photon ionization occurs with reasonably low probability and thus contributes significantly only to the initiation stage (at least at moderate pressures—say, around one atmosphere). At lower pressures, N-photon ionization should contribute in increasing amounts to the growth of the discharge due to its relative weak pressure dependence compared to cascade ionization processes (see, for example, Fig. 20 of Ref. 6).

The photon flux F (photons cm^{-2} sec^{-1}) required to produce a given transition rate W (transitions cm^{-3} sec^{-1}) is given by

$$F=N_0^{-1/N}(W/\delta^{(N)})^{1/N}, \qquad (13)$$

where N_0 is the atomic number density (roughly proportional to pressure) and $w^{(N)}=\delta^{(N)}F^N$ is the transition rate per atom. For low-order processes—say, $N=2$ or 3 (as appropriate for photo-ionization of the alkali gases with ruby laser light)—the flux required to produce a substantial transition rate W is significantly lower than for the higher order processes appropriate to the rare gases. Also, the pressure dependence for the lower order processes is much stronger, in accordance with Eq. (13). Hence, multiple-photon ionization should play a more dominate role (over appreciable pressure ranges) in the growth of gas discharges in the alkali gases than in the rare gases. The alkali gases thus seem to be interesting candidates for gas-breakdown experiments as well as for direct photo-ionization experiments.

ACKNOWLEDGMENTS

The author expresses his appreciation to Professor A. Gold and to J. O'Brien for several helpful discussions.

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Electron Photodetachment from O$^-$ and Elastic Scattering from Atomic Oxygen

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Cross sections have been determined for the photodetachment of an electron from the negative atomic-oxygen ion. Calculations are made for the three transitions O$^-$ ^2P to O ^3P, O ^1D, and O ^1S with photon energies from threshold to 13.6 eV. A method is used wherein wave functions for both bound-state and continuum electrons are obtained through a modified version of Slater's approximation to the Hartree-Fock equations. Correlation effects are included through a polarization potential obtained from an application of first-order perturbation theory to the Hartree-Fock atomic system. Results are compared with the experiments of Smith and of Branscomb, Smith, and Tisone, giving very good low-energy agreement. In addition, the elastic-scattering cross section for neutral oxygen, the dipole polarizability, the attachment cross section, and attachment coefficient for electron capture were also determined. Agreement is quite good between these observables and available experimental data.

I. INTRODUCTION

BECAUSE of their importance in terrestrial and stellar atmospheres, the cross sections for photodetachment of the negative atomic-oxygen ion and cross sections for low-energy electron scattering by atomic oxygen have been studied by a number of investigators both experimentally and theoretically.[1] In treating either of these problems theoretically there is the usual difficulty of adequately describing the continuum solutions at low energies, the ordinary Hartree-Fock treatment being inadequate because of correlation effects. In the case of the negative ion there is the added problem of obtaining acceptable wave functions for the initial negative-ion state since, again because of neglect of correlation, Hartree-Fock solutions are not particularly accurate.

In the present treatment of these problems, a method is utilized wherein the bound-state system is described through a modification of the Hartree-Fock-Slater (HFS) technique and correlation effects are determined by a polarization potential obtained from the perturbation of the bound-state system by the detached (or scattered) electron. The latter has been applied with some success in low-energy electron scattering from alkali atoms[2] where polarization terms in the interaction potential are quite large.

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[1] See review by L. M. Branscomb, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962), p. 100.

[2] W. R. Garrett, Phys. Rev. **140**, A705 (1965); hereafter referred to as I.

II. PHOTODETACHMENT CROSS SECTION: FORMULATION

In the present analysis we are interested in the cross section for the process

$$O^- + h\nu \rightarrow O + e^-$$

with photon energies ranging from threshold to about 1 Ry. For these energies we need only consider ionization from the outer $2p$ shell where the removal of a $2p$ electron from an O^- ion in its normal $1s^2 2s^2 2p^5 (^2P)$ state leaves an oxygen atom in its normal ^3P state or in either of the ^1D or ^1S exicted states. The threshold energies for excitation from O^- to each of these states of O are 1.465, 3.432, and 5.66 eV, respectively.[3] If we denote by ψ_i the wave function for the initial ion normalized to a unit cloud, and by ψ_f the wave function for the final system normalized to represent a unit core with an outgoing wave of unit amplitude, then the usual dipole formula for the absorption cross section has the form[4]

$$\sigma_d(\nu) = \frac{32\pi^4 m^2 e^2}{3h^3 c} \frac{\xi_c \nu v}{(2L_i+1)(2S_i+1)} \times \sum_{mL_i} \sum_{mL_f, mS_f} \left| \psi_i^* \sum_{q=1}^{5} \mathbf{r}_q \psi_f d\tau_1 \cdots d\tau_5 \right|^2 . \quad (1)$$

