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THEORETICAL PHOTODETACHMENT CROSS SECTION FOR
THE NEGATIVE ATOMIC OXYGEN ION

by

H. T. Jackson, Jr.

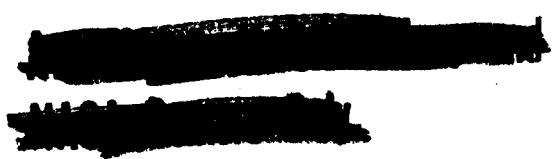W. R. Garrett

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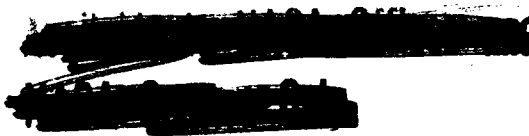
University of Alabama Research Institute

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Foreword

The results contained in this paper are being submitted for journal publication under an abbreviated format. Issued as a Research Report, this material constitutes a preprint and is given limited distribution in order to provide an early dissemination of current information.

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ABSTRACT

The theoretical photodetachment cross section for the negative atomic oxygen ion in its normal ground state, $(1s)^2 (2s)^2 (2p)^5$, has been investigated for the three transitions; $O^-(^2P) + h\nu \to O(^3P) + e$, $O^-(^2P) + h\nu \to O^-(^1D) + e$, and $O^-(^2P) + h\nu \to O(^1S) + e$ in the photon energy range up to 12 ev. In addition, the scattering cross section for the neutral oxygen atom, the polarizability, the attachment cross section and the attachment coefficient have also been determined. Results are compared with available experimental and other theoretical data. Excellent agreement has been obtained with the latest reliable experimental data.

The Hartree-Fock treatment utilizing a modified form of the Slater approximation for exchange was used to compute the bound state radial functions for the neutral atom and negative ion. The polarization potential was developed from first order perturbation theory in conjunction with the adiabatic approximation. The continuum wave functions for the outgoing electron were derived from Schrödinger's equation utilizing the modified Hartree-Fock-Slater and polarization potentials.

The agreement of the photodetachment and neutral atomic oxygen cross sections with experimental data as well as the agreement of the polarizability calculation with experiment is a most favorable indication for the validity of this work.

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CHAPTER I

GENERAL INTRODUCTION

An atom or molecule may absorb a photon of sufficient energy so that a bound electron may be removed and become free. The absorption of such a photon of energy $h\nu$ by a negative ion N^- leads to the production of a neutral atom or molecule N^0 and a free electron with velocity v.

$$h\nu + N^- \rightarrow N^0 + e^-. \qquad (1.1)$$
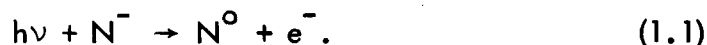
The resulting free electron will have a translational energy equal to the difference between the photon energy and the energy expended in removing the electron from the negative ion. If E_b is the binding energy of the electron, then

$$h\nu = E_b + mv^2/2, \qquad (1.2)$$

where it is assumed that the neutral atom or molecule is so massive compared with the electron that the kinetic energy of the final neutral state may be ignored.

This process, whereby a negative ion absorbs a photon causing an electron to undergo a transition from a bound state to the continuum, is known as photo-detachment. The initial state is a negative ion in a radiation field and the final state is a neutral atom or molecule and a free electron. If a beam of radiation passes through a gas composed of negative ions, the ions act as though they had a cross section $\sigma_{PD}(\nu)$ (photodetachment) for the incoming photons of energy $h\nu$. This cross section is defined in such a way that each encounter between an ion and a photon removes a photon from the beam.[1] Thus, light of frequency ν is reduced

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[1] S. S. Penner, Quantitative Molecular Spectroscopy and Gas Emissivities, Addison-Wesley, Reading, Mass., 1959, p. 162.

by a factor[2] $\exp(\sigma_{PD,\nu} nt)$ in passing through a gas of thickness t containing n atoms per cubic centimeter. In practice,[3] a beam of mass-separated negative ions is irradiated with a light source of known spectral intensity distribution. In the region of intersection between the photon and the ion beams a current of free electrons is produced. This current may then be measured and used to calculate the photodetachment cross section as a function of the incident photon energy. This paper is concerned with the theoretical calculation of this photodetachment cross section σ_{PD}.

In particular, this paper is concerned with the calculation of electron photodetachment from the negative oxygen ion, O^-. Considerable efforts have recently been directed toward obtaining good theoretical calculations and improved experimental measurements of the photodetachment cross section at different wavelengths.[4-9] The work reported here was initiated in order to (1) gain a better understanding of the importance of various parameters in the calculation of photodetachment cross sections, and (2) hopefully obtain better agreement between theory and experiment. It is to be noted that excellent agreement between the present work and the latest reliable experimental data has been obtained.

The early development of related negative ion processes for atomic and molecular oxygen as applicable to the formulation of the present problem is given

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[2] D. R. Bates, Monthly Notices, Roy. Astron. Soc. 109, 432 (1946).

[3] S. J. Smith and L. M. Branscomb, Rev. Sci. Inst. 31, 733 (1960).

[4] J. W. Cooper and J. B. Martin, Phys. Rev. 123, 1482 (1962).

[5] L. M. Branscomb and S. J. Smith, Phys. Rev. 98, 1127 (1955).

[6] M. M. Klein and K. A. Brueckner, Phys. Rev. 111, 1115 (1958).

[7] L. M. Branscomb, D. S. Bruch, S. J. Smith, and Sydney Geltman, Phys. Rev. 111, 504 (1958).

[8] L. M. Branscomb, S. J. Smith, and G. Tisone, J. Chem. Phys. (to be published) (1965).

[9] S. J. Smith, in Proc. Fourth Int'l. Conf. on Ionization Phenomena in Gases, Uppsala, 1959, edited by N. R. Nilsson (North-Holland Publishing Co., Amsterdam, 1960), p. 219.

by Bates and Massey.[10] The experimental study of photodetachment processes originated in 1953.[3] These first laboratory observations were concerned with negative hydrogen ions and soon afterwards cross sections were determined for negative ions of other gases. Only recently[3] has improved and relatively sophisticated instrumentation become available enabling more reliable measurements to be made of the photodetachment cross section. All the published work done in this connection has been by Branscomb, Smith, et al., of the National Bureau of Standards. Their latest data on oxygen are presently unpublished,[8] but the results will be given in this paper for comparison with the results of the present theoretical work.

In order to adequately introduce the present work, it is felt necessary to briefly sketch the need for such calculations. Emphasis on photodetachment or negative ion bound-free transitions has, in the past, been placed largely on atomic hydrogen. This is important in astrophysics because quanta of energy in the ultraviolet, visible and near infrared spectral regions can photodissociate the hydrogen ion into a neutral hydrogen atom and a free electron. These negative ions of hydrogen account for most of the continuous absorption in late-type stars.[11] Speculation as to the astrophysical importance of O^- absorption has been suggested,[7] but a more recent commentary[11] states that it is unlikely that this is important in any of the stars.

The absorption of continuous radiation by O^- accounts for the release of electrons and destruction of negative ions in the sunlit ionosphere, and can be a source of opacity in certain regions of the spectrum for high temperature plasmas or gas caps containing oxygen. In order to completely understand the earth's upper atmosphere it is necessary to know the photoabsorption cross section of the various gaseous constituents.[12-14] Atomic oxygen is important since it is the

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

[11] L. H. Aller, Astrophysics, The Atmospheres of the Sun and Stars, Ronald Press New York (1963), p. 194.

[12] P. J. Nawrocki and R. Papa, Atmospheric Processes, Geophysics Corporation of America, GCA No. 61-37-A, Bedford, Massachusetts (1961).

[13] D. R. Bates and H. S. W. Massey, Trans. Roy. Soc. A192, 1 (1947).

[14] R. B. Crains and J. A. R. Samson, Phys. Rev. 139, A1403 (1965).

dominant constituent above 160 km. The theoretical background for interpreting and understanding the physical processes capable of producing radiation in the hot flow field surrounding a reentering ballistic vehicle comes, in part, from the bound-free continuum of negative ions.[15] The photodetachment cross section is of particular interest in connection with emissivity calculations for heated air.[1] Comparison of experimental and calculated values of the photodetachment cross section are also very valuable in the theoretical study and modeling of related effects which do not readily lend themselves to experimental investigation.[7] Such difficulties necessitate the need for good theoretical calculations.

Various semitheoretical models presently exist for computing photodetachment cross sections.[4,6,9,10] Cooper and Martin[4] have stated, "Our understanding of the related processes of ... photodetachment from negative ions is at present fragmentary. Even though much progress has been made ... for the important case of atomic hydrogen, little has been done for heavier atomic systems." These various methods and the subsequent results will be discussed and compared with available experimental data along with the results of this paper. The primary difficulty in treating such problems is in determining the distortion of the wave functions of the neutral atom by the outgoing electron and calculating the resulting polarization potential. The photodetachment cross section is very sensitive to this term in the total final state interaction. Because of its importance, this paper will review briefly a recently developed method[16] for determining the polarization potential. This method is used in the present calculations and results in excellent agreement being obtained with the latest reliable experimental data. The development of the present model will be given in considerable detail with emphasis on the development of the polarization potential, continuum wave functions and bound state radial functions for O^-.

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[15]R. G. Breene, Jr., _RVIP Reentry Radiation Measurements. A Theoretical Background_ (U). Physical Studies, Inc., SR No. 1, Kettering, Ohio (1964).

[16]W. R. Garrett, Phys. Rev. __140__, A705, (1965).

In addition, the elastic scattering cross section for the neutral oxygen atom is calculated and compared with various other theoretical and experimental results. This is computed by calculating the phase shifts of the partial waves at various electron energies. The attachment coefficient, α_A, is also calculated as a function of electron energy for atomic oxygen. This is given by $v\sigma_A$ where v is the velocity of the incident electron and σ_A is the cross section for the capture of an incident electron of energy $mv^2/2$ into a level belonging to the ground state of O^- by a normal O atom. This is important in the study of the formation of negative oxygen ions[10] and again finds application in our understanding the ionosphere. The relation between photodetachment and electron absorption cross sections may be derived by considering detailed balancing at equilibrium between electron capture and photoionization.[1]

CHAPTER II

DEVELOPMENT OF THE CROSS SECTION EQUATION

1. Introduction

To compute the cross section for photodetachment the initial state is taken as a negative ion in a radiation field and the final state is a neutral atom and a free electron. The electromagnetic energy of the radiation field acts as a small perturbation on the negative ion and time dependent perturbation theory can be used to calculate the probability per unit time that this perturbation will produce a transition. This is the transition rate for absorption. An ion in a field of electromagnetic radiation experiences interactions between its magnetic moments and the magnetic field and between its electric charges and the electric field. Only the latter will be considered since the magnetic interaction is very small compared to the electric interaction.

The wavelengths to be considered are large compared to the dimensions of the atom so that the electric field can be considered constant over any region occupied by the atom. The interaction energy H' can be obtained by adopting the Hamiltonian for a charged particle in a radiation field where the momentum operator $\overline{P}$ is replaced by the usual expression $\overline{P} - e\overline{A}$, where $\overline{A}$ is the vector potential. Thus the whole radiation field can be put into the vector potential which is perpendicular to the direction of propagation. This chapter will develop the normalized vector potential, from this find the interaction energy, then derive the general photodetachment cross section, and finally reduce this general equation to the particular form applicable to the present problem.

2. Vector Potential

The electromagnetic field will be treated classically by assuming that the vector potential can be specified without any uncertainty at any space-time point by using Maxwell's equations in free space.

In free space the vector potential can be made to satisfy

$$\nabla^2 \overline{A} - (1/c^2)\overline{A} = 0 \quad \text{and} \quad \nabla \cdot \overline{A} = 0. \tag{2.1}$$

A typical plane wave solution of the above is

$$\overline{A}(\overline{r}, t) = \hat{e}a \cos(\overline{k} \cdot \overline{r} - \omega t) \quad \text{with} \quad \hat{e} \cdot \overline{k} = 0, \tag{2.2}$$

where (a) is a constant scalar amplitude, $\hat{e}$ is a unit vector perpendicular to $\overline{k}$ and $\omega = kc$. The electric field $\overline{E} = -\overline{A}$ is

$$\overline{E}(t) = -\hat{e}akc \sin(\overline{k} \cdot \overline{r} - \omega t). \tag{2.3}$$

The energy density is defined by the usual equation where the average energy residing in the electric and magnetic fields are equal.

$$\xi = \overline{E} \cdot \overline{D} = (1/4\pi)k^2 c^2 a^2 \sin^2(\overline{k} \cdot \overline{r} - \omega t). \tag{2.4}$$

and its magnitude averaged over a period $(2\pi/\omega)$ of the oscillation gives the time average of the energy density

$$\xi = (1/8\pi)k^2 c^2 a^2. \tag{2.5}$$

The photon density (ρ_p) is the average energy density (ξ) divided by the energy per photon $(\hbar ck)$

$$\rho_p = \frac{kca^2}{8\pi\hbar} \tag{2.6}$$

The amplitude a in the vector potential may thus be expressed in terms of the photon density by normalizing to one photon per unit volume and calling this

volume τ.*

$$\frac{1}{\tau} = \frac{kca^2}{8\pi\hbar} \tag{2.7a}$$

Solving for a gives

$$a = \left(\frac{8\pi\hbar}{kc\tau}\right)^{1/2} \tag{2.7b}$$

Then the normalized vector is

$$\overline{A}(\bar{r}, t) = \hat{e}\left(\frac{8\pi\hbar}{ck\tau}\right)^{1/2} \cos(\bar{k}\cdot\bar{r} - \omega t). \tag{2.8}$$

3. Matrix Elements for the Transition

Expanding the above cosine term into its exponential parts and keeping only that portion which makes the final state energy greater than the initial state energy and leads to absorption,[15] yields

$$\overline{A}(\bar{r}, t) = \hat{e}\left(\frac{8\pi\hbar}{kc\tau}\right)^{1/2} \frac{1}{2} \exp(i\bar{k}\cdot\bar{r} - i\omega t). \tag{2.9}$$

The Hamiltonian operator describing a charged particle in a radiation field is

$$H = (1/2m)\left[\overline{P} - e\overline{A}(\bar{r}, t)\right]^2 + V(\bar{r}). \tag{2.10}$$

