

quadrupole shielding and antishielding occurs although no simple trends are discernible.

In Table IV the sensitivity of the calculated polarizabilities and shielding factors to the choice of zeroth-order Hartree-Fock function is demonstrated. This sensitivity is most pronounced in the negative ions (note the Cl^- values), although some of the inert gas functions give substantial disparity in the results. The energy of the outermost orbital and the total energy of a given atom or ion is listed to exhibit the relationships of the polarizabilities and shielding factors to these quantities. Polarizability effects are primarily dependent upon the

outermost regions of an atomic-charge distribution and, therefore, constitute a sensitive test of the relative accuracy of zeroth-order functions as is evident from Table IV.

It should be noted that the calculated values for α_{24} and γ_{24} are quite large in some cases and, therefore, for field strengths attainable in the laboratory (10^6 V/cm and higher), the quadrupole moments induced in S -state atoms and ions are of the same order of magnitude as permanent molecular quadrupole moments. The method discussed by Buckingham⁶ should, therefore, be quite feasible for measuring these parameters.

Excitation of the Spin Multiplets of the Ground State of Oxygen by Slow Electrons*

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Electron excitation cross sections of the transitions between the three spin multiplets $J=0, 1, 2$, of the $[(1s)^2(2s)^2(2p)^4]^3P$ ground state of the neutral oxygen atom have been calculated by using the continuous-state Hartree-Fock formulation for electron energies of 500–10 000°K. Partial-wave analysis is performed in a coupled representation characteristic of the total angular momentum of the entire system. The scattering equations are further simplified by neglecting the coupling between the different partial waves of the incident electron. Under an exact-resonance approximation, the scattering equations for the s wave can be completely decoupled and the solutions obtained by numerical iteration. The p -wave manifold consists of three sets of simultaneous equations. Exact solutions (close-coupling) are obtained for selected scattering equations and are compared with the corresponding collision strengths calculated by a modified distorted-wave treatment to examine the validity of the latter approximate method. Final collision strengths for the p wave are evaluated from appropriate combinations of the close-coupling and weak-coupling schemes. Partial cross sections for the d wave are found to be of minor importance and may be obtained with the Born approximation. Corrections for the energy differences between atomic states are found to be small. The calculated cross sections are somewhat larger than the values estimated by Gershberg and provide evidence for the importance of the role of neutral oxygen atoms in the cooling of the interstellar media.

I. INTRODUCTION

FORBIDDEN transitions between the spectral terms of the ground configuration of neutral atomic oxygen give rise to some of the most prominent lines in the spectrum of auroras, and the excitation of these metastable states by electron impact has been a subject of considerable interest. Yamanouchi, Inui, and Amemiya¹ calculated the excitation and de-excitation cross sections for the 3P , 1D , and 1S terms of the ground configuration $(1s)^2(2s)^2(2p)^4$ by the Born-Oppenheimer approximation, but considered only potential distortion and assumed the free-electron wave functions to be orthogonal to the bound-state orbitals. Bates *et al.*,²

however, later have pointed out that these cross sections were overestimated by several orders of magnitude. The errors originated from the incorrect assumptions of weak distortion and weak coupling and the failure to consider the orthogonality requirements. To correct the situation, Seaton³ formulated the electron-atom collision problem in a manner analogous to the Hartree-Fock method for bound atomic states. Continuous-state Hartree-Fock equations were obtained by adopting antisymmetrized basis wave functions in the appropriate expansions. The strength of the exchange coupling for p wave was found to be so great that the usual weak-coupling approximations could not be relied upon. By retaining only the strong spherically symmetric exchange terms and assuming equal energies for all three atomic states (exact-resonance approximation), the scattering equations were uncoupled by transformation and solved numerically. In later papers,

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¹ T. Yamanouchi, Y. Inui, and A. Amemiya, *Proc. Phys. Math. Soc. Japan* **22**, 847 (1940).

² D. R. Bates, A. Fundaminsky, J. W. Leech, and H. S. W. Massey, *Phil. Trans. Roy. Soc. London* **A243**, 93 (1950).

³ M. J. Seaton, *Phil. Trans. Roy. Soc. London* **A245**, 469 (1953).

TABLE I. Composite states for values of $l \leq 2$.

Designation				Designation			
J_T	J	j	l ($M_T=J_T$)	J_T	J	j	l ($M_T=J_T$)
$\frac{1}{2}$	1	0	0	$\frac{3}{2}$	2	0	2
	0	0	0		1	2	11
	2	1	1		0	2	12
	1	1	1		2	0	A
	1	1	1		2	1	B
	0	1	1		1	1	C
	2	2	2		2	1	D
	2	2	2		2	2	E
	1	2	2		1	2	F
	2	2	0		1	0	G
$\frac{3}{2}$	1	0	2	2	2	H	
	2	1	3	1	2	P	
	1	1	4	2	2	I	
	0	1	5	2	2	II	
	2	1	6	1	2	III	
	1	1	7	2	2	IV	
	2	2	8				
	1	2	9				

Seaton^{4,5} employed a modified type of distorted-wave method and perturbation techniques to correct for the coupling terms which had been omitted in the earlier work.

The O^{++} ion (O_{III}) with a ground configuration of $(1s)^2(2s)^2(2p)^2$ has the same set of spectral terms as O_I . Hebb and Menzel⁶ calculated the transition probabilities between the 3P , 1D , and 1S terms using the Born-Oppenheimer approximation, with the free plane-wave appropriately replaced by the continuous Coulomb wave functions. Seaton⁴ has subsequently refined these calculations in a manner analogous to the procedures adopted for O_I .

Another interesting process is the electron excitation of the spin-multiplets of the 3P state. The cross sections for these transitions in O_{III} were important in determining the conditions under which the Bowen fluorescent mechanism would operate. The calculations by Hebb and Menzel⁶ were found to overestimate these cross sections by about an order of magnitude. In Seaton's improved calculations,^{4,5} the distorted-wave Born-Oppenheimer approximation was used with exchange distortion neglected. However, no calculations of the spin-multiplet transitions of O_I have yet been made.

Recently Gershberg⁷ has postulated that the excitation of the spin-multiplet components of the 3P ground state of O_I by electron impact may be an important cooling mechanism in the H_I regions of interstellar space. The behaviors of the O_{III} cross sections near threshold were corrected empirically and ratios were established for associated transitions between the 3P , 1D , 1S states of the ground configurations in O_I and O_{III} . The unknown cross sections for the spin-multiplet

transitions of O_I could thus be roughly estimated. With only order of magnitude accuracy expected, Gershberg concluded that the contributions to the cooling rate from neutral oxygen atoms and carbon ions may be of comparable size. However, the cross sections of neutral atoms and ions are known to behave quite differently for low energy, and the approach taken by Gershberg could result in considerable error at the low temperatures considered. The spin-multiplet spacings are 0, 0.00072, 0.00103 atomic units (a.u.) for the $J=2, 1, 0$ components of O_I , thus excitation can take place with very slow electrons. The smaller degree of penetration of the slow electrons tends to de-emphasize the exchange effect and consequently causes the potential coupling to play a more important role. A detailed calculation of these excitation cross sections is reported in this paper and the effects of the different coupling terms on the cross sections are examined.

II. GENERAL FORMULATION

The Hartree-Fock equations for continuous states developed by Seaton³ are used as the starting point in the formulation. To clarify the notation, a brief resume of Seaton's development is given here. Hartree atomic units are used throughout the work.

Consider an electron moving in the field of a neutral atom of nuclear charge Z with N electrons. Let us denote the incident electron by i and the totality of the N atomic electrons by i^{-1} . The Hamiltonian of the $(N+1)$ -electron system may be written as

$$H = H_i + H(i^{-1}) + \sum_{j=1, j \neq i}^{N+1} 1/r_{ij}, \quad (1)$$

where

$$H_i = -\frac{1}{2}\nabla_i^2 - Z/r_i, \quad (2)$$

$$H(i^{-1}) = \sum_{j=1, j \neq i}^{N+1} [H_j + \sum_{k>j, k \neq i}^{N+1} 1/r_{jk}].$$

The wave functions of the isolated atom are denoted by $\psi_n(i^{-1})$, i.e.,

$$H(i^{-1})\psi_n(i^{-1}) = E_n\psi_n(i^{-1}). \quad (3)$$

To solve the Schrödinger equation for the $(N+1)$ -electron problem,

$$(H - E)\Psi(1, 2, \dots, N, N+1) = 0, \quad (4)$$

we shall perform the usual expansion

$$\Psi = \sum_n \mathcal{A}\phi_n(i)\psi_n(i^{-1}), \quad (5)$$

where \mathcal{A} is the antisymmetrizing operator. Upon multiplying Eq. (4) by $\psi_m^*(i^{-1})$ and integrating over all coordinates except those of electron 1, we obtain

$$[H_1 - \frac{1}{2}k_m^2]\phi_m(1) + \sum_n \{V_{mn}(1)\phi_n(1) - W_{mn}(1)\} = 0, \quad (6)$$

⁴ M. J. Seaton, Proc. Roy. Soc. (London) A218, 400 (1953).

⁵ M. J. Seaton, Proc. Roy. Soc. (London) A231, 37 (1955).

⁶ M. H. Hebb and D. H. Menzel, Astrophys. J. 92, 408 (1940).