Here ν is the frequency of the incident radiation, and v is the velocity of the detached electron. For the initial $O^-(^2P)$ state we have $L_i = 1$ and $S_i = \frac{1}{2}$. In the summation over magnetic quantum numbers, use has been made of the selection rule that the integrals vanish unless $S_i = S_f$ and $m_{S_i} = m_{S_f}$. Finally, ξ_c is the overlap integral for the core electrons arising from the slight relaxation of the inner electrons when detachment occurs. If we represent wave functions for the core by $\phi(c)$, then $\xi_c = |\int \phi_i^*(c) \phi_f(c) d\tau_c|^2$, which is very nearly equal to 1. If we adopt atomic units, write $mv = \hbar k$, and carry out the angular integrals in the matrix elements for a given final-state multiplet, Eq. (1) can be written in the form

$$\sigma_d(\nu) = \tfrac{4}{3}\pi \alpha_f a_0^2 k (E_b + E_e) \xi_c \xi_p \times (C_{l-1} M_{l-1}^2 + C_{l+1} M_{l+1}^2) \text{ cm}^2, \quad (2)$$

where α_f is the fine-structure constant and a_0 the Bohr radius (which is introduced in order to express the cross section in cm^2). E_b and E_e are the binding energy and outgoing energy, respectively, of the detached electron in rydbergs. The dipole matrix elements $M_{l\pm1}$ for the final-state multiplet are of the form

$$M_{l\pm1} = \int_0^\infty R_{nl}(r) r R_{k,l\pm1}(r) r^2 dr, \quad (3)$$

where $R_{nl}(r)$ and $R_{k,l\pm1}(r)$ are the radial parts of the bound and continuum wave functions of the electron in its initial and final states with normalization:

$$\int_0^\infty R_{nl}^2(r) r^2 dr = 1 \quad (4)$$

and

$$R_{k,l}(r) \underset{kr\rightarrow\infty}{\longrightarrow} (kr)^{-1} \sin(kr + \delta_l - \tfrac{1}{2} l\pi). \quad (5)$$

TABLE I. Values of C_0 and C_2 for each final state of O.

Transition	C_0	C_2
$O^-(^2P) \rightarrow O(^3P) + e^-$	1	2
$O^-(^2P) \rightarrow O(^1D) + e^-$	5/9	10/9
$O^-(^2P) \rightarrow O(^1S) + e^-$	1/9	2/9

The constants $C_{l\pm1}$ result from the angular integration in Eq. (1) and depend on the final-state multiplet of the residual neutral atom. These have been tabulated by Bates[4] for the transitions of interest here. Finally, ξ_p is the overlap integral for the outer electrons which are in the same state both before and after detachment. In the present context we have

$$\xi_p = \left(\left| \int_0^\infty R_{nl}^i R_{nl}^f r^2 dr \right|^2 \right)^4 ,$$

where R_{nl}^i is the initial $2p$ radial function for O^-, and R_{nl}^f is the final $2p$ radial function for O.

Since a p electron ($l=1$) is being removed in the O^- detachment, the matrix elements $M_{l\pm1}$ are M_0 and M_2, corresponding to outgoing s and d waves in the continuum. The constants C_0 and C_2 depend on the final-state multiplet of the neutral atom. These are tabulated in Table I for the ^3P, ^1D, and ^1S states of the ground configuration of O.

The determination of $\sigma_d(\nu)$ is dependent on an adequate knowledge of the bound-state O^- wave function and of the continuum functions for the detached electron.

III. THE POLARIZATION POTENTIAL

In both the problem of photodetachment of an electron from a negative ion and in the scattering of a free electron by an atomic system, one needs to know the wave function for the free electron in the field of the neutral atom. As is well known, both the photodetachment cross section and the low-energy elastic-scattering cross section are extremely sensitive to the potential function describing the interaction between the free electron and the atomic system. At low energies exchange effects as well as effects due to the distortion of the neutral atom by the electric field of the free electron are very important. In the present problem we describe the interaction by a perturbed Hartree-Fock potential wherein the perturbation by the free electron is used to calculate a polarization potential in

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[3] L. Branscomb, D. S. Burch, S. J. Smith, and S. Geltman, Phys. Rev. **111**, 504 (1958).

[4] D. R. Bates, Monthly Notices Roy. Astron. Soc. **106**, 432 (1946).

the adiabatic approximation. This method has been used effectively in low-energy electron scattering by alkali atoms where the polarization term is quite large.[2]

Under the influence of an incident or outgoing free electron, the Hartree-Fock (HF) one-electron orbitals and the HF energy depend on the coordinates of the free electron. The perturbed orbitals ψ_i of the HF determinant for the atomic system satisfy the following equation[5] (in atomic units) which depends on the free-electron coordinate r_f:

$$\left[-\nabla_1^2+V(r_1,r_f)-A(r_1,r_f)+\frac{2}{r_{1f}}\right]\times\psi_i(\mathbf{r}_1,\mathbf{r}_f)=\epsilon_i(\mathbf{r}_f)\psi_i(\mathbf{r}_1,\mathbf{r}_f)\,,\quad(6)$$

where

$$V(r_1,r_f)=-\frac{2Z}{r_1}+\sum_j\int|\psi_j(\mathbf{r}_2,\mathbf{r}_f)|^2\frac{2}{r_{12}}d\mathbf{r}_2\,,\quad(7)$$

and

$$A(\mathbf{r}_1,\mathbf{r}_f)g(\mathbf{r}_1,\mathbf{r}_f)=\sum_j\int\left(\psi_j^*(\mathbf{r}_2,\mathbf{r}_f)g(\mathbf{r}_2,\mathbf{r}_f)\frac{2}{r_{12}}d\mathbf{r}_2\right)\psi_j(\mathbf{r}_1,\mathbf{r}_f)\,.\quad(8)$$

