

Elastic Scattering from Atomic Oxygen and Photodetachment from O^- †

RONALD J. W. HENRY

Kitt Peak National Observatory, Tucson, Arizona*

(Received 19 May 1967)

A method developed by Temkin to allow for polarization effects in low-energy scattering of electrons from atoms has been extended to include all direct contributions from the polarized orbitals and the exchange contribution from the most important type of polarized orbital. The analysis has been applied to atoms with configurations $1s^2 2s^2 2p^q$. Cross sections for the elastic scattering of slow electrons by atomic oxygen are given for energies < 6.5 eV. The additional direct polarization terms are found to be important in calculating s -wave elastic cross sections for O, as they decrease the cross section by a factor of 2 near threshold; but the exchange d orbitals of the oxygen atom are relatively unimportant in relation to all direct polarization terms. Photodetachment cross sections for O^- are given for photon energies in the range 1.47 to 5.5 eV, and are found to be in good agreement with experiment when polarization terms are included and the dipole velocity approximation is used.

I. INTRODUCTION

LOW-ENERGY scattering of electrons by atomic systems has been the subject of a number of recent theoretical and experimental investigations. In particular, theoretical attempts¹⁻⁷ have been made to improve upon the results obtained using the exchange approximation. This approximation neglects the reaction of the scattered electron on the atomic system. The long-range polarization effects which are induced by this reaction are important for low-energy electron scattering.

In their study of low-energy elastic scattering of electrons from atomic oxygen and the photodetachment of O^- , Bates and Massey⁸ introduced an additional potential which had the asymptotic form $-\alpha r^{-4}$, where α is the polarizability of the atom. This is the anticipated form of a potential due to the polarization effect. They computed phase shifts and photodetachment cross sections as a function of the polarizability, which was regarded as an adjustable parameter.

A similar approach was used by Klein and Brueckner.⁹ They uniquely determined the polarizability by requiring that α is the eigenvalue in the solution of the bound-state equation for the radial functions for O^- . In this equation they assumed that the electron affinity is known, and used the value given by the experimental determination of Branscomb *et al.*¹⁰ The phase shifts for s -wave electrons were only calculated

at a few energies by Klein and Brueckner, a wider range of energy being obtained by using an effective-range formula. The formula used was incorrect, since a modified effective-range theory¹¹ must be used for a central potential with asymptotic form $-\alpha r^{-4}$. Cooper and Martin¹² corrected and extended the results of Klein and Brueckner. They obtained photodetachment cross sections for O^- which are in good agreement with the experimental results of Smith.¹³

An approximate method for inclusion of dipole distortion effects was developed by Temkin.¹ He applied the polarized orbital method to atomic oxygen, and made allowance for the d orbitals of the oxygen atom. These orbitals contribute about 70% to the polarizability. Only s -wave scattering cross sections were computed.

The method employed by Temkin has been extended to include all direct contributions from the polarized orbitals and the exchange contribution from the most important type of polarized orbital. The analysis has been applied to atoms with configurations $1s^2 2s^2 2p^q$, and is given in Sec. II. The numerical methods employed to solve the coupled integrodifferential equations are given in Sec. III. Cross sections for the elastic scattering of slow electrons by atomic oxygen and photodetachment cross sections for O^- are presented in Secs. IV and V, respectively. The effect of inclusion of additional direct polarization terms and the correct inclusion of exchange d orbitals of the oxygen atom is discussed in Sec. VI.

II. THEORY

We will consider the collision of an electron with an atomic system which has nuclear charge Z and N electrons. The totally antisymmetric $(N+1)$ -electron wave function is defined as

$$|\Gamma; \mathbf{X}_1 \mathbf{X}_2 \cdots \mathbf{X}_{N+1}\rangle \equiv \Psi(\Gamma; \mathbf{X}),$$

¹¹ L. Spruch, L. Rosenberg, and T. F. O'Malley, Phys. Rev. Letters **5**, 375 (1960).

¹² J. W. Cooper and J. B. Martin, Phys. Rev. **126**, 1482 (1962).

¹³ S. J. Smith, in *Proceedings of the Fourth International Conference on Ionization Phenomena in Gases*, Uppsala (North-Holland Publishing Company, Amsterdam, 1960), p. 219.

† Contribution No. 259 from the Kitt Peak National Observatory.

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

¹ A. Temkin, Phys. Rev. **107**, 1004 (1957).

² A. Temkin and J. C. Lamkin, Phys. Rev. **121**, 788 (1961).

³ I. H. Sloan, Proc. Roy. Soc. (London) **A281**, 151 (1964).

⁴ R. W. LaBahn and J. Callaway, Phys. Rev. **135**, A1539 (1964); **147**, 28 (1966).

⁵ P. M. Stone, Phys. Rev. **141**, 137 (1966).

⁶ D. G. Thompson, Proc. Roy. Soc. (London) **A294**, 160 (1966).

⁷ J. Lawson, H. S. W. Massey, J. Wallace, and D. Wilkinson, Proc. Roy. Soc. (London) **A294**, 149 (1966).

⁸ D. R. Bates and H. S. W. Massey, Phil. Trans. Roy. Soc. (London) **A239**, 269 (1943).

⁹ M. M. Klein and K. A. Brueckner, Phys. Rev. **111**, 115 (1958).

¹⁰ L. M. Branscomb, D. S. Burch, S. J. Smith, and S. Geltman, Phys. Rev. **111**, 504 (1958).

where \mathbf{X}_i denotes the spatial and spin coordinates of the i th electron, and $\Gamma \equiv \gamma k l L S L' S' M_L M_{S'}$ is the complete set of quantum numbers required to specify the atomic system. The atomic term is labeled LS , and the wave number and orbital angular momentum of the projectile are k and l , respectively. The total orbital and spin quantum numbers are L' and S' , and we shall work in a representation where the Hamiltonian H_{N+1} is diagonal in L' and S' .

