

Calculations on the Scattering of Electrons by Atomic Systems with Configurations $2p^{q*†}$

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The continuum Hartree-Fock equations which describe the radial motion of an electron incident on carbon, nitrogen, and oxygen atoms, and on singly ionized oxygen, all in the ground-state configuration, have been solved. The resulting elastic and inelastic cross sections among the three ground-state terms of the atoms are presented and compared with previous calculations and experiment. The auto-ionization levels in atomic oxygen are calculated and found to be in good agreement with the experimental determinations of the corresponding atomic-oxygen absorption-line series.

1. INTRODUCTION

IN a previous paper,¹ we have developed the theory for describing transitions induced by electron impact between all the ground-state terms of atoms and ions with configurations $(np)^q$, where $n=2$ or 3 and $0 \leq q \leq 6$. In addition, a description was given of the numerical methods which have been developed to solve the resultant coupled integro-differential equations. In the present work, we report the results obtained from the computer code for the neutral target atoms carbon, nitrogen, and oxygen, and for singly ionized oxygen. As outlined in Ref. (1) the interest in these systems is primarily astrophysical.

In the collision problem, the wave functions of the target systems are assumed to be known. Roothaan and Kelly² have presented SCF (self-consistent-field) functions in analytical form for all *discrete* states arising from configurations $1s^2 2s^m 2p^n$, where m and n may be any integers provided there are at most eight electrons for nuclear charge seven, and nine for nuclear charge eight. The physical systems under consideration in this paper are the continuum states of C^- , N^- , O^- , and O , with the parent atom or ion in its ground-state configuration. In this paper, the emphasis is on determining the optically forbidden transition probabilities among the

ground-state terms of the parent atom, using SCF functions for the target atom.

In addition, a direct quantitative comparison can be made with experiment for the atomic-oxygen absorption-line series which is obtained from the solutions of the e^-O^+ system, where we use SCF functions for the target ion.

The ground-state configuration of carbon in the independent-particle model is $(1s)^2 (2s)^2 (2p)^2$, which leads to the ground-state terms 3P , 1D , 1S which will be denoted collectively by $^{2s+1}L_1$. Since the Hamiltonian is diagonal in the set of the total quantum numbers $LS\pi$, then the number of radial equations coupled together for a particular set will depend on the allowed range of the quantum numbers $L_1S_1l_2$, where the orbital angular momentum of the projectile $l_2=L+L_1$ and $S_1=S+\frac{1}{2}$. We recall that the parity quantum number is defined in terms of the behavior of the wave function under a reflection of the coordinate axes in the origin. Consequently, when the wave function of the target atomic system is approximated by products of one-electron Hartree-Fock orbitals, then the parity is $(-1)^{\sum i l_i}$, where the sum is over all the orbital quantum numbers of the individual electrons. For carbon, this means $\pi=(-1)^{l_2}$. In Table I we list the l_2 values and the number of radial equations coupled together for $L \leq 3$.

In the calculations reported here, we have assumed that the orbitals of the atomic electrons are accurately represented by analytic SCF functions.³ That is to say, we assume that

$$P_i(r) = \sum_{\alpha} \tilde{C}(i,\alpha) r^{I(i,\alpha)} e^{-\xi(i,\alpha)r}, \quad (1)$$

where $i=1s, 2s, 2p, \dots$ and α denotes the number of

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§ Operated by the Association of Universities for Research in Astronomy, Inc., under contract with the National Science Foundation.

¹ K. Smith, R. J. W. Henry, and P. G. Burke, Phys. Rev. **147**, 21 (1966).

² C. C. J. Roothaan and P. S. Kelly, Phys. Rev. **131**, 1177 (1963).

³ See C. C. J. Roothaan, Rev. Mod. Phys. **32**, 179 (1960); C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, *ibid.* **32**, 186 (1960).

TABLE I. Orbital quantum numbers l_2 of the projectile in the various $LS\pi$ states, together with the number of radial equations coupled together in those states for electrons incident on either carbon or oxygen.

L	S	π	3P	1D	1S	No. of equations
0	$\frac{1}{2}$	Even		2	0	Two
		Odd	1			One
	$\frac{3}{2}$	Even				None
		Odd	1			One
1	$\frac{1}{2}$	Even	0,2	2		Three
		Odd	1	1,3	1	Four
	$\frac{3}{2}$	Even	0,2			Two
		Odd	1			One
2	$\frac{1}{2}$	Even	2	0,2,4	2	Five
		Odd	1,3	1,3		Four
	$\frac{3}{2}$	Even	2			One
		Odd	1,3			Two
3	$\frac{1}{2}$	Even	2,4	2,4		Four
		Odd	3	1,3,5	3	Five
	$\frac{3}{2}$	Even	2,4			Two
		Odd	3			One

terms taken to represent an orbital. The functions are normalized such that

$$\int_0^\infty P_i(r)P_j(r)dr = \delta_{ij}. \quad (2)$$

In Table II we present the SCF parameters we have used in our production runs on e^-C scattering; they were taken from Clementi.⁴ In addition, we have presented the experimental energy differences between the terms, taken from the tables of Moore.⁵ These were used in our calculations rather than the consistent set of SCF values in order that a direct comparison can be made with experiment. The \bar{C} 's of Eq. (1) are related to

TABLE II. Clementi parameters (Ref. 4) for the SCF functions used for production runs on carbon. The SCF energies for the terms are $E(^3P)=37.68861$ a.u.; $E(^1D)=37.6313$ a.u.; $E(^1S)=37.5495$ a.u., and the experimental energy differences between the terms are $\Delta E(^3P-^1D)=0.0929$ Ry, $\Delta E(^3P-^1S)=0.19728$ Ry.

Orbital, i	$C(i,\alpha)$	$I(i,\alpha)$	$\xi(i,\alpha)$
1s	0.92695	1	5.41250
	0.07665	1	9.28630
	0.00073	2	1.0311
	-0.00167	2	1.5020
	0.00539	2	2.58975
	0.00210	2	4.2595
2s	-0.20786	1	5.4125
	-0.01175	1	9.2863
	0.06494	2	1.0311
	0.74109	2	1.5020
	0.34626	2	2.58975
	-0.13208	2	4.2595
2p	0.24756	2	0.9554
	0.57774	2	1.4209
	0.23563	2	2.5873
	0.0109	2	6.3438

⁴ E. Clementi, IBM J. Res. Develop. **9**, 2 (1965).

⁵ C. E. Moore, Natl. Bur. Std. (U. S.) Circ. No. 467, I (1949).

the C 's in Table II by

$$\bar{C}(i,\alpha) = C(i,\alpha) \{ [2I(i,\alpha)]! \}^{-1/2} [2\xi(i,\alpha)]^{n_i+1/2}, \quad (3)$$

where n_i is the principal quantum number of the atomic orbital i .

The ground-state configuration of oxygen in the independent-particle model is $(1s)^2(2s)^2(2p)^4$, which leads to the same ground-state terms as carbon. Thus, the l_2 values and the number of radial equations coupled together are the same as those of Table I. The SCF functions computed by Roothaan and Kelly² for the 3P state of oxygen were used to describe the terms of the ground-state configuration. Once again, the calculations reported here were carried out with the experimental energy differences which results in $E(^1D) = -74.73722$ a.u. (atomic units), and $E(^1S) = -74.65556$ a.u. relative to the SCF value for $E(^3P) = -74.80915$ a.u.

The ground-state configuration of nitrogen and O^+ is $(1s)^2(2s)^2(2p)^3$ and leads to the three terms 4S , 2D , 2P . While the set of l_2 values is different from those presented in Table I, a similar table can readily be constructed. Calculations on e^-N scattering were carried out using the SCF functions and energies of Roothaan and Kelly.²

Calculations on e^-O^+ scattering were carried out also using the SCF functions of Roothaan and Kelly, but in order to compare directly with experiment, the experimental energy differences between the terms were used.⁵ Thus, relative to the SCF value for $E(^4S) = -74.37253$ a.u., $E(^2D) = -74.25036$ a.u. and $E(^2P) = -74.18818$ a.u.

In Sec. 2 we discuss in detail the tests we used to ensure that the results of the computer code are correct. In Secs. 3 and 4 we present our results for the inelastic and elastic cross sections, respectively, for electrons scattered from the three ground-state terms of carbon, nitrogen, and oxygen atoms. The positions and widths of the auto-ionization levels in atomic oxygen are tabulated in Sec. 5 for the partial waves $^3S^o$, $^3P^o$, and $^3D^o$, and are compared with experimental determinations of the corresponding atomic-oxygen absorption-line series.

2. CHECKING THE CODE

The only previously published calculations which are identical in formulation to a small subset of those reported here are those of Myerscough and McDowell.⁶ These authors have solved a single integro-differential equation. Their results for the carbon phase shift $\delta(^4S^o)$ are plotted as dots in Fig. 1 and joined by a smooth curve in the two regions; their phase shift is positive between 0.6 and 0.7 Ry and is not shown in Fig. 1. These calculations were performed using the parameters quoted in Ref. 7 for the orbitals of the atomic electrons.

⁶ V. P. Myerscough and M. R. C. McDowell, Proc. Phys. Soc. (London) **84**, 231 (1964).

⁷ V. P. Myerscough and M. R. C. McDowell, Monthly Notices Roy. Astron. Soc. **128**, 287 (1964).

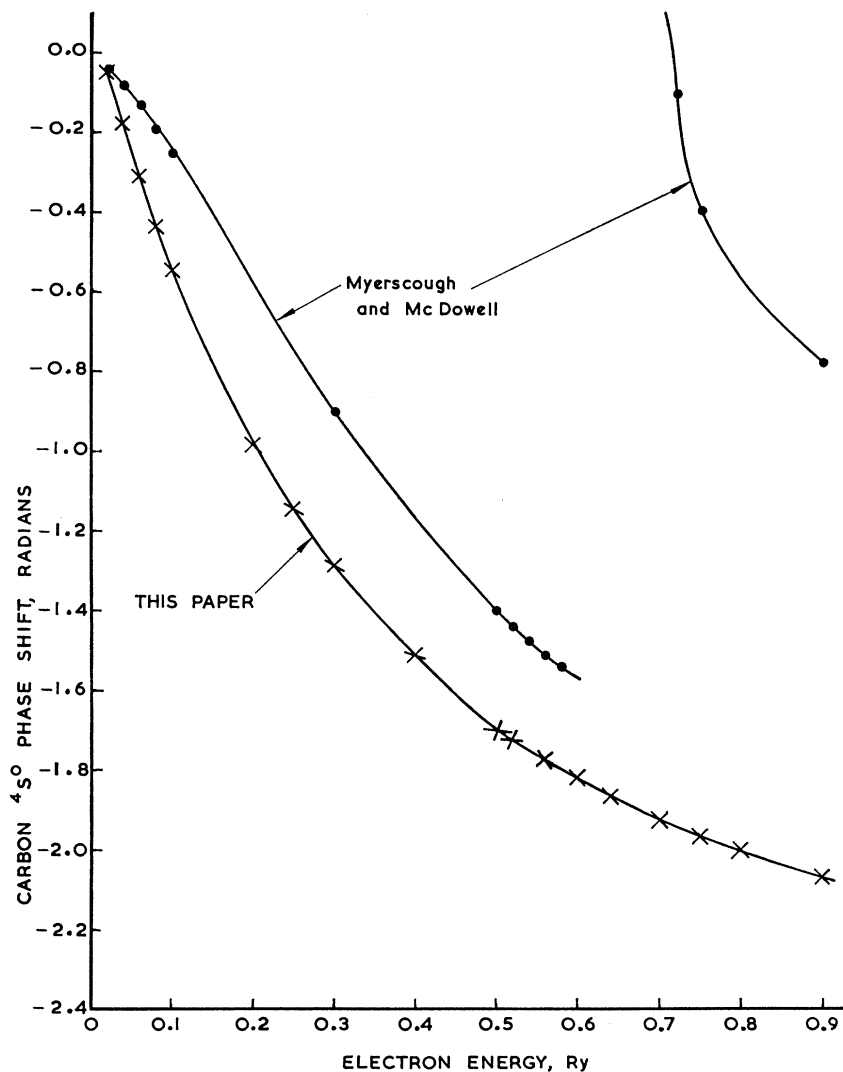


FIG. 1. The energy variation of the $4S^0$ phase shift for electrons incident on carbon atoms calculated by Myerscough and McDowell (Ref. 6) compared with our results.