Here the coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ are those of bound electrons and $\mathbf{r}_f$ that of the free electron. In order to simplify the perturbed HF equations, we utilize first-order perturbation theory and write the perturbed orbital $\psi_i(\mathbf{r}_1,\mathbf{r}_f)$ in the form

$$\psi_i(\mathbf{r}_1,\mathbf{r}_f)=\phi_i(\mathbf{r}_1)+\chi_i(\mathbf{r}_1,\mathbf{r}_f)\,,\quad(9)$$

where $\phi_i(\mathbf{r}_1)$ is the unperturbed HF orbital, assumed known. In order to make the calculations feasible, we treat both the perturbed HF equations [Eq. (1)] and the equations for the unperturbed set $\phi_i(\mathbf{r}_1)$ in a modified version of the Slater exchange approximation to the HF equations. In Slater's free-electron-exchange approximation to the HF equations an exchange term proportional to $\rho^{1/3}$, where ρ is the electron density, is used in place of the exchange integrals.[6] A recent derivation,[7] wherein a different average over electron momenta is taken, yields an exchange potential which is $\frac{2}{3}$ as great as that of Slater. Since both techniques are only approximations, we have written the exchange term $A(r_1)$ in the form

$$A_{s'}(r_1)=\lambda_s 6\left[\frac{3}{8\pi}\sum_j\phi_j^*(\mathbf{r}_1)\phi_j(\mathbf{r}_1)\right]^{1/3},\quad(10)$$

where λ_s is a variable coefficient. $\lambda_s=1$ corresponds to Slater's potential and $\lambda_s=\frac{2}{3}$ corresponds to that of Kohn and Sham.[7] In the present calculations the coefficient λ_s was varied over a small range below 1.0 in several self-consistent calculations. Thus, with this technique one may calculate HFS wave functions yielding orbital energies which can be made to match a predetermined criterion of a "good" wave function simply by varying λ_s in several successive calculations. The criterion used herein will be discussed below.

The unperturbed solutions $\phi_i(\mathbf{r}_1)$ were taken as solutions to the HFS′ equation,

$$[-\nabla_1^2+V(r_1)-A_{s'}(r_1)]\phi_i(\mathbf{r}_1)=\epsilon_i^0\phi_i(\mathbf{r}_1)\,,\quad(11)$$

with

$$V(r_1)=-\frac{2Z}{r_1}+\sum_j\int|\phi_j(\mathbf{r}_2)|^2\frac{2}{r_{12}}d\mathbf{r}_2\quad(12)$$

and $A_{s'}(r_1)$ given by Eq. (10).

Our objective is to determine the first-order perturbations $\chi_i(\mathbf{r}_1,\mathbf{r}_f)$ of the single electron orbitals ϕ_i. The term $2/r_{1f}$ of Eq. (6) is treated as a perturbation on the HF system and the perturbations χ_i are obtained as solutions to a set of integro-differential equations. Substituting (9) into (6) and making use of (11), one obtains a set of equations for χ_i which are excessively complicated due to perturbed Coulomb and exchange integrals.[5] These terms are, however, small as compared to the direct terms[5] and will be dropped, leaving an equation for the perturbation χ_i of the ith orbital of the form[2]

$$[-\nabla_1^2+V(r_1)-A_{s'}(r_1)-\epsilon_i^0]\chi_i(\mathbf{r}_1,\mathbf{r}_f)=\left[\int|\phi_i(\mathbf{r}_1)|^2\frac{2}{r_{12}}d\mathbf{r}_1-\frac{2}{r_{1f}}\right]\Phi_i(\mathbf{r}_1)\,.\quad(13)$$

In this equation we expand the perturbation term $2/r_{1f}$ in the multipole expansion

$$\frac{2}{r_{1f}}=\frac{2}{r_>}+\frac{2r_<}{r_>^2}\cos\theta+\frac{2r_<^2}{2r_>^2}(3\cos^2\theta-1)+\cdots\,,\quad(14)$$

where $r_<$ is the lesser and $r_>$ is the greater of r_1 and r_f, and θ is the angle between r_1 and r_f. We make the dipole approximation in (13) and drop all quadrupole and higher-order terms of (14), leaving a set of inhomogeneous differential equations[2] for the perturbation χ_i of an atomic orbital ϕ_i:

$$[-\nabla_1^2+V(r_1)-A_{s'}(r_1)-\epsilon_i^0]\chi_i(\mathbf{r}_1,\mathbf{r}_f)=-\frac{2r_1}{r_f^2}\cos\theta\,\phi_i(\mathbf{r}_1),\quad(r_f>r_1)\quad(15a)$$

$$[-\nabla_1^2+V(r_1)-A_{s'}(r_1)-\epsilon_1^0]\chi_i(\mathbf{r}_1,\mathbf{r}_f)=-\frac{2r_f}{r_1^2}\cos\theta\,\phi_i(\mathbf{r}_1).\quad(r_f<r_1)\quad(15b)$$

These equations must be solved in the two regions—$r_1<r_f$ and $r_1>r_f$—and matched at the boundary $r_1=r_f$.