Where $V(\bar{r})$ describes the coulomb or other interactions. Expanding,

$$H = (1/2m)(P^2 - e\overline{P}\cdot\overline{A} - e\overline{A}\cdot\overline{P} + e^2 A^2) + V(\bar{r}).$$

Now in the present gage

$$(\overline{P}\cdot\overline{A} - \overline{A}\cdot\overline{P})\Psi = -i\hbar\{\nabla\cdot(\overline{A}\Psi) - \overline{A}\cdot\nabla\Psi\} = -i\hbar(\nabla\cdot\overline{A})\Psi = 0. \tag{2.11}$$

Thus

$$H = H_o - (e/m)\overline{P}\cdot\overline{A} + (e^2/2m)A^2, \tag{2.12}$$

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*The normalized volumes will be carried because of their units.

where H_o is the unperturbed Hamiltonian. Making the usual assumption that

$$(e/m)\overline{P} \cdot \overline{A} \gg (e^2/2m) A^2, \tag{2.13}$$

then

$$H' = -(e/m)\overline{P} \cdot \overline{A} = -(e/m)\frac{1}{2}\left(\frac{8\pi\hbar}{kc\tau}\right)^{1/2} \overline{P} \cdot \hat{e} \exp\{i(\overline{k} \cdot \overline{r} - \omega t)\}, \tag{2.14}$$

and the matrix elements for the transition probabilities are, considering only one component of $\overline{P}$ and taking $\exp(i\overline{k} \cdot \overline{r}) \simeq 1$ (dipole approximation).

$$\left|H'_{fi}\right|_x^2 = \frac{2\pi e^2 \hbar}{m^2 kc\tau} \left|<f|P_x|i>\right|^2. \tag{2.15}$$

But [17]

$$<f|P_x|i> = im\omega_p <f|x|i>,$$

since $\left|<r>\right|^2 = \left|<x>\right|^2 + \left|<y>\right|^2 + \left|<z>\right|^2$ and on the average all are equal then $\left|<r>\right|^2 = 3\left|<x>\right|^2$ and it follows that

$$\left|H'_{fi}\right|^2 = \frac{2\pi\hbar e^2 \omega_p}{3\tau} \left|<f|r|i>\right|^2. \tag{2.16}$$

4. General Cross Section Equation

The transition rate or transition probability per unit time for absorption of a quantum of energy $\hbar\omega$ from the radiation field and finding the system in the desired final state is given by the familiar expression[17]

$$\dot{W} = \frac{2\pi}{\hbar} \left|H'_{fi}\right|^2 \rho(E), \tag{2.17}$$

where $\rho(E)$ is the density of final states for the electrons and is given by

$$\rho(E)\,dE = \frac{L^3 d\overline{P}}{(2\pi\hbar)^3} = \frac{L^3 P^2 dPd\Omega}{(2\pi\hbar)^3}, \tag{2.18}$$

[17] L. I. Schiff, <u>Quantum Mechanics</u>, McGraw-Hill Book Co., Inc., New York, 1955, p. 261.

where L^3 represents the volume that confines the particle in the energy range dE and $d\Omega$ is the solid angle into which the ejected electron with velocity $\bar{v}$ and momentum $\bar{P}$ goes. Taking $E = P^2/2m$ then

$$\frac{dP}{dE} = \frac{1}{v},$$

giving

$$\rho(E) = \frac{L^3 m^2 v d\Omega}{(2\pi\hbar)^3}, \tag{2.19}$$

and

$$W = \frac{4\pi^2 m^2 v e^2 \omega_p^2 L^3}{(2\pi\hbar)^3 \tau} \frac{\left|<f|r|i>\right|^2}{3} d\Omega. \tag{2.20}$$

Now dividing W by the incident photon flux I gives the cross section

$$d\sigma = W/I \quad \text{where } I = c/\tau. \tag{2.21}$$

Combining terms, the expression for the cross section becomes

$$d\sigma = \frac{me^2 \omega_p k}{6\pi c\hbar^2} \frac{\left|<f|r|i>\right|^2}{3} d\Omega, \tag{2.22}$$

where the momentum, mv, has been written as $\hbar k$.

Taking L^3 as a unit volume, expressing r and L in atomic units and the energies in Rydberg units, the above equation becomes

$$\sigma = (4\pi/3) k \alpha_f a_o^2 (E_b + E_e) F(i, f), \tag{2.23}$$

where α_f is the fine structure constant and E_e is the electron energy. The quantity $F(i, f)$ in the above equation involves the initial and final states. Since there are a number of initial and final states, this expression must be averaged over the possible initial states and summed over the final states.

$$F(i, f) = \frac{P}{\omega_i} \sum_i \sum_f \left| \langle f | r | i \rangle \right|^2, \tag{2.24}$$

where ω_i is the number of initial states and P is the appropriate overlap integral of the electrons which are in the same state both before and after detachment. If one-electron central field orbitals are used, then F is conveniently expressed as[2]

$$F(i, f) = P(C_{\ell-1} M_{\ell-1}^2 + C_{\ell+1} M_{\ell+1}^2), \tag{2.25}$$

where the C_ℓ's are obtained by evaluating the angular portion of the dipole matrix elements for each transition of interest and the M_ℓ's are the radial integrals

$$M_{\ell \pm 1} = \int_o^\infty R_{n\ell}(r) \, r \, R_{k,\ell \pm 1} \, r^2 \, dr. \tag{2.26}$$

The selection rule on the azimuthal quantum number ℓ comes from considering only an electric dipole transition where an $n\ell$ electron is removed from a bound state orbital into the continuum. $R_{n\ell}$ is the radial bound state orbital for the $n\ell$ electron and $R_{k,\ell \pm 1}$ is the radial wave function for the free electron with angular momentum quantum number $\ell \pm 1$. Each of these is normalized so that

$$\int_o^\infty R_{n\ell}^2(r) \, r^2 \, dr = 1, \tag{2.27a}$$

and

$$R_{k,\ell} \xrightarrow[kr \to \infty]{} (kr)^{-1} \left\{ \sin(kr + \delta_\ell - \frac{\ell \pi}{2}) \right\}. \tag{2.27b}$$

Combining these various terms the general cross section equation may be written as

$$\sigma = (4\pi/3) \alpha_f a_o^2 k \, (E_b + E_e) \, P \, (C_{\ell-1} M_{\ell-1}^2 + C_{\ell+1} M_{\ell+1}^2). \tag{2.28}$$

5. O^- Photodetachment Cross Section

The stable bound state of the negative oxygen ion is the 2p ground state which arises from the $(1s)^2 (2s)^2 (2p)^5$ configuration. An electric dipole transition is made in the photodetachment process whereby a 2p electron is removed from a bound state orbital to a continuum state. This continuum may become either a free

s-wave or a free d-wave depending on the final angular momentum state it occupies since the azimuthal quantum number (l) must change by one unit for this transition. However, for O^-, there are three transitions possible since the neutral oxygen atom may be left in the ^3P, ^1D or ^1S states after detachment. The threshold excitation energies (E_b) for each of these are 1.465 ev, 3.432 ev and 5.66 ev respectively.[9] Because of experimental difficulties in accurately measuring the latter two, this paper will emphasize the ^3P state, i.e., $O^-(^2P_{1/2}) \rightarrow O(^3P_2)$, which occurs at longer wavelengths than the other transitions. The cross section for the other states can be obtained by using the same radial matrix elements, the appropriate angular parts of the dipole matrix elements and the binding energies corresponding to each threshold. This will be done and certain conclusions drawn concerning the general behavior of the resulting cross section curves.

In order to calculate the cross section for photodetachment, integrations must be performed over the passive electrons (overlap integral) and the active electron. This involves calculations of the radial wave function for the bound and free orbitals. Products of one-electron central field orbitals will be used to describe the wave function of an individual bound $n\ell$ orbital for both the ion and neutral atom. The method of calculating these functions will be described in Chapter IV. The continuum wave functions for a given angular momentum state are obtained by solving the Schrödinger wave equation for the free electron at the desired electron energies in the potential field due to the residual neutral atom. This interaction is most important and must be treated very carefully. The cross section is extremely sensitive to the exact form of the total interaction potential. The polarization interaction used in the calculation of the continuum wave functions is developed in the next chapter.

The overlap integral P, previously mentioned, gives a correction to the cross section by allowing for the distortion of the wave functions of the passive electrons due to the ejection of the active electron.[3] Since product wave functions are being used and there are four 2p electrons in the same state before and after detachment, the square of the matrix element involving the product of each of these gives the value of P.

$$P_{2p} = \prod_{i=1}^{4} \left| \int_0^\infty R_{2p}^i \, R_{2p}^f \, r^2 dr \right|_i^2 . \qquad (2.29)$$

This distortion is only slight and the distortion of the inner core (1s) and (2s) electrons will therefore be neglected and the overlap integrals P_{1s} and P_{2s} will be taken as unity.

The values of the C_ℓ's mentioned in the previous section are determined by considering the relative probabilities for the three transitions of O^- going to neutral O plus a free electron. The following transitions are possible (see Table I) and the number of possible final states is given by $(2S + 1)(2L + 1)$ which are 9, 5 and 1 respectively for the ^3P, ^1D, and ^1S states. The relative probability for each of these may then be taken as 1, 5/9, and 1/9 respectively. By combining the ^3P, ^1D and ^1S states of O with first the s and then the d states of the continuum waves, it is found that 1 and 2 states respectively exist for these additions.

The values of C_o and C_2 for the above three transitions are tabulated below.[2]

TABLE I

Values of C_o and C_2 for the Various Final State Configurations

Transition	C_o	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

CHAPTER III

POLARIZATION POTENTIAL

1. Introduction

Existing models[4,6] for the theoretical calculation of photodetachment cross sections correct for polarization (the interaction potential due to the distortion of the neutral atom by the outgoing electron) by semiempirical means which do not arise naturally from the formalism of the problem. These methods have not yielded cross sections which are in complete agreement with experiment. Results are completely unreliable if this interaction is neglected, however when these semiempirical parameters are introduced, the only criteria for their accuracy is, of course, agreement with available experimental data. This section will consider the distortion of the neutral atom by the outgoing electron and develop a polarization potential from this interaction which describes the effect of the polarized atom on the scattered electron. First order perturbation theory will be used in conjunction with the adiabatic approximation.

The adiabatic model is based on the ability of the neutral atom to polarize in response to the instantaneous position of the outgoing electron. Thus assumes that the velocity of the free electron is small compared to the orbital velocity of the bound electrons. Since the energies of the outgoing detached electron are small (~ 10 ev or less), the bound state wave functions have sufficient time to adjust or respond to the influence of the perturbing field. This method has been applied to yield the low energy scattering cross section for electron-cesium atom collisions by Garrett and Mann[18] and very recently to electron scattering from lithium and sodium by Garrett.[16]

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[18]W. R. Garrett and R. A. Mann, Phys. Rev. 130, 658(1963).

2. Formulation of the Problem

Consider a bound electron of the negative ion as having been detached so that the system now consists of a neutral atom and a free electron of relatively low energy.

The Hamiltonian for the entire problem is

$$H = H_a(\bar{r}) + H_f(\bar{r}_f) + W(\bar{r}, \bar{r}_f). \qquad (3.1)$$

H_a is the Hamiltonian for the atom, H_f is the free-particle Hamiltonian, and W the interaction Hamiltonian representing the interaction of the outgoing electron with the bound electrons.

$$W(\bar{r}, \bar{r}_f) = \sum_{i=1}^{Z} \frac{1}{|\bar{r}_i - \bar{r}_f|}. \qquad (3.2)$$

The vectors $\bar{r}_f$ and $\bar{r}_i$ represent the positions of the free electron and one of the bound electrons, respectively.

Initially a one-electron atom will be considered and this will then be extended to an atom with atomic number Z.

$$H_a \phi_o(\bar{r}) = E_o \phi_o(\bar{r}), \qquad (3.3)$$

where the eigenvalue E_o and the normalized eigenfunction $\phi_o(r)$ for the neutral atom are supposedly known.

The Schrödinger equation for the complete system may be written as

$$[H_a(\bar{r}) + H_f(\bar{r}_f) + W(\bar{r}, \bar{r}_f)] \; \psi(\bar{r}, \bar{r}_f) = E \; \psi(\bar{r}, \bar{r}_f), \qquad (3.4)$$

where $\Psi(\bar{r}, \bar{r}_f)$ is the complete wave function for the system.

Neglecting exchange, the complete wave function may be written

$$\Psi(\bar{r}, \bar{r}_f) = \phi(\bar{r}, \bar{r}_f) \; \psi(r_f), \qquad (3.5)$$

where the perturbed wave function, $\phi(\bar{r}, \bar{r}_f)$, for the bound state considers the influence of the perturbing field by its dependency on $\bar{r}_f$ and $\psi(\bar{r}_f)$ is the

free-particle wave function. The perturbed wave function will now be written as

$$\Phi(\bar{r}, \bar{r}_f) = \Phi_o(\bar{r}) + \chi(\bar{r}, \bar{r}_f), \tag{3.6}$$

where $\Phi_o(\bar{r})$ has previously been defined and $\chi(\bar{r}, \bar{r}_f)$ is the perturbed part of the orbital wave function resulting from the outgoing electron which is at the position $\bar{r}_f$. The requirement is also imposed that

$$<\Phi_o, \chi> = 0. \tag{3.7}$$

The Hamiltonian for the entire problem may now be written as

$$[H_a(\bar{r}) + H_f(\bar{r}_f) + W(\bar{r}, \bar{r}_f)] \; [\Phi_o(\bar{r}) + \chi(\bar{r}, \bar{r}_f)] \; \psi(\bar{r}_f)$$

$$= E \; [\Phi_o(\bar{r}) + \chi(\bar{r}, \bar{r}_f)] \; \psi(\bar{r}_f). \tag{3.8}$$

3. The Polarization Potential

If the above equation is multiplied from the left by $\Phi_o^*(\bar{r}) \; \psi^*(\bar{r}_f)$ and integrated over all space, the following result is obtained

$$\langle \psi, <\Phi_o, w\Phi_o> \psi \rangle + \langle \psi, <\Phi_o, w\chi> \psi \rangle + <\psi, H_f \psi> = (E - E_o) <\psi, \psi>, \tag{3.9}$$

where use has been made of the facts that Φ_o is normalized, Φ_o and χ are orthogonal and hermitian, and Φ_o is the eigenfunction of H_a with eigenvalue E_o.