The time-independent Schrödinger equation is given by

$$H_{N+1}\Psi = E\Psi,$$

where

$$H_{N+1} = -\frac{1}{2}\nabla_{N+1}^2 - \frac{Z}{r_{N+1}} + \sum_{k=1}^N \frac{1}{r_{k,N+1}} + H_N$$

and E is the total energy of the system.

The wave function Ψ may be expanded in terms of the complete set of orthonormal eigenfunctions Φ of the atomic system, these functions also being correctly antisymmetrized. Thus,

$$\Psi(\Gamma; \mathbf{X}) = A\psi(\Gamma; \mathbf{X}), \quad (1)$$

where A is the antisymmetrization operator, and

$$\begin{aligned} \psi(\Gamma; \mathbf{X}) = & \sum C(S\frac{1}{2}S'; M_S m_s M_{S'}) \\ & \times C(LL'L'; M_L m_l M_{L'}) Y_{l m_l}(\hat{r}_{N+1}) \chi_{1/2}^{m_s}(N+1) \\ & \times \Phi(\gamma LS | X_{N+1}^{-1}; X_{N+1}) F(r_{N+1}) r_{N+1}^{-1}. \quad (2) \end{aligned}$$

Here $C(abc; \alpha\beta\gamma)$ is a Clebsch-Gordan coefficient,¹⁴ $Y_{l m_l}(\hat{r})$ is a spherical harmonic, and $\chi_{1/2}^{m_s}(i)$ is a spin function.

Solutions for the scattered electron wave function F are obtained by requiring that

$$\int \psi^*(\Gamma; X_{N+1}^{-1}) [H_{N+1} - E] \Psi(\Gamma; \mathbf{X}) dr_{N+1}^{-1} = 0, \quad (3)$$

where $\int dr_i^{-1}$ denotes integration over all coordinates except r_i . We define

$$\frac{1}{2}k^2 = E - E_0,$$

where E_0 is the energy (in atomic units) of the atomic state LS , and we make use of the result that

$$H_N \Phi = E_0 \Phi.$$

If only the ground-state term is retained in the expansion (2), then the Hartree-Fock or exchange approximation is obtained. Within this approximation, (3) may be reduced to

$$(\mathcal{L} + k^2)F(r) + W(r, F) = 0, \quad (4)$$

where

$$\mathcal{L} \equiv \frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + \frac{2Z}{r} - 2V(r).$$

¹⁴ G. Racah, Phys. Rev. **63**, 367 (1943). For Clebsch-Gordan and Racah coefficients we use the phase conventions of M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957).

For systems which have configuration $1s^2 2s^2 2p^a$, the direct potential V is given by¹⁵

$$\begin{aligned} V(r) = & 2Y^0(1s, 1s; r) + 2Y^0(2s, 2s; r) \\ & + 3q(2l+1)(2L+1) \sum_{\lambda} (2\lambda+1)^{-1} C(l\lambda; 000) \\ & \times C(11\lambda; 000) W(lLL; L'\lambda) \sum_{L_2 S_2} (-1)^{L'+L_2} \\ & \times (qLS | \} L_2 S_2 \}^2 W(1L1L; L_2 \lambda) Y^\lambda(2p, 2p; r), \quad (5) \end{aligned}$$

where $W(abcd; ef)$ is a Racah coefficient,¹⁴ $(qLS | \} L_2 S_2 \}$ is the coefficient of fractional parentage, and Y^λ is defined by

$$\begin{aligned} Y^\lambda(nl, n'l'; r) = & r^{-\lambda-1} \int_0^r P_{nl}(s) P_{n'l'}(s) s^\lambda ds \\ & + r^\lambda \int_r^\infty P_{nl}(s) P_{n'l'}(s) s^{-\lambda-1} ds. \quad (6) \end{aligned}$$

The exchange potential W is given by¹⁵

$$\begin{aligned} W(r, F) = & -(2l+1)^{-1} Y^l(1s, F; r) P_{1s}(r) \\ & - (2l+1)^{-1} Y^l(2s, F; r) P_{2s}(r) \\ & - 3q(2l+1)(2L+1)(2S+1) \sum_{L_2 S_2} (qLS | \} L_2 S_2 \}^2 \\ & \times W(S\frac{1}{2} \frac{1}{2} S; S' S_2) \sum_{\lambda} (2\lambda+1)^{-1} C(1\lambda; 000)^2 \\ & \times X(L_2 1L; 1\lambda; L l L') Y^\lambda(2p, F; r) P_{2p}(r), \quad (7) \end{aligned}$$

where $X(abc; pqr; xyz)$ is the Wigner $9j$ function.

The exchange approximation neglects the reaction of the scattered electron on the atomic system. This reaction is important for low-energy electron scattering. It may be accounted for by taking more terms in the expansion of ψ , Eq. (2). We may include, for example, configurations $1s^2 2s^2 2p^{a+1}$ and $1s^2 2s^2 2p^{a-1} 3d$. However, this would necessitate solving many coupled integro-differential equations.¹⁶

An alternative approach has been suggested by Temkin.¹ He replaced Φ in Eq. (2) by $[\Phi + \Phi_p]$, where Φ_p is included to take account of the dipole distortion of the atom by the incident electron. We will now outline the procedure used to calculate the polarization function Φ_p .

