PHYSICAL REVIEW VOLUME 115, NUMBER 1 JULY 1, 1959

Wave Function for the Free Electron. I. The Coulomb Potential*

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(Received January 26, 1959)

The wave function for a free electron in the presence of an atom is considered for the case of the Coulomb potential, a potential which ignores both the effects of electron exchange and core polarization. A sample calculation involving the neutral oxygen atom is carried through. From the single-determinant wave function for the ^3P ground state of this atom the Coulomb potential is developed, and the important parts of the potential for the s- and d-wave portions of the free-electron wave function are considered. The relevant Schrödinger equations are solved by means of an IBM 704 program which is written so as to be readily adaptable to electrons in the presence of other atoms or ions having electrons through $2p$. In our oxygen example the wave function calculations were carried out for values of the free-electron linear momentum ranging from 0.01 through 0.80 atomic unit.

I. INTRODUCTION

In two previous papers[1] we have described the programs developed for the computation of analytic atomic wave functions; these programs were written primarily with an eye toward their subsequent utilization in free-electron wave function calculation. It is our purpose in this and succeeding papers to describe the manner in which we may use the wave functions obtainable from these programs in order to determine the wave function for the free electron in the presence of the atom described by the wave function. In this paper we shall consider the free electron under the influence of a Coulomb potential. In two subsequent papers we shall consider the effect of the introduction of exchange and polarization. Throughout the calculations and considerations we shall be referring specifically to a free electron in the presence of oxygen, but bear in mind that this is merely being used as a convenient and interesting example and that the calculations could equally well be carried out for electrons in the presence of other atoms or ions having electrons through $2p$. The same statement applies to somewhat more complex atoms, but here the potentials will contain certain additional terms.

Our general procedure has been about as follows: We obtain a potential for the electron by utilizing a single-determinant wave function for the ^3P ground configuration of the unperturbed neutral oxygen atom. This potential is obtained under the assumption of a Coulomb potential which infers the neglect of (1) exchange forces and (2) forces due to atomic polarization by the free electron. An expansion in terms of Legendre polynomials is assumed for the free-electron wave function, and this is substituted into the Schrödinger equation which contains our computed potential. Two coupled equations for the s- and d-waves in this Legendre expansion for the electron are obtained. Investigation shows this coupling to be of no real importance, so that the two equations may simply be solved independently. The equations are solved numerically and fitted to the familiar asymptotic solutions. A general program for the calculation has been written for the IBM 704 electronic data processing machine, and, using this program, the wave functions for several values of the electronic translational energy have been computed.

The program in question is easily adaptable to the computation of the p-wave functions, for example, and has, on occasion, been so adapted. However, it will be rather obvious from what is to follow that waves of higher order than s correspond so closely to Born approximation as to be practically indistinguishable therefrom.

II. SCHRÖDINGER EQUATION FOR THE *s* AND *d* WAVES OF THE FREE ELECTRON

A first step in setting up the Schrödinger equation for the free electron is, of course, the determination of the potential field in which the free electron exists. Let us first outline our procedure in obtaining this potential.

We suppose our potential due only to the Coulombic forces of the nucleus and orbital electrons. Quite obviously then, we are neglecting (1) exchange effects and (2) atomic polarization effects.[2] Under these conditions our potential function will be of the general form:

$$V=-\frac{Z}{r}+\int\frac{|\Psi_{^3P}(\mathrm{O})|^2}{r_{e\tau}}d\tau. \tag{1}$$

In Eq. (1), the first term on the right represents the nuclear portion of the potential while the second term is accounted for by the orbital electrons in our oxygen atom. The ^3P wave function which appears under the integral sign is our eighth order determinant, the orbitals of which were obtained from our simple vari-

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

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[1] R. G. Breene, Jr., Phys. Rev. **111**, 1111 (1958); **113**, 809 (1959).