Considering the first two terms in the above equation, the first represents the mutual interaction energy of the outgoing electron with the atomic electron and the second term is identified as the mutual interaction of the free electron with the perturbation of the atomic wave function. Therefore the polarization potential seen by the outgoing electron due to the distortion of the atom is

$$V_p(\bar{r}_f) = <\Phi_o, w\chi>. \tag{3.10}$$

Equation (3.9) may be written in the form

$$\langle \psi, (H_f + E_o + \langle \Phi_o, w\Phi_o \rangle + \langle \Phi_o, wX \rangle - E) \psi \rangle = 0.$$

From this it follows that

$$E = E_o + E_f + \langle \Phi_o, w\Phi_o \rangle + \langle \Phi_o, wX \rangle , \qquad (3.11)$$

and substituting the result for E from the above equation into equation (3.8) and simplifying

$$\psi H_f X + w\Phi_o X + H_a X\psi = [E_o X + \langle \Phi_o, w\Phi_o \rangle \Phi_o + \langle \Phi_o, w\Phi_o \rangle X$$

$$+ \langle \Phi_o, wX \rangle \Phi_o + \langle \Phi_o, wX \rangle X] \psi. \qquad (3.12)$$

This equation may now be simplified by making use of the adiabatic approximation mentioned at the beginning of this section. Since the Hamiltonian for the free electron changes relatively slowly, then solutions of the above equation will be obtained by fixing r_f, thus $\nabla^2 r_f = 0$. This results in the first term of the above equation being zero. This equation now becomes

$$[(H_a - E_o) X] \psi = [\langle \Phi_o, w\Phi_o \rangle + \langle \Phi_o, wX \rangle - w] (\Phi_o + X) \psi. \qquad (3.13)$$

The interaction $w(\bar{r}, \bar{r}_f)$ can now be considered as a perturbation on the unperturbed system H_a. Since this term as well as the polarization perturbation X is small, then only terms through first order will be retained in the differential equation for determining X. With this approximation equation (3.13) becomes

$$[H_a(\bar{r}) - E_o] X(\bar{r}, \bar{r}_f) = [\langle \Phi_o(\bar{r}), w(\bar{r}, \bar{r}_f) \Phi_o(\bar{r}) \rangle - w(\bar{r}, \bar{r}_f)] \Phi_o(\bar{r}). \qquad (3.14)$$

4. Multielectron Atom

For a multielectron atom the polarization potential will be developed from first order perturbation theory utilizing a modified form of the Hartree-Fock theory. The Hamiltonian for the complete atom will be written as follows:

$$H_a(\bar{r}) = \sum_i H_i(\bar{r}) ,$$

where

$$H_i \phi_i = -\nabla_i^2 \phi_i(\bar{r}_i) - \frac{2Z}{r_i} \phi_i(\bar{r}_i) + \sum_j \int \phi_j^*(\bar{r}_j) \frac{2}{r_{ij}} \phi_j(\bar{r}_j) d\tau_j \phi_i(\bar{r}_i)$$

$$- \sum_j [\int \phi_j^*(\bar{r}_j) \frac{2}{r_{ij}} \phi_i(\bar{r}_j) d\tau_j] \phi_j(\bar{r}_i). \qquad (3.15)$$

$H_i(\bar{r}_i)$ depends on the coordinates of the ith electron and the average effect of the other electrons. The first term is the kinetic energy of the ith electron, the second term is the potential energy in the field of the nucleus where r_i is the distance from the nucleus to the ith electron, the third term is the repulsive coulomb potential interaction between the ith and Z-1 other electrons. A spherical average of this repulsive interaction is taken. The final term is the exchange integral which arises from using determinantal functions in the Hartree-Fock model. The wave function for the atom will then be written as a determinant

$$\Phi_0(r) = D \left| \phi_1(\bar{r}_1) \phi_2(\bar{r}_2) \cdots \phi_n(\bar{r}_n) \right|, \qquad (3.16)$$

with

$$H_i \phi_i = E_i \phi_i . \qquad (3.17)$$

The complete wave function is written

$$\Phi_0 + X = D \left| (\phi_1 + X_1)(\phi_2 + X_2) \cdots (\phi_n + X_n) \right|, \qquad (3.18)$$

where

$$<\phi_i, X_i> = 0 \quad \text{and} \quad <\phi_i, \phi_i> = 1. \qquad (3.19)$$

Utilizing this model the first order equation (3.15) becomes

$$(H_i - E_i) X_i(\bar{r}_i, \bar{r}_f) = [<\phi_i, w_i \phi_i> - w_i] \phi_i(\bar{r}_i), \qquad (3.20)$$

where

$$W = \sum_i w_i \quad \text{and} \quad w_i = \frac{1}{|\vec{r}_f - \vec{r}_i|}$$

Equation (3.20) is the differential equation for determining the perturbation X_i of the single electron orbital ϕ_i of the neutral atom. The total polarization potential is then

$$V_p(\vec{r}_f) = \sum_i \int \phi_i \, w_i \, X_i \, d\tau_i, \tag{3.21}$$

or

$$V_p(\vec{r}_f) = \sum_i V_{p_i}(\vec{r}_f).$$

This polarization potential can thus be calculated for an atom by considering the contribution due to each orbital which is determined from the modified Hartree-Fock solution for the atom.

An estimate of the exchange term in the Hartree-Fock theory can be obtained very conveniently by using wave functions given by the Thomas-Fermi model of the atom.[19] This is known as the simple Slater approximation. The essential features of the Hartree-Fock method are retained by replacing the exchange potentials by a universal exchange potential. This is obtained by suitably averaging over the individual exchange potentials to get an average charge density and exchange potential. This average of exchange potential is spherically symmetric and may be represented by

$$6\left[\frac{3}{8\pi} \sum_i \phi_i^*(\vec{r}_i) \, \phi_i(\vec{r}_i)\right]^{1/3} \phi_i(\vec{r}_i). \tag{3.22}$$

When equation (3.22) is inserted into (3.15) very close approximations to the Hartree-Fock solutions are obtained. Agreement of the subsequent calculated photodetachment cross-sections and scattering cross sections with experimental data provide a useful criterion for the validity of this model.

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[19] J. C. Slater, Quantum Theory of Atomic Structure, Vol. II, McGraw-Hill, New York, 1960.

5. The Radial Equations

At this point the differential equation for determining χ_i for an orbital may be written as

$$(H_i - E_i) \, \chi_i(\bar{r}_i, \bar{r}_f) = \left[<\phi_i, \frac{2}{r_{if}} \phi_i> - \frac{2}{r_{if}} \right] \phi_i(\bar{r}_i). \qquad (3.23)$$

This equation can be separated and the radial equations for the various angular momentum states written. A coordinate system is chosen which has the Z-axis parallel to the position vector r_f of the outgoing free electron. The interaction $2/r_{if}$ can be written as polynomials in terms of $P_\lambda(\cos \theta_{if})$ by making use of the expansion

$$\frac{2}{r_{if}} = \sum_\lambda \left(\frac{4\pi}{2\lambda+1} \right)^{1/2} \frac{2r_<^\lambda}{r_>^{\lambda+1}} \, Y_\lambda^o (\theta, 0)$$

$$= \frac{2}{r_>} + \frac{2r_<}{r_>^2} \cos \theta + \frac{r_<^2}{r_>^3} (3 \cos^2 \theta - 1) + \cdots. \qquad (3.24)$$

where $r_<$ is the lesser and $r_>$ the greater of r_i and r_f. The quadrupole and higher order terms in the above expansion will be dropped leaving only the first two terms in the series. When these two terms are substituted into the bracketed term of equation (3.20), the term becomes

$$\left[\int \phi_i^*(\bar{r}_i) \, \frac{2}{r_>} \, \phi_i(\bar{r}_i) \, d\tau_i - \frac{2}{r_>} - \frac{2r_<}{r_>^2} \cos \theta \right]. \qquad (3.25)$$

It can now be noted that the first term above can be written as

$$\frac{2}{r_f} \int_\Omega \int_0^{r_f} \phi_i^* \, \phi_i \, r^2 \, dr \, d\Omega + \int_\Omega \int_{r_f}^\infty \phi_i^* \, \frac{2}{r_i} \phi_i \, r^2 \, dr \, d\Omega. \qquad (3.26)$$

Since the ϕ_i's are normalized the first term in the above equation goes to $2/r_f$ for large values of r_f and the second term goes to zero. The $2/r_f$ term then calcels the second term in the equation leaving only the dipole term $(2r_</r_>^2) \cos \theta$. For smaller values of r_f, the monopole term becomes appreciable but will be small

compared to the coulomb potential term. Thus the dipole approximation will be made at this point and only the third term in equation (3.25) will be retained.

The following pair of equations is now obtained for determining the perturbed wave X_i.

$$\left[-\nabla_i^2 + V(\bar{r}_i) - A_s(\bar{r}_i) - E_o \right] X_i(\bar{r}_i, \bar{r}_f) = -\frac{2r_i}{r_f^2} \cos\theta \, \phi_i(\bar{r}_i) \quad \text{for } r_f > r_i, \quad (3.27a)$$

and

$$\left[-\nabla_i^2 + V(\bar{r}_i) - A_s(\bar{r}_i) - E_o \right] X_i(\bar{r}_i, \bar{r}_f) = -\frac{2r_f}{r_i^2} \cos\theta \, \phi_i(\bar{r}_i) \quad \text{for } r_i > r_f. \quad (3.27b)$$

where $V(\bar{r}_i)$ is the coulomb potential and $A_s(\bar{r}_i)$ is the Slater exchange term. These may now be solved and the solutions joined at $r_i = r_f$ to obtain the first order perturbation of each electron orbital ϕ_i. The dipole polarization potential may now be determined from equation (3.21).

$$V_p(\bar{r}_f) = \sum_i \int \phi_i^*(\bar{r}_i) \frac{2r_<}{r_>^2} \cos\theta \, X_i(\bar{r}_i, \bar{r}_f) \, d\tau_i. \quad (3.28)$$

The individual perturbation of the electron orbitals for the various allowed angular momentum states must now be considered. First, equations (3.27) will be reduced into radial equations and appropriate radial integrals by writing ϕ_i and X_i in the form

$$\phi_i(\bar{r}_i) = R_{n\ell} Y_\ell^m(\theta, \phi), \quad (3.29)$$

and

$$X_i(\bar{r}_i, \bar{r}_f) = \sum_{\ell', m'} X_{n\ell \to \ell'}(r_i, r_f) \, C_{n\ell \to \ell'}^{m \to m'} Y_{\ell'}^{m'}(\theta, \phi), \quad (3.30)$$

and for convenience the following change in variables will be made

$$P_{n\ell}(r)/r = R_{n\ell}(r),$$

and

$$U_{n\ell\to\ell'}(r, r_f)/r = X_{n\ell\to\ell'}(r, r_f) \qquad (3.31)$$

When these functions are substituted into the differential equations (3.27), they separate into the following two radial equations

$$\left[\frac{d^2}{dr_i^2} - \frac{\ell'(\ell'+1)}{r_i^2} + V(\bar{r}_i) - A_s(\bar{r}_i) - E_o\right] U_{n\ell\to\ell'}(r_i, r_f) = \frac{2r_<}{r_>^2} P_{n\ell}(r_i). \qquad (3.32)$$

This is actually two equations for $r_f > r_i$ and $r_i > r_f$ which must be solved and matched at $r_i = r_f$. The constants C in equation (3.30) are determined by the Clebsch-Gordon coefficients which occur in the angular integrations. These coefficients are zero[20] unless $\Delta\ell = \pm 1$ for $\ell \neq 0$ and $\Delta\ell = 1$ for $\ell = 0$. The polarization potential can now be written as

$$V_{P_{n\ell\to\ell'}}(\bar{r}_f) = K_{n\ell\to\ell'} \left[\frac{2}{r_f^2} \int_0^{r_f} P_{n\ell}(r_i) U_{n\ell\to\ell'}(r_i, r_f) dr_i \right.$$

$$\left. + r_f \int_{r_f}^{\infty} P_{n\ell}(r_i) U_{n\ell\to\ell'}(r_i, r_f) r_i^{-2} dr_i\right], \qquad (3.33)$$

or

$$V_p(\bar{r}_f) = \sum_{n\ell\ell'} V_{P_{n\ell\to\ell'}}(\bar{r}_f).$$

In the above equation, K depends on ℓ' and the number of electrons in a given $n\ell$ shell. These constants have been tabulated by Sternheimer.[20] The accuracy of the polarization potential can be conveniently checked by noting that as $r_f \to \infty$, V_p should approach the value $-\alpha/r^4$ where α is the dipole polarizability. A value of 0.762 Å^3 was obtained for the oxygen atom as compared to the latest experimental value of 0.77 Å^3.[21]

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[20]R. M. Sternheimer, Phys. Rev. 96, 951 (1954).

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

6. Polarization Calculations

The unperturbed wave functions used to calculate the polarization potential were taken as the Hartree-Fock-Slater functions obtained from a program originally written by Herman and Skillman[22] and modified by Garrett. This program furnished the functions $V(r)$, $A_s(r)$, E_o and $P_{n\ell}(r)$ in equations (3.32) to calculate the perturbations $U_{n\ell \to \ell'}$ of an orbital whose radial function is $P_{n\ell}$.

The electronic configuration of the normal oxygen atom is $(1s)^2 (2s)^2 (2p)^4$. The total polarization was taken to be that contributed by the two outermost 2s and 2p shells. The 2s shell, in Sternheimer's notation, can undergo the perturbation $2s \to p$ and the radial equation must be solved for $U_{2,0 \to 1}$. This notation indicates the unperturbed character is s being perturbed in such a way that the perturbed wave U has p character. There are two modes of excitation for the 2p electrons, $2p \to d$ and $2p \to s$, and the radial equation must be solved for the perturbations $U_{2,1 \to 2}$ and $U_{2,1 \to 0}$. Thus the pair of equations (3.32) must be solved and matched for each of these three perturbations for each value of r_f to obtain the polarization potential as a function of r_f. This obviously involves a great deal of computation time. In the actual solution the unperturbed equations were solved over a 441 point mesh for r_i and for 110 or every fourth point for r_f. An interpolation program was then used to bring the polarization potential $V_p(r_f)$ back to a 441 point mesh system to be compatible with the functions necessary for obtaining continuum wave solutions for the outgoing electron.

