statistical errors for w are approximately $\pm 2\%$. These errors, as seen from Table I, would not change appreciably the values quoted above for ϵ_1 and A. However, the significance of the consistency between the results of the beam experiment and the present swarm experiment is closely related to the validity of the electron energy distribution function used in the analysis of the swarm experiment. In support of the distribution function, we note that Bowe[13] has shown that for Ar the calculated distribution function gave values for the electron drift velocity which agree well with experiment.

The present method of analysis of the swarm data in terms of a strongly peaked function for the cross sections does not provide a unique assignment of the width of the capture region, e.g., in Table I it is seen that a solution to Eq. (5) could be expressed in terms of the sum of three strongly peaked functions taken at 6.3, 6.4, and 6.5 ev. This would, however, leave unchanged the peak energy and the magnitude of the total cross-section integral A. It is likely that the true width of the capture region is less than that reported by Buchel'nikova. Unfortunately, the potential energy curves[15] for H_2O are not well established; therefore, the width of the capture region cannot be realistically estimated.[16]

A further consistency check using the electron energy distribution functions in argon was made by comparing the swarm results for electron capture in Ar-O_2 mixtures reported in reference 7 with the beam experiment reported in reference 6. Even though the check involved only a small fraction of the total number of electrons in the high-energy tail, both the magnitude and the dependence of α (for O_2) on E/P were in very good agreement with the beam experiment.

In summary, we have found no evidence of internal inconsistency between the swarm experiments and the beam experiments for electron capture in both H_2O and O_2, provided that the swarm experiments are conducted in mixtures with argon for which the electron energy bistribution is established from independent considerations. This suggests the swarm method as a means of establishing the energy scale and absolute cross section for various electron capture reactions, provided that the swarm experiments are performed under conditions where good information is available on the electron energy distribution.

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Wave Functions for the Free Electron. II. The Inclusion of Polarization and Exchange*

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The effect of the polarization of the atomic core by the free electron on the free-electron wave function and the effect of the exchange of the free electron with the bound orbitals on this wave function are treated by perturbation theory. Polarization must be considered first. Its effect on the atomic charge cloud is introduced through an expansion over the bound wave functions for the atom in terms of the free-electron separation as a parameter. This parametric treatment of electron separation means we cannot accept the solution at small separations from the nucleus although this is not a serious restriction. From this wave function we obtain a polarized Coulomb potential from which a solution for the free-electron function may be obtained using our old programs. Having solved the free-electron wave equation with the exchange potential terms supposed zero, we use this solution to compute the exchange integrals. The equation including these integrals is then solved to obtain approximate wave functions for free electrons containing both exchange and polarization.

I. INTRODUCTION

IN a previous paper we have detailed the programs developed by us[1] for the determination of the wave function for an electron in the field of a neutral atom where the atom is supposed to give rise only to a Coulomb potential. In that paper we deliberately neglected the effects of (1) the polarization of the atomic charge cloud by the free electron and (2) the exchange of the free electron with the various bound electrons in the atomic charge cloud. In what is to follow we shall discuss the inclusion of these effects.

In recent years several methods for the inclusion of polarization and exchange have been used, and we shall touch briefly on a few of them. First we remark

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* Based on work performed under the auspices of the U. S. Air Force Ballistic Missiles Division.

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[1] R. G. Breene, Jr., and Maria C. Nardone, Phys. Rev. 115, 93 (1959).

the work of Kivel and his associates.[2] This author included exchange by means of a method introduced by Slater[3] for bound orbitals. This method hypothesizes a charge-free sphere about the electron in question, the charge from this region being redistributed throughout the system to effect the same energy change as would the straightforward introduction of exchange. Kivel found it necessary to adjust to other results for the hitherto untried free-electron exchange case. This same author introduced polarization through the Buckingham potential whose parameters were obtained by adjustment to conductivity experiments. Klein and Brueckner[4] determined the parameters in the Buckingham polarization potential for oxygen by adjusting to the binding energy of O^-.