The radial equation included terms which allowed explicit orthogonalization of the solution to the s -discrete orbitals, and was solved using an iterative numerical procedure. The anomalous behavior of the solution in the region of 0.65 Ry was interpreted by the authors as a resonance. For such a narrow resonance the background phase should be smooth and Fig. 1 shows that their background phase has a discontinuity in the first derivative.

The resonance explanation does not seem plausible for additional reasons. Those narrow resonances which have been predicted by theoretical calculations on electron-atom collisions, and subsequently confirmed by experiment, have always been consequences of many (≥ 2 -) channel formulations. In other words, the single-equation model of Myerscough and McDowell does not have the usual resonance mechanism built into it. While resonances can be generated in single-channel

problems,⁸ it requires a particular structure to the potential (strong short-range attraction, together with longer-range repulsive barrier) which is not met here. Consequently, on the above physical arguments alone, we would expect the phase shift $\delta(4S^0)$ to vary smoothly with energy over the entire range. In Fig. 1 we present our results as crosses and it is seen that the conjecture of a smooth curve is confirmed. These results were obtained by solving the same equation and using the same parameters for the Hartree-Fock orbitals as Myerscough and McDowell, but not orthogonalizing the solutions to the s orbitals. We have also performed calculations including s orthogonalization and the results are very close to the crosses. Runs were also made using Clementi⁴ parameters and the results agreed very well, differences less than 5%, with our results presented in Fig. 1.

⁸ See M. Ross and G. L. Shaw, *Ann. Phys. (N. Y.)* **13**, 147 (1961).

From Table I we see that the set $(LS\pi) = (1 \frac{3}{2} \text{ even})$ results in a pair of coupled radial equations. Myerscough and McDowell's formalism⁶ neglected the equation for $l_2=2$, as well as its coupling to $l_2=0$. Their results are reproduced in Table III, as well as the more recent values published by Myerscough,⁹ who used a noniterative numerical technique to solve the radial equation, but did not orthogonalize her solutions to the s states. While the difference between these two sets of results is enormous, they have one feature in common: smooth variation with energy over the range considered. Because of this, it is very surprising that the noniterative technique⁹ gives different answers from the iterative method.⁶ We should expect such large differences only where the phase shift varied dramatically with energy, which would be manifest in the iterative method jumping wildly from one iteration to another. In Table III we have presented some phase shifts from a completely independent code written by one of us (R. J. W. H.) in collaboration with Dalgarno and Stewart. See Ref. 10 for the formalism, which includes orthogonalization to the s states and uses an iterative technique. These results agree very well with the original results of Myerscough and McDowell. In Table III, column SHB, we present also the results of the present code limiting it to a single equation with no s orthogonalizing. The agreement between columns MD, H, and SHB confirms the reliability of all three. The same analytic Hartree-Fock orbitals of the atomic electrons⁷ were used in all calculations.

Further conclusions can be drawn from Table III: Columns MD and H are, in principle, based on identical formalisms and numerical procedures—they agree. The agreement of SHB with MD and H confirms the conjecture that the numerical procedure should not alter the results when the variation of phase shift with energy is smooth; and demonstrates that s orthogonalization is unimportant. The above evidence indicates that the results in column M are wrong.

A very valuable check on the accuracy of the calculations reported here, and which has not been possible for any previous work, is the symmetry of the R matrix.

TABLE III. 4P phase shift for electron-carbon scattering in the single-equation approximation. Column M, Myerscough (Ref. 9); column MD, Myerscough and McDowell (Ref. 6); column H, Henry (unpublished); column SHB (this paper).

k^2 (Ry)	M	MD	H	SHB
0.02	-0.389	-0.27	-0.27	-0.275
0.04	-0.575	-0.39	-0.39	-0.387
0.06	-0.708	-0.48	-0.48	-0.472
0.08	-0.824	-0.56	-0.55	-0.545
0.10	-0.926	-0.63	-0.61	-0.608
0.30		-1.15		-1.036
0.50		-1.46		-1.310
0.70		-1.58		-1.517

⁹ V. P. Myerscough, Phys. Letters 18, 262 (1965).

¹⁰ A. Dalgarno, R. J. W. Henry, and A. L. Stewart, Planet. Space Sci. 12, 235 (1964).

Of course, this symmetry is only a necessary condition which the numerical results must satisfy; it is not sufficient to guarantee their correctness. A glance at Table I shows the order of the various sets of equations which must be solved for given $LS\pi$. For example, in the case we have just been comparing with previous results, 4P , there are two coupled equations. We found that the matrices were symmetric to six significant figures. The stability of this symmetry has been investigated when the integration step size H is increased or decreased, when the matching point r_0 of the numerical method is varied, and when the point r_a at which the exponential potentials are neglected is varied. (As an illustration of the variation, some of these tests are given in Table IV for oxygen.)

In the over-all quantum state 2P we see from Table I that in our model there are three coupled radial functions. Myerscough and McDowell⁶ in their formalism neglected the two equations with $l_2=2$ as well as the coupling to $l_2=0$. Their results,¹¹ as well as the noniterative results of Myerscough,⁹ are compared with ours, limited to one equation in Table V. Once again, we see that the two sets of these authors' results differ enormously, while the results of one of us (R.J.W.H.), column H, which used procedures which are numerically equivalent to MD, agree very well with those of the present code SHB which is numerically equivalent to M. Further evidence in support of our results comes from the symmetry of the full 3×3 R matrix. However, none of the models used in the first three columns of Table V could make such a check. We conclude that the results of Refs. 9 and 11 are wrong; furthermore, the results in columns H and SHB are mere approximations to those discussed in the next section.

Calculations on the elastic scattering of slow electrons by oxygen atoms have been performed by Myerscough,¹² using the numerical technique of Ref. 9; her results are reproduced in Table IV, column M, where they are compared with results obtained using the present code, columns a, b, c, and A. That is to say, we restrict our code to solve precisely Myerscough's equation. The single radial equations solved by Myerscough can be seen from Table I; they are $(L=1, S=0.5, \pi=\text{even}, l_2=0)$ and $(L=1, S=1.5, \pi=\text{even}, l_2=0)$. While Myerscough orthogonalized her solutions to $P_{2s}(r)$, the code giving the results in columns a-c did not, but the results in column A were obtained by a code which orthogonalized the radial function to both P_{1s} and P_{2s} .

Columns a to A of this table are further evidence in support of the statements made earlier that orthogonalization to closed subshells is not important. While our results for the 2P phase shifts differ from Myerscough by 10%, the 4P results differ by a factor of 2. When we include the full set of three radial equations ($S=0.5$)

¹¹ V. P. Myerscough and M. R. C. McDowell, Proc. Phys. Soc. (London) 84, 622 (1964).

¹² V. P. Myerscough, Phys Letters 19, 120 (1965).

TABLE IV. 2P and 4P phase shifts for electron-oxygen scattering in the single-equation approximation. Column M, Myerscough (Ref. 12); column H, independent code of Ref. 10; column a, $H=0.01$, $r_0=1.0$, $r_a=15.0$; column b, $H=0.02$, $r_0=0.5$, $r_a=5.1$; column c, $H=0.04$, $r_0=1.0$, $r_a=10.2$; column A, $H=0.01$, $r_0=0.5$, $r_a=16.0$ and includes s orthogonalization. Columns LAC were taken from the results of a code (noniterative, no orthogonalization) written by L. A. Conway (unpublished): LAC1, $H=0.125$; LAC2, $H=0.05$; LAC3, $H=0.0125$. (We are indebted to Miss Conway for allowing us to use these results.)

k^2 (Ry)	M	LAC1	LAC2	LAC3	H	(a)	(b)	(c)	(A)
					$\delta({}^2P)$				
0.03	-0.343	-0.344	-0.295	-0.292	-0.291	-0.293	-0.292	-0.295	-0.310
0.04	-0.395	-0.396	-0.340	-0.336	-0.336	-0.337	-0.336	-0.340	-0.351
0.06	-0.482	-0.483	-0.414	-0.410	-0.410	-0.411	-0.411	-0.414	-0.418
0.08	-0.556	-0.556	-0.477	-0.472	-0.471	-0.473	-0.473	-0.476	-0.475
0.10	-0.618	-0.619	-0.531	-0.526	-0.525	-0.526	-0.527	-0.530	-0.525
					$\delta({}^4P)$				
0.03	-0.075	-0.290	-0.233	-0.229		-0.230	-0.234	-0.233	-0.214
0.04	-0.100	-0.335	-0.269	-0.264		-0.265	-0.270	-0.268	-0.257
0.06	-0.143	-0.409	-0.329	-0.324		-0.325	-0.330	-0.328	-0.327
0.08	-0.179	-0.472	-0.380	-0.374		-0.375	-0.381	-0.379	-0.387
0.10	-0.209	-0.526	-0.425	-0.419		-0.419	-0.426	-0.424	-0.440

and pair of equations ($S=1.5$), we obtain symmetrical \mathbf{R} matrices—a check not possible in Myerscough's work. Furthermore, our results are stable under wide variations of the parameters. Additional support for the correctness of our results can be seen in Table IV, where we give the unpublished results of one of us (R.J.W.H.) and of L. A. Conway, using completely independent codes. We conclude that Myerscough's results are numerically incorrect.

The symmetry of the \mathbf{R} matrix for all our results was checked in an analogous manner to the case of carbon to ensure that it was stable when the integration step size was increased or decreased, when the matching point of the numerical method was varied, and when the point at which the exponential potentials are neglected was varied.

Seaton¹³ solved two coupled equations for oxygen at an energy of 0.3 Ry for the set $(LS\pi)=(1\frac{1}{2}\text{ odd})$, which restricts the calculation to p waves in the two open channels and ignores the coupling to the closed 1S channel. His resulting collision strengths were $\Omega({}^3P, {}^1D)=1.06$ and $\Omega({}^1D, {}^3P)=0.90$. These dimensionless parameters are related to the collision cross sections through

$$\sigma(n, n') = (\pi/k_n^2 \omega_n) \Omega(n, n'), \quad (4)$$

where ω_n is the statistical weight of the initial state. The collision strengths should be equal, but in Seaton's calculation some of the exchange terms were neglected, thus destroying the symmetry of the \mathbf{R} matrix. At this energy our program gives $\Omega({}^3P, {}^1D)=0.925=\Omega({}^1D, {}^3P)$ when the *two* coupled equations are solved. There is no post-prior discrepancy, since all the exchange interactions between the terms are included.

As mentioned previously, the calculations reported in the next section on carbon and oxygen used SCF functions, but experimental energy differences. For nitrogen we use the SCF energy differences. In Fig. 2 we present the excitation cross section (${}^4S^{\circ}-{}^2D^{\circ}$) calculated

using SCF energies and compare it with calculations using experimental energy differences between the two terms. We see that the result is insensitive to these parameters.

A further qualitative check on the correctness of the code comes from $(LS\pi)=(0\frac{1}{2}\text{ even})$ in carbon. In Table VI we present the phase shifts and cross sections for $k^2 < 1.0$ Ry. At low energies we see that the phase shift has an interesting structure; very close to threshold it is positive, but it changes sign around 0.11 Ry. This type of behavior has been observed previously in electron-hydrogen atom scattering.¹⁴ Qualitatively, this phenomenon can be understood as follows: At very low energies, the colliding electron will be influenced by the long-range part of the potential only. The higher the incident energy, the deeper will be the penetration of the projectile into the atomic charge cloud, where exchange effects are very important. From the sign of the phase shift, the code predicted that, while the long-range potential is attractive, the short-range forces are repulsive. The code gave the long-range attractive polarization as $(2.9982 r^{-3})$, which was verified.

A somewhat remarkable prediction of the code was that the ${}^2S^{\circ}$ phase shift was identical to the ${}^4S^{\circ}$ phase shift in the electron-oxygen system. It was verified that this was caused by chance cancellations in the exchange terms.