⁷ R. E. Gershberg, Izv. Krymsk. Astrofiz. Observ. 26, 324 (1961).

where

$$V_{mn}(1) = \int \psi_m^*(1^{-1}) \left[\sum_{j \neq 1} 1/r_{j1} \right] \psi_n(1^{-1}) dx_1^{-1}, \quad (7)$$

$$W_{mn}(1) = N \int \psi_m^*(1^{-1}) [H - E] \psi_n(2^{-1}) \phi_n(2) dx_1^{-1}, \quad (8)$$

$$E - E_m = \frac{1}{2} k_m^2. \quad (9)$$

The notation appearing in these equations implies that the integration is to be performed over all coordinates except those of electron 1. The functions V and W are referred to as the potential and exchange integrals, respectively. Equation (8) can be simplified into either of two forms:

$$W_{mn}(1) = N \int \psi_m^*(1^{-1}) \left[H_2 - \frac{1}{2} k_m^2 + \sum_{j \neq 2} 1/r_{j2} \right] \times \psi_n(2^{-1}) \phi_n(2) dx_1^{-1}, \quad (10)$$

$$W_{mn}(1) = N \int \psi_m^*(1^{-1}) \left[H_1 - \frac{1}{2} k_m^2 + \sum_{j \neq 1} 1/r_{j1} \right] \times \psi_n(2^{-1}) \phi_n(2) dx_1^{-1}. \quad (11)$$

Although Eqs. (10) and (11) give identical results when exact wave functions are used, in numerical work a choice must be made between the two forms, and, as only approximate wave functions are available, the final cross sections will vary depending upon the particular selection. Equations (10) and (11) correspond, respectively, to the well-known "prior" and "post" interactions. In the present calculation, Eq. (10) has been employed to evaluate the exchange matrix elements.

For the problem of excitation of the J components of the ground state of Or by slow electrons, we shall include only the manifold of the $[(1s)^2(2s)^2(2p)^4]^3P$ group in the summation of Eq. (5). It is customary at this point to decompose the wave function of the incident electron into a series of partial waves characterized by l and m_l . However, since the electron spin plays an important role in these transitions, it is advantageous to couple \mathbf{l} with the spin of the incident electron to form \mathbf{j} , i.e., to construct a new set of basis functions $\Phi(ljm_j|\theta_i\phi_i)$ from $Y_{l,m_l}(\theta_i\phi_i)$ and the spin functions. In order to simplify the scattering equations we further couple \mathbf{j} with \mathbf{J} of the neutral atom to form the total angular momentum \mathbf{J}_T of the $(N+1)$ -electron system. The basis functions of this coupled representation are

$$\begin{aligned} X(J_T, M_T, J, j, L=1, S=1, l, s=\frac{1}{2}) \\ = \sum_{M+m_j=M_T} (JMjm_j|JjJ_T M_T) \psi_{JM}(i^{-1}) \\ \times \Phi(ljm_j|\theta_i\phi_i). \quad (12) \end{aligned}$$

Table I presents the available composite states with $l=0,1,2$.

The total wave function for the system is now expanded as

$$\Psi = \sum_n \mathcal{A} F_n(r_i) X_n(i^{-1}, \theta_i, \phi_i) / r_i. \quad (13)$$

The index n now represents the array of quantum numbers appearing in the left-hand side of Eq. (12). The differential equations for F_n are obtained by substituting Eq. (13) in the Schrödinger equation in the standard manner:

$$\mathcal{L}_m F_m(r_1) + \sum_n [\mathcal{U}_{mn} F_n(r_1) - r_1^{-1} \mathcal{W}_{mn}] = 0, \quad (14)$$

where

$$\mathcal{L}_m^l = -\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} - \frac{Z}{r} - \frac{1}{2} k_m^2, \quad (15)$$

$$\begin{aligned} \mathcal{U}_{mn} = \int X_m^*(1^{-1}, \theta_1, \phi_1) \left[\sum_{j \neq 1} 1/r_{j1} \right] \\ \times X_n(1^{-1}, \theta_1, \phi_1) dr_1^{-1}, \quad (16) \end{aligned}$$

$$\begin{aligned} \mathcal{W}_{mn} = N \int X_m^*(1^{-1}, \theta_1, \phi_1) [H - E] \\ \times X_n(2^{-1}, \theta_2, \phi_2) [F_n(r_2)/r_2] dr_1^{-1}. \quad (17) \end{aligned}$$

Again either the post- or prior-interaction may be selected in the further reduction of Eq. (17). Hereafter, the subscript 1 will be omitted in Eq. (14) and its related definitions. In this coupled representation, the Hamiltonian is diagonal in J_T and M_T and the cross sections are independent of M_T . The summation in Eq. (14) therefore includes only those states having the same value of J_T and M_T as the m state. Hence, a particular value of J_T and M_T may be selected and this subset of equations may be solved independent of the remainder of the set.

The wave functions for the bound atomic J states have been taken as linear combinations of determinantal functions. Slater⁸ gives the $M_L=0, M_S=0$ function for 3P ; the remainder of the manifold are obtained with the step-up and step-down operators. Standard vector-coupling methods yield the wave functions for the different spin-multiplet states. Procedures for evaluating Eqs. (16) and (17) in terms of the basic determinants are given by Condon and Shortley,⁹ and Seaton,³ respectively. Equation (13) may be rewritten in the following form:

$$\begin{aligned} \Psi(n'|1, 2, \dots, N+1) \\ = \sum_n \mathcal{A} F_n(n'|r_i) X_n(i^{-1}, \theta_i, \phi_i) / r_i \quad (18) \end{aligned}$$

which explicitly indicates the dependence upon the choice of the initial state n' of the composite system. The asymptotic form of F_n is related to the elements of

⁸ J. C. Slater, *Quantum Theory of Atomic Structure II* (McGraw-Hill Book Company, Inc., New York, 1960).
⁹ E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, London, 1963).

the R matrix as

$$F_n(n'|r_i) \sim k_n^{-1/2} [\sin(k_n r_i - \frac{1}{2} l_n \pi) \delta_{nn'} + R_{nn'} \cos(k_n r_i - \frac{1}{2} l_n \pi)]. \quad (19)$$

In actual practice, it is more convenient to match the solution of F at large r to a combination of Bessel functions, $J_{\pm(l+1/2)}(kr)$, rather than the above circular functions; and to describe the asymptotic function in terms of an amplitude A and a phase shift from the free-particle solution η . In terms of the T matrix, which is defined as

$$\mathbf{T} = -2i\mathbf{R}/(1-i\mathbf{R}), \quad (20)$$

the cross section for the $J' \rightarrow J$ transition can be expressed as

$$Q(J' \rightarrow J) = \pi k'^{-2} \Omega(J, J') / (2J' + 1), \quad (21)$$

where

$$\Omega(J, J') = \frac{1}{2} \sum_{\substack{l, l', j, j_T \\ j', j_T}} (2J_T + 1) |T(\alpha J j l J_T, \alpha J' j' l' J_T)|^2 \quad (22)$$

is the collision strength and α represents the remainder of the quantum numbers defining the composite state.

III. SOLUTION OF THE SCATTERING EQUATIONS

Even with the use of the coupled representation, the scattering equations in Eq. (14) are still very difficult to solve. One simplification can be made from the observation that for collisions between electrons and neutral atoms, the interaction is of sufficiently short range that only partial cross sections of small l need be considered. In the present investigation, only contributions for $l \leq 2$ have been taken into account. The transitions of interest for O_I are optically forbidden; an expansion of the interaction shows that $\Delta l = 0, \pm 2$. Generally, any interaction matrix element is dependent upon the amount of overlap for the wave functions of the incident and scattered electrons. For small values of l it is to be expected that the overlap for wave functions with $\Delta l = \pm 2$ is small compared with that for which $\Delta l = 0$. For this reason, we will neglect the coupling between partial waves of different l . When these approximations are made, the manifold of Eq. (14) can be decomposed into systems of simultaneous equations of manageable sizes. With this approximation, it is possible to write

$$\Omega(J, J') = \sum_l \Omega_l(J, J'), \quad (23)$$

where $\Omega_l(J, J')$ can be obtained from Eq. (22) and represents the contribution to the collision strength from the l partial wave. The methods for solving the scattering equations associated with $l = 0, 1$, and 2 are different and must be described separately. The analytic self-consistent-field (SCF) functions as calculated by

Clementi, Roothaan, and Yoshimine¹⁰ are used to construct the atomic wave functions, and in the discussion to follow, S_1 , S_2 , and P denote the radial functions for the $(1s)$, $(2s)$, and $(2p)$ orbitals, respectively. Before proceeding to the scattering equations it is helpful to introduce the following quantities which occur in the subsequent equations:

$$\Delta(A, B) = \int_0^\infty A(r)B(r)dr,$$

$$y_l(A, B|r_1) = r_1^{-l-1} \int_0^{r_1} A(r_2)B(r_2)r_2^l dr_2 + r_1^l \int_{r_1}^\infty r_2^{-l-1} A(r_2)B(r_2)dr_2, \quad (24)$$

$$R_l(A, B, C, D) = \int_0^\infty A(r_1)C(r_1)y_l(B, D|r_1)dr_1$$

$$= \int_0^\infty B(r_1)D(r_1)y_l(A, C|r_1)dr_1,$$

$$\mathcal{I}C_1^l(A, B) = \int_0^\infty A(r_1) \left[-\frac{1}{2} \frac{d^2}{dr_1^2} + \frac{l(l+1)}{2r_1^2} - \frac{Z}{r_1} \right] \times B(r_1)dr_1,$$

where A , B , C , and D are radial functions. The notation is equivalent to that employed by Seaton³ and is consistent with the work of Hartree¹¹ on atomic calculations. In the presentation of the final results of the cross sections, the energies of the incident electrons are expressed in units of temperature with $E = kT$.