With the solutions for the perturbations χ_i of the HF orbitals, the polarization potential is determined

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[5] J. Callaway, Phys. Rev. **106**, 868 (1957).
[6] J. C. Slater, Phys. Rev. **81**, 385 (1951).
[7] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

from the expression[2]

$$V_p(r_f)=\sum_j\int \phi_j^*(\mathbf{r}_1)\frac{2r_<}{r_>^2}\cos\theta\,\chi_j(\mathbf{r}_1,\mathbf{r}_f)d\mathbf{r}_1, \quad (16)$$

where the sum extends over all occupied orbitals ϕ_j.

Equations (15a), (15b) may be reduced to radial equations and the integrals in (16) to integrations over radial coordinates by writing

$$\phi_i(\mathbf{r}_1)=[P_{nl}(r_1)/r_1]Y_l^m(\theta,\phi), \quad (17)$$

and

$$\chi_i(\mathbf{r}_1,\mathbf{r}_f)=\sum_{l',m'}[U_{nl\to l'}(r_1,r_f)/r_1] \times C_{n,l\to l'}{}^{m\to m'}Y_{l'}{}^{m'}(\theta,\phi). \quad (18)$$

Substituting (18) into (15) gives the radial equations

$$\left[\frac{d^2}{r_1^2}-\frac{l'(l'+1)}{dr_1^2}-V(r_1)+A_{s'}(r_1)+\epsilon_i{}^0\right]U_{n,l\to l'}(r_1,r_f) =\frac{2r_1}{r_f^2}P_{nl}(r_1), \quad (r_f>r_1) \quad (19a)$$

$$\left[\frac{d^2}{r_1^2}-\frac{l'(l'+1)}{dr_1^2}-V(r_1)+A_{s'}(r_1)+\epsilon_i{}^0\right]U_{n,l\to l'}(r_1,r_f) =\frac{2r_f}{r_1^2}P_{nl}(r_1), \quad (r_f<r_1) \quad (19b)$$

which must be solved and matched at $r_1=r_f$. The constants $C_{n,l\to l'}{}^{m\to m'}$ are determined from the Clebsch-Gordan coefficients which occur from the angular integrals and are zero unless $l'=l\pm1$. These values are tabulated by Sternheimer.[8] The polarization potential can be written in terms of the solutions to Eq. (19). Thus,

$$V_p(r_f)=\sum_{nll'}V_{n,l\to l'}(r_f), \quad (20)$$

where

$$V_{n,l\to l'}(r_f)=K_{n,l\to l'}\left[\frac{2}{r_f^2}\int_0^{r_f}P_{nl}(r_1)r_1U_{n,l\to l'}(r_1,r_f)dr_1 +2r_f\int_{r_f}^{\infty}P_{nl}(r_1)U_{n,l\to l'}(r_1,r_f)r_1^{-2}dr_1\right]. \quad (21)$$

The constants $K_{n,l\to l'}$ are numbers which depend on l' and on the number of electrons in an nl shell, and have been given by Sternheimer for complete shells.[8] We note that in the case of an atomic system which is not spherically symmetric, the distortion of the atom depends on its orientation. Thus, the polarization potential is conveniently taken as the average over all orientations of the atomic system.

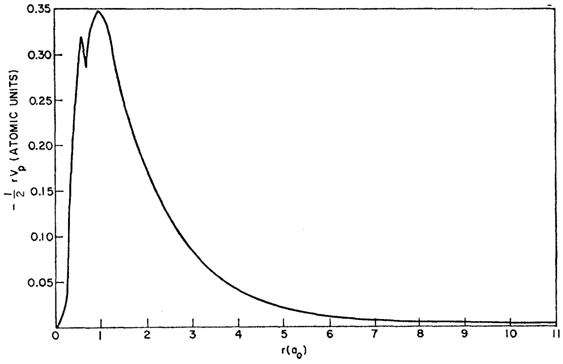

FIG. 1. Total polarization potential for neutral oxygen from the $(2s)^2(2p)^4$ orbitals. $[-\frac{1}{2}V_p(r)\times r.]$

IV. APPLICATION TO OXYGEN

The determination of the polarization potential for oxygen requires solutions of the perturbation equations (19a), (19b) for s and p electrons. The $1s$ contribution to V_p was found to be negligible, thus solutions are required for the $2s^2$ states which undergo $s\to p$ perturbations, $U_{2,0\to1}$, and for the $2p^4$ electrons which undergo $p\to s$ and $p\to d$ excitations requiring the solutions $U_{2,1\to0}$ and $U_{2,1\to2}$. The notation $U_{n,l\to l'}$ for the radial part of the perturbation of an nl orbital is that of Sternheimer.[8]