A further check on the accuracy and correctness

TABLE V. 2P phase shift, $l_2=0$ for electrons incident on carbon atoms. Column M, Myerscough (Ref. 9); column MD, Myerscough and McDowell (Ref. 11); column H, unpublished results based on the code of Ref. 10; and column SHB, this paper.

k^2 (Ry)	M	MD	H	SHB
0.02	-0.117	-0.19	-0.35	-0.3531
0.04	-0.215	-0.30	-0.49	-0.4943
0.06	-0.283	-0.41	-0.60	-0.6010
0.08	-0.348	-0.52	-0.69	-0.6894
0.10	-0.409	-0.62	-0.76	-0.7659

¹³ M. J. Seaton, Phil. Trans. Roy. Soc. London **A245**, 469 (1953).

¹⁴ See P. G. Burke and H. M. Schey, Phys. Rev. **126**, 147 (1962).

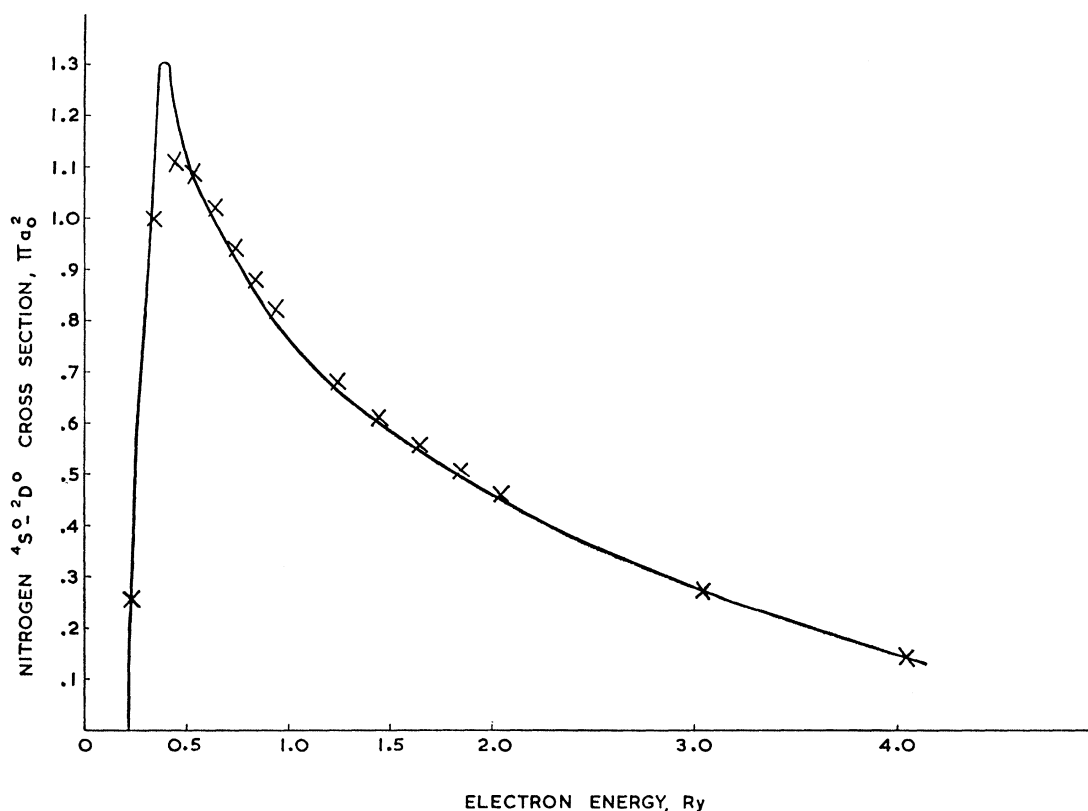


FIG. 2. Excitation cross section $4S^{\circ}-2D^{\circ}$ for electrons incident on nitrogen atoms calculated with SCF energy differences, the full curve, and experimental energy differences, crosses. (The "experimental" scale has been shifted to higher energies.)

of codes can be applied if one uses the properties of boundedness. Hahn, O'Malley, and Spruch¹⁵ have shown that if a scattering calculation is based on a variational principle in which the trial function approximates the closed-channel part of the wave function, but the open-channel portion of the trial function is determined by solving the ordinary integro-differential equations for it resulting from the variational principle,

TABLE VI. $2S^{\circ}$ phase shift for electron-carbon scattering.

k^2 (Ry)	δ , radians	σ , πa_0^2
0.04	0.06914	
0.06	0.06227	
0.08	0.03861	
0.10	0.0118	0.0006
0.12	-0.01621	
0.14	-0.0445	
0.16	-0.0727	
0.18	-0.1004	
0.20	-0.1274	0.0359
0.30	-0.2512	0.0916
0.40	-0.3563	0.1352
0.50	-0.4459	0.1653
0.60	-0.5230	0.1848
0.70	-0.5902	0.1966
0.80	-0.6492	0.2030
1.00	-0.7484	0.2058

¹⁵ Y. Hahn, T. F. O'Malley, and L. Spruch, Phys. Rev. **128**, 932 (1962).

then the approximate values for the phase shifts are always less than the true values and they monotonically approximate the true magnitudes when one increases the number of trial functions. The formalism we have used¹ satisfies these criteria. In Table VII, we present the $2P$ phase shifts in three approximations. From Table I we see that in this case, there are two channels connected to the $2P$ state and one to the $1D$ state, so that there are one, two, or three radial equations with three, seven, and eleven exchange terms, respectively. From Table VII we see that including the closed ($1D l_2=2$) channel does increase the eigenphases, as required by the bound theorems. In this table we have presented also the phase shift $2D$ which hardly changes at all as we increase the number of closed channels taken in the trial function. These results indicate that our accuracy

TABLE VII. Phase shifts at $k^2=0.05$ Ry for electron-carbon scattering in a variety of approximations. N_E is the number of distinct exchange terms; δ_a and δ_b are the eigenphases.

No. of equations	N_E	$2D$ δ_2	N_E	$2P$ δ_a	δ_b
1	4	-0.028928	3	-0.551578	
2	7	-0.028964	7	-0.541925	0.028310
3	11	-0.028963	11	-0.537622	0.028417
4	15	-0.028962			
5	19	-0.028944			

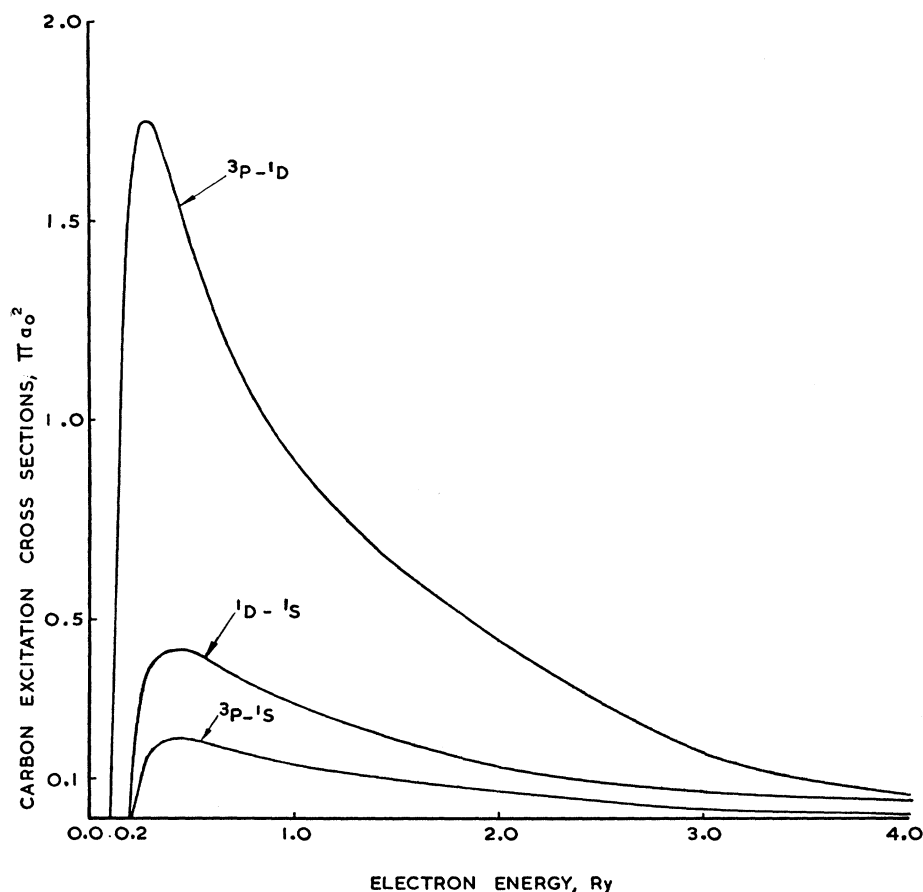


FIG. 3. Excitation cross sections among the ground-state terms of atomic carbon induced by electron impact.

is less than four significant figures. The method of Ref. 15 has been extended^{16,17} to the case where both inelastic and elastic scattering occur.

A quantitative check on the accuracy of the code is furnished by its predictions of the positions of the resonances in the e^-O^+ system. A detailed discussion of these results will be given in Sec. 5.

3. FORBIDDEN TRANSITIONS

Since we have taken the experimental energy differences between the terms of carbon, then the two inelastic thresholds are at 0.0929 Ry (1D) and 0.19728 Ry (1S) above the ground state. In Fig. 3 we have drawn the three total inelastic cross sections for the transitions among the ground-state terms induced by electron impact. Unfortunately, no experiments have been carried out to observe these transitions, although total-scattering experiments have been performed by Maecker *et al.*¹⁸ The only published theoretical calculations have

been reported by Pilyankevich.¹⁹ While the cross sections in Fig. 3 are about the same size as those of nitrogen, to be discussed below, they are three times larger than the corresponding oxygen excitation cross sections. Comments on the high-energy behavior of these cross sections are given in some detail in our presentation of the oxygen results.

For oxygen, as mentioned in the Introduction, we used the experimental separation of the terms in our calculations; the resulting thresholds for excitation are 0.14386 Ry (1D) and 0.30718 Ry (1S) above the ground state.

The total inelastic cross section ($^3P-^1D$) is presented in Fig. 4, as a function of k_1^2 . At high energies the cross section is approaching its asymptotic behavior of k_2^{-6} , which is as expected for this spin-forbidden cross section. Also shown are the results of Seaton,¹³ the dashed curve, who used the exact resonance approximation for the case of incident and final p -wave electrons, corresponding to the set $(LS\pi) = (1\frac{1}{2}\text{ odd})$. The discontinuity in Seaton's curve is due to the fact that above the 1S threshold Seaton solved three equations (p waves in each channel), whereas below it only two equations were

¹⁶ Y. Hahn, T. F. O'Malley, and L. Spruch, Phys. Rev. **134**, B397 (1964); **134**, B911 (1964).

¹⁷ M. Gailitis, Zh. Eksperim. i Teor. Fiz. **47**, 160 (1964) [English transl.: Soviet Phys.—JETP **20**, 107 (1965)].

¹⁸ H. Maecker, T. Peters, and H. Schenck, Z. Physik **140**, 119 (1955).

¹⁹ A. N. Pilyankevich, Zh. Techn. Fiz. **30**, 226 (1960) [English transl.: Soviet Phys.—Tech. Phys. **5**, 204 (1960)].