Before completing the discussion on the polarization potential, a brief explanation of the matching procedure used to solve equations (3.32) will be given. The numerical integration scheme contains an arbitrary constant in the series expansion used to start the calculations. This parameter is varied automatically in the computer program until the radial functions and their derivatives match at $r_i = r_f$ and the solution decreases exponentially at infinity. In practice, the choice was narrowed by repeated iterations until an accuracy of five to six significant figures was achieved in the starting values.

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[22]F. Herman and S. Skillman, Atomic Structure Calculations, Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1960.

7. Polarization Results

The polarization potential V_p and the electronic polarizability α are determined by first solving the set of equations (3.32) for the three perturbed radial functions $U_{n\ell \to \ell'}$. Each equation is of the form

$$\frac{d^2 U_{n\ell \to \ell'}}{dr^2} + f(r) \, U_{n\ell \to \ell'} = g(r),$$

and must be joined at the boundary $r_i = r_f$.

At large values of r, the polarizability was computed from the relation $\alpha = V_p r^4$. When α became constant, the integration of equation (3.33) was terminated. The following values were obtained for the radial portion of the integrals $r^4 R(n\ell \to \ell')$ in the asymptotic region.

$$r^4 R(\infty)(2s \to p) = -1.12235,$$

$$r^4 R(\infty)(2p \to s) = 0.575515,$$

$$r^4 R(\infty)(2p \to d) = -0.843395.$$

Sternheimer[20] gives the following coefficients for the various contributions to α for each electron at a large distance from the nucleus.

ℓ	$|m|$	K
0	0	4/3
1	0	16/15
1	1	4/5

where

$$\alpha(n\ell \to \ell') = K \, r^4 R(\infty)(n\ell \to \ell')$$

Thus, in the model being considered the oxygen atom has two 2s electrons and the value of $\alpha(2s \to p)$ and the polarization potential for the orbital is given by

$$\alpha(2s \to p) = 2 \left(\frac{4}{3}\right) r^4 R(\infty)(2s \to p), \qquad 2, |m| = 0$$

$$V_p(r)(2s \to p) = 2 \left(\frac{4}{3}\right) R(r)(2s \to p). \qquad 2, |m| = 0$$

There are four 2p electrons and the value of $\alpha(2p \to s)$, $\alpha(2p \to d)$ and the polarization potential are similarly obtained by multiplying by the angular coefficients for the various allowed values of the magnetic quantum number m and averaging over these states. There are three states these electrons may assume.

1. All electrons with $|m| = 0$

$$\alpha(2p \to d) = 4 \left(\frac{4}{5}\right) r^4 R(\infty)(2p \to d), \qquad 4, |m| = 0$$

$$V_p(r)(2p \to d) = 4 \left(\frac{4}{5}\right) R(r)(2p \to d). \qquad 4, |m| = 0$$

2. Three electrons with $|m| = 1$, one with $m = 0$

$$\alpha(2p \to d) = 3 \left(\frac{4}{5}\right) r^4 R(\infty)(2p \to d), \qquad 3, |m| = 1$$

$$V_p(r)(2p \to d) = 3 \left(\frac{4}{5}\right) R(r)(2p \to d), \qquad 3, |m| = 1$$

$$\alpha(2p \to d) = 1 \left(\frac{16}{15}\right) r^4 R(\infty)(2p \to d), \qquad 1, |m| = 0$$

$$V_p(r)(2p \to d) = 1 \left(\frac{16}{15}\right) R(r)(2p \to d), \qquad 1, |m| = 0$$

$$\alpha(2p \to s) = 1 \left(\frac{4}{3}\right) r^4 R(\infty)(2p \to s), \qquad 1, |m| = 0$$

$$V_p(r)(2p \to s) = 1 \left(\frac{4}{3}\right) R(r)(2p \to s). \qquad 1, |m| = 0$$

3. Two electrons with $|m| = 1$, two with $m = 0$.

$$\alpha(2p \to d) = 2 \left(\frac{4}{5}\right) r^4 R(\infty)(2p \to d), \qquad 2, |m| = 1$$

$$V_p(r)(2p \to d) = 2 \left(\frac{4}{5}\right) R(r)(2p \to d), \qquad 2, |m| = 1$$

$$\alpha(2p \to d) = 2 \left(\frac{16}{15}\right) r^4 R(\infty)(2p \to d), \qquad 2, |m| = 0$$

$$V_p(r)(2p \to d) = 2 \left(\frac{16}{15}\right) R(r)(2p \to d), \qquad 2, |m| = 0$$

$$\alpha(2p \rightarrow s) = 2 \left(\frac{4}{3}\right) r^4 R(\infty)(2p \rightarrow s), \qquad 2, |m| = 0$$

$$V_p(r)(2p \rightarrow s) = 2 \left(\frac{4}{3}\right) R(r)(2p \rightarrow s). \qquad 2, |m| = 0$$

The polarizability is then obtained by adding the contribution from the 2s orbital to the average contribution from the 2p orbital. If the polarizabilities computed from items 1, 2 and 3 above are all summed and divided by three and this added to the contribution from the 2s orbital, a value of $5.1493 \, a_o^3$ is obtained. Taking $a_o = 0.529 \text{Å}$ gives a value of $\alpha = 0.767 \text{Å}^3$. The latest experimental value is $0.77 \pm .006 \text{Å}^3$.[21] The polarization potential is obtained in a similar manner and is shown in Figure 1.
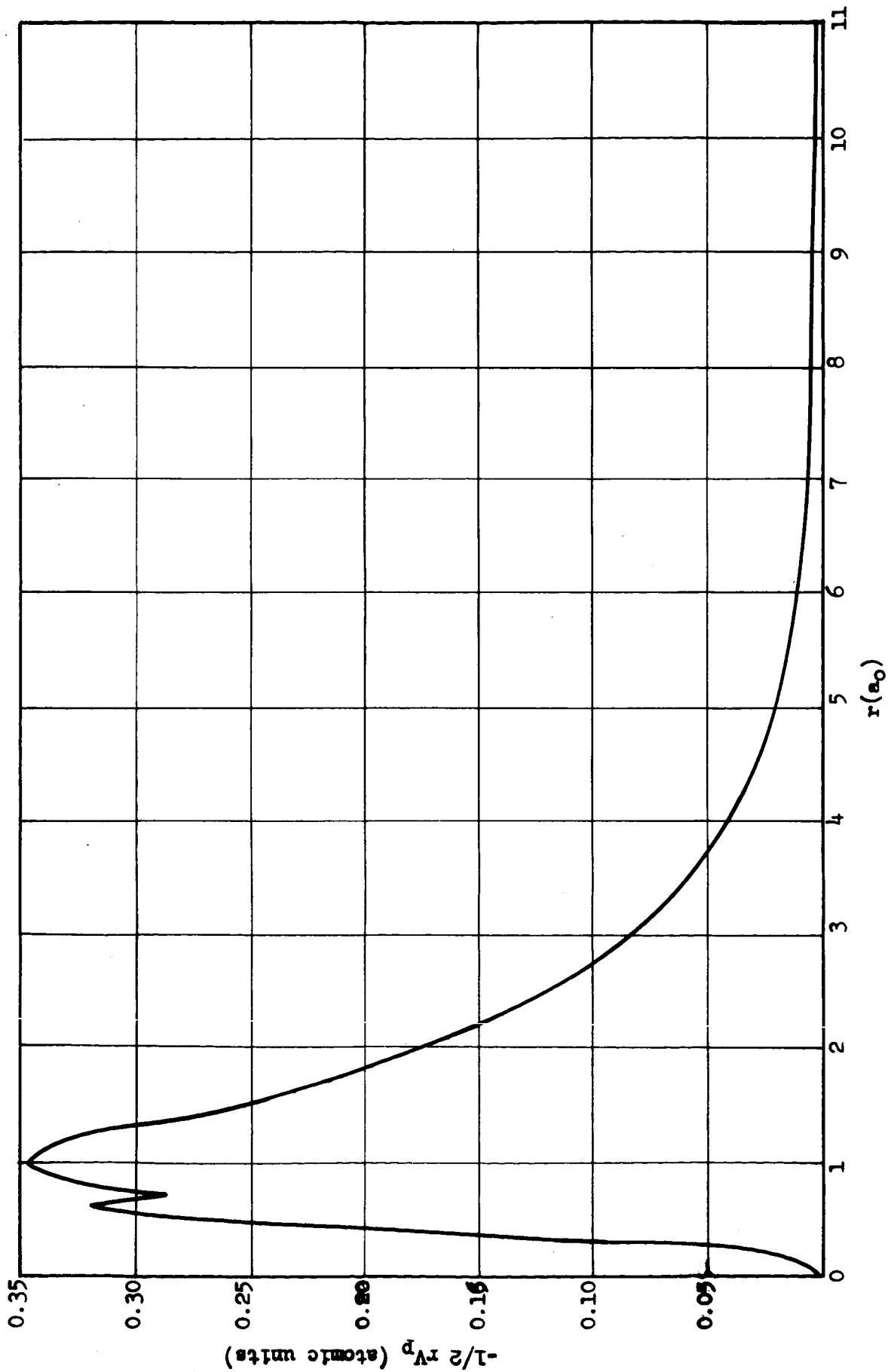
Figure 1   Total polarization potential for the oxygen atom
from the $(2S)^2 (2P)^4$ orbitals.

CHAPTER IV

BOUND STATE FUNCTIONS

1. Introduction

The bound state radial functions for the negative atomic oxygen ion must be accurately determined in order to calculate the dipole matrix elements, equation (2.26). In calculating these matrix elements the 2p eigenfunctions of the ion are required. The eigenfunctions for the neutral atom are also required to compute the overlap integral equation (2.29) for the passive electrons. In the present calculations the modified Hartree-Fock-Slater equations utilizing the free-electron exchange discussed in Chapter III were used to compute the self-consistent solutions for each orbital by varying the exchange potential until the correct eigenvalues were obtained. Simple product functions were then used to describe the complete state of the atomic system. The computer program for carrying out the computations was originally written by Herman and Skillman[22] and modified by Garrett. The same radial wave function is used for both sets of spins for a particular $n\ell$ orbital.

2. Method of Solution

With distances measured in Bohr units and energies in Rydberg units, the Hartree-Fock wave equation is written[19]

$$[-\nabla_i^2 + V(\bar{r}_i) - A(\bar{r}_i)]\,\psi_i(\bar{r}_i) = E_i\,\psi_i(\bar{r}_i), \qquad (4.1)$$

where $V(\bar{r}_i)$ is the sum of the nuclear and electronic coulomb potentials

$$V(\bar{r}_i) = \frac{-2Z}{r_i} + \sum_i \int \psi_i^*(\bar{r}_i)\,\frac{2}{r_{ij}}\,\psi_i(\bar{r}_i)\,d\tau_i, \qquad (4.2)$$

and the exchange potential is given by

$$A(\bar{r}_i)\ \psi_i^*(\bar{r}_i)\ \psi_i(\bar{r}_i) = \sum_j\ [\int \psi_i^*(\bar{r}_i)\ \psi_j(\bar{r}_i)\ \frac{2}{r_{ij}}\ \psi_j(\bar{r}_i)\ \psi_i(\bar{r}_i)\ d\tau_j]\ \psi_i(\bar{r}_i). \quad (4.3)$$

The exchange integrals are now replaced by a term known as the Slater exchange potential[19] which is, of course, somewhat less accurate, but makes the equations much simpler for computation purposes.

$$A_s\ \psi_i^*(\bar{r}_i)\ \psi_i(\bar{r}_i) = 6\left[\frac{3}{8\pi}\ \sum_i\ \psi_i(\bar{r}_i)\ \psi_i(\bar{r}_i)\right]^{1/3}\ \psi_i(\bar{r}_i). \quad (4.4)$$

These equations are reduced to radial equations by writing the function

$$\psi_k(\bar{r}_k) = \frac{P_{n\ell}(r_k)}{r_k}\ Y_\ell^m(\theta,\ \phi). \quad (4.5)$$

With this substitution the differential equations separate into the radial equations

$$\left[-\frac{d^2}{dr_i^2} + V(r_i) - \frac{\ell(\ell+1)}{r_i^2} - A_s(r_i)\right] P_{n\ell}(r_i) = E_i\ P_{n\ell}(r_i), \quad (4.6)$$

where it is required that

$$\int_0^\infty P_{n\ell}^2(r)\ dr = 1. \quad (4.7)$$

These radial equations were numerically solved using a 441 mesh point coordinate system scaled to $Z^{-1/3}$. The system of equations was then iterated until a set of self-consistent potentials was obtained. The Slater exchange potential was varied until the correct eigenvalues for both the atom and ion were obtained.

3. Results

The results for the $2p$ orbitals of the neutral atom and ion are shown in Figure 2. The results of the overlap integral for a single passive electron gave a value of 0.9575 and the square of the matrix element taken over all four electrons gives the subsequent value of 0.7064.