[2] We shall detail our treatment of these effects in later papers. For an interesting recent treatment of (2) see A. Temkin, Phys. Rev. **107**, 1004 (1957).

ation calculation. The $r_{e\tau}$ represents the separation of the free electron from the element of atomic charge $d\tau$.

It is rather apparent that the evaluation of this potential is a matter of the evaluation of the integral in Eq. (1). In evaluating this integral we might first write the orbitals which we have obtained for neutral oxygen:

$$R_{1s}=2(7.661)^{\frac{3}{2}}r\exp[-7.661r], \tag{2a}$$

$$R_{2s}=\frac{1}{2\sqrt{2}}(5.4961)^{\frac{3}{2}}[1.5673-5.4961r]r \times\exp[-2.859r], \tag{2b}$$

$$R_{2p}=\frac{1}{2\sqrt{6}}(4.389)^{\frac{5}{2}}r^2\exp[-2.1945r]. \tag{2c}$$

These orbitals will, of course, go to make up our simple determinantal function which may be represented as the antisymmetric product:

$$\Psi_{^3P}(\mathrm{O})=\frac{1}{(8!)^{\frac{1}{2}}}P(-)\prod_i\psi_i. \tag{3}$$

We now utilize Eqs. (2) and (3) within the framework of Eq. (1) to obtain the following rather lengthy potential:

$$V_{\mathrm{O}}=-\left(15.322+\frac{2}{r}\right)e^{-15.322r}-\left(38.330r^2+18.368r+8.930+\frac{2}{r}\right)e^{-5.718r}-\left(14.092r^2+19.264r+13.168+\frac{4}{r}\right)e^{-4.389r}-(3\cos^2\vartheta-1)\left(1.761r^2+2.409r+2.200+\frac{1.500}{r}+\frac{1.684}{r^2}+\frac{0.15552}{r^3}\right)e^{-4.389r}+\frac{0.15552}{r^3}(3\cos^2\vartheta-1). \tag{4}$$

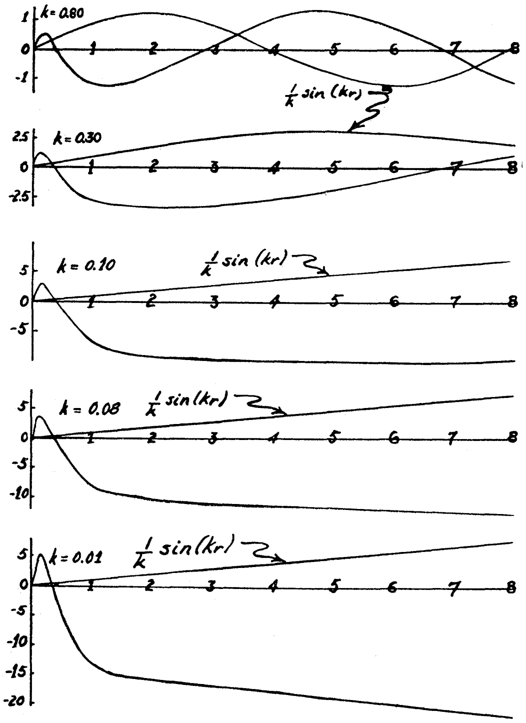

FIG. 1. The radial portion of the s wave function for the free electron in the presence of the oxygen atom for the indicated values of the momentum, in atomic units. The Born approximation $[k^{-1}\sin(kr)]$ has been drawn in for comparison and is so labeled.

