

A Relativistic Self-Consistent Field for Cu^+ *

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An improvement can be made in the Hartree self-consistent field solution of the many-electron atom by substituting the Dirac relativistic one-electron equation for the Schrödinger one-electron equation. It has been shown earlier that in the solution without exchange the necessary potential function can be found just as in the nonrelativistic case. The numerical solution for the inner shells of Cu^+ is outlined, and tables of the resulting energy parameters and charge density distribution are given. The corrections introduced into the charge density distribution are small, except near the nucleus, for this comparatively light ion. The energy parameters are noticeably affected, and the known splitting of the (*p*) and (*d*) energy parameters is shown. Approximate calculations of the magnetic interaction energies between two electrons show the results to be negligible, to the order of accuracy of the main calculations.

I. INTRODUCTION

IT was first suggested by Swirles¹ that the simple substitution of the Dirac one-electron equation² for the Schrödinger equation in the Hartree method³ of the self-consistent field would give results of considerable value in predicting relativistic corrections in the energy levels and charge density distributions of heavy atoms. The questions of exchange effects, retarded potentials, and interactions of the magnetic moments of the electrons have been further discussed by Swirles,⁴ following in part work by Bethe and Fermi.⁵

The equations necessary for the Hartree treatment with relativistic corrections, both with and without exchange, were given in the articles mentioned.^{3,4} The present article outlines the procedures used in solving the equations without exchange, and presents some numerical results for the inner shells (those most affected by relativistic corrections) of Cu^+ . This ion was chosen as the heaviest yet treated both with and without exchange (by Hartree⁶).

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¹ B. Swirles, Proc. Roy. Soc. **A152**, 625 (1935).

² P. A. M. Dirac, Proc. Roy. Soc. **A117**, 610; **A118**, 351 (1928).

³ D. R. Hartree, Proc. Camb. Phil. Soc. **24**, 89, 111 (1928).

⁴ B. Swirles, Proc. Roy. Soc. **A157**, 680 (1936).

⁵ H. A. Bethe and E. Fermi, Zeits. f. Physik **77**, 296 (1932).

⁶ D. R. Hartree, Proc. Roy. Soc. **A141**, 282 (1933); **A157**, 490 (1936).

II. RELATIVISTIC EQUATIONS

The Dirac matrix equation for an electron in a central field of electrostatic potential V can be written in the form of four nonmatrix equations, in terms of four components $\psi_1, \psi_2, \psi_3, \psi_4$ of the matrix wave function.

It has been shown⁷ that the equations are separable as follows:

$$\begin{aligned}\psi_1 &= F_l(r)f_1(\theta, \phi) \\ \psi_2 &= F_l(r)f_2(\theta, \phi) \\ \psi_3 &= G_l(r)f_3(\theta, \phi) \\ \psi_4 &= G_l(r)f_4(\theta, \phi).\end{aligned}\tag{1}$$

The exact forms of f_1, f_2, f_3, f_4 , which are spherical harmonics, have four sets of values,^{1,7} depending on the quantum numbers l, j, u . The radial portions F_l, G_l satisfy the two equations

$$\begin{aligned}\left(\frac{W+V(r)}{c}+c\right)F_l+\frac{d}{dr}G_l-\frac{l}{r}G_l=0 \\ -\left(\frac{W+V(r)}{c}-c\right)G_l+\frac{d}{dr}F_l+\frac{l+2}{r}F_l=0\end{aligned}\tag{2}$$

for $j=l+\frac{1}{2}$. For $j=l-\frac{1}{2}$, the corresponding F_{-l-1}, G_{-l-1} satisfy similar equations with $-l-1$ substituted for l throughout.

The units of (2) are atomic.⁸ W represents the total energy of the electron, including its rest

⁷ C. G. Darwin, Proc. Roy. Soc. **A118**, 654 (1928).

⁸ E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge, 1935), p. 428.

energy, c is the velocity of light, and $V(r)$ the spherically symmetrical electrostatic potential.

The complete wave functions are listed in several places.^{1,7} Their orthogonality properties have been discussed by Hartree.⁹ Examination of each $f(\theta, \varphi)$ shows that, for a given total quantum number, n , the quantum number l can be 0, 1, 2, \dots , $(n-1)$, just as in Schrödinger's theory. The number of solutions for a given l depends on l and on j ($l+\frac{1}{2}$ or $l-\frac{1}{2}$). The results

TABLE I. Comparison of energy parameters E .

STATE	REL. E_{nl}	NON REL. ϵ_{nl}	NON REL. EXCH. ⁶ $\epsilon_{nl, nl}$	OBSERVED X-RAY LEVEL
1s	332.4	329.0	329.2	330.8
2s	39.76	39.22 ₅	41.15	40.50
1/2	35.33			35.1 ₅
2p		34.93	35.91 ₅	
3/2	34.57			34.4 ₅
3s	4.489	4.484	5.325 ₅	4.4 ₅
1/2	3.006			
3p		3.039	3.639 ₅	2.8 ₅
3/2	2.909			
3/2	0.510			
3d		0.5975	0.8065	0.2
5/2	0.500			

can be summarized thus: for s electrons, with $l=0$, $j=l+\frac{1}{2}$ only, and there are two independent orthogonal solutions; for p electrons with $l=1$, there are two solutions for $j=l-\frac{1}{2}$ and four for $j=l+\frac{1}{2}$; for d electrons, with $l=2$, there are four solutions for $j=l-\frac{1}{2}$ and six for $j=l+\frac{1}{2}$. The several solutions for a certain n , l , j have the same radial portion for their wave functions, and the same energy, differing only in their dependence on angle. The two sets of solutions for a certain n , l arising from $j=l-\frac{1}{2}$ or $l+\frac{1}{2}$ differ in energy, as well as in their functional form.