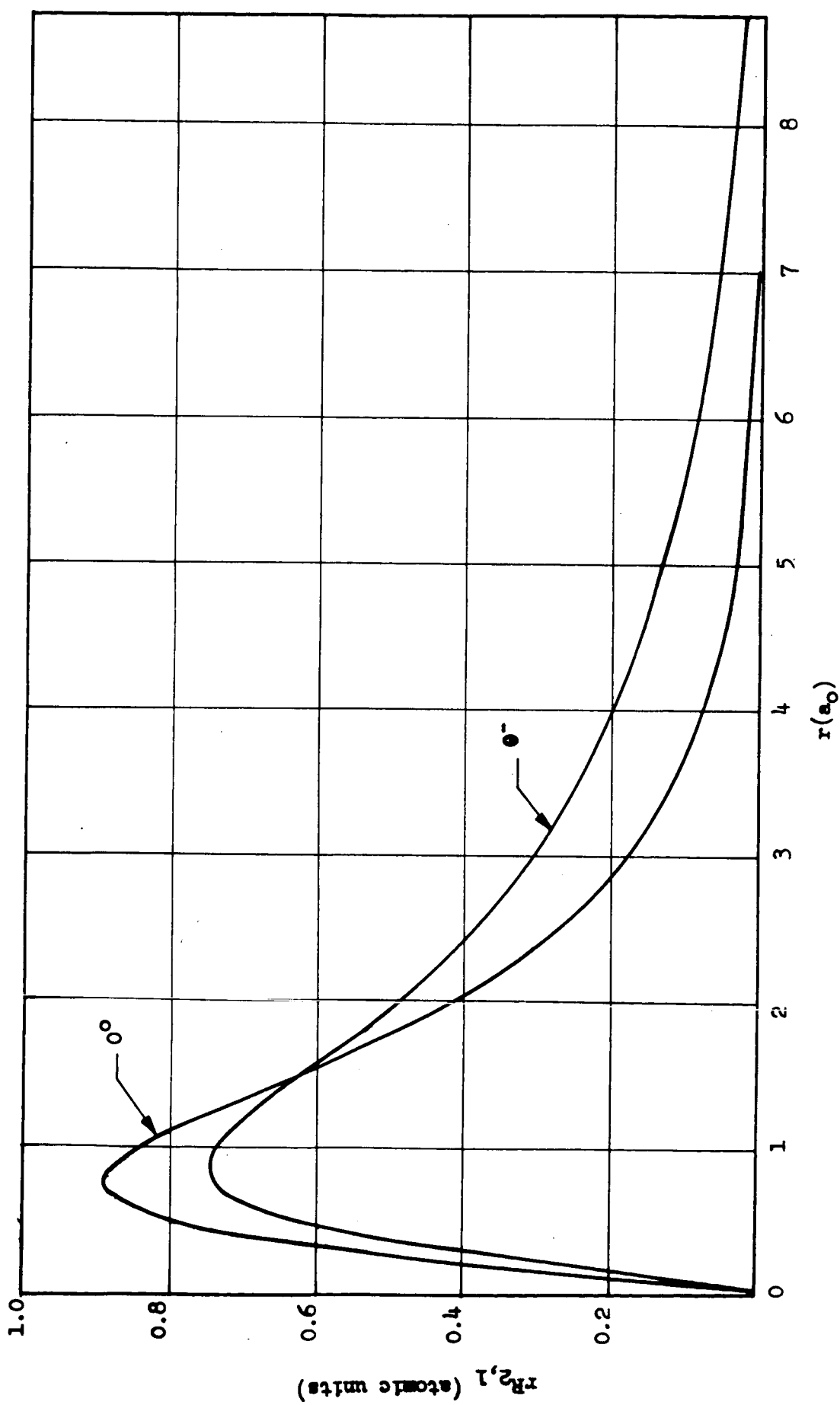$$\int_0^\infty P_{2p}^f\ P_{2p}^i\ dr = 0.9575. \quad (4.8)$$

Figure 2   2P bound state radial wave functions for the neutral oxygen atom and the negative atomic oxygen ion.

CHAPTER V

CONTINUUM WAVE FUNCTIONS

1. Introduction

The free wave radial equations for the outgoing electron of energy k^2 must be evaluated at various energies and used in equation (2.26) to evaluate the M_ℓ's used in obtaining the photodetachment cross section, equation (2.28). Since a 2p electron is detached, then this electron must have an angular momentum quantum number of $\ell = 0$ or $\ell = 2$ corresponding to an s or d wave, respectively. The shape of these functions, particularly the s waves, is very sensitive to the potential function used in the calculations. The s-state scattering is the major contributor to the cross section at relatively low energies. Thus, because of the absence of the centrifugal potential, the total interaction potential which includes the polarization potential strongly affects the scattering phase shift (δ_s) which in turn affects both the magnitude and spectral dependence of the cross section. The interaction potential acting on the detached electron is taken to be the potential obtained from the modified Hartree-Fock-Slater method for the ion plus the polarization potential calculated in Chapter III.

This chapter will duscuss the method of obtaining the free wave solutions, the normalization procedure used, the calculation of the phase shifts which are used to calculate the scattering cross section of neutral oxygen and list some of the typical results.

2. Method of Solution

In this formulation the problem is to determine the radial functions which satisfy the Schrödinger radial equation

$$\left[\frac{d^2}{dr^2} + V(r) + V_p(r) - \frac{\ell(\ell+1)}{r^2} + k^2\right] P_{k\ell}(r) = 0, \qquad (5.1)$$

where $P_{k\ell}(r) = rR_{k\ell}(r)$ and which have the asymptotic form

$$P_{k\ell}(r) \xrightarrow[kr \to \infty]{} k^{-1} \sin(kr - \frac{\ell\pi}{2} + \delta_\ell). \qquad (5.2)$$

For a given partial wave, equation (5.1) is solved by the Numerov process for various values of the energy k^2 over the same coordinate mesh as that of the Hartree–Fock–Slater program which furnished the unperturbed bound functions. The arbitrary constant used in the starting series expansion was adjusted to give the correct asymptotic behavior at large values of kr, equation (5.2). The numerical integration was continued until the ratio $V_T/k^2 \leq 10^{-4}$ at $r = R_o$ was reached, where V_T is the total potential. At this point the absence of a scattering potential was assumed and the solutions of equation (5.1) may be obtained analytically subject to the boundary condition (5.2) and by joining the numerical solution with the analytical at R_o.

3. Method of Normalization

In the region where the scattering potential is taken to vanish, the radial equation (5.1) can be written

$$\left[\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} + k^2\right] P_{k\ell}(r) = 0. \qquad (5.3)$$

By making the change in variables $X = kr$ and $Y = X^{-1/2}P$, equation (5.3) can be transformed into the familiar Bessel's equation

$$X^2 Y'' + XY' + \left[X^2 - (\ell+\frac{1}{2})^2\right] Y = 0, \qquad (5.4)$$

which has the general solution

$$Y = AJ_{\ell+1/2}(x) + BJ_{-\ell-1/2}(x), \qquad (5.5)$$

where the J's are half-odd order Bessel functions. Transforming this equation back to the variables kr and $P_{k\ell}(r)$, it becomes

$$P_{k\ell}(r) = A\sqrt{kr}\, J_{\ell+1/2}(kr) + B\sqrt{kr}\, J_{-\ell-1/2}(kr). \tag{5.6}$$

For the photodetachment process, the s and d waves are of interest. These half-odd order functions are listed below.

ℓ	$\sqrt{\dfrac{\pi x}{2}}\, J_{\ell+1/2}(x)$	$\sqrt{\dfrac{\pi x}{2}}\, J_{-\ell-1/2}(x)$
0	$\sin x$	$\cos x$
2	$\left(\dfrac{3}{x^2} - 1\right)\sin x - \left(\dfrac{3}{x}\right)\cos x$	$\left(\dfrac{3}{x}\right)\sin x + \left(\dfrac{3}{x^2} - 1\right)\cos x$

The s and d wave solutions of equation (5.3) may now be written

$$P_{sk} = A_s \sin(kr) + B_s \cos(kr), \tag{5.7a}$$

or

$$P_{sk} = C_s \sin(kr + \delta_s), \tag{5.7b}$$

and

$$P_{dk} = A_d \left\{ \left[\frac{3}{(kr)^2} - 1\right] \sin kr - \frac{3}{kr}\cos kr \right\} + B_d \left\{ \left[\frac{3}{(kr)^2} - 1\right] \cos kr + \frac{3}{kr}\sin kr \right\} \tag{5.8a}$$

or

$$P_{dk} = C_d \left\{ \left[\frac{3}{(kr)^2} - 1\right] \sin(kr + \delta_d) - \frac{3}{kr}\cos(kr + \delta_d) \right\}, \tag{5.8b}$$

where

$$C_i = (A_i^2 + B_i^2)^{1/2} \quad \text{and} \quad \tan\delta_i = B_i/A_i.$$

Note that each of the equations (5.7b) and (5.8b) have the asymptotic behavior

$$P_{k\ell}(r) \xrightarrow[kr \to \infty]{} k^{-1}\sin\left(kr - \frac{\ell\pi}{2} + \delta_\ell\right),$$

where each of the coefficients C are chosen as k^{-1}. The normalization and determination of the phase shifts are now easily accomplished by numerically integrating equation (5.1) until the scattering potential vanishes and then utilizing two points of the computed eigenfunctions, $P_{k\ell}(r_1)$ and $P_{k\ell}(r_2)$ in this region to determine the coefficients in equations (5.7a) and (5.8a). The normalized continuum functions P_η are now obtained from the unnormalized solutions P_u by the relationship

$$P_\eta = \frac{P_u}{k(A^2 + B^2)^{1/2}}, \tag{5.9}$$

and the phase shifts from the relationship

$$\delta = \tan^{-1} B/A, \tag{5.10}$$

at each of the various energies for the desired partial wave. This method guarantees the correct normalization and is advantageous in that the numerical integration need not extend beyond a prescribed point since numerical errors can accumulate.

4. Results

The phase shifts for several of the partial waves at various electron energies are tabulated in Table II. Figures 3 and 4 show typical s and d free waves at two values of the energy k^2 of the outgoing electron. The total potential function $V(r) + V_p(r)$ used in the calculations is shown in Figure 5.

TABLE II

Phase Shifts for the Continuum Wave

| E(Ry)	L = 0	L = 1	L = 2	L = 3	L = 4	L = 5	L = 6	L = 7	L = 8	L = 9	L = 10
.00025	.046										
.00050	.064	.001									
.0010	.087	.001									
.0030	.135	.005									
.0075	.174	.013	.001								
.010	.182	.018	.002	-.001							
.020	.180	.039	.005	.001							
.030	.157	.058	.008	.002	.001						
.050	.099	.089	.018	.004	.001	.001					
.065	.055	.104	.026	.005	.002	.001	.001				
.10	-.038	.122	.048	.011	.003	.001	.001	.001			
.20	-.237	.112	.104	.033	.012	.004	.002	.001	.001	.001	
.35	-.449	.068	.180	.058	.028	.013	.005	.003	.002	.001	.001
.50	-.628	-.004	.242	.079	.038	.022	.012	.005	.003	.002	.001
.75	-.842	-.096	.354	.114	.054	.030	.019	.012	.007	.003	.002
1.00	-1.010	-.174	.457	.147	.069	.039	.024	.016	.011	.007	.004
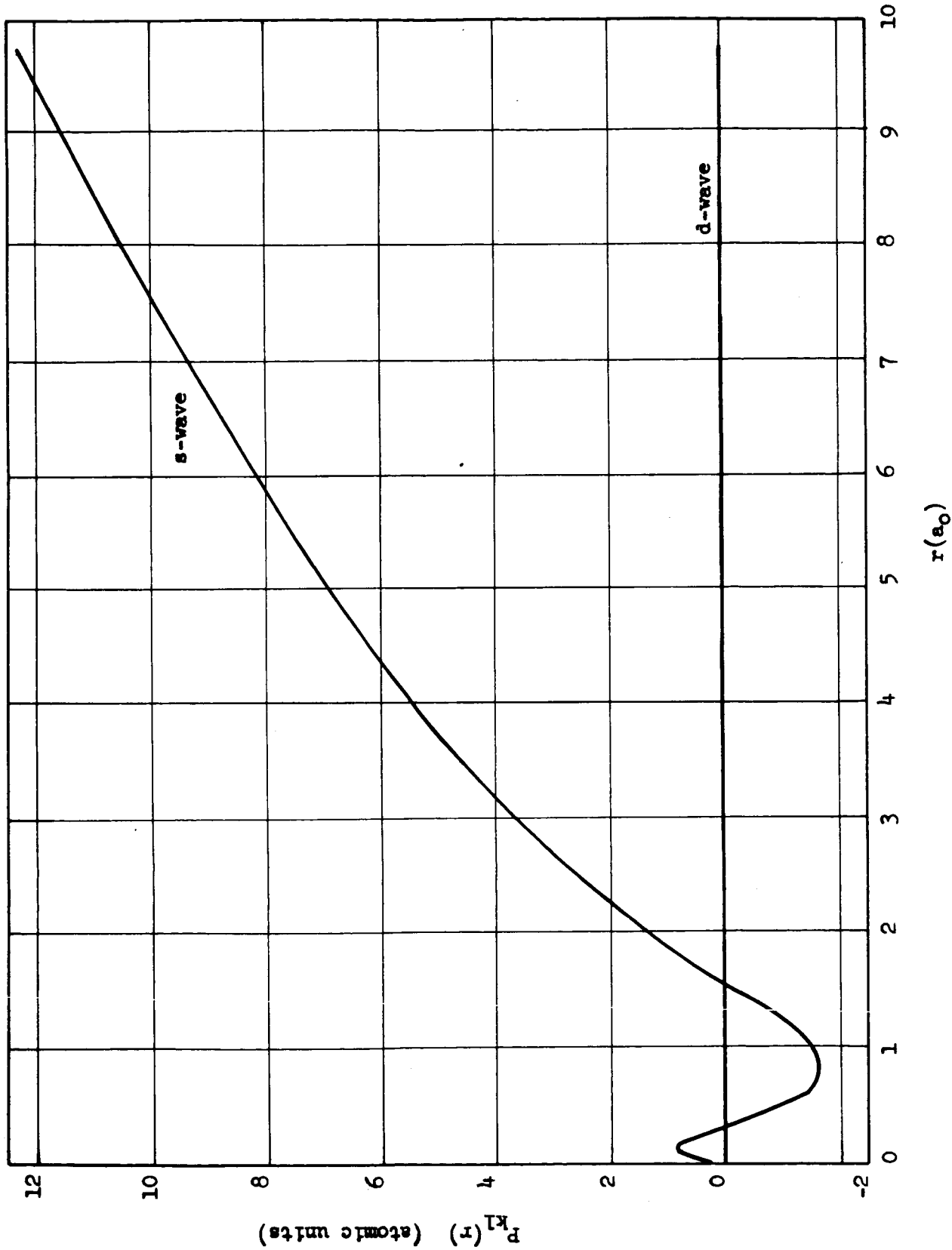
Figure 3   Free electron radial wave functions for the s and d
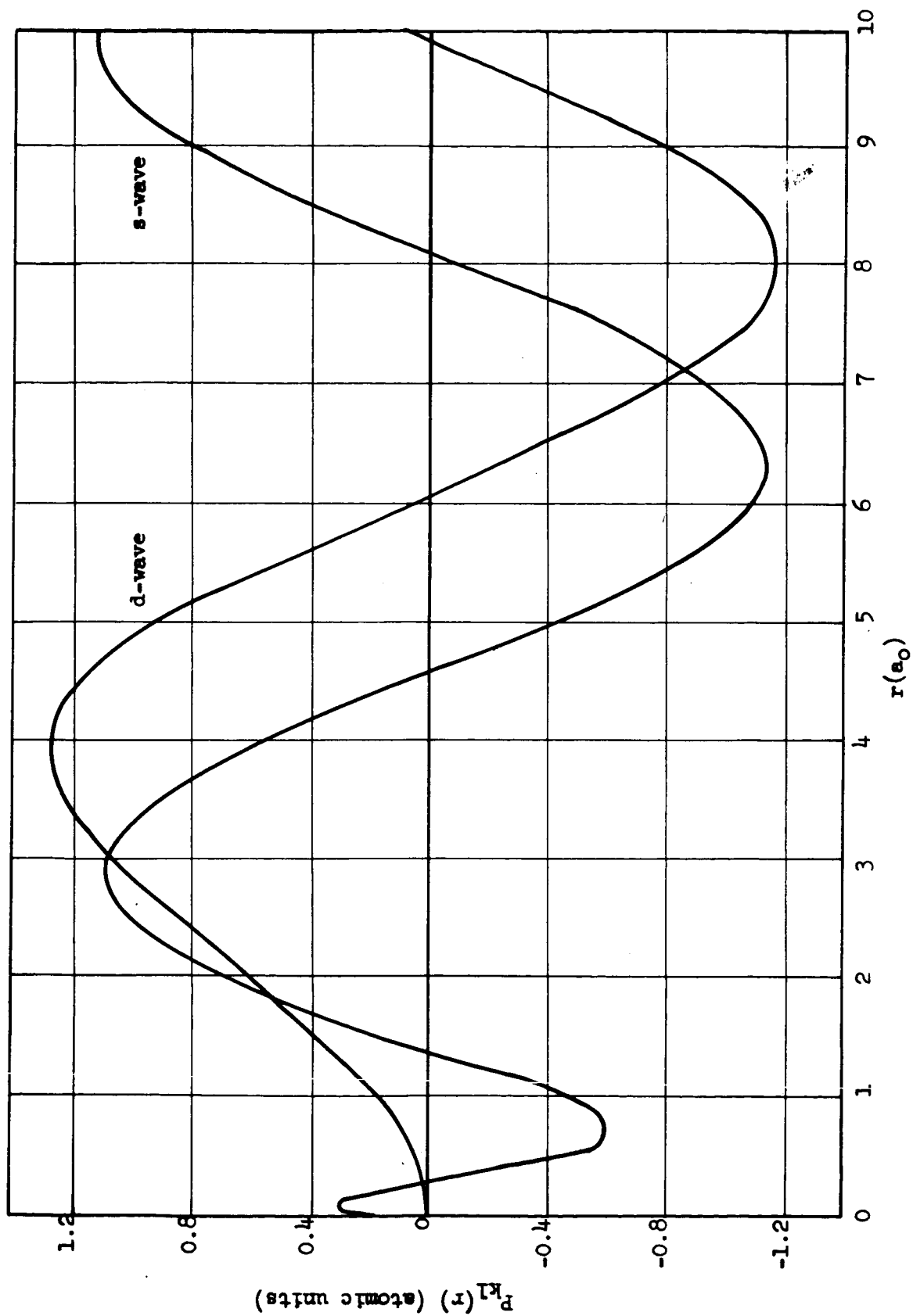waves, $E_e = 0.0004$ Ry