We shall now make use of Eq. (4) in obtaining wave functions for the free electron in the field of the oxygen atom much after the fashion in which these wave functions were obtained in the field of the hydrogen atom by Chandrasekhar and Breen.[3]

TABLE I. The s-wave phase shifts. In the case of the Robinson phase shifts, the corresponding k value is in parentheses to the right.

k (atomic units)	δ_0 (calculated here)	δ_0 (Klein and Brueckner)	δ_0 (Robinson)
0.08	3.941		
0.10	4.033	6.128	
0.30	4.250	5.798	5.14 ($k=0.25$)
0.80	4.011	5.128	4.42 ($k=1.00$)

We now assume a solution for the free-electron wave function of the following familiar form:

$$\psi_e=\sum_l\frac{\chi_l(r)}{r}P_l(\vartheta). \tag{5}$$

In Eq. (5), $P_l(\vartheta)$ are Legendre polynomials while $\chi_l(r)$ are the unknown radial wave functions for which we must solve the Schrödinger equation. At this point, we intend limiting ourselves to a consideration of the s- and d-wave portions of this free-electron solution, although our demonstration of the method is equally applicable to other combinations of solution. As a consequence, after our assumed solution is substituted into the Schrödinger equation containing the potential as given by Eq. (4), we multiply through on the left by P_0 and P_2, respectively, and integrate over the polar

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[3] S. Chandrasekhar and F. H. Breen, Astrophys. J. **103**, 41 (1946).

angle to obtain the following:

$$\frac{d^2\chi_0}{dr^2}+k^2\chi_0 -2\sum_l\left(\int d\tau\, P_0P_lV_0\right)\chi_l\bigg/\int d\tau\, P_0P_0=0, \tag{6a}$$

$$\frac{d^2\chi_2}{dr^2}+\left[k^2-\frac{6}{r^2}\right]\chi_2 -2\sum_l\left(\int d\tau\, P_2P_lV_0\right)\chi_l\bigg/\int d\tau\, P_2P_2. \tag{6b}$$

Since our potential V_0 is equivalent in form to a sum of the first and second Legendre polynomials, it is apparent that the only term existing in the Eq. (6a) are those terms having $l=0$ and $l=2$. The situation is somewhat different in Eq. (6b), but it can be shown that the terms in the sum in this equation making the most appreciable contribution are those having $l=0$ and $l=2$. This means that we now have two equations in our two functions χ_0 and χ_2, the two equations being coupled by the angular terms in the potential.

Actual calculation has shown that the terms in these equations arising from the angular portions of the potential have a negligible effect, which is more or less apparent from inspection. Therefore, we have dropped the terms from both equations. Now our equations to be solved are

$$\frac{d^2\chi_0}{dr^2}+[k^2+2V_0(r)]\chi_0=0, \tag{7a}$$

$$\frac{d^2\chi_2}{dr^2}+\left[k^2-\frac{6}{r^2}+2V_0(r)\right]\chi_2=0. \tag{7b}$$

III. CALCULATIONS OF THE WAVE FUNCTIONS AND RESULTS

A numerical solution to these two equations has been programmed for the IBM 704 and carried out in the regions $0\leqslant r\leqslant 8$ for the s wave and d wave for values of the free-electron translational energy ranging from 0.01 through 0.80 atomic unit.

We have joined the numerical solution of the s wave at the outer end of its range to the familiar asymptotic solution:

$$\chi_l(r)=\frac{1}{k}\sin(kr-\tfrac{1}{2}l\pi+\delta_l). \tag{8}$$

Since the numerical solution for the d wave remains dependent on the centrifugal potential, it was necessary to connect the numerical solution to an asymptotic solution by some other method.

At the point where our potential is essentially zero, the equation becomes

$$\frac{d^2\chi_2}{dr^2}+\left[k^2-\frac{6}{r^2}\right]\chi_2=0, \tag{9}$$

which we recall has the familiar solution:

$$\chi_2=(\pi r/2)^{\frac{1}{2}}J_{\frac{5}{2}}(r)=\left(\frac{3}{r^2}-1\right)\sin r-\frac{3}{r}\cos r. \tag{10a}$$

TABLE II. The s and d wave functions for a free electron in the presence of an oxygen atom for the case $k=0.01$ atomic unit.