If the perturbation due to the incident electron is adiabatic and if the predominant polarization effects occur exterior to the space occupied by the atomic electrons, then the static Hamiltonian may be written

$$H_{N+1}(\text{static}) = H_N - z r_{N+1}^{-1} + \lambda \sum_k V_k \epsilon(r_{N+1}, r_k),$$

¹⁵ K. Smith, R. J. W. Henry, and P. G. Burke, Phys. Rev. **147**, 21 (1966).

¹⁶ K. Smith, R. J. W. Henry, and P. G. Burke, Phys. Rev. **157**, 51 (1967). These authors have solved up to five coupled integrodifferential equations which arise when all terms of the ground-state configuration are included in the expansion of ψ . Since these terms all belong to the same configuration, no polarization effects are included.

where $z=Z-N$ is the excess charge, $\lambda=r_{N+1}^{-2}$ is a small perturbation,

$$V_k = r_k P_1(\hat{r}_k \cdot \hat{r}_{N+1}),$$

and

$$\begin{aligned} \epsilon(r_{N+1}, r_k) &= 1 \quad (r_{N+1} > r_k) \\ &= 0 \quad (r_{N+1} < r_k). \end{aligned}$$

The step function ϵ ensures that the scattered electron is always outside the atomic electrons.

The wave functions for the atomic system may be expressed as sums of Slater determinants, and an unperturbed ground-state orbital may be written as

$$\Phi_k = r_k^{-1} P_{n l'}(r_k) Y_{l', m'}(\hat{r}_k) \chi_{1/2}^{m_s}(k).$$

Expanding the single-electron perturbed functions in the series

$$\Phi_k + \Phi_k' + \dots \text{ terms of higher order,}$$

then

$$\begin{aligned} \lambda \Phi_k' &= \sum_{l'' m''} C(n l' \rightarrow l''; m' \rightarrow m'') r_k^{-1} \\ &\quad \times u_{n l' \rightarrow l''}(r_k) Y_{l'', m''}(\hat{r}_k) \\ &\quad \times Y_1^{m' - m''}(\hat{r}_{N+1}) \chi_{1/2}^{m_s}(k) r_{N+1}^{-2} \epsilon(r_{N+1}, r_k), \end{aligned}$$

in which

$$\begin{aligned} C(n l' \rightarrow l''; m' \rightarrow m'') \\ = 2(-1)^{1+m''-m'} \{4\pi(2l'+1)[3(2l''+1)]^{-1}\}^{1/2} \\ \times C(1 l' l''; m' - m'' m'') C(1 l' l''; 000). \end{aligned} \quad \text{where}$$

$$\alpha_{2s \rightarrow p}(r) = -\frac{4}{3} \left[\int_0^r P_{2s} s u_{2s \rightarrow p} ds - \int_0^r P_{2s} s P_{2p} ds \int_0^r P_{2p} u_{2s \rightarrow p} ds \right] \quad (11a)$$

and

$$\begin{aligned} \alpha_{2p \rightarrow l''}(r) &= -6q(2l+1)(2L+1)C(1 l''; 000)^2 \sum_l C(1 l t; 000)^2 \sum_{L_2 S_2} (q L S | \} L_2 S_2)^2 \sum_f (2f+1) W(1 l'' l t; 1 f)^2 \\ &\quad \times W(L_2 1 L' l; L f)^2 \left[\int_0^r P_{2p} s u_{2p \rightarrow l''} ds - \delta_{l'' 0} \int_0^r P_{2p} s P_{2p} ds \int_0^r P_{2p} u_{2p \rightarrow l''} ds \right]. \end{aligned} \quad (11b)$$

In Eq. (9) W_p is the exchange potential. In calculating W_p , we have only considered the most important type of polarized orbital, $2p \rightarrow d$. Then W_p is given by

$$W_p(r, F) = \beta_{2p \rightarrow d} Z^\lambda (2p, F; r) u_{2p \rightarrow d}(r) + \delta_{l_2} X_p(r, F), \quad (12)$$

where

$$\begin{aligned} \beta_{2p \rightarrow d} &= 2(\sqrt{6})q(2l+1)(2L+1)(2S+1) \sum_{L_2 S_2} (q L S | \} L_2 S_2)^2 W(S \frac{1}{2} \frac{1}{2} S; S' S_2) C(\lambda l 2; 000) \\ &\quad \times \sum_t C(\lambda 1 t; 000) C(1 t; 000) \sum_f (-1)^f (2f+1) W(L_2 1 L' l; L f)^2 W(1 2 l t; 1 f) W(1 l 2; \lambda f), \end{aligned} \quad (13)$$

and

$$Z^\lambda (2p, F; r) = r^\lambda \int_r^\infty P_{2p} F s^{-\lambda-3} ds. \quad (14)$$

The function X_p arises from the operation of the Laplacian operator on the step function ϵ . We find

$$\begin{aligned} X_p(r, F) &= -2q(2L+1)(2S+1) \sum_{L_2 S_2} (q L S | \} L_2 S_2)^2 W(S \frac{1}{2} \frac{1}{2} S; S' S_2) X(112; 1 L_2 L; 2 L L') \\ &\quad \times \left\{ \int_r^\infty F s^{-2} \left(\frac{d^2}{ds^2} + \frac{2Z}{s} - \frac{2}{s^2} \right) P_{2p} ds u_{2p \rightarrow d}(r) + \left[\left(\frac{1}{r^2} \frac{dP_{2p}}{dr} - \frac{2}{r^3} \right) u_{2p \rightarrow d}(r) + \frac{2}{r^2} P_{2p}(r) \frac{du_{2p \rightarrow d}}{dr} \right] F(r) \right. \\ &\quad \left. + \frac{1}{r^2} P_{2p}(r) u_{2p \rightarrow d}(r) \frac{dF}{dr} + \int_r^\infty P_{2p} s^{-2} F ds \left(\frac{d^2}{dr^2} + \frac{2Z}{r} - \frac{6}{r^2} \right) u_{2p \rightarrow d}(r) \right\}. \end{aligned}$$

¹⁷ R. M. Sternheimer, Phys. Rev. **96**, 951 (1954).