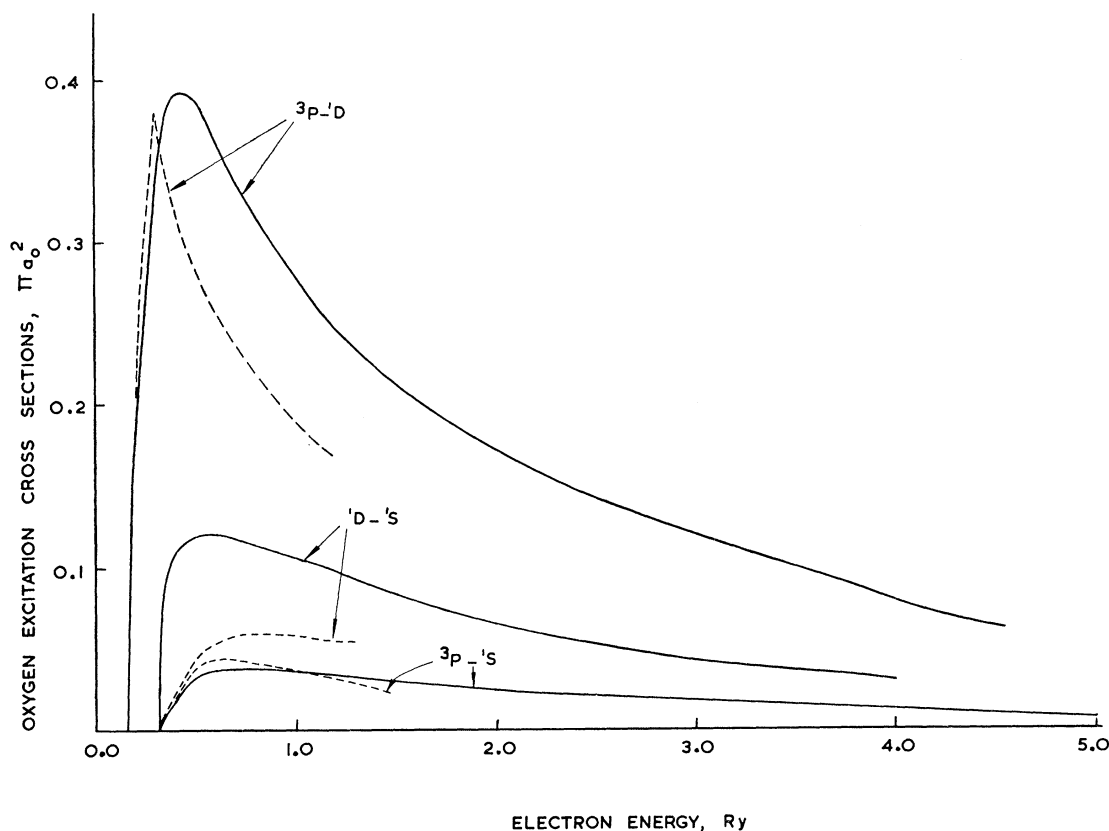


Fig. 4. Excitation cross sections among the ground-state terms of atomic oxygen induced by electron impact, the full curves. Dashed curves are the calculations of Seaton (Ref. 13).

solved; thus the effect of the exponentially decreasing function in the closed channel was ignored. In this case we solved four coupled equations both below and above the 1S threshold. It was found that this set ($LS\pi$) = ($1 \frac{1}{2}$ odd) dominated the total inelastic cross section throughout the energy range, contributing 90% at 1.0 Ry and 60% at 5 Ry.

The total inelastic cross sections (3P - 1S) and (1D - 1S) are also drawn in Fig. 4 and again compared with Seaton's results—the dashed curves. At high energies the spin-forbidden transition falls off at k_3^{-6} , while the cross section (1D - 1S) goes as k_3^{-2} . At low energies the dominant contribution to the cross section for 1D - 1S is ($LS\pi$) = ($0 \frac{1}{2}$ even) which was neglected by Seaton; hence, his results are smaller than those presented here. We note, as for carbon, that (1D - 1S) is greater than (3P - 1S) which implies that in LS coupling the spin selection rule is more rigidly obeyed than the orbital selection rule.

While no experiments have been reported on these transitions, total-cross-section measurements have been performed by Maecker *et al.*,¹⁸ Lin and Kivel,²⁰ Neynaber *et al.*,²¹ Sunshine *et al.*,²² and Daiber.²³ Previous

²⁰ S. C. Lin and B. Kivel, Phys. Rev. **114**, 1026 (1959).

²¹ R. H. Neynaber, L. L. Marino, E. W. Rothe, and S. M. Trujillo, Phys. Rev. **123**, 148 (1961).

²² G. Sunshine, B. B. Aubrey, and B. Bedersen, in *Proceedings*

calculations have been carried out by Yamanouchi,^{24,25} Seaton,²⁶ and Percival²⁷ on the excitation of oxygen atoms by electron impact.

Seaton²⁶ estimated the contributions to these transitions from various terms he had neglected in his classic paper.¹³ Since his earlier work agrees as well as it does with the elaborate calculations we have performed keeping all terms in the equations, we have not included the slight changes of Ref. 26 in the dashed curves of Fig. 4. Percival²⁷ has calculated the collision strengths for low-energy excitation of oxygen from the ground-state term $(2p)^4 \ ^3P$ to the excited configurations $(2p)^3 \ ^4S(3p) \ ^3P$ and $(2p)^3 \ ^4S(3p) \ ^5P$, and so his work lies outside the scope of the calculations reported here. Yamanouchi *et al.*²⁴ calculated the probability for the excitation of the metastable states 1D and 1S from the ground state 3P , using a modified distorted-wave Born-Oppenheimer approximation. Their results were shown

of the Fourth International Conference on the Physics of Electronic and Atomic Collisions (Science Bookcrafters, Inc., Hastings-on-Hudson, New York, 1965), p. 130.

²³ J. W. Daiber, in *Proceedings of the Gaseous Electronics Conference*, University of Minnesota, 1965 (unpublished).

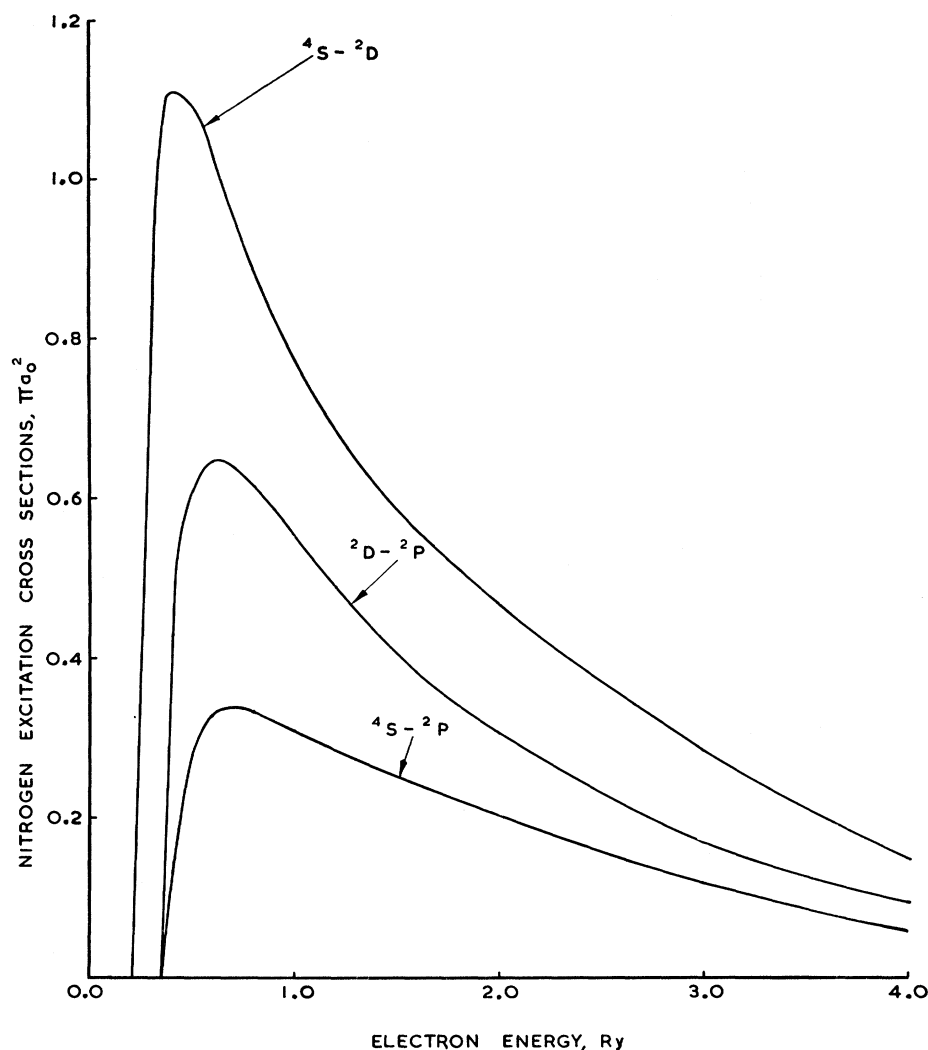
²⁴ T. Yamanouchi, T. Inui, and A. Amemiya, Proc. Phys. Math. Soc. Japan **22**, 847 (1940).

²⁵ T. Yamanouchi, J. Phys. Soc. Japan **5**, 154 (1950).

²⁶ M. J. Seaton, Proc. Roy. Soc. (London) **A231**, 37 (1955).

²⁷ I. C. Percival, Proc. Phys. Soc. (London) **A70**, 241 (1957).

FIG. 5. Excitation cross sections among the ground-state terms of atomic nitrogen induced by electron impact.



to exceed the conservation limit by Bates *et al.*²⁸ and are not included here. Similarly drastic numerical approximations were made in Ref. 25.

In Fig. 5 we present the inelastic cross sections for the forbidden transitions among the ground-state terms of nitrogen induced by electron impact. The only reported experiment on the excitation of nitrogen atoms by electron impact²⁹ is concerned with the configuration change $3p\ 4P^o-3s\ 4P$ and so is outside the scope of this paper. No previous theoretical calculations on these excitation processes have been carried out.

Finally in Tables VIII-X we give the most important partial-wave cross-section contributions for the forbidden transitions in carbon, oxygen, and nitrogen, respectively. It can now be seen from Table IX why Seaton¹³ obtained reasonable results for the transitions

²⁸ D. R. Bates, A. Fundaminsky, J. W. Leech, and H. S. W. Massey, *Phil. Trans. Roy. Soc. London* **A243**, 93 (1951).

²⁹ W. F. Sheridan, O. Oldenberg, and N. P. Carleton, in *Proceedings of the Second International Conference on the Physics of Electronic and Atomic Collisions* (W. A. Benjamin, Inc., New York, 1961), p. 159.

($3P-1D$) and ($3P-1S$) while considerably underestimating the cross section for ($1D-1S$). He essentially considered only the $2P^o$ contribution and for the latter transition this contributes less than half the total value over the energy range considered, with the biggest error being made close to the threshold. As expected, the spin-allowed transitions, since they contain a direct interaction, involve many more high partial waves than the spin-changing transitions. It is these contributions from higher partial waves which change the high-energy behavior of the cross section from k^{-6} to k^{-2} .