Seaton[5] introduced the effects of exchange and polarization without an appeal to experiment for parameter determination by first supposing the function for the system, free electron plus bound atom, to be of the form:

$$\Psi=\sum_{n=1}^{n_0}\mathcal{A}\psi_n(i^{-1})\varphi_n(i),$$

in which the $\mathcal{A}$ is a specific antisymmetrizing operator; the ψ_n are the bound wave functions, and the φ_n are the free-electron wave functions. We remark that the expansion in individual functions is truncated for practicality, although the author compares the effects of such truncation. The specific point of importance to us in Seaton's further development is that he obtains equations for the determination of the bound orbitals with the polarization effect included in them in what we might consider zeroth order. Temkin[6] later objected to this truncation as leaving out important contributions to the wave function and suggested taking polarization into account by a sum of the following form:

$$\Psi=\varphi(1)[\Psi_0(2,\cdots,Z+1)+\Psi^{(\mathrm{pol})}(1,\cdots,Z+1)],$$

wherein the chief concern is with the construction of the function $\Psi^{(\mathrm{pol})}$. Here, too, the individual bound orbitals are considered as polarized in zeroth order.

Mittleman and Watson[7] and Lippmann *et al.*[8] have developed descriptions of the system, free electron plus atom, which involve an expansion in terms of incoherent scattering processes, the adiabatic case corresponding to the first term in such an expansion. We shall only consider the adiabatic case for the relatively slow electrons of our interest. Finally, we mention the review by Allen[9] of Hartree-Fock equations containing a perturbing electric field. Additional work concerned with zeroth-order solutions including polarization effects is described therein.

All the methods discussed above may well be superior to the work which we shall discuss, but they will not suit our purpose. Basically, our intent is to include the effects of polarization and exchange through modification of our atomic and free-electron wave functions rather than through recalculation. In what follows we detail our method of doing this.

II. INCLUSION OF POLARIZATION AND EXCHANGE

In a general way the means of our inclusion of the effects of polarization will be ordinary perturbation theory, while the inclusion of exchange will appeal to an iterative procedure. We begin with the form of our wave function which is to describe a system composed of a neutral atom of Z electrons and the free electron. We choose an antisymmetric product as follows:

$$\Psi_n^{(0)}=\frac{1}{[(Z+1)!]^{\frac{1}{2}}}P\prod_{i=1}^{Z}\psi_{in}^{(0)}\varphi_e, \tag{1}$$

wherein P is the permutation operator; ψ_i are the bound orbitals, and φ_e is the free electron wave function. Our first-order wave function will be

$$\Psi^{(1)}=\frac{1}{[(Z+1)!]^{\frac{1}{2}}}\sum_n a_nP\prod_{i=1}^{Z}\psi_{in}^{(0)}\varphi_e, \tag{2}$$

where it is to be remarked that we expand only over those states arising from different bound orbitals. To this we add the further restriction on Eq. (2), namely, only those $\Psi_n^{(0)}$ are included for which but one orbital is different from the set of ground-state orbitals. For our purposes this will pose no serious restriction.

The Coulomb Hamiltonian for the system in atomic units is

$$H=\sum_{i=1}^{Z+1}H_{ci}+\sum_{i>j=1}^{Z}\frac{1}{r_{ij}}+\sum_{i=1}^{Z}\frac{1}{r_{i,\,Z+1}}, \tag{3a}$$

$$H_{ci}=-\frac{1}{2}\nabla_i^2-\frac{Z}{r_i}. \tag{3b}$$

The first two terms in the Hamiltonian of Eq. (3a) are, according to our viewpoint, of zeroth order. The third term will be broken up into terms of zeroth and first order at a later stage in the development.

We wish to make use of the atomic wave functions available from our earlier programs.[10] This means we

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[2] P. Hammerling, W. W. Shine, and B. Kivel. J. Appl. Phys. **28**, 760 (1957); S. C. Lin and B. Kivel. Phys. Rev. **114**, 1026 (1959); B. Kivel, Phys. Rev. **116**, 1484 (1959); **116**, 926 (1959).