The total polarization function is a sum of products of the single-electron unperturbed orbitals, in which each orbital is replaced consecutively by its polarized part. Thus,

$$\Phi_p = \lambda \sum \Phi_1 \cdots \Phi_{k-1} \Phi_k' \cdots \Phi_N.$$

The differential equation for $u_{n l' \rightarrow l''}(r)$ was first obtained by Sternheimer.¹⁷ It is

$$\begin{aligned} \left\{ \frac{d^2}{dr^2} \frac{1}{P_{n l'}} \left[\frac{d^2 P_{n l'}}{dr^2} \right] + \frac{[l'(l'+1) - l''(l''+1)]}{r^2} \right\} \\ \times u_{n l' \rightarrow l''}(r) = -r P_{n l'}(r). \end{aligned} \quad (8)$$

When Φ is replaced by $(\Phi + \Phi_p)$, then from (2) and (3) we obtain the following scattering equation for the function F :

$$\begin{aligned} (\mathcal{L}^1 + k^2)F(r) + W(r, F) + W_p(r, F) \\ + \sum_{n=1}^2 \sum_{l_1=0}^{n-1} \delta_{l_1} \mu_{n l} P_{n l}(r), \end{aligned} \quad (9)$$

where $\mathcal{L}^1 = \mathcal{L} - 2V_p(r)$. Here $V_p(r)$ is the direct polarization potential. In calculating V_p we assume that there is no contribution from the closed $1s^2$ shell. Then V_p is given by

$$V_p(r) = r^{-4} [\alpha_{2s \rightarrow p}(r) + \alpha_{2p \rightarrow s}(r) + \alpha_{2p \rightarrow d}(r)], \quad (10)$$

Sloan³ has shown that no special effects arise from the unphysical discontinuity which the step function produces in the total wave function.

We have also required that the continuum wave function be orthogonal to all the ground-state orbitals, so we have included in (9) terms of the form $\delta_{il}\mu_{nl}P_{nl}(r)$, where μ_{nl} are the Lagrange undetermined multipliers. They are adjusted so that

$$\int_0^{\infty} P_{nl}Fdr=0.$$

III. NUMERICAL METHODS

In order to calculate the polarization potentials we have to solve Eq. (8) for the polarized orbital function. The boundary conditions for $u_{nl \rightarrow l'}$ are

$$u_{nl \rightarrow l'}(r) \sim r^{l'+1}, \quad (15a)$$

$$\lim_{r \rightarrow \infty} u_{nl \rightarrow l'}(r) = 0. \quad (15b)$$

The limit of large r cannot be employed exactly due to rounding errors, so we must obtain an approximate form for it. The unperturbed atomic wave functions have the asymptotic form

$$P_{nl}(r) \sim Ar^n e^{-\beta r}.$$

When we use this in (8) instead of (15b) we obtain the boundary condition

$$u_{nl \rightarrow l'}(r) \sim -A(4\beta)^{-1} r^{n+2} e^{-\beta r}.$$

The integration of (8) is then straightforward, except for unphysical singularities due to the $P_{nl}(r)^{-1} d^2 P_{nl}/dr^2$ term. These singularities were smoothed out, but we do not expect to have introduced any large errors as a result of this procedure.

We are required to solve the scattering equation given by (9) in order to obtain the continuum wave function F . The boundary conditions which F must satisfy are

$$\begin{aligned} F(r) &\sim r^{l+1}, \\ F(r) &\sim k^{-1/2}(\sin\theta + \tan\delta_l \cos\theta), \end{aligned} \quad (16)$$

where

$$\theta = kr - l\pi/2 - \eta \ln 2kr + \sigma_l,$$

$$\eta = -z/k,$$

and

$$\sigma_l = \arg\Gamma(1+l+i\eta).$$

We note that the Y^λ functions [Eq. (6)], satisfy the following second-order differential equation¹⁸

$$\frac{d^2}{dr^2}(rY^\lambda) = \frac{\lambda(\lambda+1)}{r^2}(rY^\lambda) - \frac{(2\lambda+1)}{r}P_{nl}(r)F(r), \quad (17)$$

¹⁸ D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957), p. 51.

with the boundary conditions

$$\begin{aligned} rY^\lambda(nl', F; r) &\sim r^{\lambda+1}, \\ rY^\lambda(nl', F; r) &\sim r^{-\lambda}. \end{aligned} \quad (18)$$

The Z^λ functions [Eq. (14)], may be treated in an analogous manner to the Y^λ functions. Thus the functions Z^λ satisfy

$$\begin{aligned} \frac{d^2}{dr^2}(r^2Z^\lambda) &= \frac{(\lambda+2)(\lambda+1)}{r^2}(r^2Z^\lambda) \\ &- \left[\frac{(\lambda+1)}{r^2}P_{nl}(r) + \frac{1}{r} \frac{dP_{nl}}{dr} \right] F(r) - \frac{1}{r} P_{nl}(r) \frac{dF}{dr} \end{aligned} \quad (19)$$

and are subject to the boundary conditions,

$$\begin{aligned} r^2Z^\lambda(nl', F; r) &\sim r^{l'+l+2}, \\ r^2Z^\lambda(nl', F; r) &\sim r^{-\lambda-1}. \end{aligned} \quad (20)$$

The integrals which occur in the X_p function may be handled in a similar manner.