4. ELASTIC SCATTERING

For oxygen and carbon the quartet states make no contribution to the inelastic cross section because only the $3P$ term is allowed and it is decoupled from the other two terms. (See Table I.) The dominant contribution comes from the set $(LS\pi) = (1\ \frac{3}{2}\ \text{even})$. In Figs. 6 and 7 we present the total elastic cross section ($3P-3P$). In Fig. 7 the dashed curve is the total cross section, as the

TABLE VIII. Partial-wave contributions to the excitation cross sections of carbon atoms by electrons.

k^2 (Ry)	0.15	0.2	0.25	0.3	0.4	0.5	0.6	0.8	1.0	1.4	2.0	3.0	4.0
$^3P-^1D$													
2P	0.000	0.001	0.002	0.004	0.007	0.011	0.015	0.022	0.026	0.027	0.020	0.009	0.005
$^2P^\circ$	0.330	0.484	0.514	0.502	0.446	0.389	0.338	0.261	0.210	0.150	0.103	0.040	0.012
2D	0.003	0.004	0.005	0.006	0.008	0.008	0.008	0.008	0.007	0.005	0.004	0.002	0.001
$^2D^\circ$	0.849	1.143	1.225	1.217	1.104	0.977	0.858	0.673	0.546	0.387	0.236	0.069	0.019
2F	0.000	0.002	0.005	0.010	0.024	0.041	0.058	0.087	0.103	0.104	0.078	0.039	0.019
$^3P-^1S$													
$^2P^\circ$		0.003	0.110	0.169	0.200	0.196	0.179	0.146	0.120	0.085	0.054	0.017	0.004
2D		0.000	0.000	0.000	0.002	0.004	0.007	0.013	0.017	0.020	0.017	0.009	0.004
$^1D-^1S$													
2S		0.085	0.147	0.112	0.071	0.051	0.040	0.028	0.021	0.014	0.008	0.003	0.001
$^2P^\circ$		0.005	0.110	0.146	0.175	0.183	0.178	0.155	0.131	0.090	0.045	0.008	0.004
2D		0.000	0.048	0.084	0.104	0.101	0.091	0.070	0.053	0.031	0.017	0.009	0.007
$^2F^\circ$			0.011	0.027	0.041	0.047	0.048	0.047	0.045	0.038	0.029	0.019	0.014
2G			0.004	0.010	0.018	0.021	0.022	0.023	0.022	0.020	0.017	0.014	0.011
$^2H^\circ$			0.001	0.004	0.010	0.012	0.013	0.013	0.013	0.013	0.012	0.010	0.008

TABLE IX. Partial-wave contributions to the excitation cross sections of oxygen atoms by electrons.

k^2 (Ry) =	0.2	0.25	0.3	0.35	0.4	0.5	0.6	0.8	1.0	1.5	2.0	3.0	4.0
$^3P-^1D$													
2P	0.000	0.000	0.001	0.001	0.001	0.003	0.004	0.007	0.010	0.015	0.017	0.015	0.011
$^2P^\circ$	0.159	0.269	0.336	0.371	0.383	0.376	0.352	0.297	0.255	0.177	0.133	0.083	0.051
2D	0.001	0.001	0.002	0.003	0.003	0.004	0.006	0.009	0.012	0.017	0.019	0.017	0.013
$^2D^\circ$	0.000	0.001	0.001	0.002	0.002	0.002	0.002	0.003	0.003	0.003	0.002	0.002	0.002
$^3P-^1S$													
$^2P^\circ$				0.010	0.021	0.033	0.038	0.037	0.034	0.025	0.019	0.012	0.007
2D				0.000	0.000	0.000	0.000	0.001	0.002	0.005	0.006	0.006	0.004
$^1D-^1S$													
2S				0.059	0.053	0.038	0.029	0.019	0.014	0.008	0.006	0.003	0.002
$^2P^\circ$				0.023	0.034	0.040	0.041	0.041	0.039	0.030	0.022	0.011	0.005
2D				0.005	0.015	0.026	0.030	0.031	0.028	0.020	0.015	0.008	0.005
$^2F^\circ$				0.001	0.004	0.009	0.011	0.013	0.013	0.013	0.012	0.009	0.007
2G				0.000	0.001	0.004	0.005	0.006	0.006	0.006	0.006	0.005	0.005
$^2H^\circ$				0.000	0.001	0.002	0.002	0.003	0.004	0.004	0.004	0.003	0.003
2J				0.000	0.000	0.001	0.002	0.002	0.002	0.002	0.002	0.002	0.002

TABLE X. Partial-wave contributions to the excitation cross sections of nitrogen atoms by electrons.

k^2 (Ry)	= 0.3	0.4	0.5	0.6	0.8	1.0	1.4	2.0	3.0	4.0
$^4S-^2D$										
$^3S^\circ$	0.000	0.001	0.001	0.002	0.002	0.002	0.002	0.001	0.000	0.000
3P	0.837	1.100	1.076	1.001	0.836	0.700	0.513	0.357	0.202	0.095
$^3D^\circ$	0.004	0.009	0.015	0.024	0.045	0.066	0.096	0.103	0.075	0.047
3F	0.000	0.000	0.000	0.000	0.001	0.001	0.003	0.004	0.005	0.005
$^4S-^2P$										
3P		0.133	0.281	0.327	0.323	0.290	0.224	0.157	0.084	0.036
$^3D^\circ$		0.000	0.001	0.003	0.011	0.021	0.036	0.044	0.035	0.022
$^2D-^2P$										
1P		0.027	0.037	0.035	0.027	0.021	0.014	0.009	0.005	0.004
$^1P^\circ$		0.047	0.038	0.031	0.024	0.020	0.015	0.010	0.006	0.004
3P		0.039	0.087	0.114	0.129	0.122	0.096	0.061	0.022	0.005
$^3P^\circ$		0.149	0.110	0.085	0.058	0.042	0.027	0.014	0.007	0.004
1D		0.070	0.151	0.180	0.182	0.165	0.127	0.087	0.045	0.018
$^1D^\circ$		0.004	0.011	0.014	0.018	0.019	0.020	0.017	0.011	0.007
3D		0.062	0.077	0.069	0.055	0.046	0.034	0.025	0.016	0.012
$^3D^\circ$		0.011	0.028	0.031	0.029	0.024	0.017	0.010	0.005	0.003
1F		0.031	0.003	0.004	0.004	0.004	0.004	0.004	0.003	0.003
$^1F^\circ$		0.004	0.009	0.009	0.006	0.005	0.004	0.005	0.005	0.003
3F		0.003	0.009	0.011	0.012	0.012	0.011	0.009	0.006	0.005
$^3F^\circ$		0.014	0.035	0.042	0.047	0.047	0.042	0.031	0.019	0.013

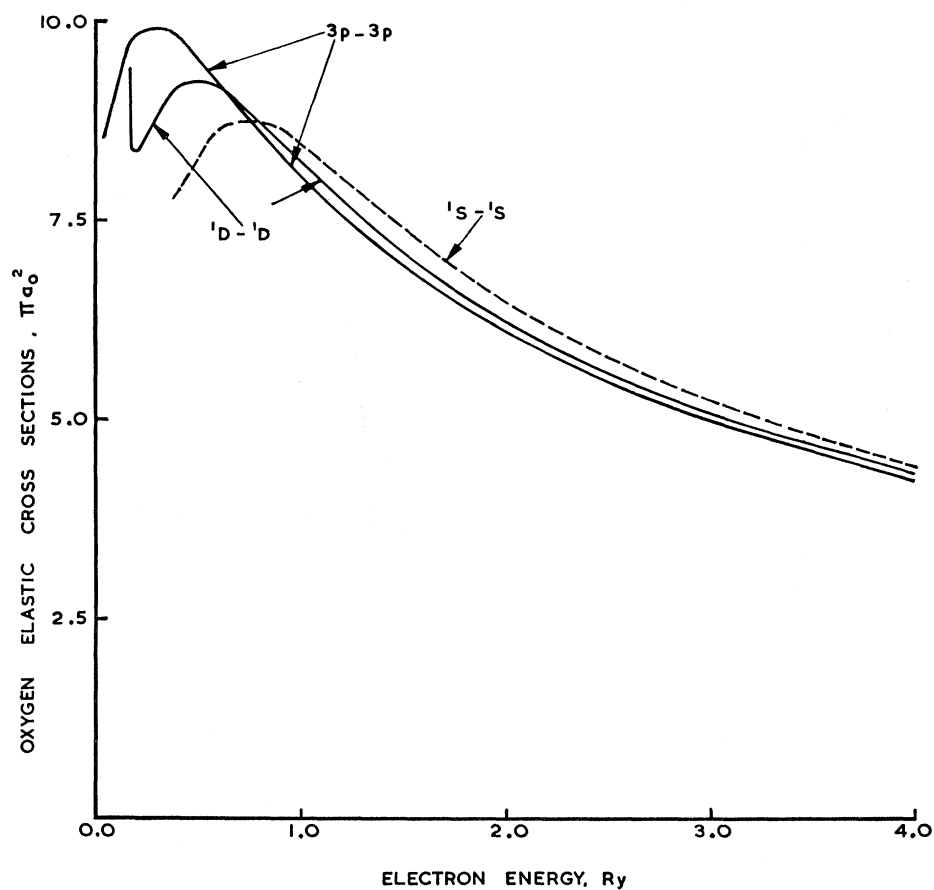


FIG. 6. Elastic cross sections for electrons incident on the ground-state terms of oxygen.

inelastic cross sections (${}^3P-1D$) and (${}^3P-1S$) have been added to the elastic cross section. This can be compared with the experimental results for the total cross section, obtained by Sunshine *et al.*²² (open circles), and it is seen that the theoretical curve overestimates the cross

section at low energies. This can in part be attributed to the neglect of polarization, i.e., the reaction of the scattered electron back on the atom. Temkin³⁰ attempted to include this effect by the method of polarized orbitals and applied the formalism to the scattering of s -wave

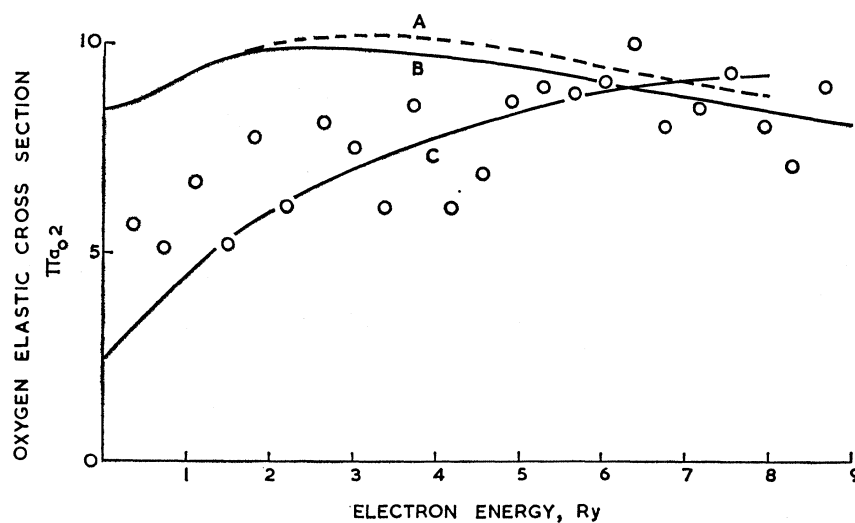


FIG. 7. Total cross sections for electrons incident on oxygen atoms. Curve B is the total elastic cross section ${}^3P-3P$, while curve A includes the excitation cross sections ${}^3P-1D$ and ${}^3P-1S$. The circles are the experimental points of Sunshine *et al.* (Ref. 22); curve C was taken from the calculations of Bauer and Browne (Ref. 35).

³⁰ A. Temkin, Phys. Rev. 107, 1004 (1957).

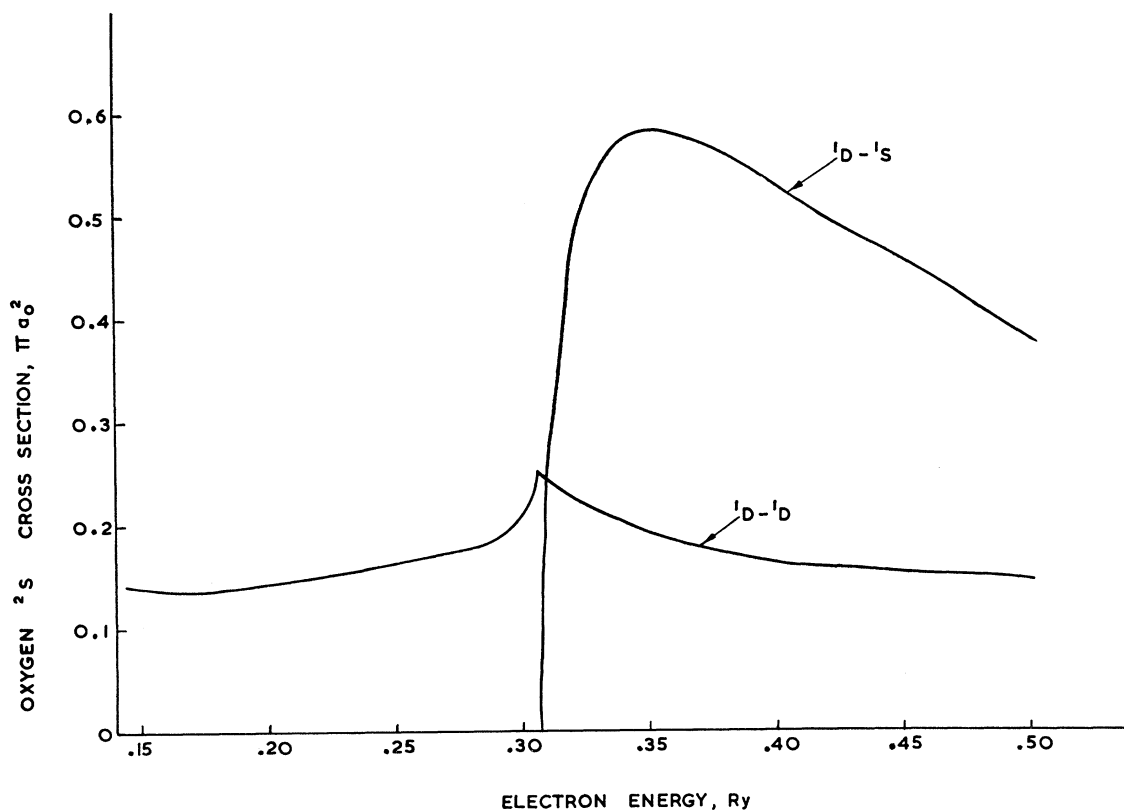


FIG. 8. 2S partial-wave cross sections for electrons incident on atomic oxygen.