The solutions to Eqs. (19a), (19b) for the appropriate $U_{n,l\to l'}$ functions were obtained by the method described in I. The unperturbed functions $\phi_i(r_1)$ were obtained by the modified HFS′ method described in Sec. III. Here the Slater exchange term was varied in successive calculations until solutions were obtained which yielded an ionization energy in agreement with experimental values for the weighted average of the ground-state configuration of oxygen. The resultant value of the coefficient of Eq. (10) was found to be $\lambda_s=1.118$. Since oxygen is not a closed-shell system, the polarization potential was calculated as the average over all orientations of the atomic system. As a check on the accuracy of the potential function, the asymptotic value of V_p was compared with $V_p\sim\alpha/r^4$ and the resultant value of the polarizability α was obtained as $\alpha=r_f^4V_p(r_f)$ at $r_f=25a_0$. The results converted to Å^3 are

$$\alpha=0.767\text{ Å (calculated)},$$
$$\alpha=0.77\pm0.01\text{ Å (experiment)}.^9$$

Thus, the agreement with experiment is very good. The polarization potential multiplied by $-r/2$ is shown in Fig. 1.

V. CONTINUUM FUNCTIONS

Having obtained the polarization potential experienced by a free electron in the field of the neutral atom, the continuum functions were obtained by a straight-

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[8] R. M. Sternheimer, Phys. Rev. **96**, 951 (1954); **115**, 1198 (1959).

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

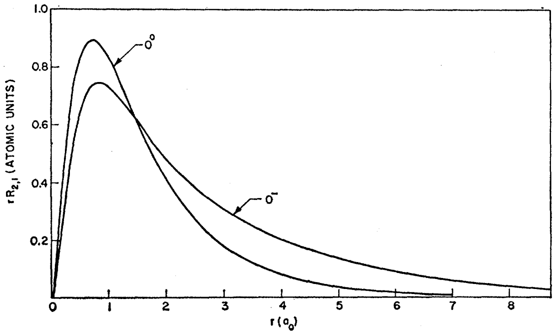

FIG. 2. 2*p* bound-state radial wave function for neutral oxygen and for the negative ion.

forward integration of the Schrödinger equation for the lth partial-wave $P_{kl}(r)$:

$$\left[\frac{d^2}{dr^2}-V'(r)-V_p(r)-\frac{l(l+1)}{r^2}+k^2\right]P_{kl}(r)=0, \quad (22)$$

where $P_{kl}(r)=rR_{kl}(r)$, which is normalized so that asymptotically

$$P_{kl}(r) \underset{kr\to\infty}{\longrightarrow} k^{-1}\sin(kr-\tfrac{1}{2}l\pi+\delta_l). \quad (23)$$

Here the potential $V(r)$ is the total HFS′ potential, including the exchange term as in Eq. (11), and $V_p(r)$ is the polarization potential of Sec. IV. The equation for $P_{kl}(r)$ was solved by the Numerov process for various values of k^2. The numerical integration was carried out to a point R_0 where the ratio $|V_T/k^2|\leq 10^{-4}$. Here V_T is the total interaction potential $V'+V_p$. At this point the solutions were normalized and the phase shifts δ_l determined by matching the functions of a linear combination of the regular and irregular spherical Bessel functions. The distance R_0 varied from about $35a_0$ to as much as 500 a_0 for the various values of k^2.

VI. BOUND-STATE FUNCTION OF O^-

The bound-state functions for the oxygen negative ion were obtained by the modification of the HFS method outlined in Sec. III. Here, however, the "self-energy" was subtracted out of the interaction potential for each electron; thus the calculation made was effectively a modification of the Hartree method wherein a variable exchange term of the Slater form [Eq. (10)] is added in the self-consistent calculation. The procedure was repeated with different coefficients λ_s on the exchange part of the potential until an eigenvalue of the 2*p* electron was obtained which corresponded to the experimental ionization energy of O^-(1.465 eV).

This method differs from that used by Klein and Brueckner[10] or Cooper and Martin[11] in that a self-consistent calculation was made each time the variable parameter was adjusted rather than taking a single equation and adjusting a parameter in the total potential function in order to match the 2*p* eigenvalue. However, the present technique is not expected to be appreciably better than that of Ref. 10 or 11, though both are probably better than ordinary HF. In Fig. 2 the 2*p* functions of O and O^- are plotted for comparative purposes. The overlap integrals

$$\int_0^\infty R_{2p}{}^i R_{2p}{}^f r^2 dr$$

which describe the relaxation of the passive electrons were found to be 0.9575 for a single electron. This is significantly less than one, and when the product of the squares is taken, the resultant value of ξ in Eq. (2) is 0.71. Thus, in the case of negative ions a considerable error is made by assuming ξ to be unity.[10,11]

VII. RESULTS

A. Photodetachment Cross Section

Having obtained bound-state and continuum solutions, the matrix elements for $\sigma_d(\nu)$ yield the photodetachment cross section. The results of the cross-section calculations are shown in Fig. 3 along with the experimental results of Branscomb, Smith, and Tisone[12] and of Smith.[13] The *s*- and *d*-wave contribution to $\sigma_d(\nu)$ are shown separately along with the total detachment cross section.