This treatment of integrals of the form \int_r^∞ , avoids the difficulties encountered by Temkin and Lamkin² and Sloan,³ who wrote the integrals in the form

$$\int_r^\infty = - \int_\epsilon^r + \int_\epsilon^\infty,$$

where ϵ is a small, arbitrary, nonzero constant.

We thus have to solve Eqs. (9), (17), and (19) subject to the above boundary conditions. We note that a first derivative is present. The coupled integrodifferential equations were solved using an extension of a method given by Sloan³ for a single integrodifferential equation. The numerical solution was obtained by integrating outwards and inwards with subsequent matching to obtain a final continuous solution.¹⁹ The integral terms in the equations were treated noniteratively following Marriott.²⁰ The asymptotic expansion method of Burke and Schey²¹ was used to determine the phase shift δ_l from the function F . The combination of these methods has been outlined by Smith *et al.*¹⁵

IV. ELASTIC-SCATTERING CROSS SECTIONS: OXYGEN

We have applied the theory presented in Sec. II to atomic oxygen. The self-consistent-field (SCF) wave functions given by Roothaan and Kelly²² were used for the unperturbed ground-state term of oxygen.

¹⁹ K. Smith and P. G. Burke, *Phys. Rev.* **123**, 174 (1961).

²⁰ R. Marriott, *Proc. Phys. Soc. (London)* **72**, 121 (1958).

²¹ P. G. Burke and H. M. Schey, *Phys. Rev.* **126**, 163 (1962).

²² C. C. J. Roothaan and P. S. Kelly, *Phys. Rev.* **131**, 1177 (1963).

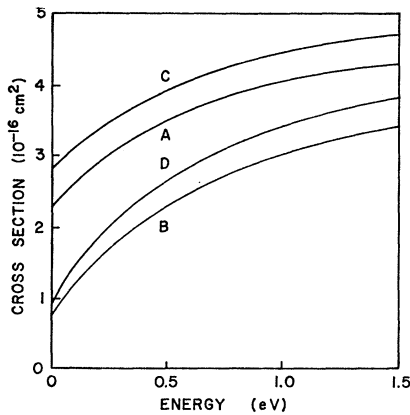


FIG. 1. Energy variation of s -wave elastic cross section for electrons incident on atomic oxygen. Polarization potential terms are included as follows: Curve A : $2p \rightarrow d$ direct term only; curve B : All direct terms; curve C : $2p \rightarrow d$ direct and exchange terms; curve D : All direct and exchange terms.

The polarized orbital functions were obtained by solving Eq. (8). These solutions were then used to calculate the direct polarization potential. Thus we obtained $2V_p \sim -5.15r^{-4}$. This value compares very favorably with the experimental value²³ for the polarizability of $5.19\alpha_0^3$.

The ground state of oxygen is a 3P state, and so for an s -wave electron, the total spin quantum number can have the values $S = \frac{1}{2}$ or $S = \frac{3}{2}$. In Fig. 1 we present our results for the elastic scattering of s -wave electrons by atomic oxygen. The curves A through D represent the sum of the 2P and 4P contributions to the cross sections, in various approximations. Curve A is obtained by including only the $\alpha_{2p \rightarrow d}$ term in the direct polarization potential and neglecting the exchange polarization terms. For curve B all the direct polarization terms have been retained, but W_p has been omitted. Curve C was calculated by including W_p and only the d -orbital contribution to V_p . For curve D all contributions to the potentials were retained. In all the approximations the direct and exchange potentials, V and W , respectively, have been fully included.

Curve A has previously been calculated by Temkin,¹ who sought to obtain, within the framework of s -wave scattering, a quantitative estimate of the relative importance of the exchange polarization terms, compared to the direct polarization terms. However, he erroneously considered integrals of the form $\int_0^r P_{2p} F s^\lambda ds$ for W_p , instead of those contained in Eq. (12). Thus curve C differs from that computed by Temkin. When the exchange polarization terms are included correctly, the s -wave elastic cross sections are increased by 10% over those computed using the direct $2p \rightarrow d$ potential (curve A).

The effect of the additional $\alpha_{2s \rightarrow p}$ and $\alpha_{2p \rightarrow s}$ terms in the direct polarization potential is large. The corre-

sponding cross sections (curve B) are lower than curve A by about 25% at 1.5 eV and over a factor of 2 smaller at threshold. When the exchange polarization terms are included (curve D), there is a small increase over those cross sections calculated without the exchange terms.

Smith, Henry, and Burke¹⁶ calculated cross sections for scattering of s -wave electrons from atomic oxygen, omitting all the polarization terms. They found a threshold value of $7.5 \times 10^{-16} \text{ cm}^2$, and observed a gradual decrease in the cross section to $3.3 \times 10^{-16} \text{ cm}^2$ at 13.6 eV. As can be seen from Fig. 1, in all the approximations used in the present analysis, the cross sections are much less than these values, and they increase with energy. Thus, the effect of the inclusion of polarization terms on the s -wave cross sections is significant at low energies.

The effect of the exchange polarization terms on higher partial waves was investigated at several energies and was found to be less than 4%. Thus, we shall neglect all exchange polarization terms for $l > 0$.

In Fig. 2 we present our results for the total elastic scattering of electrons by atomic oxygen. All direct and exchange polarization potentials were retained in the calculation of the s -wave contribution. For the p and d waves, the exchange polarization terms were omitted. The integrodifferential equations were not solved for $l > 2$. The contribution from these higher-order partial waves was estimated in the Born approximation⁶ using only a polarization potential.

The results of three other theoretical calculations are shown in Fig. 2. Variations on the Hartree-Fock-Slater (HFS) model were used in these calculations.