electrons from oxygen. His results indicate that when polarization corrections are included, the cross section is lowered by a factor of 2 near threshold, and is scaled to about a 10% reduction at an energy of 0.4 Ry. Neynaber *et al.*²¹ have measured the total collision cross sections for electrons scattered by atomic oxygen. Over the range 0.169 to 0.85 Ry they observed a cross section which was almost constant at $(6.2 \pm 0.5)\pi a_0^2$. This lies well below our results in Fig. 7, and is 30% smaller than the results of Sunshine *et al.*²² for incident electron energies greater than 0.5 Ry. Nevertheless, for energies below 0.4 Ry, it is clear that the distortion (polarization) of the atomic charge cloud has not been fully taken into account in our model of one configuration. Preliminary theoretical attempts to include more distortion have been reported by Bates and Massey,³¹ Hammerling, Shine, and Kivel,³² and Klein and Brueckner,³³ as well as Temkin, mentioned above. The theory for including any number of excited (real or virtual) configurations within the Hartree-Fock approach has been developed by Smith and Conway.^{33a}

In Fig. 6 we have compared the total elastic cross section for 3P - 3P with the cross sections for scattering from the two higher terms 1D and 1S . From Table I we see which sets of $(LS\pi)$ contribute to $\sigma({}^1D$ - ${}^1D)$ and $\sigma({}^1S$ - ${}^1S)$; the set 2S is particularly interesting in that it gives rise to a cusp³⁴ (see Fig. 8).

The salient features of our oxygen results, as presented in Fig. 7, curves A (total) and B (elastic), are in disagreement with the experiment of Sunshine *et al.*²² at very low energies and excellent agreement for energies above 0.6 Ry. The disagreement is confirmed by the result of Lin and Kivel,²⁰ who, via indirect observations, quote the cross section to be about $2.0\pi a_0^2$ at $k^2=0.04$ Ry. Bauer and Browne,³⁵ curve C, have drastically simplified the Hartree-Fock equations by deriving effective potentials for exchange and correlation. They obtained good agreement with experiment (at the intermediate energies), as seen in Fig. 7. An additional feature of interest is the dip in the 1D - 1D cross section just above threshold, as drawn in Fig. 6.

There are two coupled equations and two reaction channels for the 2S over-all state. For incident energies greater than 0.163 Ry both channels are open; this is

³¹ D. R. Bates and H. S. W. Massey, Proc. Roy. Soc. (London) **A192**, 1 (1947).

³² P. Hammerling, W. W. Shine, and B. Kivel, J. Appl. Phys. **28**, 760 (1957).

³³ M. M. Klein and K. A. Brueckner, Phys. Rev. **111**, 1115 (1958).

^{33a} K. Smith and L. A. Conway (unpublished).

³⁴ L. D. Landau and E. M. Lifshitz, *Non-Relativistic Quantum Mechanics* (Pergamon Press, Ltd., London, 1958).

³⁵ E. Bauer and H. N. Browne, *Atomic Collision Processes* (North-Holland Publishing Company, Amsterdam, 1964), p. 16.

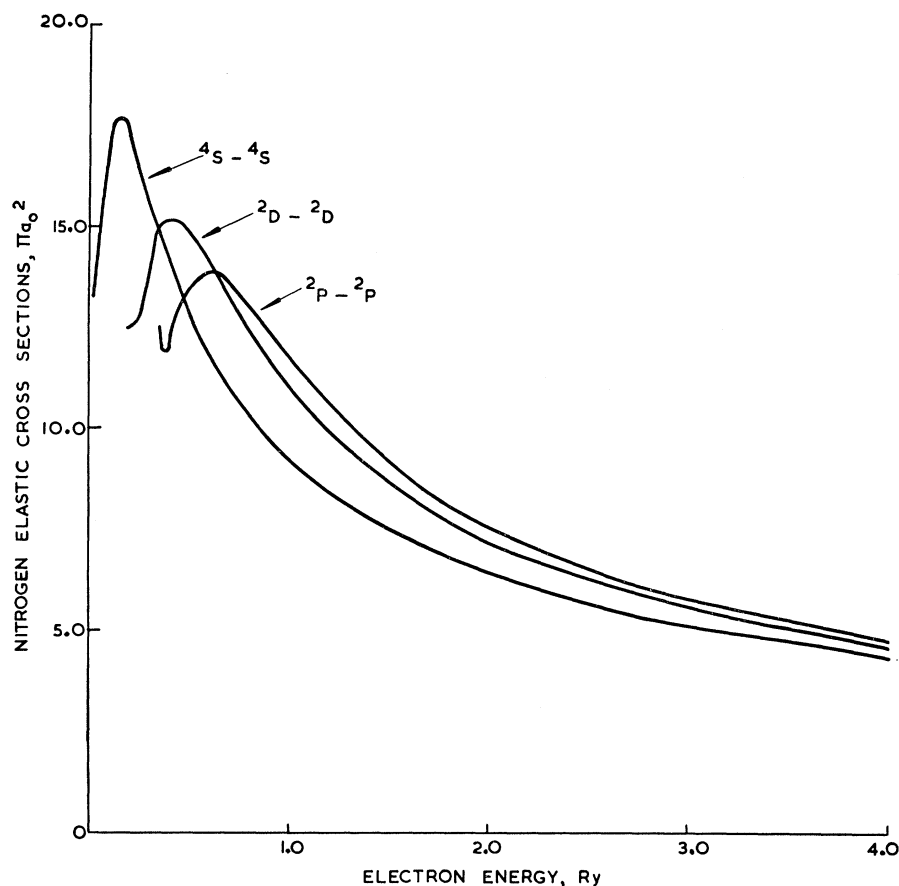


FIG. 9. Elastic cross sections for electrons incident on the ground-state terms of atomic nitrogen.

the threshold energy required to excite the oxygen atom from the 1D to the 1S state. In Fig. 8 we have plotted the elastic cross section $\sigma({}^1D-{}^1D)$ and the excitation cross section $\sigma({}^1D-{}^1S)$ in the vicinity of the inelastic cross section, but no suggestion on a resonance.

The contribution of this set to the total inelastic cross section $\sigma({}^1D-{}^1S)$ is found to be dominant for low energies ($k_s^2 < 0.05$ Ry).

In Fig. 9 we present the three elastic cross sections from the ground state 4S of nitrogen and from the pair of metastable states, 2D and 2P . All $(LS\pi)$ combinations which contribute to these cross sections have been included. In Fig. 10, the dashed curve represents our calculated total collision cross section versus energy for electrons incident on the ground-state term, 4S . On this graph we have plotted the calculations of Klein and Brueckner³³ and of Bauer and Browne,³⁶ as well as the experimental results of Neynaber *et al.*³⁷ As for oxygen, the single configuration Hartree-Fock model we have used grossly overestimates the cross section at very low energies, but does seem to tend to the experimental values beyond 10 eV. The model of Bauer and Browne

seems to be good at low energies, but is still rising at 10 eV. From these results it is clear that our model is neglecting the effect of long-range forces which are dominant at low energy. It is however, surprising that our results are so far in error when it is remembered that the equivalent single configuration result for e^- -H scattering is only 10% in error. It is suggested therefore that part of the discrepancy is experimental.

In Fig. 11 we present the three elastic cross sections for electrons incident on the three terms 3P , 1D , 1S of carbon. The curves have the same structure as for nitrogen and oxygen. The previous calculations of Myerscough and McDowell have been discussed extensively in Sec. 2 and since their work, as well as that of Cooper and Martin,³⁸ are approximations to our model, they will not be discussed further. Malik and Trefftz³⁹ have calculated the s -wave contribution to the total cross section for the scattering of electrons by carbon (and nitrogen) atoms; their results bear no resemblance to the experimental curve quoted in Fig. 7 and give huge cross sections at zero energy, about $80\pi a_0^2$. In Fig. 12 we show the 2S partial-wave cross sections where a cusp effect

³⁶ E. G. Bauer and H. N. Browne, as discussed in Ref. 37.

³⁷ R. H. Neynaber, L. L. Marino, E. W. Rothe, and S. M. Trujillo, Phys. Rev. **129**, 2069 (1963).

³⁸ J. W. Cooper and J. B. Martin, Phys. Rev. **126**, 1482 (1962)

³⁹ F. B. Malik and E. Trefftz, Z. Naturforsch. **16**, 492 (1961)

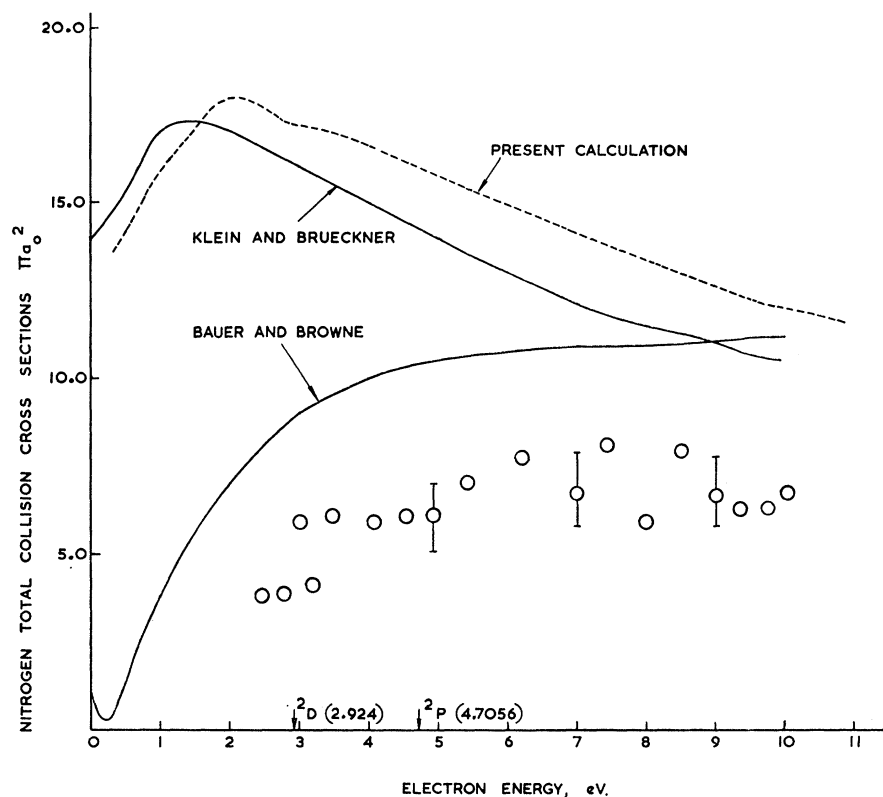


FIG. 10. Total cross sections for electrons incident on nitrogen atoms, dashed curve, compared with previous theoretical calculations of Klein and Brueckner (Ref. 33) and Bauer and Browne (Ref. 36) and the experimental results of Neynaber *et al.* (Ref. 37), circles.

similar to that discussed in oxygen occurs. It is interesting to note that it is an inversion of the oxygen cusp.