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[6] A. Temkin, Phys. Rev. **116**, 358 (1959); **107**, 1004 (1957).

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[8] B. A. Lippmann, M. H. Mittleman, and K. M. Watson, Phys. Rev. **116**, 920 (1959).

[9] L. C. Allen, Phys. Rev. **118**, 167 (1960).

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must require that

$$H_c\psi_k^{(0)}+\sum_{j>i=1}^{Z}\frac{\psi_k^{(0)}}{r_{ij}}-E_a^{(0)}\psi_k^{(0)}=0, \tag{4}$$

where we suppose our analytic wave functions solutions to Eq. (4). The Schrödinger equation is set up and we multiply through on the left by $\prod_{i=1}{}^{Z}\psi_{i0}^{(0)}$ and integrate to obtain

$$\int\prod_{i=1}^{Z}\psi_{i0}^{(0)}[H-E]\Psi d\tau=0, \tag{5a}$$

where:

$$E=E^{(0)}+\lambda E^{(1)}=E_a^{(0)}+E_e^{(0)}+\lambda E^{(1)}, \tag{5b}$$

$$\Psi=\Psi^{(0)}+\lambda\Psi^{(1)}. \tag{5c}$$

Equation (5a) separates into zeroth-, first-, and higher-order terms in the normal fashion for all portion of H. However, after removing our defining Eq. (4) from the zeroth-order result we are left with a term containing a bound orbital as follows:

$$\sum_{i=1}^{Z}\left[\int\frac{|\psi_{i0}^{(0)}|^2}{r_{i,\,Z+1}}d\tau\varphi_e-\int\frac{\Psi_{i0}^{(0)}\varphi_e}{r_{i,\,Z+1}}d\tau\psi_{i0}^{(0)}\right]. \tag{6}$$

If Eq. (4) is to be maintained, we must either (1) relegate this second term to first order or (2) declare it zero. It appears reasonable to consider the third term on the right of Eq. (3a) of mixed order for the following reasons: (1) We suppose the polarizing effect of the free electron on the neutral atom to be a perturbation which it certainly is both in type and magnitude of effect. This polarization must come from this third term, and hence we are justified in looking to this term for the first-order portion of the Hamiltonian. (2) On the other hand, if we treat this term as first-order insofar as the free electron is concerned we will have a completely unperturbed free electron described by a plane wave in zeroth order. This will not be very helpful, so we ask that a part of this third term in Eq. (3a) be of zeroth order.

The result of our considerations of the previous paragraph is the relegation of the second term in Eq. (6) to the first order. Therefore we obtain the following zeroth-order equation.

$$H_c\varphi_e-\sum_{i=1}^{Z}\int\Psi_{i0}^{(0)}[H_c-(E_a^{(0)}+E_e^{(0)})]\varphi_e d\tau\psi_{i0}^{(0)}+\sum_{i=1}^{Z}\int\frac{|\psi_{i0}^{(0)}|^2}{r_{i,\,Z+1}}d\tau\varphi_e=E_e^{(0)}\varphi_e. \tag{7}$$

We now make the following approximations: (1) The off-diagonal elements of H_c are of higher order and (2) the overlap of the bound and free wave functions are of higher order. The first is probably of little importance, and the second at most will restrict us to large separations from the nucleus. The result is the zeroth-order equation for the free electron which we have applied previously[1]:

$$H_c\varphi_e+\sum_{i=1}^{Z}\int\frac{|\psi_{i0}^{(0)}|^2}{r_{i,\,Z+1}}d\tau\varphi_e-E_e^{(0)}\varphi_e=0. \tag{8}$$