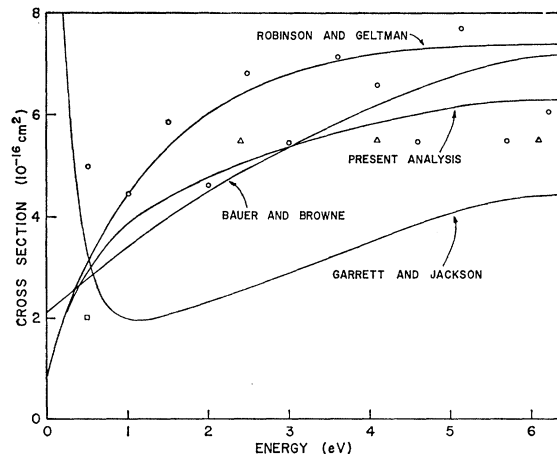


FIG. 2. Total elastic cross sections for electrons incident on oxygen atoms, compared with theoretical calculations of Bauer and Browne (Ref. 24), Robinson and Geltman (Ref. 25), and Garrett and Jackson (Ref. 26), and with experimental results: Δ Neynaber *et al.* (Ref. 27); \circ Sunshine *et al.* (Ref. 28); \square Lin and Kivel (Ref. 30).

²⁴ E. Bauer and H. N. Browne, in *Atomic Collision Processes*, edited by M. R. C. McDowell (North-Holland Publishing Company, Amsterdam, 1964), p. 16.

²³ R. A. Alpher and D. R. White, *Phys. Fluids* **2**, 153 (1959).

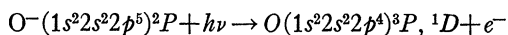
Bauer and Browne²⁴ introduced adjustable parameters to take account of exchange, correlation, and exchange correlation interactions. Robinson and Geltman²⁵ modified the HFS potential by including two additional terms which also had adjustable parameters. One term removes the Coulomb tail in the HFS potential and the other term introduces the effect of polarization. Garrett and Jackson²⁶ obtained an equation which is an approximation to Eq. (9). In their treatment exchange was included through the use of a modified Slater exchange term.

In Fig. 2 the theoretical calculations are compared with the results of three different experiments on the total scattering of electrons by atomic oxygen. Neynaber *et al.*²⁷ and Sunshine, Aubrey, and Bederson²⁸ used crossed-beam techniques to obtain the ratio of atomic to molecular oxygen cross sections. They calculated the absolute atomic values by multiplying these ratios by the molecular cross sections obtained by other investigators who used single-beam methods.²⁹ The datum point of Lin and Kivel³⁰ was deduced from measurements with shock-tube techniques. At this energy, 0.5 eV, Sunshine *et al.* obtained a cross section of $5.0 \pm 1.5 \times 10^{-16}$ cm². Another experiment which used shock tube methods was reported by Daiber and Waldron.³¹ They obtained cross sections which varied from 9×10^{-16} cm² to 17×10^{-16} cm² in the energy range 0.43–0.49 eV.

The present calculations agree well with all the existing experimental results except those of Daiber and Waldron. Also the theoretical calculations reported by Robinson and Geltman²⁵ and by Bauer and Browne²⁴ are in good agreement with the results of the present analysis.

V. PHOTODETACHMENT OF O⁻

We are concerned with the transitions



for the ejection of an outer-shell electron. The threshold energies for excitation from O⁻ to ³P and ¹D states of atomic oxygen are at 1.465 and 3.432 eV, respectively.

The photodetachment cross sections may be calculated using the expression given by Henry and Lipsky.³² For single-channel photodetachment, this expression may be written in the form

$$\sigma_p = 3.42 \times 10^{-18} C_p^2 (I + k^2)^{-1} [C_0 M_0^2 + C_2 M_2^2] \text{ cm}^2. \quad (21)$$

²⁵ E. J. Robinson and S. Geltman, *Phys. Rev.* **153**, 4 (1967).

²⁶ W. R. Garrett and H. T. Jackson, *Phys. Rev.* **153**, 28 (1967).

²⁷ R. H. Neynaber, L. L. Marino, E. W. Rothe, and S. M. Trujillo, *Phys. Rev.* **123**, 148 (1961).

²⁸ G. Sunshine, B. B. Aubrey, and B. Bederson, in *Proceedings of the Fourth International Conference on Physics of Electronic and Atomic Collisions, Quebec* (Science Bookcrafters, Hasting-on-Hudson, New York, 1965), p. 130.

²⁹ E. Bruche, *Ann. Physik* **83**, 1065 (1927).

³⁰ S. C. Lin and B. Kivel, *Phys. Rev.* **114**, 1026 (1959).

³¹ J. W. Daiber and H. F. Waldron, *Phys. Rev.* **151**, 51 (1966).

³² R. J. W. Henry and L. Lipsky, *Phys. Rev.* **153**, 51 (1967).

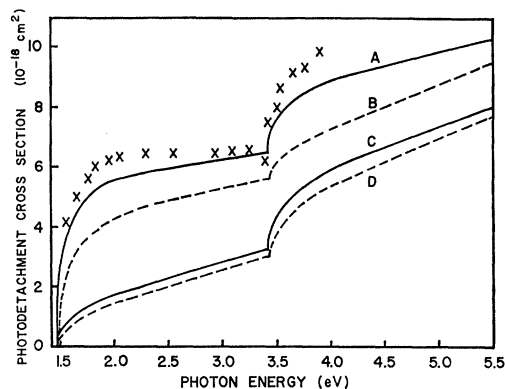


FIG. 3. Photodetachment cross sections for O⁻. Curves A and B were calculated using the dipole velocity approximation, and C and D using the dipole length approximation. Solid curves were obtained on retaining all polarization terms in Eq. (9), and dashed curves on neglecting all polarization terms. The crosses represent experimental results of Branscomb *et al.* (Ref. 34).