1. The s -Wave Collision Strengths

The sets of equations expressing the contributions to the cross sections from the s waves have a particularly simple form. From Table I it is seen that coupling occurs only between states a and b of $J_T = \frac{1}{2}$ and between 1 and 2 of $J_T = \frac{3}{2}$. In each case we have a set of two simultaneous equations of the form

$$\mathcal{L}_m^0 F_m + \sum_n (\mathcal{U}_{mn} F_n - r^{\mathcal{W}}_{mn}) = 0, \quad (25)$$

$$\mathcal{U}_{mn} = \rho_{mn} [4y_0(PP) + 2y_0(S_1 S_1) + 2y_0(S_2 S_2)], \quad (26)$$

$$r^{\mathcal{W}}_{mn} = \alpha_{mn} [\gamma_1(PF_n)P - R_1(S_1 PPF_n)S_1 - R_1(S_2 PPF_n)S_2 + \rho_{mn} \{ [\gamma_0(S_1 F_n) + \lambda_{mn}^{(1)}(S_1 F_n)]S_1 + [\gamma_0(S_2 F_n) + \lambda_{mn}^{(2)}(S_2 F_n)]S_2 \}, \quad (27)$$

¹⁰ E. Clementi, C. C. J. Roothaan, and M. Yoshimine, Phys. Rev. **127**, 1618 (1962).

¹¹ D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957).

with

$$\begin{aligned} \lambda_{mn}^{(1)}(S_1F_n) = & \mathfrak{I}C_2^0(S_1F_n) - \frac{1}{2}k_n^2\Delta(S_1F_n) \\ & + 4R_0(PS_1PF_n) + R_0(S_1S_1S_1F_n) \\ & + 2R_0(S_2S_1S_2F_n) - R_0(S_1S_2S_2F_n), \end{aligned} \quad (28)$$

$$\begin{aligned} \lambda_{mn}^{(2)}(S_2F_n) = & \mathfrak{I}C_2^0(S_2F_n) - \frac{1}{2}k_n^2\Delta(S_2F_n) \\ & + 4R_0(PS_2PF_n) + R_0(S_2S_2S_2F_n) \\ & + 2R_0(S_1S_2S_1F_n) - R_0(S_2S_1S_1F_n). \end{aligned} \quad (29)$$

The values of ρ and α are summarized in Table II. It should be noted that the coupling is provided by exchange alone while the Coulomb potential elements produce only distortion. Because of the short-range nature of the coupling, good numerical results can be achieved with a reasonably low limit on the radial variable.

As a first approximation we shall neglect the energy difference between the incident and scattered electrons, i.e., set $k_n^2 = k_m^2 = k^2$ because of the small spin-multiplet splittings. When this exact-resonance approximation¹² is made, the scattering equations can be decoupled by means of the following transformation:

$$\begin{aligned} J_T = \frac{1}{2}: \quad F_a = & -\sqrt{2}n_1G_1 + n_2G_2, \\ F_b = & n_1G_1 + \sqrt{2}n_2G_2; \end{aligned} \quad (30)$$

$$\begin{aligned} J_T = \frac{3}{2}: \quad F_1 = & -(\sqrt{5})n_3G_1 + n_4G_2, \\ F_2 = & n_3G_1 + (\sqrt{5})n_4G_2; \end{aligned} \quad (31)$$

where the constants n are to be selected in order to provide the proper asymptotic behaviors for F . In both cases ($J_T = \frac{1}{2}, \frac{3}{2}$) the differential equations for G are

$$\begin{aligned} [\mathcal{L}^0 + 4y_0(PP) + 2y_0(S_1S_1) + 2y_0(S_2S_2)]G_1 \\ = [y_0(S_1G_1) + \lambda^{(1)}(S_1G_1)]S_1 \\ + [y_0(S_2G_1) + \lambda^{(2)}(S_2G_1)]S_2, \end{aligned} \quad (32)$$

$$\begin{aligned} [\mathcal{L}^0 + 4y_0(PP) + 2y_0(S_1S_1) + 2y_0(S_2S_2)]G_2 \\ = [y_0(S_1G_2) + \lambda^{(1)}(S_1G_2)]S_1 \\ + [y_0(S_2G_2) + \lambda^{(2)}(S_2G_2)]S_2 + y_1(PG_2)P. \end{aligned} \quad (33)$$

Here $\lambda^{(1)}$ and $\lambda^{(2)}$ are as defined by Eqs. (28) and (29) with the m index omitted, and

$$\lambda^{(i)}(S_iG_2) = \lambda^{(i)}(S_iG_2) - R_1(S_iPPG_2). \quad (34)$$

When we multiply Eq. (32) on the left by S_1 and integrate over the radial variable, we obtain an equation for $\lambda^{(1)}(S_1G_1)$ which is identical to Eq. (28). Because of this indeterminacy we may choose to make G_1 orthogonal to S_1 . The same conclusion can be drawn for $\lambda^{(2)}(S_2G_1)$, $\lambda^{(1)}(S_1G_2)$, and $\lambda^{(2)}(S_2G_2)$. Accordingly we can set

$$\Delta(S_1G_1) = \Delta(S_2G_1) = \Delta(S_1G_2) = \Delta(S_2G_2) = 0. \quad (35)$$

¹² In the present work, the term "exact-resonance" indicates equal energies for the bound atomic states being considered. This differs from the terminology employed by Seaton (Ref. 3), who includes an omission of the y_2 and R_2 potential and exchange terms in the definition.

TABLE II. Coefficients in the potential and exchange matrix elements for s wave ($M_T = J_T$).

J_T	m, n	ρ_{mn}	α_{mn}
$\frac{1}{2}$	a, a	1	$\frac{1}{3}$
	a, b	0	$\frac{1}{3}\sqrt{2}$
	b, a	0	$\frac{1}{3}\sqrt{2}$
	b, b	1	$\frac{2}{3}$
$\frac{3}{2}$	1, 1	1	$\frac{1}{6}$
	1, 2	0	$\frac{1}{6}\sqrt{5}$
	2, 1	0	$\frac{1}{6}\sqrt{5}$
	2, 2	1	$\frac{5}{6}$

The expressions for λ and λ [Eqs. (28), (29), (34)] can be simplified in the following manner. By multiplying the Hartree-Fock radial differential equations⁸ for S_1 and S_2 through by G_1 and by G_2 on the left and integrating, we obtain four equations which upon substitution into Eqs. (28), (29), and (34) give

$$\begin{aligned} \lambda^{(1)}(S_1G_1) = & \frac{2}{3}R_1(S_1PPG_1), \\ \lambda^{(2)}(S_2G_1) = & \frac{2}{3}R_1(S_2PPG_1), \\ \lambda^{(1)}(S_1G_2) = & -\frac{1}{3}R_1(S_1PPG_2), \\ \lambda^{(2)}(S_2G_2) = & -\frac{1}{3}R_1(S_2PPG_2). \end{aligned} \quad (36)$$

Equations (32) and (33) are solved by the method of Numerov¹³ with coupling and exchange terms requiring numerical iteration. Solutions were initiated by small-value expressions near the origin; the interval of integration was increased to 0.1 a.u. for regions exterior to the atom and the routine continued until the influence of the atom was insignificant relative to free-particle behavior. A limit of $r = 50$ is sufficient for s waves. Side conditions given in Eqs. (35) were imposed after each step of the iteration with the resulting convergence rapid enough to provide four figures of accuracy for the phases after five to eight passes. The asymptotic boundary conditions yield the final s -wave collision strengths in terms of η_1 and η_2 , the phases of G_1 and G_2 , respectively. Under exact resonance, the final expressions for these collision strengths are

$$\begin{aligned} \Omega_s(1,2) = & (10/9) \sin^2(\eta_1 - \eta_2), \\ \Omega_s(0,1) = & (8/9) \sin^2(\eta_1 - \eta_2), \\ \Omega_s(0,2) = & 0. \end{aligned} \quad (37)$$

Numerical values of Ω_s at various electron energies are summarized in Table III. The collision strengths depend heavily upon the asymptotic difference in phase between the G_1 and G_2 solutions; this difference in phase is dictated solely by the effect of exchange terms involving the G_2 and P functions. These short-range terms are sensitive to the precise value of G_2 interior to the atom, hence are substantially affected by short-range distortion and the orthogonal restrictions (with respect to S_1

¹³ D. R. Hartree, *Numerical Analysis* (Clarendon Press, Oxford, England, 1952).