We now multiply the third term in Eq. (3a) on the right by $\Psi_0^{(0)}$ and on the left by $\prod'\Psi_{j0}^{(0)}\varphi_e$, where the product is taken over $j=1$ to Z and the prime indicates that the ith bound orbital has been left out of the product. The result is

$$\sum_{j=1}^{Z}\int\frac{|\psi_j^{(0)}|^2|\varphi_e|^2}{r_{je}}d\tau\psi_{i0}^{(0)}+\int\frac{|\varphi_e|^2}{r_{ie}}d\tau\psi_{i0}^{(0)}-\sum_{j=1}^{Z}{}'\int\frac{\bar{\psi}_{j0}^{(0)}(l)\psi_{i0}^{(0)}(l)|\varphi_e|^2}{r_{le}}d\tau\psi_{j0}^{(0)}-\int\frac{\bar{\varphi}_e\psi_{i0}^{(0)}}{r_{ie}}d\tau\varphi_e. \tag{9a}$$

We ignore the first and third terms in Eq. (9) as of higher order, and first consider the second term. If we again restrict ourselves to some distance from the nucleus, then a classical path[11] may be assumed:

$$\int\frac{|\varphi_e|^2}{r_{ie}}d\tau\psi_i\rightarrow\frac{1}{r_{ie}}\int|\varphi_e|^2d\tau\psi_i=\frac{1}{r_{ie}}\psi_i.$$

Now Eq. (9a) becomes

$$\frac{1}{r_{ie}}\psi_i-\int\frac{\bar{\varphi}_e\psi_i}{r_{ie}}d\tau\varphi_e, \tag{9b}$$

and the equations for the bound orbitals and free-electron wave functions are still coupled through the second term. We treat this as follows:

First we obtain the wave functions for the bound orbitals perturbed by the first term in Eq. (9b). These wave functions will contain the free-electron separation from the nucleus as a parameter. In addition, they will reflect the polarization of the neutral atom's charge cloud by the free electron. They will be used in the solution of the following equation:

$$H_c\varphi_e+\int\frac{|\Psi|^2}{r_{ie}}d\tau\varphi_e-E_e^{(0)}\varphi_e=\sum_{i=1}^{Z}\int\frac{\bar{\varphi}_e\psi_{i0}^{(0)}}{r_{ie}}d\tau\varphi_e, \tag{10}$$

an obvious adaptation of Eq. (8) wherein Eq. (5c) has replaced the bound orbitals appearing in Eq. (8). The assumption that the right side is zero allows us to consider only the effects of polarization on the free electron. The solution thus found is used in the evaluation of the integral on the right of Eq. (9). The entire equation is then solved for φ_e. The result should now contain the effects of both polarization and exchange.

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[11] R. G. Breene, Jr., *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1961), Vol. 27, p. 37.

III. POLARIZATION OF OXYGEN

We now consider the wave function for a free electron in the presence of neutral oxygen as an example of our program for the inclusion of polarization. We refer to our earlier oxygen-electron calculations.[1]

We suppose the O atom in its ^3P ground state, and we must first obtain the atomic wave function for this state perturbed by the free electron. We take the first term in Eq. (9b) as the perturbing Hamiltonian and appeal to the familiar Legendre expansion. As justified by our earlier work, we cut off this expansion after the first term. Ordinary perturbation theory then yields for the atomic wave function:

$$\Psi_{ii}=a_{ii}\Psi_i^{(0)}+a_{ii}\sum_j\frac{H_{ij}'}{E_i^{(0)}-E_j^{(0)}}\Psi_j^{(0)}, \qquad (11)$$

where the sum is to be carried only over the reasonably close lying levels. Our ^3P ground state is, of course, a single eighth-order determinant. Under the aegis of the perturbing Hamiltonian it will combine with none of the determinants representative of oxygen with three $2p$ and one $3s$ electrons. It will combine with two of the determinants corresponding to oxygen with three $2p$ electrons and one $3p$ electron, namely,

$$\Psi_{\mathrm{IV}}[(-1^+0^+1^+)(1^-)] \qquad \Psi_{\mathrm{V}}[(-1^-0^+1^+)(1^+)].$$