In Tables XI–XIII we give the most important partial-wave cross-section contributions to the elastic scattering by electrons in carbon, oxygen, and nitrogen. It is interesting to note that for many of these cross sections the quadrupole interaction, which behaves asymptotically as r^{-3} , dominates the low-energy cross section, giving a finite partial-wave cross section at threshold even when the orbital angular momentum of the incident electron is not zero. Mott and Massey⁴⁰ show that for potentials of the form

$$V(r) = c/r^s$$

the phase shift δ_l varies as

$$\delta_l \sim k^{s-2} \quad (k \rightarrow 0)$$

provided $2l > s-3$. For $s=3$, as in our case, this gives $\delta_l \sim k$ for all l and thus the cross section $\sigma_l \propto (\sin^2 \delta_l)/k^2$, which is finite at threshold. We find that potentials of the appropriate form are obtained provided the triangular relations $\Delta(L_i L_j 2)$ and $\Delta(l_i l_j 2)$ are satisfied, where $(L_i l_i)$ and $(L_j l_j)$ are the atomic and incident orbital angular momenta of the initial and final states, respectively. For elastic scattering $L_i = L_j$ but l_i does

not necessarily equal l_j (see Table I). Examples of this finite behavior at threshold can readily be found in the tables, e.g., in oxygen for the process (3P - 3P) we note that for $k^2 = 0.1$ Ry the cross sections for $^2S^\circ$ and $^4S^\circ$ scattering are large even though $l_i = l_j = 1$ from Table I. More detailed calculations closer to threshold than those given in Table XII show that at $k^2 = 0.02$ Ry for (3P - 3P) the $^2S^\circ$ contribution is $0.077 \pi a_0^2$ and the $^4S^\circ$ contribution is $0.155 \pi a_0^2$.

5. AUTO-IONIZATION LEVELS OF ATOMIC OXYGEN

The theoretical model¹ which we have employed in these calculations is the close-coupling approximation. This method has been shown by Feshbach⁴¹ to give rise naturally to resonances when some of the channels are closed. In particular, the dominant mechanism which produces resonances is the long-range Coulomb force. This is present in the e^-O^+ system which is under consideration in this section. In close-coupling expansion we only include the terms which arise from the ground-state configuration, but these terms are well isolated and weakly coupled to the other (neglected) states. We can thus expect accurate results for the scattering cross sections and the positions of the auto-ionization levels if the above assumptions are valid.

⁴⁰ N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford University Press, New York, 1965), 3rd ed., p. 89.

⁴¹ H. Feshbach, *Ann. Phys. (N. Y.)* 5, 357 (1958); 19, 287 (1962).

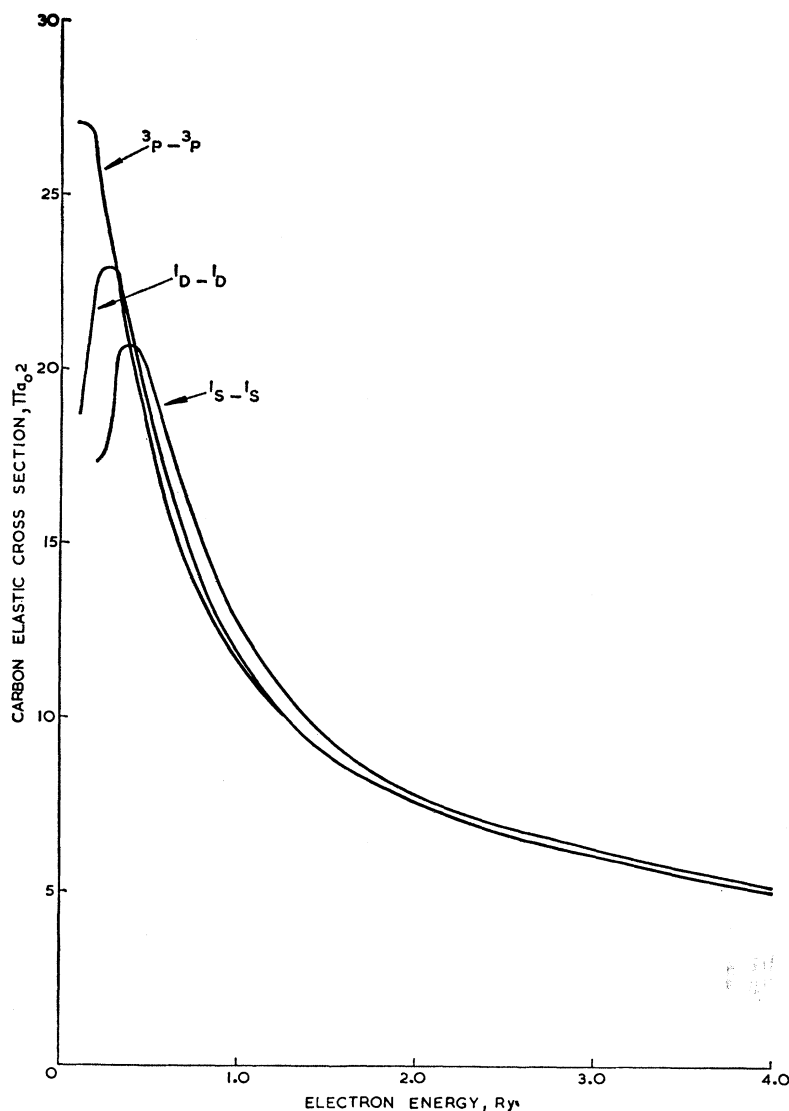


FIG. 11. Elastic cross sections for electrons incident on the ground-state terms of atomic carbon.

Since we wish to compare with experiment, we have taken the experimental energy differences between the terms of O^+ , and the two inelastic thresholds are at 0.24432 Ry (2D), and 0.36870 Ry (2P) above the ground state.

The coupled integro-differential equations for the e^-O^+ system have been solved in the energy regions where the 2D and 2P channels are closed and the 4S channel open, and where the 2P channel is closed and both the 4S and 2D channels open. This yielded resonances in the elastic (and inelastic) scattering of electrons by O^+ . The phase shifts were obtained as a function of energy for the set of total quantum numbers $S=1$, $\pi=\text{odd}$, and $L=0, 1$, and 2, and a Breit-Wigner resonance fit was carried out for each level.⁴² In order to calculate the atomic-oxygen absorp-

⁴² P. G. Burke, D. D. McVicar, and K. Smith, Proc. Phys. Soc. (London) 84, 749 (1964).

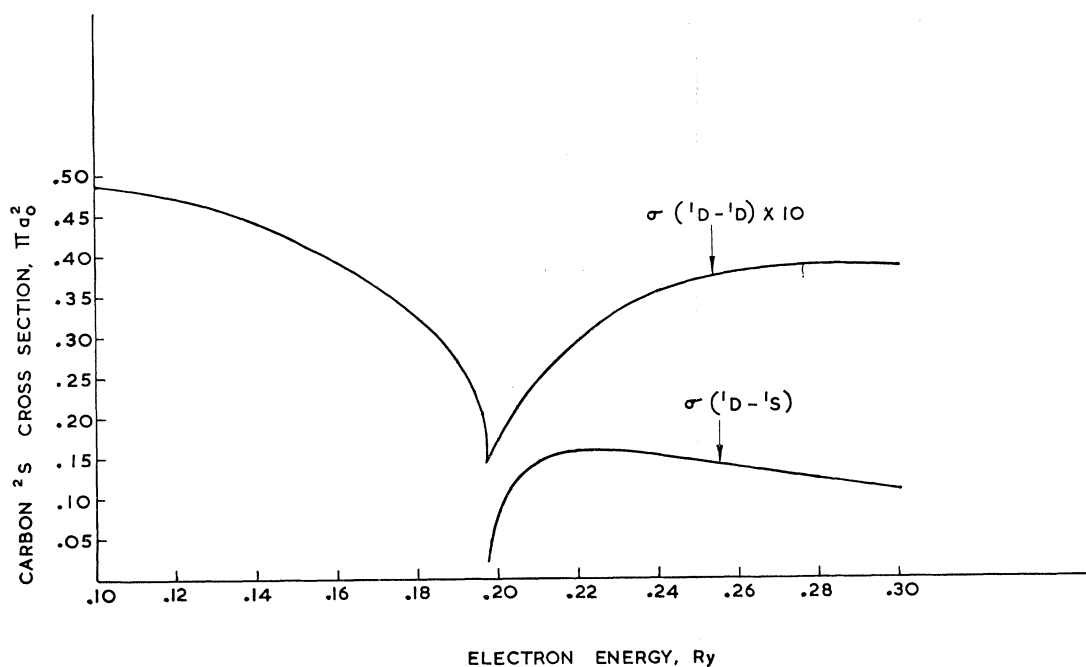
tion-line series from the positions of the auto-ionization levels, we have used a value of $109837.03 \text{ cm}^{-1}$ for the ionization energy of the ground state of atomic oxygen, 3P_2 , as measured by Eriksson and Isberg,⁴³ and the Rydberg constant for oxygen was taken to be $109737.31 \text{ cm}^{-1}$.

Six Rydberg series due to allowed transitions from the atomic-oxygen ground state have been calculated and are given in Table XIV. The upper states of these transitions are given in the first column. The results are compared with the experimental determinations of Huffman *et al.*,^{44,45} who have observed the absorption spectrum of atomic oxygen, from which they have ob-

⁴³ K. B. S. Eriksson and H. B. S. Isberg, Arkiv Fysik 24, 549 (1963).

⁴⁴ R. E. Huffman, J. C. Larrabee, and Y. Tanaka, Phys. Rev. Letters 16, 1033 (1966).

⁴⁵ R. E. Huffman, J. C. Larrabee, and Y. Tanaka, J. Chem. Phys. 46, 2213 (1967).

FIG. 12. 2S partial-wave cross sections for electrons incident on atomic carbon.

tained the Rydberg series due to the allowed transitions. They have also observed three additional Rydberg series, the upper states being $(^4S^{\circ})ns\ ^3S^{\circ}$, $(^4S^{\circ})nd\ ^3D^{\circ}$, and $(^2D^{\circ})nd'\ ^3P^{\circ}$. These series are inaccessible in our present treatment, since they correspond to all the channels being closed.

The calculated widths of the resonances are also given in Table XIV. No comparison of these can be made with experiment, since the lines observed were too narrow to show the characteristic Beutler-Fano profile. The narrowness of the lines is confirmed at least qualitatively by the present calculations, and furthermore we note

TABLE XI. Partial-wave contributions to the elastic cross sections of electrons on carbon.

k^2 (Ry)	0.1	0.15	0.2	0.25	0.3	0.4	0.5	0.6	0.8	1.0
	$^3P-^3P$									
$^2S^{\circ}$	0.001	0.010	0.036	0.065	0.092	0.135	0.165	0.185	0.203	0.206
$^4S^{\circ}$	2.462	3.005	3.096	2.950	2.735	2.215	1.754	1.392	0.914	0.658
2P	6.215	5.526	4.935	4.425	3.983	3.262	2.707	2.274	1.654	1.246
$^2P^{\circ}$	3.898	3.747	3.344	2.804	2.364	1.681	1.208	0.884	0.516	0.344
4P	8.534	8.045	7.537	7.050	6.588	5.752	5.027	4.404	3.412	2.683
$^4P^{\circ}$	1.038	1.290	1.485	1.631	1.737	1.861	1.906	1.903	1.823	1.704
2D	0.036	0.037	0.037	0.037	0.036	0.034	0.031	0.027	0.019	0.011
$^2D^{\circ}$	4.163	4.169	3.970	3.629	3.240	2.501	1.916	1.488	0.965	0.703
4D	0.049	0.031	0.015	0.004	0.000	0.013	0.051	0.106	0.236	0.354
$^4D^{\circ}$	0.621	1.053	1.432	1.745	1.995	2.339	2.532	2.624	2.638	2.543
	$^1D-^1D$									
2S	0.049	0.042	0.017	0.037	0.039	0.032	0.023	0.015	0.005	0.001
2P	0.037	0.038	0.033	0.029	0.024	0.015	0.008	0.003	0.001	0.001
$^2P^{\circ}$	0.893	2.215	2.858	3.060	2.994	2.598	2.192	1.854	1.397	1.132
2D	16.934	15.621	14.435	13.295	12.244	10.403	8.881	7.622	5.710	4.378
$^2D^{\circ}$	0.404	1.393	3.194	4.064	4.297	3.907	3.253	2.642	1.803	1.355
2F	0.124	0.127	0.143	0.161	0.182	0.232	0.287	0.342	0.439	0.509
$^2F^{\circ}$	0.275	1.027	1.809	2.467	2.980	3.649	3.981	4.109	4.048	3.813
	$^1S-^1S$									
2S			17.220	14.419	13.351	11.500	9.862	8.454	6.261	4.697
$^2P^{\circ}$			0.028	3.321	6.364	9.124	9.693	9.367	8.197	7.146
2D			0.000	0.002	0.005	0.031	0.095	0.197	0.480	0.795