TABLE III. Collision strengths for s wave.^a

Energy of scattered electron (°K)	Exact resonance		Allowance for energy differences	
	$\Omega_s(1,2)$	$\Omega_s(0,1)$	$\Omega_s(1,2)$	$\Omega_s(0,1)$
10 000	0.0084	0.0067	0.0085	0.0067
5000	0.0045	0.0036	0.0046	0.0037
1000	0.00096	0.00077	0.00106	0.00081
500	0.00048	0.00038	0.00058	0.00042

^a The parameter $\Omega_s(0,2)$ is zero.

and S_2) imposed upon the free wave functions. To examine this point more quantitatively, calculations were made of the collision strengths ignoring the S_1 and S_2 exchange terms and the associated orthogonality conditions. The results exceed those listed in Table III by over a factor of 5.

The exact-resonance approximation which has been used to obtain Eqs. (37) can be corrected to allow for energy differences between the various bound atomic states with a technique suggested by Seaton.³ If we introduce a subscript on k^2 referring to the $J=0, 1, 2$ specification of the bound atomic state, the suggested

procedure is to solve for G_1 and G_2 successively with $k=k_0, k_1$, and k_2 . Approximate expressions for F_a and F_b are obtained from a modified version of Eqs. (30) as

$$\begin{aligned} F_a(k_1^2) &= -\sqrt{2}n_1G_1(k_1^2) + n_2G_2(k_1^2), \\ F_b(k_0^2) &= n_1G_1(k_0^2) + \sqrt{2}n_2G_2(k_0^2). \end{aligned} \quad (38)$$

Equations (38) are valid solutions if the term on the right-hand side of Eqs. (32) and (33) are nearly independent of small variation of k^2 . For s waves this k^2 independence can be achieved by a suitable normalization procedure.³ A similar method would be applicable for the $J_T=\frac{3}{2}$ set of equations. The collision strengths calculated with allowance for energy differences are included in Table III. Deviations from the corresponding exact-resonance values should be important only at the lower end of the energy range being considered, and this has proved to be generally true.

2. The p -Wave Collision Strengths

For the p waves, there are three values of J_T which lead to transition between the $J=0, 1, 2$ levels, namely, $J_T=\frac{1}{2}, \frac{3}{2}$, and $\frac{5}{2}$ (Table I). For each block the resulting

TABLE IV. Coefficients in the potential and exchange matrix elements for p wave ($M_T=J_T$).

J_T	m,n ($=n,m$)	ρ_{mn}	σ_{mn}	α_{mn}	β_{mn}	γ_{mn}	κ_{mn}
$\frac{1}{2}$	c,c	1	7/50	$\frac{1}{5}$	1	19/60	-3/50
	c,d	0	$(3\sqrt{5})/50$	$\frac{1}{2}\sqrt{5}$	1	$(\sqrt{5})/20$	-9/50
	c,e	0	$(3\sqrt{10})/50$	1	0	0	$(3\sqrt{10})/50$
	c,f	0	$(2\sqrt{5})/25$	$\frac{1}{3}\sqrt{5}$	1	$(\sqrt{5})/30$	-3/50
	d,d	1	-1/10	$-\frac{1}{2}$	1	$\frac{1}{4}$	$\frac{1}{10}$
	d,e	0	$\sqrt{2}/10$	1	0	0	$\sqrt{2}/10$
	d,f	0	0	-1	1	$-\frac{1}{10}$	$-\frac{3}{10}$
	e,e	1	0	1	1	$\frac{2}{5}$	$-\frac{2}{5}$
	e,f	0	0	1	0	0	0
	f,f	1	0	$\frac{1}{3}$	1	$\frac{1}{3}$	$-\frac{2}{3}$
$\frac{3}{2}$	3,3	1	0	$-\frac{2}{3}$	1	13/75	-6/25
	3,4	0	3/25	1	0	3/25	0
	3,5	0	$(\sqrt{10})/25$	$\frac{1}{6}\sqrt{10}$	1	$-(\sqrt{10})/75$	3/25
	3,6	0	-7/50	$-\frac{5}{6}$	1	-17/150	-21/125
	3,7	0	$-(3\sqrt{5})/50$	$-\frac{1}{2}\sqrt{5}$	1	$-(\sqrt{5})/50$	-3/25
	4,4	1	2/25	1	1	4/25	-2/25
	4,5	0	0	1	0	$(3\sqrt{10})/50$	$-(3\sqrt{10})/50$
	4,6	0	-9/50	1	0	3/50	-6/25
	4,7	0	$-(\sqrt{5})/50$	1	0	$-(3\sqrt{5})/50$	$(\sqrt{5})/25$
	5,5	1	0	$\frac{5}{6}$	1	7/30	-6/25
	5,6	0	$-(\sqrt{10})/25$	$(\sqrt{10})/12$	1	$-(\sqrt{10})/150$	$-\frac{2}{3}$
	5,7	0	0	$\frac{1}{4}\sqrt{2}$	1	$\sqrt{2}/10$	$-\frac{2}{3}$
	6,6	1	0	7/12	1	103/300	-156/350
	6,7	0	0	$-\frac{1}{4}\sqrt{5}$	1	$-(\sqrt{5})/100$	-6/25
7,7	1	0	$\frac{1}{4}$	1	$\frac{1}{4}$	$-\frac{2}{3}$	
$\frac{5}{2}$	B,B	1	-1/10	1	1	19/100	-29/100
	B,C	0	$-(\sqrt{21})/50$	1	0	$(3\sqrt{21})/100$	$-(\sqrt{21})/20$
	B,D	0	$(\sqrt{14})/50$	1	0	$-(3\sqrt{14})/50$	$(2\sqrt{14})/25$
	C,C	1	-1/50	1	1	31/100	-33/100
	C,D	0	$(\sqrt{6})/50$	1	0	$(3\sqrt{6})/50$	$-(\sqrt{6})/25$
	D,D	1	0	1	1	4/25	-4/25

reduced radial differential equations may be expressed as

$$\mathcal{L}_m^1 F_m + \sum_n [\mathcal{U}_{mn} F_n - r^2 \mathcal{W}_{mn}] = 0, \quad (39)$$

$$\mathcal{U}_{mn} = \rho_{mn} [4y_0(PP) + 2y_0(S_1 S_1) + 2y_0(S_2 S_2)] + \sigma_{mn} y_2(PP), \quad (40)$$

$$r^2 \mathcal{W}_{mn} = \{ \alpha_{mn} [\beta_{mn} y_0(PP_n) + \lambda_{mn}(PF_n)] + \gamma_{mn} y_2(PF_n) \} P + \frac{1}{3} \rho_{mn} [y_1(S_1 F_n) S_1 + y_1(S_2 F_n) S_2], \quad (41)$$

$$\lambda_{mn}(PF_n) = \beta_{mn} [\mathcal{J} C_2^1(PF_n) - \frac{1}{2} k_n^2 \Delta(PF_n) + 3R_0(PPPF_n) + 2R_0(S_1 P S_1 F_n) + 2R_0(S_2 P S_2 F_n) - \frac{1}{3} R_1(P S_1 S_1 F_n) - \frac{1}{3} R_1(P S_2 S_2 F_n)] + \kappa_{mn} R_2(PPPF_n). \quad (42)$$

The values of the various coefficients are listed in Table IV.

It will be shown that the p -wave interaction is the most significant in establishing the total cross sections. However, these equations are also the most complex, with both exchange and potential coupling of comparable magnitude. Before proceeding to the solution of these equations, it is instructive to consider a special approximation which, though not applicable to the present problem, does furnish a useful starting point for the mathematical procedure. This approximation consists of neglecting the energy differences between the spin-multiplets and also omitting the y_2 and R_2 terms. Under these assumptions, the scattering equations can be completely decoupled by means of the transformations:

$$J_T = \frac{1}{2}: \quad \begin{aligned} F_c &= -2n_a G_a - (\sqrt{5}) n_d G_d, \\ F_d &= -2n_b G_b + 3n_a G_a, \\ F_e &= n_c G_c, \\ F_f &= -(\sqrt{5}) n_a G_a + 3n_b G_b + 2n_d G_d; \end{aligned} \quad (43)$$

$$J_T = \frac{3}{2}: \quad \begin{aligned} F_3 &= n_4 G_4 + 2(\sqrt{5}) n_5 G_5, \\ F_4 &= n_2 G_2, \\ F_5 &= 3n_3 G_3 - \sqrt{2} n_5 G_5, \\ F_6 &= -3n_1 G_1 - 2n_4 G_4 + (\sqrt{5}) n_5 G_5, \\ F_7 &= (\sqrt{5}) n_1 G_1 + \sqrt{2} n_3 G_3 + 3n_5 G_5; \end{aligned} \quad (44)$$

$$J_T = \frac{5}{2}: \quad F_i = n_i G_i, \quad i = B, C, D. \quad (45)$$

This transformation is an effective method of taking into account the strong coupling contributed by the spherical $y_0(PP)$ terms. Seaton³ has found these coupling terms to completely dominate the transition probabilities between the 3P , 1D , and 1S terms of the ground configuration of Or. Hence, as a zeroth-order approximation, he made the assumptions of exact resonance and nonimportance of the asymmetric potential and exchange terms. In later work,⁴ a correction was made for the omitted coupling terms with perturbation methods.