The perturbed atomic wave function is

$$\Psi_{^3P}=a_{33}\Psi_{^3P}^{(0)}+\frac{a_{33}}{\Delta_4}H_{34}'\Psi_{\mathrm{IV}}+\frac{a_{33}}{\Delta_5}H_{35}'\Psi_{\mathrm{V}}, \qquad (12a)$$

where

$$a_{33}^2+\frac{a_{33}^2}{\Delta_4^2}H_{34}'^2+\frac{a_{33}^2}{\Delta_5^2}H_{35}'^2=1, \qquad (12b)$$

and where

$$H=\sum_{i=1}^{8}\frac{1}{r_{ei}}$$

is now understood to depend on the free-electron separation R with the result:

$$\Psi_{^3P}=((\Delta_4\Delta_5)^{\frac{1}{2}}/A)\Psi_{^3P}^{(0)}+(\Delta_5H_{34}'/A\Delta_4)\Psi_{\mathrm{IV}}+(\Delta_4H_{35}'/\Delta_5A)\Psi_{\mathrm{V}}, \qquad (13a)$$

$$A=(\Delta_4^2\Delta_5^2+H_{34}'^2+H_{35}'^2)^{\frac{1}{2}}. \qquad (13b)$$

This is our perturbed atomic wave function, and we may obtain our Coulomb potential for the free electron from it as

$$V(0)=-\frac{Z}{r}+(\Delta_4^2\Delta_5^2/B)V_{\mathrm{Coul}}+(\Delta_5^2H_{34}'^2/B)\times\int\frac{|\Psi_{\mathrm{IV}}|^2}{r_{ei}}d\tau+(\Delta_4^2H_{35}'^2/B)\int\frac{|\Psi_{\mathrm{V}}|^2}{r_{ei}}d\tau+2(H_{34}'^2+H_{35}'^2)\Delta_4\Delta_5/B, \qquad (14a)$$

$$B=\Delta_4^2\Delta_5^2+\Delta_5^2H_{34}'^2+\Delta_4^2H_{35}'^2. \qquad (14b)$$

Let us note that for some determinant "j":

$$\int\frac{|\Psi_j|^2}{r_{ei}}d\tau=2V_{1s}^{(j)}+2V_{2s}^{(j)}+3V_{2p}^{(j)}+V_{3p}^{(j)}, \qquad (15)$$

since the integrals in Eq. (14) correspond to sums over the individual orbital integrals. Now we make the approximation that the effective nuclear charges for the $1s$ and $2s$ electrons are the same for all considered. This assumption and Eq. (15) yield, for Eq. (14a):

$$V=-\frac{8}{R}+2V_{1s}^{(0)}+2V_{2s}^{(0)}+B^{-1}[4\Delta_4^2\Delta_5^2V_{2p}^{(0)}+3\Delta_5^2H_{34}'^2V_{2p}^{(4)}+3\Delta_4^2H_{35}'^2V_{2p}^{(5)}+\Delta_5^2H_{34}'^2V_{3p}^{(4)}+\Delta_4^2H_{35}'^2V_{3p}^{(5)}+2\Delta_4\Delta_5(H_{34}'^2+H_{35}'^2)]. \qquad (16)$$

$V_{1s}^{(0)}$ and $V_{2s}^{(0)}$ may be obtained from reference 1. H_{3i}' may readily be evaluated as

$$H_{3i}'=\frac{Z_4^{\frac{5}{2}}Z_{11}^{\frac{5}{2}}}{2\sqrt{6}}\left[Z_{12}\int_0^\infty\frac{r^4}{r_>}e^{-Zr}dr-Z_{11}Z_{13}\int_0^\infty\frac{r^5}{r_>}e^{-Zr}dr\right], \qquad (17a)$$

where

$$Z=\tfrac{1}{2}Z_{13}+\tfrac{1}{3}Z_{11}. \qquad (17b)$$

Finally, the remaining portion of the potential may be worked out as

$$V_{2p}^{(i)}=-\frac{e^{-Z_3r}}{24}\left(Z_3^3r^2+6Z_3^2r+18Z_3+\frac{24}{r}\right)+\frac{1}{r}, \qquad (18)$$