Figure 4   Free electron radial wave functions for the s and d waves, $E_e = 0.7743$ Ry
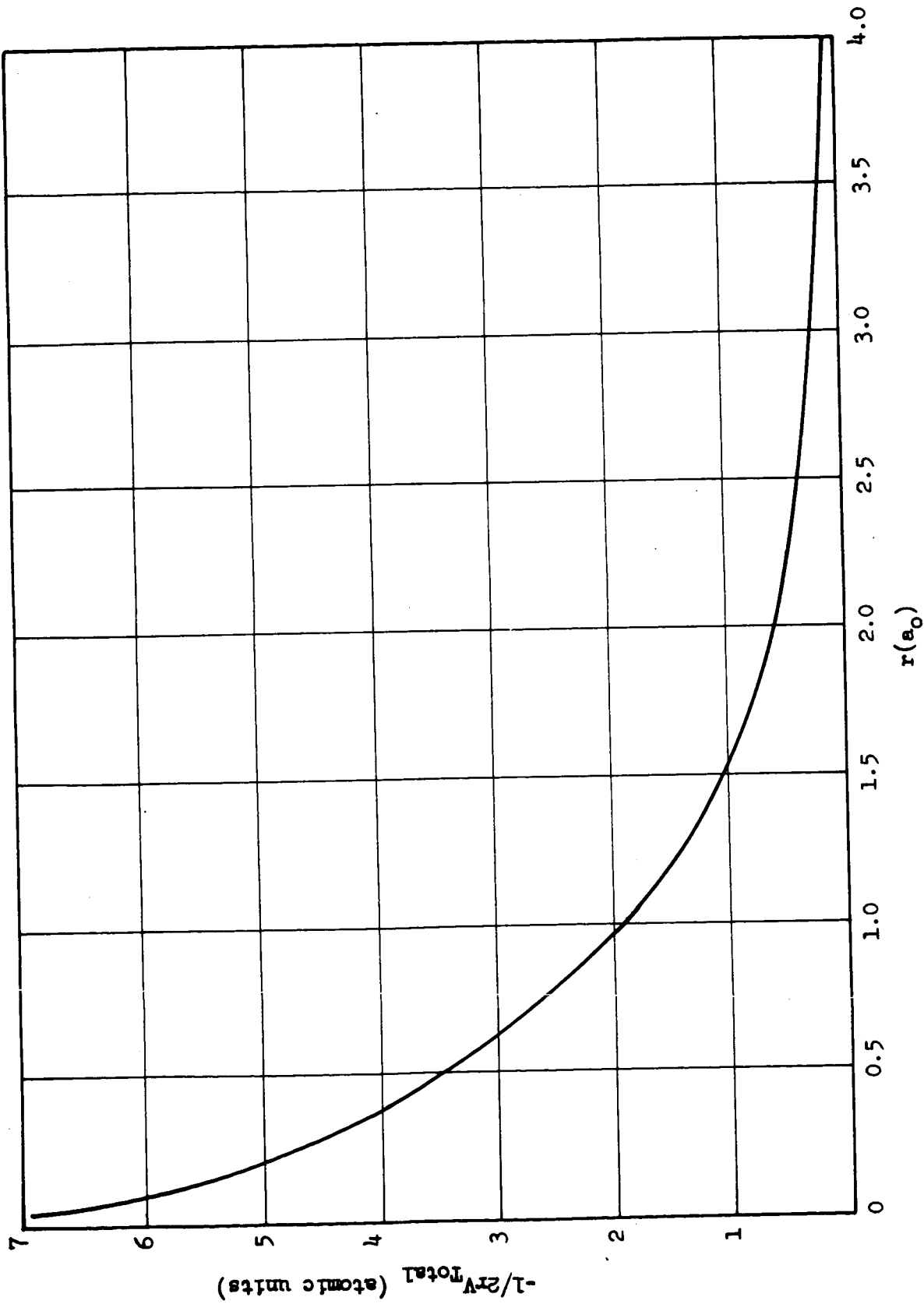
Figure 5   The total potential function for the oxygen atom (Hartree - Fock - Slater + polarization).

CHAPTER VI

RESULTS

1. Photodetachment Cross Section

The results of the photodetachment cross section calculations are shown in Figure 6 along with the experimental results of Branscomb, Smith and Tisone[8] and Smith.[9] It should be pointed out that the results of the crossed-beam experiment of Reference 8 at the higher energies should be eyed with caution since photoelectric effects from the walls of the instrumentation make calibration difficult above 3.7 ev.[8]

At higher photon energies the oxygen atom may be left in the excited ^1D or ^1S states of the ground "configuration." Using the appropriate values of the binding energy E_b and the C_ℓ's in Table I, estimates of the cross section are obtained by performing the same set of calculations that leave the atom in its ^3P ground state. These results are plotted in Figure 7 where the results of this paper are compared with the theoretical results of Cooper and Martin.[4]

The method of Klein and Brueckner assumes that the d-wave shifts are small and may be considered zero in the energy range of their investigation. They thus use the Born approximation, equation (5.8b) with $\delta_d = 0$, for the continuum d-wave. They also define a range of interaction R and consider the integrals in equation (2.26) to be zero for $r < R$ ($R = 3a_o$). Outside this region the bound-state wave function is taken to be the tail of the radial wave function.

$$R_{2p} = \frac{Ne^{-E_b^{1/2}r}}{r}\left[1 + \frac{1}{E_b^{1/2}r}\right],\qquad(6.1)$$
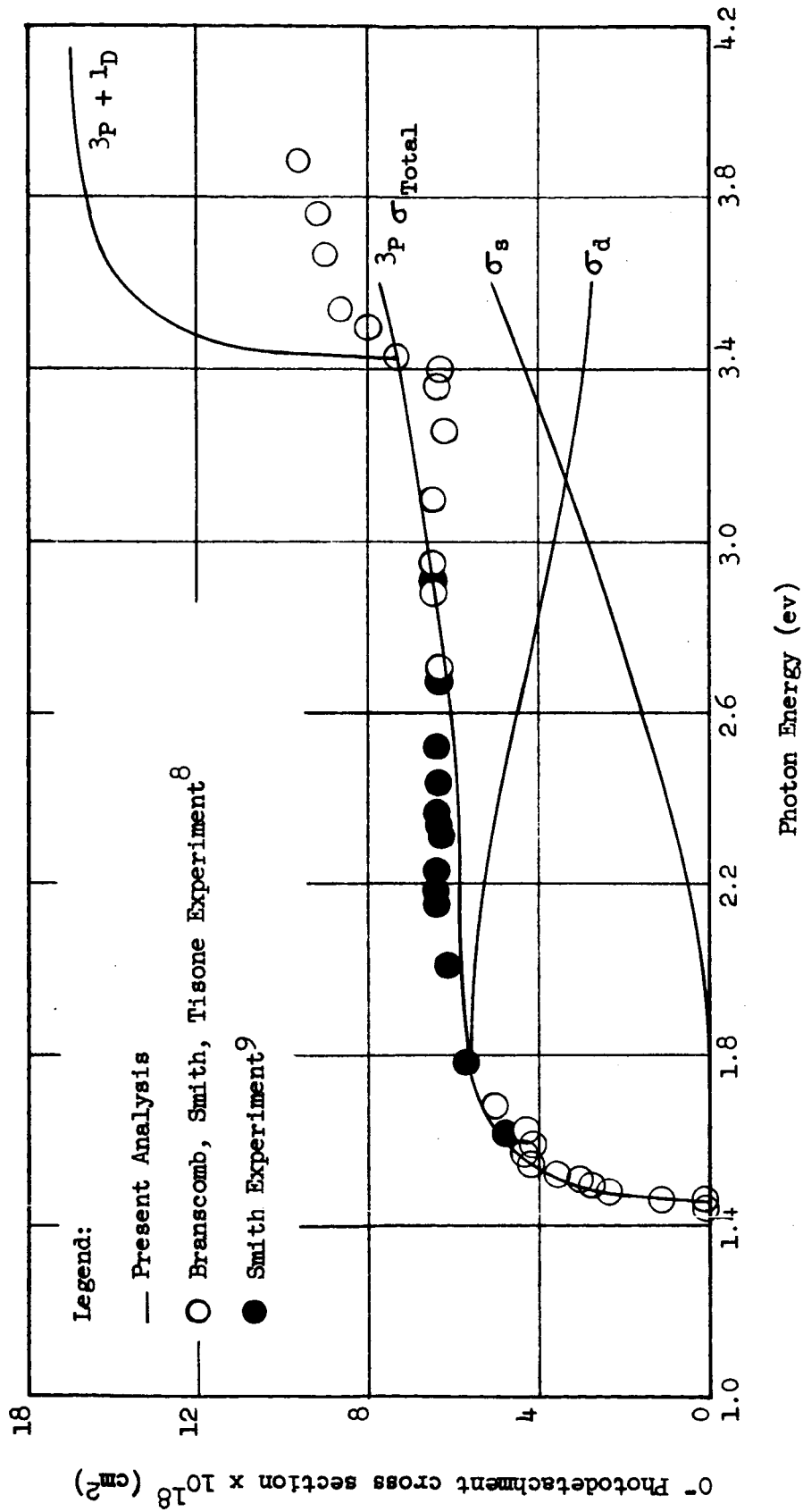
where N is the normalization constant.