This approximation scheme, however, is not applicable to the present problem as the long-range potential

coupling are of more significance here and may even contribute more to the cross sections than the spherical exchange terms. Hence a consideration of the symmetric exchange terms alone is certainly not sufficient and the treatment of the potential coupling by perturbation is of doubtful value. Nevertheless, in precise calculations, the transformations described by Eqs. (43)–(45) can be effectively used to initiate an iteration procedure, since they do remove the spherically symmetric part of the coupling. For convenience, they are referred to as the “basic transformations.”

In the following analysis, we shall first adopt the exact-resonance approximation. Under the assumption of exact-resonance, selected scattering equations are solved “exactly” (close-coupling solution). For comparison the collision strengths are also calculated by a modified distorted-wave treatment, and the validity of this approximation is examined. Final collision strengths for p wave are evaluated from appropriate combinations of the close-coupling and weak-coupling schemes. Finally the nonresonance effect is taken into account by the approximate procedure used for s waves.

A. $J_T = \frac{5}{2}$ —Close-Coupling Solutions

We shall begin with the group of equations corresponding to $J_T = \frac{5}{2}$, since the “basic transformation” for this case has the simplest form, i.e., an identity transformation. The scattering equations for F_B , F_C , F_D can be partly decoupled under exact resonance through the transformation

$$\begin{aligned} F_B &= \sqrt{2} n_C G_C + (\sqrt{7}) n_D G_D, \\ F_C &= \sqrt{2} n_B G_B + \sqrt{3} n_D G_D, \\ F_D &= \sqrt{3} n_B G_B + (\sqrt{7}) n_C G_C - \sqrt{2} n_D G_D. \end{aligned} \quad (46)$$

The differential equations for G_B , G_C , and G_D are

$$\begin{aligned} &[\mathcal{L}^1 + 4y_0(PP) + 2y_0(S_1 S_1) + 2y_0(S_2 S_2)] G_B \\ &= [y_0(PG_B) + \Lambda_B(PG_B)] P \\ &\quad + \frac{1}{3} y_1(S_1 G_B) S_1 + \frac{1}{3} y_1(S_2 G_B) S_2 \\ &\quad - (1/25) y_2(PP) G_B + (49/100) y_2(PG_B) P \\ &\quad + [(9\sqrt{21})/100] (n_C/n_B) y_2(PG_C) P, \\ &[\mathcal{L}^1 + 4y_0(PP) + 2y_0(S_1 S_1) + 2y_0(S_2 S_2)] G_C \\ &= [y_0(PG_C) + \Lambda_C(PG_C)] P \\ &\quad + \frac{1}{3} y_1(S_1 G_C) S_1 + \frac{1}{3} y_1(S_2 G_C) S_2 \\ &\quad - (1/25) y_2(PP) G_C - (23/100) y_2(PG_C) P \\ &\quad - [(3\sqrt{21})/100] (n_B/n_C) y_2(PG_B) P, \\ &[\mathcal{L}^1 + 4y_0(PP) + 2y_0(S_1 S_1) + 2y_0(S_2 S_2)] G_D \\ &= [y_0(PG_D) + \Lambda_D(PG_D)] P + \frac{1}{3} y_1(S_1 G_D) S_1 \\ &\quad + \frac{1}{3} y_1(S_2 G_D) S_2 + \frac{1}{5} y_2(PP) G_D + \frac{2}{5} y_2(PG_D) P. \end{aligned} \quad (47)$$

The Λ parameters have the same general form as Eq. (42) with some additional terms which are shown in Table V. It is found to be possible to impose again the orthogonality condition between G and P and to

TABLE V. Coefficients and coupling terms for $\Lambda_i(PG_i)$ parameters.

J_T	Parameter	β	κ	Coupling terms, $\Lambda_i - \lambda_i$
$\frac{1}{2}$	Λ_a	1	-3/50	$-\left[(3\sqrt{5}/50)(n_b/n_a)R_2(PPPG_b) - [(3\sqrt{10})/100](n_c/n_a)R_2(PPPG_c)\right]$
	Λ_b	1	-1/2	$[(3\sqrt{5})/50](n_a/n_b)R_2(PPPG_a) - (\sqrt{2}/20)(n_c/n_b)R_2(PPPG_c)$
	Λ_c	1	-2/5	$-\left[(3\sqrt{10})/25\right](n_a/n_c)R_2(PPPG_a) - (\sqrt{2}/5)(n_b/n_c)R_2(PPPG_b)$
	Λ_d	1	-3/20	0
$\frac{3}{2}$	Λ_1	1	-7/25	$-\left[(\sqrt{10})/20\right](n_3/n_1)R_2(PPPG_3) - (7/50)(n_4/n_1)R_2(PPPG_4)$
	Λ_3	1	-3/10	$[(\sqrt{10})/25](n_4/n_3)R_2(PPPG_4)$
	Λ_4	1	-3/25	$-(3/25)(n_1/n_4)R_2(PPPG_1) + [(3\sqrt{10})/25](n_3/n_4)R_2(PPPG_3)$
	Λ_5	1	-3/20	0
	Λ_B	1	-9/20	$-\left[(9\sqrt{21})/100\right](n_C/n_B)R_2(PPPG_C)$
$\frac{5}{2}$	Λ_C	1	27/100	$[(3\sqrt{21})/100](n_B/n_C)R_2(PPPG_B)$
	Λ_D	1	-3/5	0

obtain quick convergence of the numerical iteration by satisfying this requirement after each iteration.⁴ The numerical procedures for solving these equations become more complex because of the coupling between G_B and G_C . Also the (n_B/n_C) ratio is determined from the boundary conditions and must be treated by an additional iteration process since theoretically it is not known until the final G functions have been computed. For the p waves the numerical solutions of the differential equations are carried out to $r=200$ a.u. The interaction between the states with total angular momentum of $\frac{5}{2}$ can lead to $J=1 \leftrightarrow 2$ transitions only, and hence will provide a correction to only $\Omega_p(1,2)$. These contributions are included in Table VI.

B. $J_T = \frac{5}{2}$ —Method of Distorted Waves

Since the functions F_B , F_C , and F_D in Eqs. (39)–(42) are coupled only through the y_2 type of potential and exchange terms but not the y_0 terms, it should be possible to obtain accurate collision strengths with a refined weak-coupling approximation. A modified version of the method of distorted waves will be used. We shall introduce the \mathcal{Y} functions which are defined as the solutions of F_B , F_C , and F_D in Eqs. (39)–(42) with all of the y_2 coupling and distortion terms omitted, and which have the asymptotic behavior,

$$F \sim k^{-1/2} \sin(kr + \eta). \quad (48)$$

The T -matrix elements are then given by

$$T(m,n) = 4i \int_0^\infty \mathcal{Y}_m \mathcal{U}_{mn} \mathcal{Y}_n dr, \quad (49)$$

where \mathcal{U}_{mn} represents the coupling terms, including both potential and exchange, between the states m and n . The results of the distorted-wave calculations with exact resonance are included in Table VI, along with the close-coupling values. The only significant difference between the two methods appears at the higher energy limit and the over-all agreement indicates the applicability of the chosen method of distorted

waves for states which are connected only through the y_2 terms.

C. $J_T = \frac{1}{2}$ —Approximate Solution

On applying the appropriate “basic transformation” to the set of scattering equations for $J_T = \frac{1}{2}$, we obtain

$$\begin{aligned} & [\mathcal{L}^1 + 4y_0(PP) + 2y_0(S_1S_1) + 2y_0(S_2S_2)]G_a \\ &= [y_0(PG_a) + \Lambda_a(PG_a)]P - (17/50)y_2(PP)G_a \\ & \quad + \frac{2}{5}y_2(PG_a)P + \frac{1}{3}y_1(S_1G_a)S_1 + \frac{1}{3}y_1(S_2G_a)S_2 \\ & \quad + [(3\sqrt{5})/50](n_b/n_a)y_2(PP)G_b \\ & \quad + [(3\sqrt{10})/100](n_c/n_a)y_2(PP)G_c, \quad (50) \end{aligned}$$

$$\begin{aligned} & [\mathcal{L}^1 + 4y_0(PP) + 2y_0(S_1S_1) + 2y_0(S_2S_2)]G_b \\ &= [y_0(PG_b) + \Lambda_b(PG_b)]P + (1/10)y_2(PP)G_b \\ & \quad + \frac{2}{5}y_2(PG_b)P + \frac{1}{3}y_1(S_1G_b)S_1 + \frac{1}{3}y_1(S_2G_b)S_2 \\ & \quad - [(3\sqrt{5})/50](n_a/n_b)y_2(PP)G_a \\ & \quad + (\sqrt{2}/20)(n_c/n_b)y_2(PP)G_c, \quad (51) \end{aligned}$$

$$\begin{aligned} & [\mathcal{L}^1 + 4y_0(PP) + 2y_0(S_1S_1) + 2y_0(S_2S_2)]G_c \\ &= [y_0(PG_c) + \Lambda_c(PG_c)]P + \frac{1}{3}y_1(S_1G_c)S_1 \\ & \quad + \frac{1}{3}y_1(S_2G_c)S_2 + \frac{2}{5}y_2(PG_c)P \\ & \quad + [(3\sqrt{10})/25](n_a/n_c)y_2(PP)G_a \\ & \quad + (\sqrt{2}/5)(n_b/n_c)y_2(PP)G_b, \quad (52) \end{aligned}$$

$$\begin{aligned} & [\mathcal{L}^1 + 4y_0(PP) + 2y_0(S_1S_1) + 2y_0(S_2S_2)]G_d \\ &= -2[y_0(PG_d) + \Lambda_d(PG_d)]P + \frac{1}{5}y_2(PP)G_d \\ & \quad + (1/10)y_2(PG_d)P \\ & \quad + \frac{1}{3}y_1(S_1G_d)S_1 + \frac{1}{3}y_1(S_2G_d)S_2. \quad (53) \end{aligned}$$

Here the parameters Λ are related to λ in Eq. (42)

TABLE VI. Collision strengths calculated by close coupling and by distorted wave $J_T = \frac{5}{2}$.