r (atomic units)	$\chi_0(r)$	$\chi_2(r)$	r (atomic units)	$\chi_0(r)$	$\chi_2(r)$
0.002	0.1927	0.7×10^{-14}	2.800	−16.4434	0.9×10^{-5}
0.006	0.5642	0.2×10^{-12}	3.000	−16.6417	0.1×10^{-4}
0.010	0.9178	0.8×10^{-12}	3.200	−16.8393	0.1×10^{-4}
0.030	2.4319	0.2×10^{-10}	3.400	−17.0366	0.2×10^{-4}
0.050	3.5699	0.9×10^{-10}	3.600	−17.2337	0.2×10^{-4}
0.080	4.6794	0.4×10^{-9}	3.800	−17.4307	0.2×10^{-4}
0.100	5.0891	0.7×10^{-9}	4.000	−17.6277	0.3×10^{-4}
0.120	5.2822	0.1×10^{-8}	4.200	−17.8245	0.3×10^{-4}
0.140	5.2927	0.2×10^{-8}	4.400	−18.0212	0.4×10^{-4}
0.160	5.1503	0.3×10^{-8}	4.600	−18.2179	0.4×10^{-4}
0.180	4.8811	0.4×10^{-8}	4.800	−18.4145	0.5×10^{-4}
0.200	4.5079	0.5×10^{-8}	5.000	−18.6111	0.5×10^{-4}
0.240	3.5266	0.8×10^{-8}	5.200	−18.8075	0.6×10^{-4}
0.300	1.6938	0.2×10^{-7}	5.400	−19.0039	0.7×10^{-4}
0.340	0.3627	0.2×10^{-7}	5.600	−19.2002	0.7×10^{-4}
0.400	−1.6464	0.4×10^{-7}	5.800	−19.3964	0.8×10^{-4}
0.600	−7.3429	0.1×10^{-6}	6.000	−19.5926	0.9×10^{-4}
0.800	−10.9181	0.2×10^{-6}	6.200	−19.7887	0.0001
1.000	−12.9218	0.5×10^{-6}	6.400	−19.9847	0.0001
1.200	−14.0259	0.8×10^{-6}	6.600	−20.1806	0.0001
1.400	−14.6643	0.1×10^{-5}	6.800	−20.3764	0.0001
1.600	−15.0727	0.2×10^{-5}	7.000	−20.5722	0.0001
1.800	−15.3701	0.2×10^{-5}	7.200	−20.7678	0.0002
2.000	−15.6146	0.3×10^{-5}	7.400	−20.9634	0.0002
2.200	−15.8341	0.5×10^{-5}	7.600	−21.1590	0.0002
2.400	−16.0417	0.6×10^{-5}	7.800	−21.3544	0.0002
2.600	−16.2439	0.7×10^{-5}	8.000	−21.5497	0.0002

We know that the asymptotic solution of Eq. (9) is of the form Eq. (8), so we may modify Eq. (10a) to the form:

$$\chi_2=\left(\frac{3}{k^3r^2}-\frac{1}{k}\right)\sin(kr-\pi+\delta_2) -\frac{3}{k^2r}\cos(kr-\pi+\delta_2). \tag{10b}$$

Equation (10b) may be solved for the phase shift:

$$\begin{aligned}\tan\delta_2=\{&-X[D\sin(kr_0-\pi)+F\cos(kr_0-\pi)]\\&+X'[B\sin(kr_0-\pi)-C\cos(kr_0-\pi)]\}/\\&\{X[D\cos(kr_0-\pi)-F\sin(kr_0-\pi)]\\&-X'[B\cos(kr_0-\pi)+C\cos(kr_0-\pi)]\},\end{aligned} \tag{11a}$$

wherein X and X' are the values of the numerical solution and its derivative, respectively, at the radial

TABLE III. The *s* and *d* wave functions for the free electron in the presence of oxygen for the case $k=0.80$ atomic unit.