Figure 6   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.
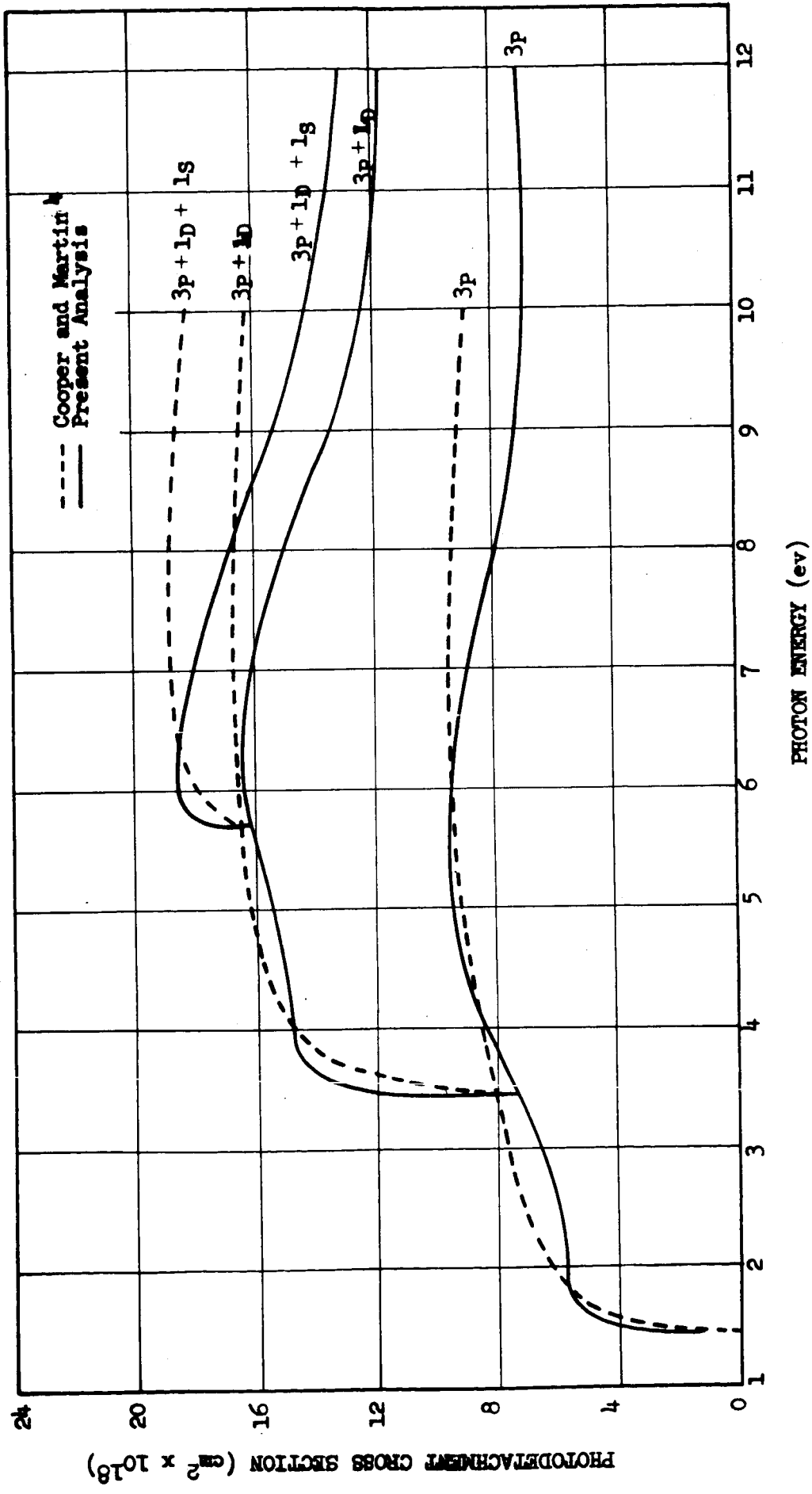
Figure 7 Photodetachment cross section for the various final state
configurations compared with the calculations of Cooper and Martin.

Schrödinger's radial equation with a polarization potential of the form

$$V_p = -\frac{1}{2}\frac{P}{(r^2 + r_p^2)^2},$$ (6.2)

was used to calculate R_{2p} out to $r = R$. In equation (6.2) r_p is the screening distance (1.2 atomic units) and P is the polarization parameter which included exchange effects. P was varied until a good fit was obtained. This procedure gave a value of $P = 5.589$ atomic units and $N = 0.374$. Numerical calculations of the free s-waves were then made for a few energies and fitted to the effective-range formula

$$k \cot \delta_s = -\frac{1}{a} + \frac{1}{2}r_o k^2.$$ (6.3)

The effective-range (r_o) and scattering-length (a) were found to be 0.860 and 0.613 atomic units respectively. From this the value of δ_s at other energies was computed. Knowing the phase shifts and using the asymptotic forms of the free and bound states, a closed form solution for the photodetachment cross section was then derived.

Cooper and Martin's method follows along the same lines with the exception of not using the asymptotic approximations previously mentioned. Schrödinger's equation for the bound state was solved treating the polarization parameter as an eigenvalue. The binding energy was assumed known. The equation was integrated out to approximately $20a_o$ and the polarization parameter adjusted until the function approached zero asymptotically. This gave a value of 5.499 for $r_p = 1.2$. Numerical integrations were then performed to calculate the free s-states, bound state and s-wave phase shifts. The d-wave phase shifts were also taken as zero in thie formulation.

The average value of these two polarization parameters was used to compute the polarization potential for these models. The results are shown in Figure 8. The results of this paper are compared with those of Cooper and Martin, and Klein and Brueckner in Figure 9.
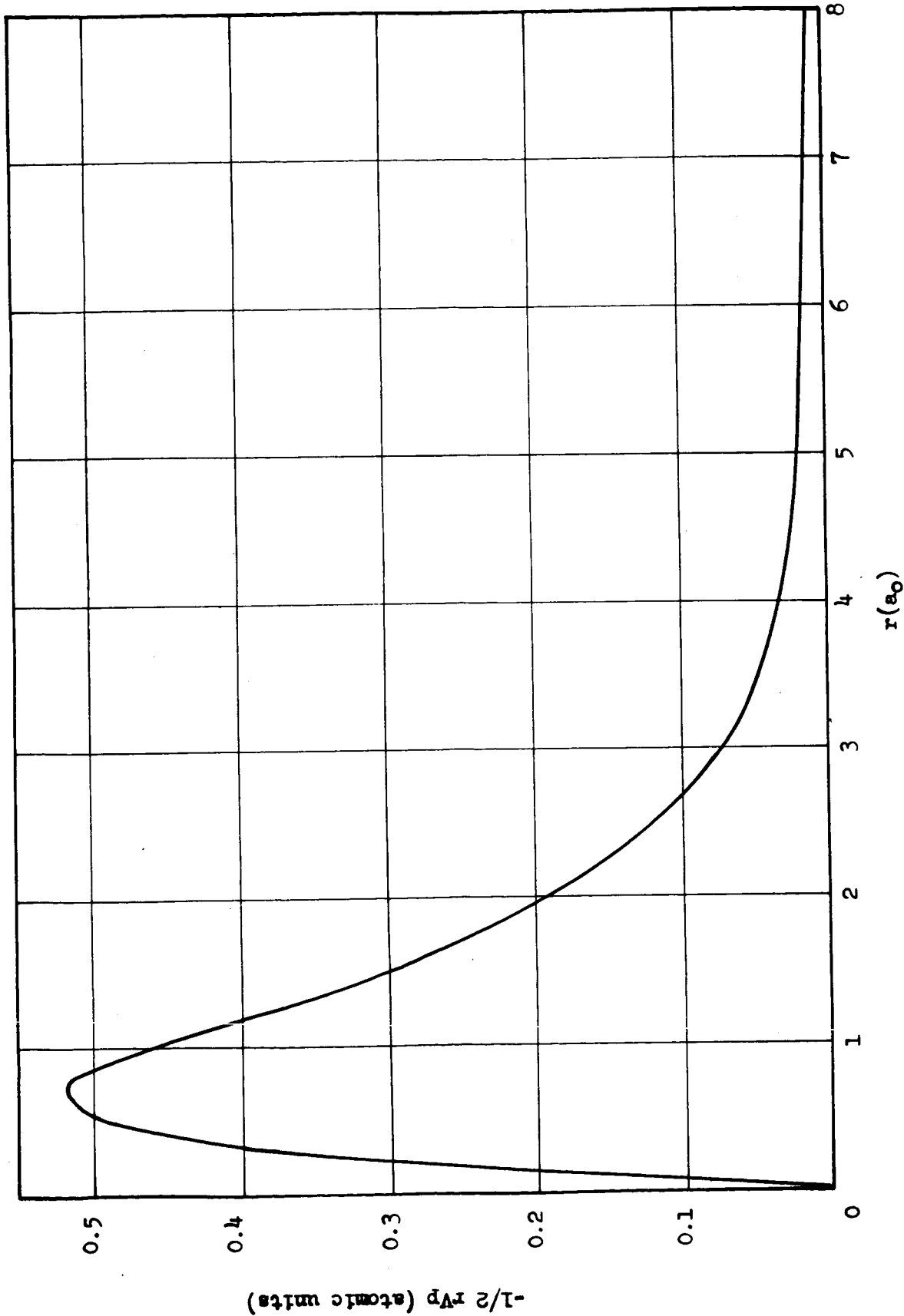
Figure 8   Polarization potential calculated from method of Klein and
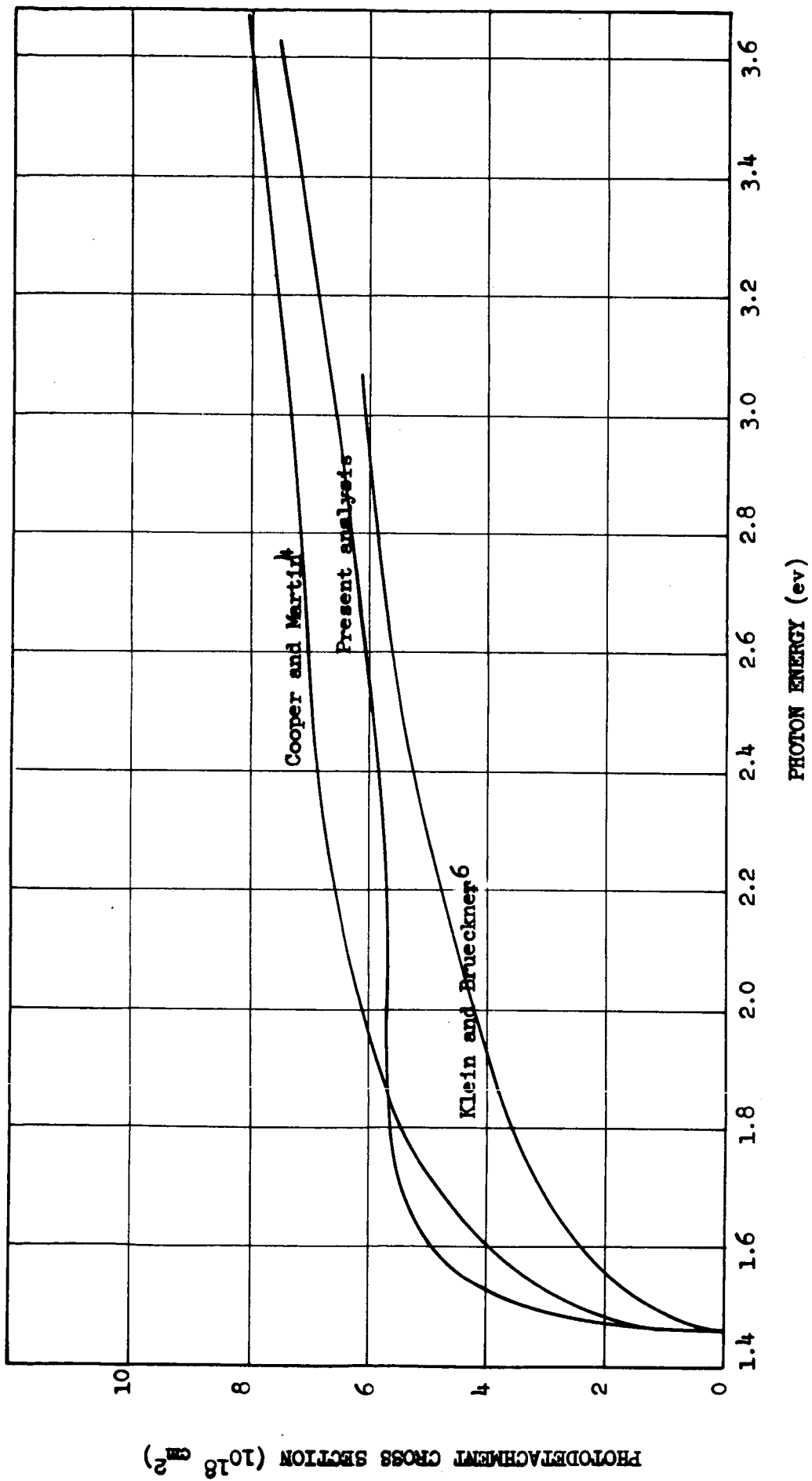Brueckner, and Cooper and Martin using the average value of
their polarizabilities.

Figure 9   Comparison of total photodetachment cross section with other theoretical results.

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2. Scattering Cross Section for Oxygen

The elastic scattering of electrons by oxygen is calculated by the method of phase shifts and compared to various other available data. The phase shifts are tabulated in Table II. In units of πa_o^2, the scattering cross section is

$$\sigma = \frac{4}{k^2} \sum_\ell (2\ell + 1) \sin^2 \delta_\ell. \qquad (6.4)$$

A detailed discussion of the various available results would be out of place in this paper. A comprehensive study to attempt to determine the latest reliable data over the energy range shown in Figure 10 was not undertaken for this paper and only the results shown in this plot were immediately available for comparative purposes. However, at the higher energies agreement with the experiment of Neynaber, Marino, Rothe, and Trujillo[23] is relatively good as well as the single point of Lin and Kivel[24] at the low energy portion of the curve. Figure 10 also shows the theoretical results of other authors.[4,6,10,25-27] Each of these contains the s and p wave contributions as explained by Neynaber, et al.[23]

3. Electron Affinity Calculations

The reverse process of photodetachment is the capture of a free electron by a neutral atom and the emission of radiation. By following an argument very similar to that outlined in Chapter II the attachment cross section for the above process may be derived. If this is carried through the photodetachment cross section and the cross section for attachment are related by the following expression[28]

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

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

[25] P. Hammerling, W. W. Shine, and B. Kivel, J. Appl. Phys. 28, 760 (1957).

[26] L. B. Robinson, Phys. Rev. 105, 922 (1957).