Exact resonance energy (°K)	$\Omega_p(1,2) = \Omega_p(2,1)$	
	Close coupling	Distorted wave
10 000	0.0078	0.0069
5000	0.0040	0.0037
1000	0.00081	0.00078
500	0.00040	0.00039

through Table V. Before proceeding to the exact solution of these equations, let us consider an approximate procedure which is based on the method of distorted waves as used for $J_T = \frac{5}{2}$. In Eqs. (39)–(42), F_e is coupled to the other three channels through only y_2 terms; one should be able to treat such coupling terms by the method of distorted waves. Hence we shall first solve the set of G equations neglecting the coupling terms to the F_e state. [This is equivalent to setting $n_c = 0$ in Eqs. (50) and (51).] The resulting scattering equations then show complete isolation of G_c and G_a and G_b ; the latter two functions can be solved by a method similar to that described to obtain the close-coupling solution of the $J_T = \frac{5}{2}$ set with the imposition of the appropriate orthogonality conditions. On the other hand, a different type of problem is encountered in the evaluation of $\Lambda_d(PG_d)$ in the G_d differential equation which is completely decoupled from the other equations by the “basic transformation.” By following a procedure equivalent to that described for G_1 in the section pertaining to s wave, it is found that this parameter is not indeterminate from the scattering equation. The differential equation for G_d specifies that

$$\Lambda_d(PG_d) = -R_0(PPPG_d) + (1/20)R_2(PPPG_d). \quad (54)$$

Also the Hartree-Fock differential equation for the bound-state P function⁸ yields

$$\Lambda_d(PG_d) = (3/20)R_2(PPPG_d) - \frac{1}{2}(\mathcal{E}_{2p} + k^2)\Delta(PG_d). \quad (55)$$

The side condition imposed on G_d is taken to be

$$\frac{1}{2}(\mathcal{E}_{2p} + k^2)\Delta(PG_d) = R_0(PPPG_d) + \frac{1}{10}R_2(PPPG_d), \quad (56)$$

and one can no longer make G_d orthogonal to P without modifying the bound-state P function.

The phase shifts and the R matrix are calculated by applying the asymptotic boundary conditions to the G functions and using Eqs. (43). However, at this stage of the approximation, the R -matrix elements connecting state “ e ” with states “ c ,” “ d ,” “ f ,” are indeterminate. These elements, however, are to be gotten by reinstating the coupling between F_e and the other channels and treating this coupling by the method of distorted waves. In other words, the T -matrix elements related to the “ e ” states are computed using Eq. (49). The \mathcal{Y} functions are now taken to be the solutions for F_c , F_d , F_e , and F_f obtained by considering only the $y_0(PG)$ coupling terms in Eqs. (50)–(53); each function is normalized to the asymptotic behavior demanded by Eq. (48). Tests confirmed the $y_2(PF)$ and $y_2(PP)$ distortion terms to be completely ineffective in this particular application. It is found that the distorted-wave integrals corresponding to excitation and de-excitation do not satisfy the requirement of detailed balance. The discrepancy is proportional to $\Delta(PG_d)$, is negligible at energies below 1000°K, and increases to about 20% at higher energies. The geometric means

between these two sets of collision strengths are chosen to compute the final cross sections. Since the contributions of these distorted-wave integrals are found to be quite small as compared with other contributions to the total collision strengths, the deviations from detailed balance constitute only minor errors in our final results. The final collision strengths are summarized in Table VII.

D. $J_T = \frac{1}{2}$ —Close-Coupling Calculations

To confirm the validity of the approximate method used in the last section, the set of differential equations for G_a , G_b , and G_c in Eqs. (50)–(52) are now solved simultaneously. (The “basic transformation” always decouples G_d from the remaining G functions.) Because of the particular form of the “basic transformation,” a difficulty is encountered in the evaluation of the n_c coefficient from the boundary conditions. For example, if the initial state were chosen to be one other than “ e ,” the absence of a sine term in Eq. (19), at first glance, seems to imply $n_c = 0$ which amounts to an effective decoupling of G_c from the remainder of the set. The answer to this paradox is that when “ e ” is not the initial state, one should look for a solution of G_c which has the special asymptotic behavior of $\cos(kr - \frac{1}{2}\pi)$ rather than the more general form of $\sin(kr - \frac{1}{2}\pi) + \zeta \cos(kr - \frac{1}{2}\pi)$. This can be accomplished as follows: Select an arbitrary value for n_c , say $n_c = n_c^{(1)}$, in the set of coupled equations. Choose, for example, F_e as the initial channel, and solve for G_a , G_b , and G_c . The n_a , n_b , and n_d coefficients are adjusted to give the correct asymptotic forms for F_c , F_d , and F_f . On the other hand, since n_c is chosen arbitrarily, F_e will not have the proper boundary behavior. The final solutions and coefficients so obtained are to be denoted by the superscript (1). Another

TABLE VII. Summary of collision strengths for p wave under exact resonance.

Exact resonance energy (°K)	Contributions to Ω_p			Total Ω_p
	$J_T = \frac{1}{2}$	$J_T = \frac{3}{2}$	$J_T = \frac{5}{2}$	
$\Omega_p(1,2)$:				
10 000	0.072	0.191	0.0078	0.271
5000	0.034	0.093	0.0040	0.131
1000	0.0028	0.0081	0.00081	0.0117
500	0.0007	0.0021	0.00040	0.0032
$\Omega_p(0,2)$:				
10 000	0.019	0.049		0.068
5000	0.008	0.025		0.033
1000	0.0003	0.0027		0.0030
500	0.000004	0.00092		0.00092
$\Omega_p(0,1)$:				
10 000	0.079	0.022		0.101
5000	0.039	0.010		0.049
1000	0.0035	0.0009		0.0044
500	0.0008	0.0002		0.0010

arbitrary value $n_c = n_c^{(2)}$ is now selected and the above routine repeated. The superscript (2) serves to distinguish these solutions. The final F functions are taken as

$$F_i = qF_i^{(1)} + (1-q)F_i^{(2)}, \quad i = c, d, e, f, \quad (57)$$

where q is adjusted to reproduce the appropriate asymptotic form of F_e , i.e., to cause the coefficient of $\sin(kr - \frac{1}{2}\pi)$ to vanish. The resulting solutions as given by Eq. (57) are thus uniquely specified and possess the required asymptotic behaviors.

Detailed calculations were performed using this scheme for an electron energy of 5000°K, with F_c selected as the initial channel. The results agree very well with those of the previous approximate method as is demonstrated by the entries in Table VIII.

E. $J_T = \frac{3}{2}$

Because of the complexity of the five-channel scattering equations of the $J_T = \frac{3}{2}$ set, we shall use the approximate method devised for the $J_T = \frac{1}{2}$ case. On applying the "basic transformation" and omitting the coupling terms between F_4 and the other four channels, the following equations result

$$\begin{aligned} & [\mathcal{E}^1 + 4y_0(PP) + 2y_0(S_1S_1) + 2y_0(S_2S_2)]G_1 \\ &= [y_0(PG_1) + \Lambda_1(PG_1)]P + \frac{1}{3}y_1(S_1G_1)S_1 \\ & \quad + \frac{1}{3}y_1(S_2G_1)S_2 + (2/25)y_2(PP)G_1 + \frac{1}{5}y_2(PG_1)P \\ & \quad + [(\sqrt{10}/20)(n_3/n_1)y_2(PG_3)P \\ & \quad \quad + (7/50)(n_4/n_1)y_2(PP)G_4], \\ & [\mathcal{E}^1 + 4y_0(PP) + 2y_0(S_1S_1) + 2y_0(S_2S_2)]G_3 \\ &= [y_0(PG_3) + \Lambda_3(PG_3)]P + \frac{1}{3}y_1(S_1G_3)S_1 \\ & \quad + \frac{1}{3}y_1(S_2G_3)S_2 + (3/10)y_2(PG_3)P \\ & \quad - [(\sqrt{10}/25)(n_1/n_3)[y_2(PP)G_1 - y_2(PG_1)P] \\ & \quad \quad - [(\sqrt{10}/25)(n_4/n_3)y_2(PP)G_4], \\ & [\mathcal{E}^1 + 4y_0(PP) + 2y_0(S_1S_1) + 2y_0(S_2S_2)]G_4 \\ &= [y_0(PG_4) + \Lambda_4(PG_4)]P + \frac{1}{3}y_1(S_1G_4)S_1 \\ & \quad + \frac{1}{3}y_1(S_2G_4)S_2 - (7/25)y_2(PP)G_4 + \frac{2}{5}y_2(PG_4)P \\ & \quad - (3/25)(n_1/n_4)[y_2(PP)G_1 - 2y_2(PG_1)P] \\ & \quad - [(3\sqrt{10}/50)(n_3/n_4)[y_2(PP)G_3 + y_2(PG_3)P], \\ & [\mathcal{E}^1 + 4y_0(PP) + 2y_0(S_1S_1) + 2y_0(S_2S_2)]G_5 \\ &= -2[y_0(PG_5) + \Lambda_5(PG_5)]P + \frac{1}{3}y_1(S_1G_5)S_1 \\ & \quad + \frac{1}{3}y_1(S_2G_5)S_2 + \frac{1}{5}y_2(PP)G_5 + \frac{1}{10}y_2(PG_5)P. \quad (58) \end{aligned}$$