and

$$V_{3p}^{(i)}=-\frac{Z_{11}e^{-\frac{2}{3}Z_{11}r}}{(2H^2-30H+135)}\left\{\frac{2}{81}Z_{11}^4r^4+\left(\frac{-4H+10}{27}\right)Z_{11}^3r^3+\left(\frac{2H^2-48H+270}{81}\right)Z_{11}^2r^2+\left(\frac{2H^2-36H+180}{9}\right)Z_{11}r+(H^2-16H+75)\right\}-\frac{1}{r}e^{-\frac{2}{3}Z_{11}r}+\frac{1}{r}, \qquad (19a)$$

where

$$H=30Z_{11}/(3Z_3+2Z_{11}). \qquad (19b)$$

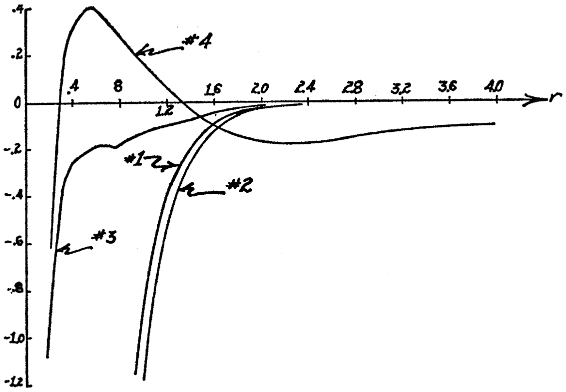

FIG. 1. Potentials for the free electron in the presence of an oxygen atom. No. 1: the Coulomb potential; No. 2: the Coulomb potential for the atom polarized by the free electron; No. 3: the potential including polarization and exchange for the electron spin down; No. 4: the potential for the electron spin up.

The substitution of Eqs. (17), (18), and (19) into Eq. (16) will, of course, yield the potential. Subsequent to such substitution one has the Coulomb potential produced by the atomic charge cloud distorted by the free-electron proximity.

Figure 1 allows a comparison of this polarized potential with the earlier Coulomb potential. When this potential is used in Eq. (8) the existing IBM 704 programs may be used to obtain the free-electron wave function. The methods of normalization of the machine solution are those of our earlier work. In Fig. 2 the effect of polarization inclusion is indicated. Only the s wave is considered here. The result is compared with the work of Klein and Brueckner.[4] In recalling the Klein and Brueckner work let us remark that we have obtained their polarization result with no normalization or reference to experiment. Their scattering results were evidently quite good, so that the agreement of our phase shifts with theirs (see Table I) is encouraging.

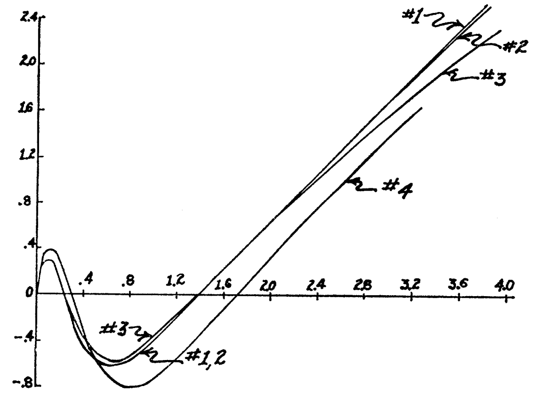

FIG. 2. Wave functions for the free electron in the presence of oxygen polarized by the free electron. No. 1: The wave function for the k value zero; No. 2: the wave function for the k value 0.1; No. 3: the wave function for the k value 0.3; No. 4: the Klein-Brueckner wave function for k value zero.

TABLE I. The s-wave phase shifts, in radians. The second column lists the phase shifts computed by us in reference 1. The third column gives the Klein and Brueckner results. The last column gives the results computed here for the polarized core.

k (atomic units)	δ (from reference 1)	δ (Klein-Brueckner)	δ (Computed here)
0.1	4.033	6.128	6.1587
0.3	4.250	5.798	5.8822

IV. EXCHANGE OF THE OXYGEN PROBLEM

Equation (10) would seem to indicate that exchange may be considered either after or before the incorporation of polarization in the calculation. Such is not the case. Because the Coulomb functions for the free electron allow excessive overlap with the bound orbitals, the exchange potentials resulting therefrom are unfortunately large. The result is a meaningless, rapidly oscillating function for the free electron. These difficulties are naturally overcome when exchange is introduced after inclusion of polarization.