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

[28] R. S. Berry, J. C. Mackie, R. L. Taylor and R. Lynch, Spin-Orbit Coupling and Electron Affinity Determination From Radiative Capture of Electrons by Oxygen Atoms. Research Report 216, AVCO-Everett Research Laboratory, July 1965.
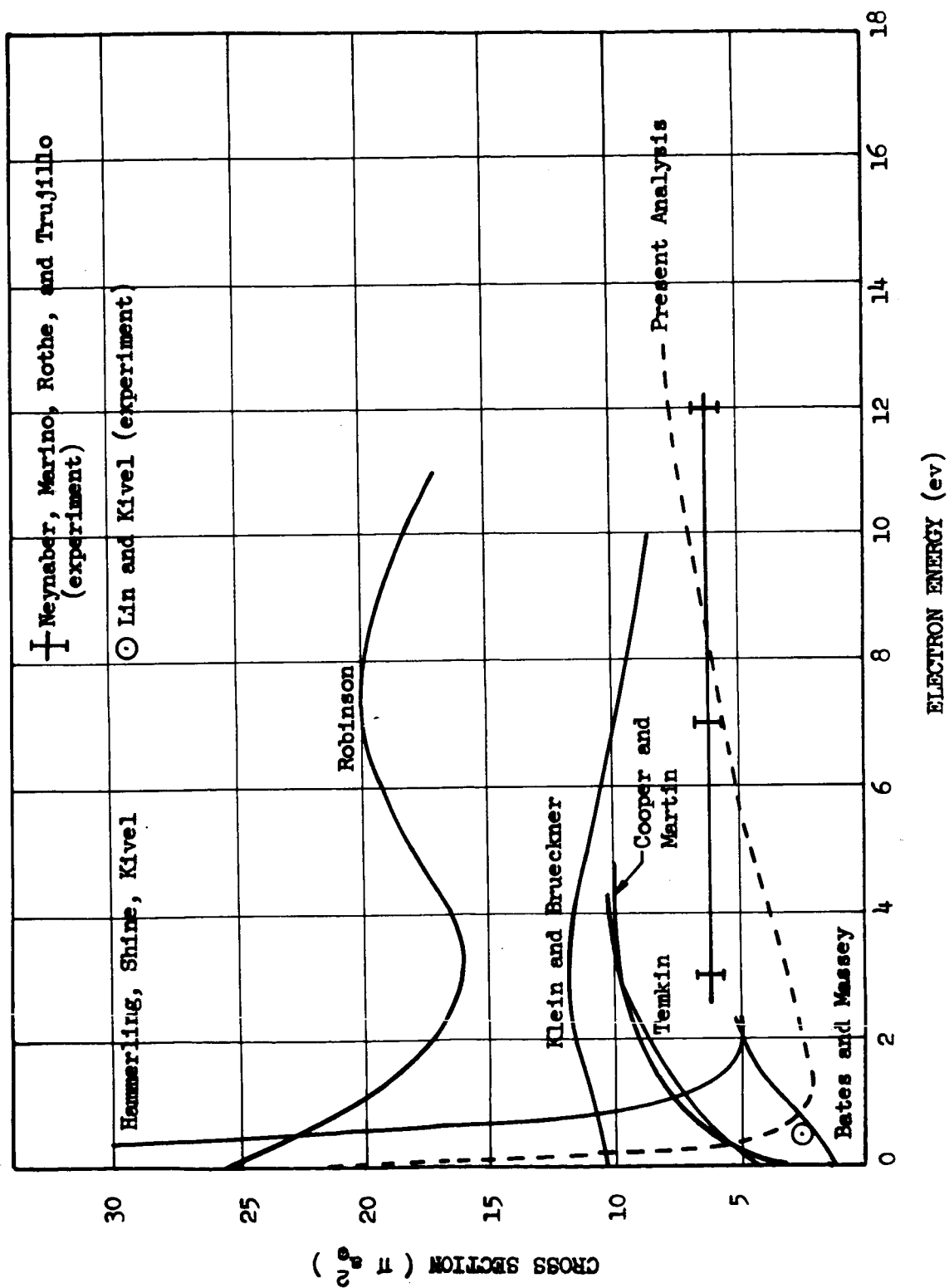
Figure 10   Scattering cross sections for oxygen

$$\sigma_{PD} = 3mc^2 \frac{E_e}{E_b^2} \sigma_A.$$

<div align="right">(6.5)</div>

In studying the emission of radiation from the above process, the rate of emission of energy $h\nu$ per unit of frequency is

$$I(\nu)/h\nu = \sigma_A V_e \, n(e) \, n(O^o) \, \rho_e,$$

<div align="right">(6.6)</div>

where $n(e)$ is the concentration of electrons, $n(O^o)$ the concentration of absorbers and ρ_e is the energy distribution of the electrons. The quantity $\sigma_A V_e$ is called the attachment coefficient and is of interest in practical applications. This coefficient, σ_A, and the absorption cross section have been computed from the previous results and are shown in Figures 11 and 12 and compared with results given by Bates.[29]

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[29]D. R. Bates (ed.) <u>Atomic and Molecular Processes</u>, Academic Press, New York, 1962, pp. 132-133.
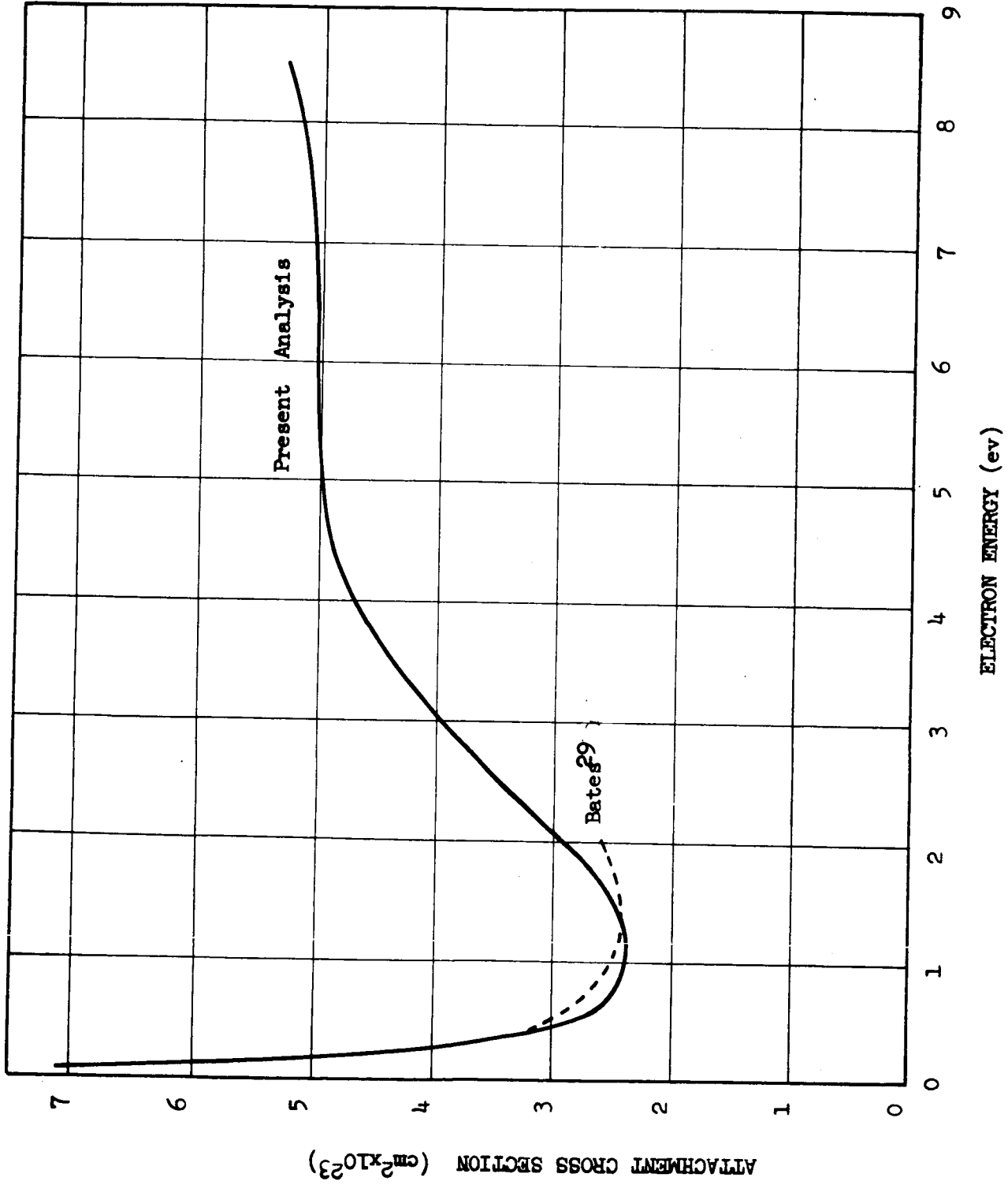
Figure 11   Attachment cross section of electrons to atomic oxygen
             calculated by detailed balancing from the photodetachment
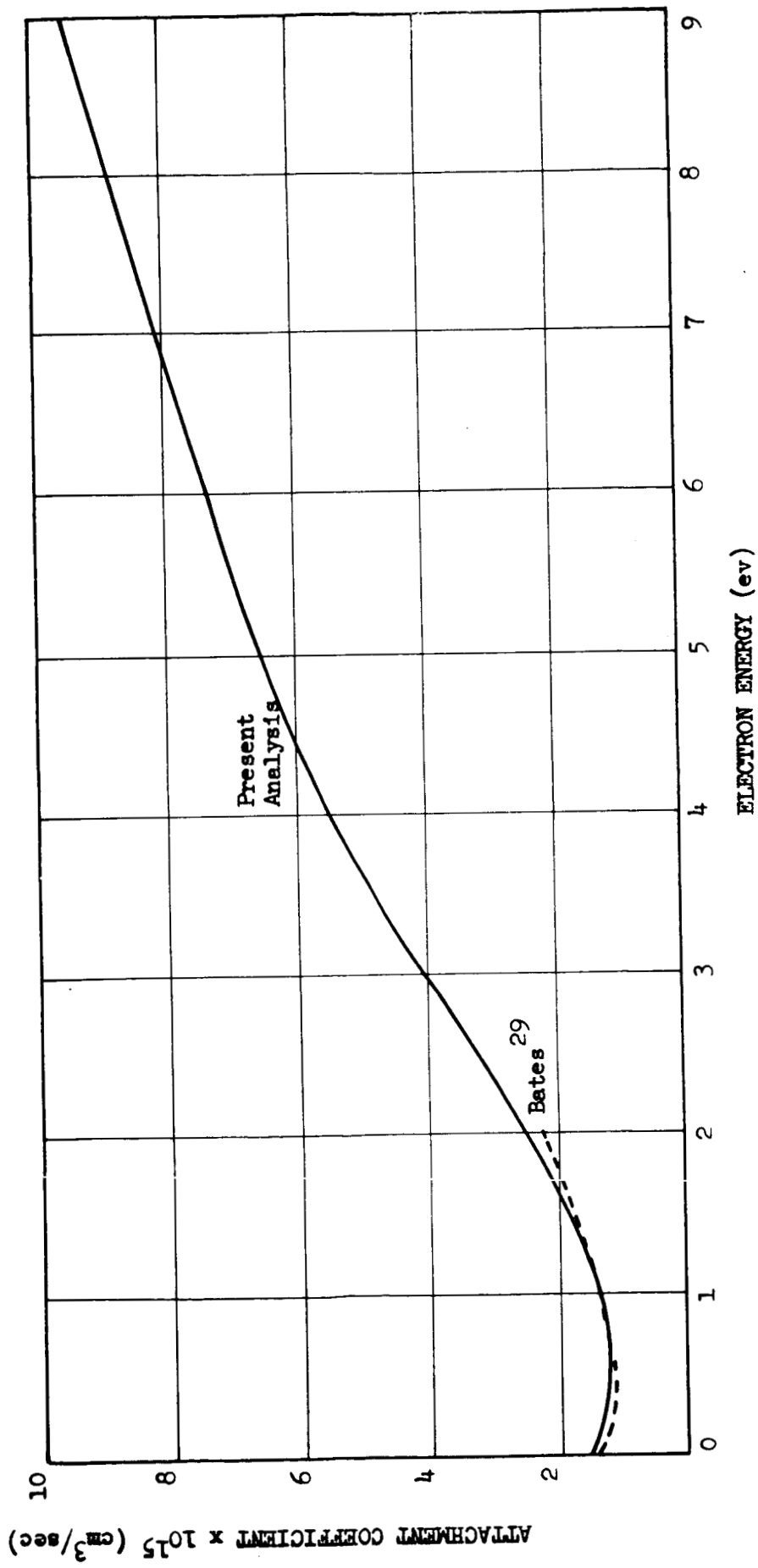   cross section.

Figure 12 Variation of attachment coefficient with electron energy for electron capture by the neutral oxygen atom.

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CHAPTER VII

CONCLUSIONS

The excellent agreement of the present results with the experimental photo-detachment data of References 8 and 9 in the region up to photon energies of 3.4 ev argues favorably for the validity of the present model. This coupled with the agreement of the scattering cross section at higher energies and the additional fact that the polarizability calculations agree so well with experiment is indeed firm confirmation for the validity of the present work.

TABLE III

Photodetachment Cross Section

$h\nu$ (ev)	^3P	^1D	$h\nu$ (ev)	^3P	^1D	^1S
1.47	1.36		3.47		4.36	
1.48	2.26		3.50		5.24	
1.49	2.82		3.55		5.98	
1.50	3.23		3.60		6.33	
1.55	4.39		3.70		6.54	
1.60	4.94		3.80		6.50	
1.65	5.25		3.90		6.39	
1.70	5.43		4.00	8.38	6.27	
1.75	5.55		4.50		5.92	
1.80	5.62		5.00	9.45	6.11	
1.85	5.67		5.50		6.55	
1.90	5.70		5.67			0.80
1.95	5.71		5.68			1.09
2.00	5.73		5.69			1.29
2.10	5.75		5.70			1.43
2.20	5.78		5.75			1.83
2.30	5.83		5.80			2.00
2.40	5.89		5.85			2.07
2.50	5.97		5.90			2.09
2.60	6.07		6.00	9.42	6.97	2.08
2.70	6.18		6.50			1.83
2.80	6.31		7.00		7.32	1.75
2.90	6.46		7.50		7.32	1.80
3.00	6.62		8.00	7.86	6.94	1.88
3.10	6.79		8.50			1.94
3.20	6.96		9.00		6.18	1.94
3.30	7.14		10.00	6.92	5.42	1.82
3.43	7.38		11.00		4.89	1.60
3.44		2.44	12.00	7.00	4.60	1.37
3.45		3.31				

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