc. Roy. Soc.* A, **192**, 1.
Bates, D. R., Massey, H. S. W. & Pearse, R. W. B. 1948 *The emission spectra of the night sky and aurorae.* London: Physical Society.
Bates, D. R. & Seaton, M. J. 1949 *Mon. Not. R. Astr. Soc.* **109**, 698.
Erskine, G. A. & Massey, H. S. W. 1952 *Proc. Roy. Soc.* A, **212**, 521.
Erskine, G. A. & Seaton, M. J. 1953 *Proc. Phys. Soc.* A, **66**, 123.
Fock, V. 1930 *Z. Phys.* **61**, 126.
Hartree, D. R. 1946–7 *Rep. Progr. Phys.* **11**, 113.
Hartree, D. R. & Hartree, W. 1936 *Proc. Roy. Soc.* A, **154**, 588.
Hartree, D. R., Hartree, W. & Swirles, B. 1939 *Phil. Trans.* A, **238**, 229.
Hebb, M. H. & Menzel, D. H. 1940 *Astrophys. J.* **92**, 408.
Huang, Kun 1945 *Astrophys. J.* **101**, 196.
Kolodziejski, R. 1951 *Acta phys. polon.* **10**, 223.
Lennard-Jones, J. E. 1930 *Proc. Camb. Phil. Soc.* **27**, 469.
Massey, H. S. W. 1950 *Negative ions*, p. 60. 2nd ed. Cambridge University Press.
Massey, H. S. W. & Mohr, C. B. O. 1952 *Proc. Phys. Soc.* A, **65**, 845.
Morse, P. M. & Allis, W. P. 1933 *Phys. Rev.* **44**, 269.
Mott, N. F. 1931 *Proc. Roy. Soc.* A, **133**, 228.
Schiff, L. I. 1949 *Quantum mechanics*, p. 236. 1st ed. New York: McGraw Hill.
Slater, J. C. 1951 *Phys. Rev.* **81**, 385.
Seaton, M. J. 1950 *Mon. Not. R. Astr. Soc.* **110**, 247.
Seaton, M. J. 1951*a* *Proc. Roy. Soc.* A, **208**, 408.
Seaton, M. J. 1951*b* *Proc. Roy. Soc.* A, **208**, 418.
Wheeler, J. A. 1937 *Phys. Rev.* **52**, 1083, 1107.
Woolley, R. v. d. R. & Allen, C. W. 1948 *Mon. Not. R. Astr. Soc.* **108**, 292.
Yamanouchi, T., Inui, Y. & Amemiya, A. 1940 *Proc. Phys. Math. Soc. Japan*, **22**, 847.
Yamanouchi, T. & Kotani, M. 1940 *Proc. Phys. Math. Soc. Japan*, **22**, 154.