The right side of Eq. (10) may be written as

$$\mathop{\mathsf{S}}\limits_{i}^{0} \int \frac{\psi_i \chi_0}{r_{ie}} d\tau, \tag{20a}$$

where we indicate a summing over all bound orbitals of the same spin as the free electron. There are, of course, two possibilities for Eq. (20a), one for a free electron spin up and the other for a free electron spin down.

$$V_- = 2\pi^{\frac{1}{2}} \int_0^\infty \frac{R_{1s}\chi_0}{r_>} dr + 2\pi^{\frac{1}{2}} \int_0^\infty \frac{R_{2s}\chi_0}{r_>} dr, \tag{20b}$$

$$V_+ = V_- + 2\left(\frac{\pi}{3}\right)^{\frac{1}{2}} \int_0^\infty \frac{r_< R_{2p}\chi_0}{r_>^2} dr. \tag{20c}$$

Equations (20b) and (20c) have been evaluated for a neutral oxygen atom in its ^3P ground state. We evaluate Eqs. (20) first with the polarized free-electron functions and the unpolarized bound functions and solve Eq. (10) using an IBM 704 program for the purpose.

The normalization of the solutions resulting from Eqs. (20b) and (20c) is somewhat more of a problem than the simple appeal to an asymptotic solution as was possible for the polarization case. The equation for the free-electron wave function takes the following form a few units of length from the nucleus:

$$\frac{d^2\chi_0}{dr^2} + \left(k^2 - \frac{a}{r} + \frac{n}{r^2}\right)\chi_0 = 0. \tag{21}$$

In the Appendix we describe the derivation of the function obtained as the solution of Eq. (21) and used by us for normalization of the machine solution. This

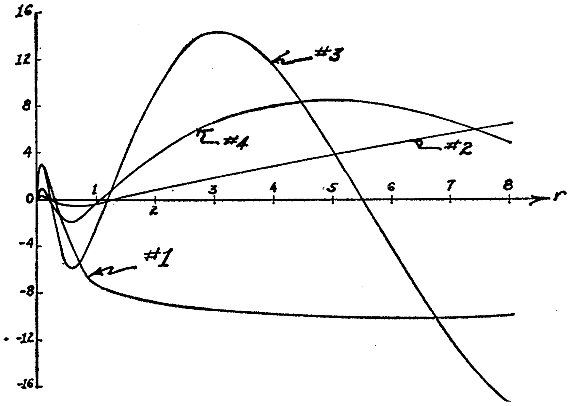

FIG. 3. Wave functions for the free electron in the presence of oxygen: No. 1: The wave function for the Coulomb potential; No. 2: the wave function for the Coulomb potential arising from the atomic core polarized by the free electron; No. 3: the wave function including polarization for the spin-up electron; No. 4: the wave function including polarization for the spin-down electron.

result is

$$\chi_0=\left|\frac{e^{i\kappa/2}\Gamma(\frac{1}{2}+il-\kappa)}{\Gamma(2il+1)}\right|\left(\frac{\rho}{2}\right)^{\frac{1}{2}}\Phi_0(\rho), \tag{22a}$$

$$\Phi_0=\sum_{j=0}^{\infty}A_j\rho^j;\quad A_0=1;\quad A_j=\frac{\eta A_{j-1}-A_{j-2}}{[j(j-1)+n]}, \tag{22b}$$

and, of course, has the required asymptotic form.

In Fig. 3 we display the wave function for (1) the free electron with polarization, (2) the free electron with polarization spin up, and (3) the free electron with polarization spin down.

ACKNOWLEDGMENTS

The author would like to express his appreciation to Miss Katherine Feucht for her work on the IBM 704 and 7090 on this problem and to Miss Maria C. Nardone for her assistance in the calculations and the computer operation.