At higher photon energies the oxygen atom may be left in the excited ^1D or ^1S state of the ground configuration. This possibility increases the cross section at the threshold energies for leaving the residual atom in these states. Using the appropriate values of the binding

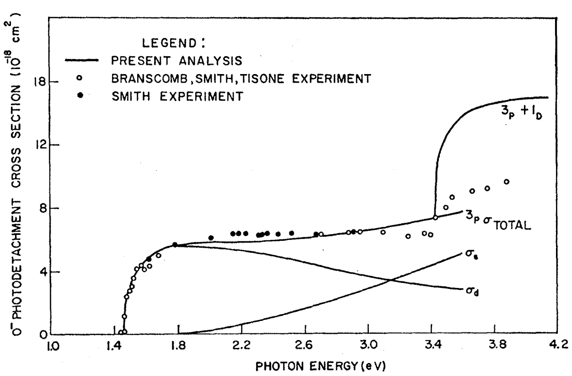

FIG. 3. Total photodetachment cross section for O^- showing contributions from the *s* and *d* waves. Experimental values are those of Branscomb, Smith, and Tisone and of Smith.

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[10] M. M. Klein and K. A. Brueckner, Phys. Rev. **111**, 115 (1958); hereafter referred to as KB.

[11] J. W. Cooper and J. B. Martin, Phys. Rev. **123**, 1482 (1962); hereafter referred to as CM.

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

[13] S. J. Smith, in *Proceedings of the Fourth International Conference on Ionization Phenomena in Gases, Uppsala, 1959*, edited by N. R. Nilsson (North-Holland Publishing Company, Amsterdam, 1960), p. 219.

energy E_b and the C_l's in Table I, estimates of the cross sections are obtained by performing the same set of calculations as for the case when the atom is left in its ^3P ground state. The approximation here is less accurate since the same bound-state radial function is used as for the ground state. Excitation to the first of these two levels is clearly shown in the experimental results of Branscomb *et al.*[12] above 3.4 eV, where the cross section shows a sudden increase. The calculated values in this region are also shown in Fig. 3. It should be noted that experimental difficulties in the high-energy region yield more uncertainty in the last few points on the right of Fig. 3. Results over a wider energy range with both ^1D and ^1S excitation are shown in Fig. 4 along with the theoretical results of Cooper and Martin.[11]

In all of the earlier treatments of photodetachment from O⁻, polarization was included by the use of a semiempirical term of the form[10,11,14]

$$V_p(r) = -P/(r^2+r_p^2)^2\,, \tag{24}$$

where the quantity r_p is the so-called screening distance (about 1.2 a.u.) and P is a polarization parameter which was adjusted in such a way as to yield an eigenvalue of E_b when put into the Schrödinger equation for the $2p$ function for O⁻. The best values obtained were $P \sim 5.7$ by Bates and Massey[14] and ~ 5.5 in later calculations.[10,11] The same term was then used in the Schrödinger equation for the continuum functions. For low energies, a comparison of earlier results with the present analysis is shown in Fig. 5. Experimental values are very close to the present results in this range.

It is worth noting that the major difference in the photodetachment cross-section calculations here as compared to those of KB[10] and CM[11] results from differences in the continuum functions rather than the bound-state functions. For comparative purposes the present calculations were repeated using our bound-state O⁻ functions and utilizing continuum functions which were solutions to the equation used by CM. The cross section thus obtained was very little different from their results, indicating that differences in the bound-state functions were only slight. A comparison was also made with the $2p$ function of KB[10] where a fit was made to an analytic function in the asymptotic region. There was little difference ($<10\%$)in the two cases. The present results correspond to a value of about 0.32 for their quantity N. Thus, the significant differences in our results stem from the continuum solutions which are sensitive to small differences in the polarization potential.

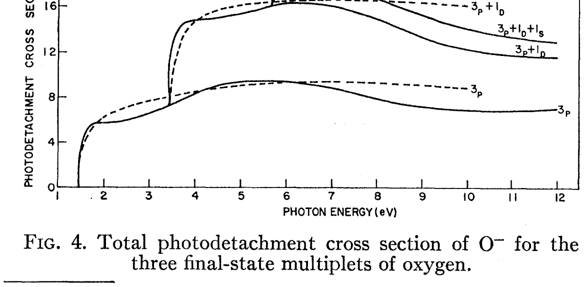

FIG. 4. Total photodetachment cross section of O⁻ for the three final-state multiplets of oxygen.

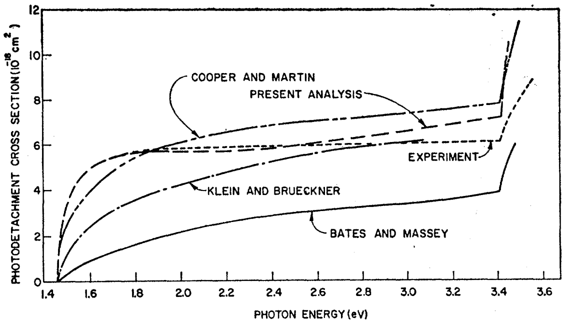

FIG. 5. Comparison of low-energy σ_d results with earlier calculations.