This is the dipole velocity approximation. The ionization potential I and the energy above threshold k^2 are in rydbergs. The overlap integral C_p is given by

$$C_p = (1s | \bar{1}\bar{s})^2 (2s | \bar{2}\bar{s})^2 (2p | \bar{2}\bar{p})^4.$$

In Eq. (21), C_0 and C_2 are constants, tabulated by Bates,³³ which depend on the initial and final states of the system. The matrix element M is given by

$$M_l = (2p | H | F) - \delta_{l0} (2s | F) (2s | \bar{2}\bar{s})^{-1} (2p | H | 2s), \quad (22)$$

where the operator

$$H = \frac{d}{dr} \left[\frac{1 + (1-l)(2l+1)}{2r} \right].$$

The terms of the form $(a|b)$ are overlaps of the radial wave functions $1s, 2s, 2p$ of O⁻ and $\bar{1}\bar{s}, \bar{2}\bar{s}, \bar{2}\bar{p}$ of O, and of the continuum wave orbital F .

The first term in (22) is the radial dipole matrix element for a single electron transition corresponding to the ejection of a $2p$ electron. The second term represents the relaxation of the ion core when photodetachment takes place. It corresponds to transitions in which the outer $2p$ electron goes to the $2s$ orbital with the ejection of an s electron. This term we shall call the s -wave core relaxation term. It is not to be confused with the direct ejection of an inner shell $2s$ electron which occurs at much higher energies than those considered here.

The corresponding expression to (21) for photodetachment in the dipole length approximation may be written

$$\sigma_L = 8.56 \times 10^{-19} C_p^2 (I + k^2) [C_0 M_0^2 + C_2 M_2^2] \text{ cm}^2. \quad (23)$$

In this form, the operator H is equal to r .

In order to calculate the matrix elements in Eq. (22) we require an accurate knowledge of the bound and

³³ D. R. Bates, *Monthly Notices Roy. Astron. Soc.* **109**, 432 (1946).

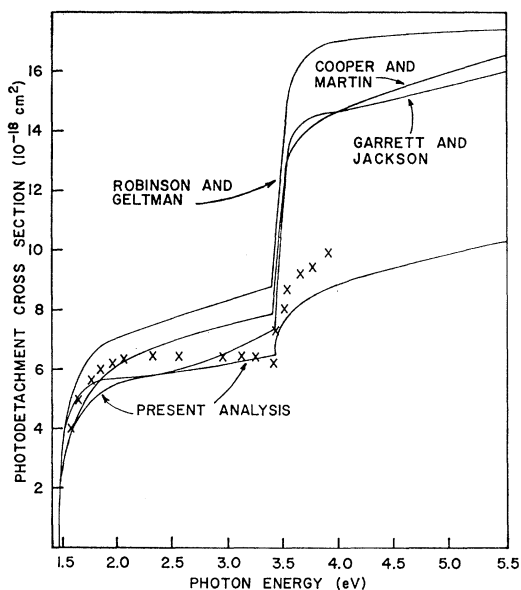


FIG. 4. Photodetachment cross sections for O^- , compared with theoretical calculations of Cooper and Martin (Ref. 12), Robinson and Geltman (Ref. 25), and Garrett and Jackson (Ref. 26). The crosses represent experimental results of Branscomb *et al.* (Ref. 34).

free radial wave functions. The SCF wave functions given by Roothaan and Kelly²² were used to describe the bound state of O^- . The continuum wave functions were obtained by solving Eq. (9).

In Fig. 3 we present our results for the photodetachment of O^- . Curves *A* and *B* represent the cross sections calculated using the dipole-velocity approximation [Eq. (21)]. Curves *C* and *D* are the cross sections calculated using the dipole-length approximation [Eq. (23)]. The effect of the polarization terms V_p and W_p in Eq. (9) was investigated. The dashed curves in Fig. 3 represent cross sections obtained when we neglected the polarization terms in the calculation of the continuum wave functions. The solid curves were obtained by retaining all the polarization terms in Eq. (9).

In Fig. 3, the experimental results of Branscomb, Smith, and Tisone,³⁴ represented by crosses, are compared with the theoretical cross sections. We note that in the dipole-velocity approximation, the cross sections are in better agreement with experiment than those calculated using the dipole-length approximation. Further, the inclusion of polarization enhances the agreement between theory and experiment, especially at energies near threshold.

The lack of agreement between the cross sections calculated in the dipole-velocity and dipole-length approximations may be due to the representation used for the bound-state wave functions for O^- . We have used Hartree-Fock orbitals for O^- , and these wave functions do not have the correct asymptotic form.¹²

³⁴ L. M. Branscomb, S. J. Smith, and G. Tisone, *J. Chem. Phys.* **43**, 2906 (1965).

This region of large r is weighted more heavily in the dipole-length approximation than in the dipole-velocity approximation. Thus, the cross sections calculated in the dipole-length approximation are not expected to be as reliable as those calculated in the dipole-velocity approximation.

The effect of the s -wave core relaxation term in Eq. (22) was also investigated. When this term is included, the s -wave contribution to the total photodetachment cross section is increased by 15% over the contribution obtained when the term is omitted. The d waves do not contain this correction term. The contribution from the d waves to the total cross sections increases as the photon energy increases. Thus, the effect of the s -wave core relaxation term is reduced as the photon energy increases. The net increase in the total cross section is 8% at a photon energy of 3.4 eV.

In Fig. 4 we compare the results of the present analysis (Fig. 3, curve *A*) with the theoretical calculations of Cooper and Martin,¹² Robinson and Geltman,²⁵ and Garrett and Jackson.²⁶ The crosses represent the results of Branscomb *et al.*³⁴ The present results appear to provide better agreement with experiment than the other theoretical calculations.