APPENDIX

The wave equation for the free electron with exchange takes the following form a few units from the nucleus:

$$\frac{d^2\chi_0}{dr^2}+\left(k^2-\frac{a}{r}+\frac{n}{r^2}\right)\chi_0=0. \tag{A.1}$$

We make the substitutions:

$$Z=2i\rho,\quad \kappa=ia/2k,\quad n=\tfrac{1}{4}-m^2,\quad m=il, \tag{A.2}$$

with the result:

$$\frac{d^2\chi_0}{dz^2}+\left\{-\frac{1}{4}+\frac{\kappa}{z}+\frac{\frac{1}{4}-m^2}{z^2}\right\}\chi_0=0. \tag{A.3}$$

The solution of this equation is given in Whittaker and Watson[12] as

$$M_{\kappa,m}(z)=z^{\frac{1}{2}+m}e^{-\frac{1}{2}z}\left\{1+\frac{\frac{1}{2}+m-\kappa}{1!(2m+1)}z+\frac{(\frac{1}{2}+m-\kappa)(\frac{3}{2}+m-\kappa)}{2!(2m+1)(2m+2)}z^2+\cdots\right\}. \tag{A.4}$$

Since $z=2i\rho$, $\arg z=\pm\pi/2$. Kummer's first formula is

$$z^{-\frac{1}{2}-m}M_{\kappa,m}(z)=(-z)^{-\frac{1}{2}-m}M_{\kappa,m}(-z), \tag{A.5}$$

and for $\arg z=\pi/2$ this becomes

$$|z|^{-\frac{1}{2}-m}e^{-(\frac{1}{2}+m)i\pi/2}M_{\kappa,m}=|z|^{-\frac{1}{2}-m}e^{[-(\frac{1}{2}+m)](-\pi i/2)}M_{\kappa,m}(-z). \tag{A.6}$$

Thus, for either argument we get

$$\arg z=\frac{\pi}{2};\quad M_{-\kappa,m}(-z)=M_{\kappa,m}(z)e^{-(m+\frac{1}{2})\pi i}, \tag{A.7a}$$

$$\arg z=-\frac{\pi}{2};\quad M_{-\kappa,-m}(z)=M_{\kappa,-m}(z)e^{(m-\frac{1}{2})\pi i}. \tag{A.7b}$$

Consequently we can use the Yost, Wheeler, and Breit[13] solution:

$$\chi_0=\frac{1}{2}\left|\frac{e^{\pi i\kappa/2}\Gamma(\frac{1}{2}+il-\kappa)}{\Gamma(2il+1)}\right|e^{-\frac{1}{2}\pi i(il+\frac{1}{2})}M_{\kappa,m}(z). \tag{A.8}$$

Let us rewrite this as

$$\chi_0=\left|\frac{e^{i\kappa/2}\Gamma(\frac{1}{2}+il-\kappa)}{\Gamma(2il+1)}\right|\left(\frac{\rho}{2}\right)^{\frac{1}{2}}e^{-i[\rho-l\ \ln 2\rho]}\{1+\cdots\}. \tag{A.9}$$

In order to re-express this equation as a series of real terms, we apply Fuchs' theorem to Eq. (3a) to obtain

$$\Phi_0=\sum_{j=0}^{\infty}A_j\rho^j;\quad A_0=1;\quad A_j=\frac{\eta A_{j-1}-A_{j-2}}{[j(j-1)+n]}, \tag{A.10a}$$

$$\chi_0=\left|\frac{e^{i\kappa/2}\Gamma(\frac{1}{2}+il-\kappa)}{\Gamma(2il+1)}\right|\left(\frac{\rho}{2}\right)^{\frac{1}{2}}\Phi_0(\rho). \tag{A.10b}$$

Equations (A.10) were used for the exchange normalization.

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[12] E. T. Whittaker and G. N. Watson, *Course of Modern Analysis* (Cambridge University Press, New York, 1927), 4th ed., p. 337.

[13] F. L. Yost, J. A. Wheeler, and G. Breit, Phys. Rev. **49**, 174 (1936).