As a final test of the sensitivity of σ_d to the bound-state functions, sample calculations were made utilizing ordinary HF wave functions for O⁻ obtained from Roothaan's method.[15,16] The matrix elements as well as the overlap integrals of Eq. (2) were re-evaluated using the analytic HF functions. The results were not appreciably different from those of Fig. 3; the photodetachment cross section maintained almost exactly the same shape as in Fig. 3 and differed by $\sim 15\%$ in magnitude.

B. Attachment Cross Section and Attachment Coefficient

The reverse process of photodetachment, i.e., radiative attachment, may be formulated in a manner similar to the above, whereby one may obtain the radiative attachment cross section σ_A describing the process $e^- + \mathrm{O} \rightarrow h\nu + \mathrm{O}^-$. The two cross sections for detachment and attachment are, in fact, related by the relationship[14]

$$\sigma_d(\mathrm{O}^{-\,2}P \rightarrow \mathrm{O}\,^3P) = \frac{3c^2m^2v^2}{2h^2\nu^2}\,\sigma_A(\mathrm{O}\,^3P \rightarrow \mathrm{O}^{-\,2}P). \tag{25}$$

Thus, one may immediately determine the radiative attachment cross section from a knowledge of the photodetachment curve. Results of σ_A obtained in the present calculations are shown in Fig. 6 along with results obtained by Branscomb[1] from experimental data in the low-energy region. One other quantity of interest in

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

[15] E. Clementi and A. D. McLean, Phys. Rev. **133**, A419 (1964).

[16] E. Clementi, C. C. J. Roothaan, and N. Yoshimine, Phys. Rev. **127**, 1618 (1962).

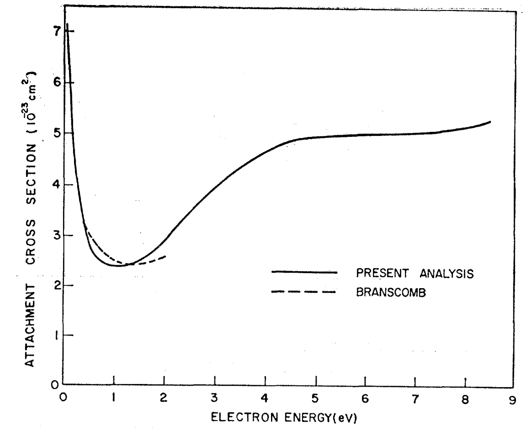

FIG. 6. Attachment cross section of electrons to atomic oxygen calculated by detailed balancing from the photodetachment cross section.

electron-attachment problems is the attachment coefficient defined as $\nu_e\sigma_A$, where ν_e is the velocity of the electron. For completeness, this quantity is also shown in Fig. 7 compared with the results of Branscomb.[1]

C. Elastic-Scattering Cross Section

The total elastic-scattering cross section for low-energy electrons can easily be obtained by the method of partial waves from the solutions for the continuum functions $P_{kl}(r)$ of Eq. (22). In units of $\pi a_0{}^2$ the scattering cross section is

$$\sigma=\frac{4}{k^2}\sum_l (2l+1)\sin^2\delta_l\,, \tag{26}$$

where δ_l is the lth partial-wave phase shift.

In the present treatment of the scattering problem, correlation effects between incident and bound electrons are included through the use of the polarization potential of Sec. IV, and exchange is included in an approximate way through the use of the modified Slater exchange term in Eq. (22). As described earlier, the exchange term was modified so as to yield a negative-ion wave function with an eigenvalue which matched a predetermined value. Thus, the phase shifts were obtained from solutions to the simple differential equation (22), which is an approximation to the integro-differential equation resulting from a more complete perturbed-HF treatment.[17]

We note that in the scattering problem it is not really appropriate to use the same continuum solutions as for the photodetachment problem. In the photodetachment process one has a continuum electron moving away from its parent negative ion which asymptotically approaches a free electron outside a neutral atom with the appropriate polarization potential $\sim\alpha/r^4$. However, in the scattering problem the target wave functions are those of a perturbed neutral atom. Thus, in the present treatment of the problem the appropriate Coulomb and exchange terms in the interaction potentials will be slightly different in the two cases. Thus, for the scattering problem the calculations of the continuum wave functions $P_{kl}(r)$ were repeated using the same polarization potential as before (appropriate for a neutral atom) but with the modified HF Slater terms of Eq. (22) being those obtained from the HFS′ calculations for neutral oxygen, as described above. Thus, the exchange term in the scattering equation was taken as that of the neutral atom modified so as to satisfy the criterion of Sec. VI. Another criterion which is very appropriate as a definition of good wave functions for the neutral atom is that they yield a dipole polarizability which agrees with experiment. The results of Sec. IV indicate that this criterion was met very well.

Results of the present determination of the elastic-scattering cross section are shown in Fig. 8. The curve labeled I was obtained using the Coulomb and exchange terms of the negative ion in the equation for the free electron. The results labeled II were obtained using the potential function obtained from neutral oxygen. The differences in the two sets of results are thus due to small differences in the Coulomb and exchange terms in the potential functions representing an electron moving in the field of its parent negative ion and an incident electron moving in the field of a neutral atom, in both cases the polarization potential term being the same. One can argue that neither of the two cases represents the actual situation for a low-energy electron and that the real potential probably lies somewhere between these extremes. The present results indicate that these small differences are in fact of considerable importance for low-energy collisions.