VI. CONCLUSIONS

The additional direct polarization potential terms are important in calculations of s -wave elastic-scattering cross sections for atomic oxygen. When these extra terms are included, the cross sections are decreased by 25% at 1.5 eV and are over a factor of 2 smaller at threshold.

The exchange d orbitals of the oxygen atom are relatively unimportant in relation to the direct polarization terms, since they increase the s -wave cross sections by only 10% over those calculated when they are omitted. Further, they have very little effect on the p - and d -wave cross sections. The $2s \rightarrow p$ and $2p \rightarrow s$ exchange terms have been omitted in the present analysis. The consequence of this omission is difficult to estimate, but in view of the small effect of the $2p \rightarrow d$ exchange terms, the results are not expected to be altered significantly.

The present results are in good accord with recent theoretical^{24,25} and experimental work.^{27,28,30} However, more experimental work at very low energies for elastic-scattering cross sections for atomic oxygen is needed, since three experiments^{28,30,31} report widely varying results at about 0.5 eV.

Photodetachment cross sections for O^- , calculated using the dipole-velocity approximation, are in good agreement with experiment when polarization potential terms are included in the calculation of continuum wave functions. The polarization terms have a significant effect, especially at low energies, where the cross sections are increased by 30% over those calculated using Hartree-Fock continuum wave functions.

At photon energies greater than 3.5 eV, the present results are in better agreement with experiment than previous theoretical calculations.^{12,25,26} However the experimental results are not reliable in this energy region, as calibration of the apparatus is difficult due to photoelectric effects from the walls of the apparatus.³⁴

In the above analysis, the exchange terms have been treated exactly, and the corrections for atomic distortion have arisen naturally in the formalism, rather than through the use of semiempirical parameters. These are the chief advantages of the polarized orbital method over previous theoretical treatments.

Schrödinger Perturbation Formalism for Exchange Interactions between Atoms or Molecules

LAURENS JANSEN

Battelle Institute, Advanced Studies Center, Geneva, Switzerland

(Received 28 December 1966; revised manuscript received 10 May 1967)

A Schrödinger perturbation expansion is developed for exchange interactions between atoms or molecules, starting from a complete, orthonormal set of symmetrized basis functions. The unperturbed Hamiltonian H_0 and the perturbation H' are defined in such a way that they are separately permutation-invariant. First- and second-order results are compared with those obtained by Eisenschitz and London for non-orthonormal basis functions, and with those derived from a Brillouin expansion.

INTRODUCTION

IN applying the Schrödinger perturbation formalism to the evaluation of intermolecular forces at large distances (large on the scale of atomic dimensions), it is possible to neglect symmetrization of the basis functions with respect to permutation of electrons and to start from a complete, orthonormal set of product-type unperturbed wave functions. Usually, these basis functions are eigenfunctions of the unperturbed Hamiltonian H_0 for the system; the unperturbed system is that of an assembly of isolated atoms (or molecules), i.e., at infinite distances from each other.

When the interatomic distances decrease, exchange becomes important, i.e., the basis functions must be chosen so that they satisfy the Pauli principle. When, however, the product-type basis vectors are symmetrized (we call any vector or function, whose space part is either symmetric or antisymmetric under exchange of two electrons, a *symmetrized* vector or function), then the new vectors do not form an orthonormal set, and they "overspan" the space of symmetrized vectors, i.e., they become linearly dependent. As early as 1930, Eisenschitz and London¹ developed an elegant method for overcoming these difficulties by a judicious choice of a particular type of basis set in symmetrized space. They derived expressions for first- and second-order perturbation energies; the first-order result is of the same form as in the case without exchange, whereas the second-order expression contains correction terms due to nonorthogonality of the basis vectors. A reformulation and an extension of the Eisenschitz-

London method has recently been undertaken by van der Avoird.²

Since the early work of Eisenschitz and London, and especially during the past ten years or so, a considerable number of different types of perturbation expansion for exchange interactions has appeared in the literature. Generally, the authors refer at most only superficially to the Eisenschitz-London paper, although several later analyses can be regarded as various approximations to the early method, or as modifications along much the same lines. This later work can be roughly divided in two categories: (a) Evaluation of exchange forces based on a Brillouin-Wigner type expansion.^{3,4} To this category belong, e.g., the analysis by Dalgarno and Lynn⁵ and that by Lynn,⁶ to which we will return later on. Convergence properties of the Brillouin series are determined by the smallness of the quantity $H_{mn}/(E-H_{mm})$, where H is the *total* Hamiltonian of the system, and where $H_{mn}(m \neq n)$ and H_{mm} are matrix elements of the total Hamiltonian with respect to a given set of basis functions. The energy E is computed by iteration. (b) Evaluation of exchange interactions on the basis of a Schrödinger type of perturbation expansion. Here, the total Hamiltonian H is split into an "unperturbed" part H_0 and a "perturbation" H' . This type of procedure immediately poses a complication, since, because of

² A. van der Avoird, *Chem. Phys. Letters* (Amsterdam) **1**, 24 (1967).

³ L. Brillouin, *J. Phys. Radium* **3**, 373 (1932); E. Wigner, *Math. Naturw. Anz. Ungar. Akad. Wiss.* **53**, 427 (1935).

⁴ P. O. Löwdin, *J. Chem. Phys.* **19**, 1396 (1951).

⁵ A. Dalgarno and N. Lynn, *Proc. Phys. Soc. (London)* **A69**, 821 (1956).

⁶ N. Lynn, *Proc. Phys. Soc. (London)* **A72**, 201 (1958).

¹ R. Eisenschitz and F. London, *Z. Physik* **60**, 491 (1930).