Expressions for Λ may be found from Eq. (42) and Table V. Like the case of $J_T = \frac{1}{2}$, G_1 , G_3 , and G_4 can be made orthogonal to P , but the side condition imposed upon G_5 must be that given by Eq. (56). The R -matrix elements between states, 3, 5, 6, and 7 are obtained by solving Eqs. (58) and using the transformation Eqs. (44). The coupling terms connecting state 4 with states 3, 5, 6, and 7 which were neglected in Eqs. (58) are then employed in conjunction with the distorted-wave method (as described for $J_T = \frac{1}{2}$) to calculate the contributions of this state to the total collision strengths. Collision

TABLE VIII. Comparison of approximate and exact (close-coupling) methods ($J_T = \frac{1}{2}$, initial state = c , energy = 5,000°K).

Element under approximate method ^a	Corresponding element under exact (close-coupling) method
$\tan\eta_{a,c} = -0.055$	-0.054
$\tan\eta_{b,c} = -0.037$	-0.036
$B(e,c) = -0.028$	$R(e,c) = -0.030$

^a The notation $\eta_{a,c}$ refers to the phase of G_a when F_c is taken to be initial state.

strengths associated with $J_T = \frac{3}{2}$ calculated under exact resonance are included in Table VII.

F. Allowance for Energy Differences

The portions of the p -wave collision strengths which are capable of being determined by the distorted-wave approximation can be corrected for the differences in energy of the bound states by simply inserting the proper wave functions with the correct electron energies into the integral of Eq. (49). Table IX displays a comparison of some typical distorted-wave calculations for the states of $J_T = \frac{3}{2}$ with the associated results from the exact-resonance approximation.

The correct treatment of the states which are connected under the strong coupling of the spherically symmetric exchange terms poses much more of a problem. This refers to the portions of the $J_T = \frac{1}{2}$ and $\frac{3}{2}$ sets which must be handled by solving the coupled differential equations. Like the case of the s -wave interactions, the method of Seaton⁸ has been used for this purpose, although for the p wave the $y_2(PP)$ long-range potential coupling terms show some sensitivity to small variations in k^2 . Nevertheless, since the energy differences are small, the Seaton approach should provide an estimate of the nonresonance effect upon the collision strengths. Another difficulty with the method is that the R matrices are no longer symmetric. We have thus symmetrized the R matrices, taking the geometric mean of the corresponding elements, and have calculated the maximum error so introduced. This percentage error has been included with the final results, and in all cases has been within the limits of the over-all accuracy expected, especially when compared with the final value for the collision strengths.

TABLE IX. Comparison of different methods of allowing for energy differences, $J_T = \frac{3}{2}$.

Energy ^a (°K)	$\Omega_p(1,2)^b$			
	Exact resonance Distorted-wave approximation	"Exact" method	Allowance for energy differences Distorted-wave approximation	Seaton's ⁸ method
5000	0.0037	0.0040	0.0037	0.0041 ± 2.6%
1000	0.00078	0.00081	0.00082	0.00089 ± 13%
500	0.00039	0.00040	0.00042	0.00048 ± 28%

^a This value represents the electron energy when the atom is in the excited ($J=1$) state.

^b The figures tabulated refer only to contributions from $J_T = \frac{3}{2}$.

^c Percent of error is the result of the asymmetry of the R matrix.

It is possible to obtain an indication of the accuracy of the above method by comparing the results so obtained for the $J_T = \frac{5}{2}$ equations with the corresponding calculations performed with the distorted-wave approximation. This comparison is exhibited in Table IX and the agreement can be viewed as acceptable.

Table X compares the exact-resonance collision strengths for p wave with similar quantities evaluated under the methods suggested in this section. It was found that allowances for energy differences were insignificant at energies of 5000°K and higher, hence detailed calculations have been performed only for the two lower energies presented. As this table well illus-

TABLE X. P -wave collision strengths with allowance for energy differences.

Electron energy ^a (°K)	Exact resonance	Ω_p Allowance for energy differences	Computed error ^b
$\Omega_p(1,2)$:			
10 000	0.271	0.271	
5000	0.131	0.131	
1000	0.0117	0.0160	<1%
500	0.0032	0.0055	4%
$\Omega_p(0,2)$:			
10 000	0.068	0.068	
5000	0.033	0.033	
1000	0.0030	0.0032	2%
500	0.00092	0.00104	13%
$\Omega_p(0,1)$:			
10 000	0.101	0.101	
5000	0.049	0.049	
1000	0.0044	0.0044	3%
500	0.0010	0.0012	5%

^a This value represents the electron energy when the atom is in the respective excited state.

^b This error arises because of the asymmetry of the R matrix.

trates, the corrections for energy differences are not of major importance.

3. The d -Wave Collision Strengths

The effects of the d -wave interactions can be ascertained quite readily. The electron having an angular momentum of $l=2$ does not penetrate substantially into the atomic force field. It is thus sufficient to neglect all of the exchange interaction, to retain only the potential matrix elements, and to calculate the collision strengths by adopting the Born approximation. The validity of the Born approximation for the d waves has been substantiated by Seaton's calculation of the transitions between the L -multiplet members of OI.⁵ The reliability is further strengthened by the fact that the magnitudes of the required integrals [Eq. (60) below] were found to be determined primarily from regions well removed from the atom.

TABLE XI. Matrix element coefficients for potential coupling terms, d wave^a ($M_T = J_T$).

J_T	m, n	$\mathcal{G}_{mn} = \mathcal{G}_{nm}$	J_T	m, n	$\mathcal{G}_{mn} = \mathcal{G}_{nm}$
$\frac{1}{2}$	g, p	$(\sqrt{30})/50$	$\frac{5}{2}$	E, F	$(6\sqrt{6})/175$
	h, p	$(3\sqrt{5})/50$		E, G	$(4\sqrt{35})/175$
$\frac{3}{2}$	8, 9	$(6\sqrt{21})/175$	$\frac{7}{2}$	E, P	$-(3\sqrt{21})/175$
	8, 11	$(\sqrt{21})/350$		H, F	$-(11\sqrt{6})/350$
	8, 12	$(\sqrt{210})/175$		H, G	$-(2\sqrt{35})/175$
	10, 9	$-3/50$		H, P	$-(\sqrt{21})/50$
	10, 11	$3/25$		$\frac{9}{2}$	II, III
10, 12	$(\sqrt{10})/25$	IV, III	$(3\sqrt{5})/175$		

^a Elements connecting the $J=0$ and $J=1$ atomic states are zero, and not included in the listing.

The potential matrix elements of interest are all proportional to $y_2(PP)$. Under the Born approximation, the T -matrix elements are related to these coupling elements as

$$T(m, n) = 2i\mathcal{G}_{mn}\Gamma(m, n), \quad (59)$$

$$\Gamma(m, n) = \pi \int_0^\infty J_{5/2}(k_m r) y_2(PP) J_{5/2}(k_n r) r dr. \quad (60)$$

Values of \mathcal{G}_{mn} are summarized in Table XI. The collision strengths for d wave then become

$$\begin{aligned} \Omega_d(1, 2) &= (144/35) |\Gamma(1, 2)|^2, \\ \Omega_d(0, 2) &= (64/35) |\Gamma(0, 2)|^2, \\ \Omega_d(0, 1) &= 0. \end{aligned} \quad (61)$$

Detailed balance immediately follows from the symmetry of the \mathcal{G}_{mn} coefficients and the $\Gamma(m, n)$ integrals. Allowance can easily be made for the differences in energy between the atomic states, and these refinements were included in the numerical work. Final values obtained for these collision strengths are summarized in Table XII. The results are sufficiently small to justify the validity of the chosen weak-coupling approximation.

IV. POLARIZATION INTERACTION

Up to this point we have neglected the effect of polarization in the excitation process. It has been shown that the polarization interaction may have a very pronounced effect on the elastic scattering of slow

TABLE XII. Collision strengths for d wave, Born approximation.^a

Energy of scattered electron (°K)	$\Omega_d(0, 2)$	$\Omega_d(1, 2)$
10 000	0.00316	0.00708
5000	0.00159	0.00358
1000	0.000291	0.000683
500	0.000122	0.000307

^a The parameter $\Omega_d(0, 1)$ is zero and does not contribute to the corresponding total cross section.