r (atomic units)	$\chi_0(r)$	$\chi_2(r)$	r (atomic units)	$\chi_0(r)$	$\chi_2(r)$
0.002	0.0177	0.9×10^{-10}	2.800	-0.0404	0.0807
0.006	0.0519	0.2×10^{-8}	3.000	0.1592	0.0935
0.010	0.0844	0.1×10^{-7}	3.200	0.3547	0.1064
0.030	0.2237	0.2×10^{-6}	3.400	0.5412	0.1191
0.050	0.3283	0.1×10^{-5}	3.600	0.7138	0.1313
0.080	0.4301	0.4×10^{-5}	3.800	0.8682	0.1425
0.100	0.4675	0.9×10^{-5}	4.000	1.0004	0.1524
0.120	0.4849	0.1×10^{-4}	4.200	1.1071	0.1607
0.140	0.4854	0.2×10^{-4}	4.400	1.1854	0.1671
0.160	0.4717	0.3×10^{-4}	4.600	1.2335	0.1712
0.180	0.4463	0.5×10^{-4}	4.800	1.2501	0.1730
0.200	0.4113	0.6×10^{-4}	5.000	1.2347	0.1721
0.220	0.3686	0.8×10^{-4}	5.200	1.1878	0.1684
0.240	0.3196	0.0001	5.400	1.1105	0.1620
0.300	0.1488	0.0002	5.600	1.0049	0.1527
0.340	0.0250	0.0003	5.800	0.8736	0.1408
0.400	-0.1612	0.0005	6.000	0.7199	0.1262
0.600	-0.6816	0.0014	6.200	0.5479	0.1092
0.800	-0.9879	0.0030	6.400	0.3619	0.0901
1.000	-1.1269	0.0056	6.600	0.1666	0.0693
1.200	-1.1585	0.0092	6.800	-0.0329	0.0470
1.400	-1.1219	0.0139	7.000	-0.2316	0.0238
1.600	-1.0390	0.0199	7.200	-0.4244	0.0002
1.800	-0.9217	0.0272	7.400	-0.6063	-0.0235
2.000	-0.7778	0.0358	7.600	-0.7727	-0.0467
2.200	-0.6126	0.0456	7.800	-0.9194	-0.0689
2.400	-0.4314	0.0565	8.000	-1.0426	-0.0896
2.600	-0.2390	0.0682			

separation in question and

$$B=3/k^3r^2-1/k, \tag{11b}$$

$$C=-3/k^2r, \tag{11c}$$

$$D=3/kr-6/k^3r^3, \tag{11d}$$

$$F=6/k^2r^2-1. \tag{11e}$$

An alternate method of obtaining the phase shift under the assumption that it is small is provided by the following equation:

$$\delta_2=\int V_{\mathrm{O}}(r)[J_{\frac{5}{2}}(kr)]^2rdr. \tag{12}$$

These phase shifts obtained by either method of calculation are quite small in accordance with the anticipated behavior of the higher order phase shifts as the free-electron velocity approaches zero.[4–6]

The *s*-wave phase shifts are displayed as Table I. We have compared them with Robinson's[4] and Klein and Brueckner's[6] results.

In Fig. 1 we have plotted the *s* wave functions for the *k* values 0.01, 0.08, 0.10, 0.30, and 0.80 atomic unit. For comparison the Born approximation is also plotted. Since the *d* wave so closely corresponds to the Born case, we have not shown it. In Tables II and III we have tabulated the computed *s* and *d* wave functions for *k* values 0.01 and 0.80 atomic unit.

ACKNOWLEDGMENTS

We wish to express our appreciation to Mrs. Rosemary Johnson for programing the calculation for the IBM 704 electronic data processing machine. It is also a pleasure to acknowledge the many stimulating discussions of the subject with Dr. R. C. Sahni and Professor Henry Margenau.

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[4] A. B. Robinson, Phys. Rev. **105**, 922 (1957).

[5] E. Fermi, *Nuclear Physics* (University of Chicago Press, Chicago, 1950), p. 118.

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