In Fig. 8 results from the present analysis are compared with the results of four different experiments on atomic oxygen. The two very low energy values of σ were obtained by shock-tube techniques[18,19]; the results of Neynaber *et al.*[20] and of Sunshine, Aubrey, and

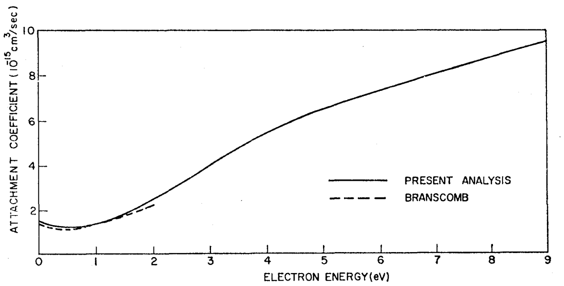

FIG. 7. Variation of attachment coefficient with electron energy for electron capture by the neutral oxygen atom.

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[17] A. Temkin, Phys. Rev. **107**, 1004 (1957).

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

[19] J. W. Daiber and H. F. Waldron, Bull. Am. Phys. Soc. **11**, 496 (1966).

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

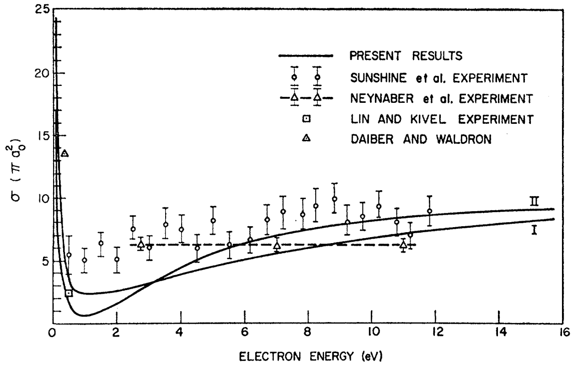

FIG. 8. Total elastic-scattering cross section for oxygen compared with available experimental data.

Bederson[21] are from crossed-beam experiments. The present results agree quite well with most of the experimental data.

One might use the results obtained in cases I and II to gain a rough idea of the magnitude of some of the errors which occur in using the adiabatic approximation as employed here. In a dynamic rather than a static treatment of the scattering problem, the atomic electrons respond to the field of a moving electron. This response depends on the velocity of the incident particle.[22–24] As the incident velocity is made smaller and smaller, the scattered electron spends more time within the atomic system, thus causing the atomic orbitals to approximate those of the negative ion. One could say that at zero incident energy the system corresponds roughly to an excited state of the negative ion, i.e., a state with zero binding energy. Thus the Coulomb and exchange integrals at zero energy should approach those for the stationary negative ion and at higher energies they should lie between the negative ion and those for the neutral atom. Thus by comparing the two cases as in I and II of Fig. 6, one can get an idea of the size of these effects by comparing the two extreme cases. However, a more important consideration in the dynamic problem is that of the effect of the velocity term on the polarization potential, where the distortion of the atomic system is reduced with increasing electron velocity.[24] This simple argument gives no information on this aspect of the scattering interaction.

VIII. CONCLUSIONS

The use of a polarized orbital-type polarization potential in both the problems of low-energy photodetachment and elastic electron scattering leads to a substantial improvement in the agreement of theory and experiment over that achieved with semiempirical corrections for atomic distortion. The use of a modified Hartree-Fock–Slater potential for the bound state as well as the continuum functions seems to have considerable merit for complicated systems where more detailed calculations would be very difficult. The present method of obtaining negative-ion solutions is somewhat unattractive, but the photodetachment cross section is apparently less sensitive to the bound-state function than to the continuum solution.

Application of the present analysis to the elastic-scattering problem yields results which are as close or closer to the experimental values than any of several earlier calculations.[25] The results of Bauer and Browne[25] for elastic scattering from oxygen are rather similar to the present results; however, their analysis is considerably different in that adjustable parameters were used in the terms of the scattering equation, whereas the exchange term is adjusted here only in the bound-state problem and is not treated as a variable function in the scattering equation. The treatment of dynamic effects on the polarization potential for more complicated systems is even more involved[24] than for H and He but should be investigated to determine their significance for the multielectron atoms.

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

[22] A. Temkin, Phys. Rev. **126**, 130 (1962).

[23] V. D. Obedkov, Zh. Eksperim. i Teor. Fiz. **43**, 649 (1962) [English transl.: Soviet Phys.—JETP **16**, 463 (1963)].

[24] R. W. LaBahn and J. Callaway, Phys. Rev. **147**, 28 (1966).

[25] E. Bauer and H. N. Browne, in *Atomic Collision Processes,* edited by M. R. C. McDowell (North-Holland Publishing Company, Amsterdam, 1964), p. 16. References to earlier theoretical results are cited here as well as a display of the cross sections.