TABLE XII. Partial-wave contributions to the elastic cross sections of electrons on oxygen.

k^2 (Ry)	0.1	0.15	0.2	0.25	0.3	0.4	0.5	0.6	0.8	1.0
	$^3P\text{-}^3P$									
$^2S^\circ$	0.107	0.125	0.140	0.153	0.163	0.179	0.188	0.193	0.195	0.192
$^4S^\circ$	0.214	0.250	0.280	0.306	0.327	0.357	0.376	0.386	0.391	0.383
2P	3.271	3.087	2.918	2.760	2.613	2.347	2.116	1.913	1.578	1.315
$^2P^\circ$	1.017	1.372	1.485	1.530	1.523	1.407	1.254	1.096	0.830	0.619
4P	4.324	4.222	4.116	4.005	3.891	3.664	3.441	3.226	2.832	2.489
$^4P^\circ$	0.000	0.016	0.050	0.090	0.134	0.220	0.297	0.362	0.460	0.523
2D	0.009	0.008	0.008	0.008	0.007	0.006	0.006	0.006	0.005	0.006
$^2D^\circ$	0.166	0.274	0.361	0.446	0.521	0.639	0.722	0.778	0.834	0.845
4D	0.021	0.025	0.030	0.036	0.044	0.062	0.085	0.111	0.170	0.230
$^4D^\circ$	0.209	0.331	0.453	0.566	0.669	0.843	0.978	1.079	1.205	1.265
	$^1D\text{-}^1D$									
2S		0.014	0.014	0.016	0.021	0.016	0.015	0.014	0.016	0.018
2P		0.010	0.010	0.011	0.011	0.014	0.016	0.020	0.028	0.038
$^2P^\circ$		0.115	0.050	0.234	0.431	0.697	0.800	0.808	0.725	0.640
2D		8.821	7.753	7.500	7.237	6.714	6.217	5.753	4.932	4.245
$^2D^\circ$		0.355	0.509	0.682	0.841	1.099	1.282	1.407	1.537	1.570
2F		0.035	0.040	0.034	0.029	0.019	0.011	0.005	0.003	0.013
$^2F^\circ$		0.032	0.044	0.149	0.291	0.595	0.862	1.076	1.362	1.515
	$^1S\text{-}^1S$									
2S						7.196	6.719	6.270	5.416	4.661
$^2P^\circ$						0.692	1.643	2.393	3.244	3.663
2D						0.001	0.002	0.009	0.049	0.124

that the series with the broadest lines is associated with the upper state ($^2P^\circ$) ns'' $^3P^\circ$, in agreement with Huffman.⁴⁶

TABLE XIII. Partial-wave contributions to the elastic cross sections of electrons on nitrogen.

k^2 (Ry)	0.1	0.2	0.3	0.4	0.5	0.6	0.8	1.0
	$^4S\text{-}^4S$							
$^3S^\circ$	5.400	4.524	3.833	3.276	2.821	2.445	1.870	1.458
$^5S^\circ$	5.506	5.069	4.653	4.260	3.894	3.557	2.968	2.481
3P	5.349	6.648	5.373	4.319	3.540	2.956	2.146	1.654
5P	0.498	1.175	1.736	2.150	2.444	2.644	2.852	2.905
$^3D^\circ$	0.000	0.000	0.000	0.000	0.001	0.003	0.010	0.021
$^5D^\circ$	0.000	0.008	0.035	0.085	0.158	0.251	0.473	0.703
	$^2D\text{-}^2D$							
$^1S^\circ$		0.000	0.000	0.001	0.001	0.004	0.007	
1P		0.034	0.084	0.134	0.172	0.216	0.233	
$^1P^\circ$		0.000	0.001	0.001	0.002	0.004	0.007	
3P		0.965	1.607	1.696	1.581	1.237	0.956	
$^3P^\circ$		0.000	0.003	0.002	0.002	0.004	0.008	
1D		1.596	2.248	2.174	1.899	1.316	0.893	
$^1D^\circ$		3.263	2.793	2.409	2.091	1.603	1.252	
3D		0.176	0.449	0.686	0.863	1.072	1.159	
$^3D^\circ$		7.631	6.847	6.148	5.529	4.501	3.703	
1F		0.125	0.311	0.455	0.554	0.655	0.682	
3F		0.301	0.765	1.141	1.409	1.705	1.808	
$^3F^\circ$		0.000	0.003	0.012	0.028	0.080	0.149	
	$^2P\text{-}^2P$							
1S			0.431	0.930	0.980	0.731	0.479	
3S			0.027	0.117	0.200	0.310	0.363	
3P			0.421	1.258	1.675	1.835	1.708	
$^3P^\circ$			7.538	6.798	6.158	5.038	4.139	
1P			0.041	0.153	0.249	0.366	0.414	
$^1P^\circ$			3.315	2.832	2.451	1.865	1.445	
1D			0.261	0.786	1.035	1.100	0.998	
$^1D^\circ$			0.000	0.000	0.001	0.009	0.023	
3D			0.160	0.661	1.121	1.708	1.970	
$^3D^\circ$			0.000	0.000	0.002	0.013	0.036	
$^3F^\circ$			0.000	0.002	0.011	0.061	0.102	

⁴⁶ R. E. Huffman (private communication).

Cairns and Samson⁴⁷ have measured the absorption cross sections for atomic oxygen at 22 wavelengths and have obtained larger values than the theoretical results of Dalgarno *et al.*,¹⁰ in particular at four wavelengths, namely, 686, 725, 736, and 780 Å. Huffman *et al.*⁴⁴ have pointed out that some of the series lines that they have observed lie close to the first three wavelengths listed

TABLE XIV. Atomic-oxygen absorption-line series (Å). The lower state is 3P_2 ; n is the principal quantum number of the upper state; Γ is the width in Å.

Upper states	n	Theory	Expt. (Ref. 45)	Γ
$(^2D^\circ)nd'$ $^3S^\circ$	3	803.60	804.27	0.0052
	4	770.53	770.79	0.0026
	5	756.13	756.24	0.0014
$(^2D^\circ)ns'$ $^3D^\circ$	6	748.52	748.63	0.0008
	4	814.13	816.86	0.0050
	5	774.37	775.32	0.0021
$(^2D^\circ)nd'$ $^3D^\circ$	6	757.96	758.41	0.0010
	3	803.92	804.77	0.020
	4	770.70	771.06	0.012
$(^2P^\circ)ns''$ $^3P^\circ$	5	756.22	756.35	0.007
	4		737.02	
	5	700.38	701.00	0.134
$(^2P^\circ)nd''$ $^3P^\circ$	6	686.91	687.20	0.064
	7	679.93	680.15	0.027
	3		724.93	
$(^2P^\circ)nd''$ $^3D^\circ$	4	697.33	697.53	0.058
	5	685.46	685.54	0.029
	6	679.17	679.20	0.019
	3		724.93	
	4	697.31	697.53	0.014
	5	685.44	685.54	0.008
	6	679.17	679.20	0.005

⁴⁷ R. B. Cairns and J. A. R. Samson, Phys. Rev. **139**, A1403 (1965).

above, but they have no evidence of a line near 780 Å. Our results are in agreement with their conclusions. For example, from Table XIV we see that there is a series line at 685.46 Å corresponding to the transition ${}^3P_2-({}^2P^\circ)5d''\ {}^3P^\circ$ and one at 685.44 Å a corresponding to ${}^3P_2-({}^2P^\circ)5d''\ {}^3D^\circ$.

The Rydberg series of levels, which belong to a discrete spectrum and which precede each threshold in the photon energy scale, provide an indirect method of ionization by absorption into a short-lived state followed by

auto-ionization. Thus, peaks in the absorption cross section can be expected near (or at) each auto-ionization level. The analysis of these resonances will be treated elsewhere.

The good quantitative agreement between theory and experiment for the absorption-line series in atomic oxygen justifies our retention of only the terms of the ground-state configuration in the close-coupling expansion. It is noted that the same approximations were made for the atoms considered in the previous sections.

Collisional Depolarization of the Rb 5*p* and Cs 6*p* Doublets*

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Using the Hanle-effect technique, the cross sections for collisional depolarization of the Rb ${}^2P_{1/2, 3/2}$ and Cs ${}^2P_{1/2}$ states by inert-gas collisions have been measured. (The natural lifetimes of these states were also obtained from the measurements.) The ${}^2P_{1/2}$ -state depolarization cross sections are much smaller than any previously reported for $L \neq 0$ states. This results from a strong selection rule governing nonresonant collisions. This selection rule is derived and its effect on $J = \frac{1}{2}$ -state depolarization is demonstrated. A relationship between the reported cross sections and sensitized fluorescence cross sections is noted.

I. INTRODUCTION

THE collisional depolarization of atomic states by thermal atom-atom collisions has been calculated in several formalisms.¹⁻³ The theories have considered isolated fine-structure states, with hyperfine components, using the adiabatic approximation to evaluate cross sections for foreign gas (nonresonant) depolarization. Franz and Franz have discussed the effect of the fine-structure interval in the nonresonant collisional depolarization of the alkali *p* doublets, and the implications to optical pumping of a $\Delta m_J = 0, \pm 2$ selection rule that occurs in several theories for collisional transfer between the *J* state of these doublets.⁴ It is demonstrated here that there exists in addition to that weak selection rule, a strong selection rule governing depolarization within a *J* level by inert gas collisions. This strong selection rule asserts that in the adiabatic approximation the entire electrostatic collisional interaction (including exchange) will not cause transitions between states *JM* and *J-M* when *J* is half-integral. The

effect of this selection rule on $J = \frac{1}{2}$ -state depolarization is very apparent, since it requires that the depolarization must be produced by smaller nonadiabatic contributions to the interaction. We present experimental results for the nonresonant collisional depolarization cross sections σ of the Rb 5*p* and Cs 6*p* fine-structure levels, verifying that the $J = \frac{1}{2}$ state cross sections are unusually small. A discussion of the extension of the present adiabatic theories to the $J = \frac{1}{2}$ problem is included, and the meaning of the Δm_J selection rules in the adiabatic theories is reviewed. The effect of the reported cross sections on ground-state optical pumping can be established by use of formulas for relaxation of hyperfine components in Ref. 2 in conjunction with procedures in Ref. 4; no discussion is included.

The theories have treated the collision Hamiltonian *V* as a perturbation that alters the populations of the electronic states of the separated atoms, using the dipole-dipole interaction and straight-line paths for $V(\mathbf{b}, \mathbf{v}, t)$ of a collision with impact parameter **b** and relative velocity **v**. For this *V*, the nonresonant collisional depolarization arises from the Van der Waals interaction, and if $[V^2(\mathbf{b}, \mathbf{v}, t), V^2(\mathbf{b}, \mathbf{v}, t')]$ is neglected,

$$S(\mathbf{b}, \mathbf{v}) = S_{ad}(\mathbf{b}, \mathbf{v}) \equiv \exp\left(-i \int_{-\infty}^{\infty} dt V_{ad}^2(\mathbf{b}, \mathbf{v}, t) / \hbar \Delta E_{av}\right)$$

is obtained,² where we represent the effect of one collision by $\psi(\infty) = S(\mathbf{b}, \mathbf{v}) \psi(-\infty)$. This integral can be evaluated in the collision frame (**b** and **v** along coordi-

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² Alain Omont, J. Phys. Radium **26**, 26 (1965).

³ M. I. D'Yakonov and V. I. Perel', Zh. Eksperim. i Teor. Fiz. **48**, 345 (1965) [English transl.: Soviet Phys.—JETP **21**, 227 (1965)].

⁴ F. Franz and J. Franz, Phys. Rev. **148**, 82 (1966).