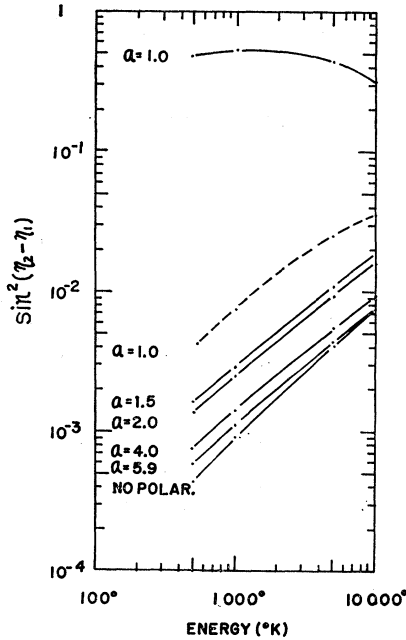


FIG. 1. Values of $\sin^2(\eta_2 - \eta_1)$ calculated by including the polarization potential with various choices of the cutoff parameter a . The solid curves result from the use of Eq. (62) and the dashed one from Eq. (65).

electrons from neutral atomic oxygen.^{14,15} The treatments of this effect in collision problems have been mostly empirical in nature. In this work a polarization potential of the form

$$V^P = -\frac{1}{2}\alpha_P r^{-4} [1 - \exp(-r/a)^8] \quad (62)$$

is chosen with $\alpha_P = 5.2$ a.u., the experimental polarization for atomic oxygen, and a is a cutoff parameter. No correct procedure has yet been established for the proper selection of this parameter. Garrett and Jackson¹⁵ give $a \approx 1$ a.u. whereas Lenander¹⁶ found that a cutoff value of 5.9 a.u. gave results compatible with the existing experimental data for elastic scattering of slow electrons by OI. Lenander essentially treated polarization as a surface effect only, while Jackson and Garrett performed a more detailed analysis in terms of polarized orbitals.

We shall first examine the polarization effect upon the s waves. If a spherically symmetrical potential such as Eq. (62) is included in the Hamiltonian, the scattering equations for s wave will be modified as follows:

$$\begin{aligned} & [\mathcal{L}^0 + 4y_0(PP) + 2y_0(S_1S_1) + 2y_0(S_2S_2) + V^P]G_1 \\ & = [y_0(S_1G_1) + \lambda_P^{(1)}(S_1G_1)]S_1 \\ & \quad + [y_0(S_2G_1) + \lambda_P^{(2)}(S_2G_1)]S_2, \quad (63) \end{aligned}$$

¹⁴ See, for example, L. B. Robinson, Phys. Rev. **105**, 922 (1957); M. M. Klein and K. A. Brueckner, *ibid.* **111**, 1115 (1958); P. Hammerling, W. W. Shine, and B. Kivel, J. Appl. Phys. **28**, 760 (1957); D. R. Bates and H. S. W. Massey, Proc. Roy. Soc. (London) **A192**, 1 (1947).

¹⁵ W. R. Garrett, and H. T. Jackson, Jr., Phys. Rev. (to be published).

¹⁶ C. J. Lenander, Phys. Rev. **142**, 1 (1966).

etc. where

$$\lambda_P^{(l)}(S_l G_l) = \lambda^{(l)}(S_l G_l) + \int_0^\infty S_l G_l V^P dr, \quad \text{etc.} \quad (64)$$

With the polarization potential included in the scattering equations for s wave as above, a series of calculations were performed for selected values of the cutoff parameter between 5.9 and 1.0 a.u. Under exact resonance the collision strengths for s wave are proportional to $\sin^2(\eta_2 - \eta_1)$. [See Eq. (37).] The results for the latter quantity have been plotted in Fig. 1 to illustrate its dependence upon the choice of the cutoff parameter. One notices a high sensitivity of the cross sections to the value of this cutoff parameter in the region $a \leq 1.5$ a.u., while above this number the variation is not so severe.

Since the dominant contribution of the polarization potential appears to originate from regions interior to the atomic charge cloud, it is interesting to investigate the role played by the near-field region of the polarization curve. A set of trial calculations was performed with the following modified formula:

$$\begin{aligned} V^P &= \text{Eq. (62)}, & r \geq a \\ V^P &= 0, & r < a. \end{aligned} \quad (65)$$

For $a > 4.0$, the results were practically identical to those obtained with Eq. (62). Deviations begin near $a = 1.5$, and for $a = 1.0$ the effects of the inner region are well emphasized by the two appropriate curves in Fig. 1.

Hence, the collision strengths depend rather strongly on the part of V^P which is inaccurate, but appear to be insensitive to the far-field region where the polarization potential is expected to give reliable results. It is questionable whether one can get meaningful results by employing an empirical polarization potential based on the asymptotic behavior of $-\alpha_P r^{-4}$. For this reason the polarization calculations will not be pursued further at this point. However, Fig. 1 shows that the polarization interaction, if it should contribute appreciably to the collision strengths, tends to increase the values of the latter. The calculated cross sections which neglect polarization can be regarded as possible lower limits to the correct magnitudes, and as such are still of considerable importance in astrophysical calculations.

V. DISCUSSION AND RESULTS

Table XIII lists the partial collision strengths Ω_s , Ω_p , and Ω_d along with the total collision strengths at four different energies. In the solution of the scattering equations (14), the two major approximations employed have been the neglect of the coupling between states of different l and the omission of the atomic states which are energetically inaccessible. The first assumption has already been discussed briefly; in general only minor corrections are involved. This is specifically demonstra-

TABLE XIII. Total collision strengths for the spin-multiplet transitions of OI.

Transition	Electron energy* (°K)	Ω_s	Ω_p	Ω_d	Ω ($\Omega_s + \Omega_p + \Omega_d$)	Ω estimated by Gershberg's method ^b
$\Omega(1,2)$	10 000	0.0085	0.271	0.0071	0.287	0.138
	5000	0.0046	0.131	0.0036	0.139	0.072
	1000	0.00106	0.0160	0.00068	0.0177	0.0043
	500	0.00058	0.0055	0.00031	0.0064	0.0011
$\Omega(0,2)$	10 000		0.068	0.0032	0.071	0.036
	5000		0.033	0.0016	0.035	0.019
	1000		0.0032	0.00029	0.0035	0.0011
	500		0.00104	0.00012	0.0012	0.0003
$\Omega(0,1)$	10 000	0.0067	0.101		0.108	0.047
	5000	0.0037	0.049		0.053	0.023
	1000	0.00081	0.0044		0.0052	0.0014
	500	0.00042	0.0012		0.0016	0.0003

* This value represents the electron energy when the atom is in the respective excited state.

^b Strictly speaking, these parameters represent the result of averaging over a Maxwellian distribution at a temperature characteristic of the tabulated electron energy, and presumably do not correspond directly to the results of the current calculations. However, the estimated parameters are only rough approximations, and differences between the two interpretations were found to be well within the order-of-magnitude accuracy claimed by Gershberg.

ted by a calculation of the s - d wave contribution for the $^3P-^1D$ transition in OIII by Seaton.⁴ For the present calculation, the dominating influence of the p -wave interaction should tend to significantly reduce this expected error.

The energetically inaccessible states of the oxygen atom which are neglected in this work presumably manifest themselves as "second-order" effects, e.g., the polarization interaction. Because of its long-range nature, the polarization interaction may cause a significant increase of the cross sections. Our analysis in the last section, however, indicates that the long-range portion of the polarization potential is rather unimportant and the cross sections are greatly affected by the magnitude of this potential near the origin. Instead of introducing an empirical polarization potential, a more fundamental approach must be used to ascertain accurately the influence of these "second-order" effects on the F functions near the origin.

It is interesting to compare the present problem with the one of transitions between the 3P , 1D , and 1S term levels of OI.³ In both cases excitation has been found to originate primarily from the p -wave interactions; for this partial-wave component, the states coupled by spherically symmetric exchange terms could be treated very effectively with an exact-resonance approximation and close-coupling techniques. The strength of this form

of coupling, the cancellation of exchange terms of comparable magnitude, and the subsequent sensitivity to wave-function behavior over a small interval, combined with the importance of orthogonality considerations have rendered the usual weak-coupling methods of limited usefulness for both sets of transitions. However, while the exchange coupling dominates the longer-range potential terms for the L -multiplet transitions, in the current problem these two effects are of about equal importance. Here the potential terms were effectively handled through an iteration procedure introduced as a refinement upon the close-coupling method. For states which display potential coupling only, the distorted-wave approximation (with a proper inclusion of exchange distortion and orthogonality restrictions) give very reliable results. In both cases the contributions from the s and d waves were found to be of only minor importance. The former result from exchange coupling alone, and were easily evaluated for the spin-multiplet transitions with a simplified version of the p -wave close-coupling technique. Born approximation proved sufficient for the longer range d -wave interactions.

Finally, it is interesting to compare our calculated cross sections with those estimated by Gershberg. In his paper the rates of energy loss are given, but not the individual estimated collision strengths. The values of the latter can be obtained readily by following his stated procedure of estimation. These "estimated" collision strengths are included in Table XIII. In all cases considered, the collision strengths calculated by solving the scattering equations exceed those estimated by Gershberg's method. Therefore assuming the validity of other phases of the energy-loss calculation, the present theoretical results substantiate, and perhaps even strengthen, the conclusion that neutral atomic oxygen plays an important part in the cooling of the interstellar media.

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