The usual Hartree preparation for numerical solution can be made, by writing $Z_p(r)/r$ for $V(r)$, and $P_l=rG_l$, $Q_l=rF_l$. Further, $W=m_0c^2-E$, or c^2-E in atomic units; $2E$ corresponds to the Hartree energy parameter ϵ . The Eqs. (2) become, after elimination of Q_l and insertion of the abbreviation

$$U(r) = 2c^2 + Z_p/r - E,$$

$$\frac{d^2 P_l}{dr^2} = P_l \left[\frac{l(l+1)}{r^2} + 2E - Z_p/r \right] - P_l \left\{ \frac{E - Z_p/r}{c} \right\}^2 + \left\{ \frac{1}{U} \left(\frac{d}{dr} (Z_p/r) \right) \left(\frac{dP_l}{dr} - \frac{l+1}{r} P_l \right) \right\}, \quad (3)$$

$$Q = -\frac{c}{U} \left(\frac{dP_l}{dr} - \frac{l+1}{r} P_l \right). \quad (4)$$

Examination of Eq. (3) shows that as $c \rightarrow \infty$ the terms in $\{ \}$ vanish, leaving the familiar nonrelativistic equation. However, near $r=0$ the equation becomes indeterminate, and in any case c is very far from being infinite—in atomic units it is about 137. More careful examination shows that the term in $[\]$ is not affected by substituting $-l-1$ for l , and that the term $[(1/c)(E-Z_p/r)]^2$ is only very slightly affected, in the main serving merely to make $2E$ exceed Hartree's ϵ . Only in the last term does a substantial change result when $-l-1$ replaces l . The change turns out to make E greater for $-l-1$, or for $j=l-\frac{1}{2}$, than for l or $j=l+\frac{1}{2}$, and hence predicts not only the existence of spin doubling of energy levels but also the relative positions of these energy levels.

III. SOLUTION OF EQUATIONS

The general procedure for numerical solution follows the Hartree method.^{3,6} $Z_p(r)$ is chosen and the equations are integrated outward from $r=0$ and inward from $r=\infty$, and joined smoothly by proper choice of E . The wave functions are normalized and used to compute a new $Z_p(r)$. The process ideally should be repeated until the initial and final Z_p 's coincide for all r to the desired degree, to give completely "self-consistent" results. The value 137.26 was chosen for c , although probably no such number of figures was necessary.

The solution can be carried out either by simultaneous integration of (2), or by use of (3) and later of (4). Both methods were tried in practice. The simultaneous integration of (2) requires starting values of P_l and Q_l , involves less work in calculating coefficients, but does not go very smoothly or converge rapidly. The integration of the second order (3) requires

⁹ D. R. Hartree, Proc. Camb. Phil. Soc. 25, 225 (1929).

starting values of P_l and dP_l/dr , and involves lengthy computations of coefficients, but converges rapidly and proceeds smoothly. Q_l need be computed only roughly, since it is small. In either case, the necessary starting values are found by assuming solutions in power series very similar to those of the corresponding hydrogenic problem, but assuming Z_p to vary linearly with r .

Once started, the integration of Eqs. (2) or (3) is continued numerically out to a point beyond the last maximum of P . For the function P_l , $n-l-1$ nodes are found, as in the nonrelativistic case, but P_{-l-1} always differs greatly from P_l . To find a solution vanishing at infinity, the Eq. (3) in a transformed variation is integrated inward, and both inward and outward integrations are repeated with different values of E until a smooth join is accomplished.

The equation used for inward integration resembles closely the Hartree η -equation.^{3,6} It is derived from (3) by the substitution of $\eta = -P'/P$, and has the form

$$\frac{d\eta}{dr} = \eta^2 + \frac{1}{U} \frac{d}{dr} (Z_p/r) \eta - \frac{l(l+1)}{r^2} + \frac{1}{U} \frac{l+1}{r} \frac{d}{dr} (Z_p/r) - \frac{U(2c^2 - U)}{c^2}. \quad (5)$$

η is a monotone function approaching the value $(2E - E^2/c^2)^{1/2}$ for very large r , and $d\eta/dr$ is both small and slowly varying in this region. Hence the integration is easily started by successive approximations, at a fairly large value of r (6 to 10 times r at the last maximum of P).

For the outward integration, the Milne method¹⁰ of integration was used. The integration of the η -equation was carried out partly by the Milne and partly by the Runge-Kutta method.¹⁰

Two complete approximations were carried out. That is, each of the nine different equations (one for each s state, two for each p and d state) was integrated and joined smoothly, starting from the nonrelativistic potential function. Then a new potential function was computed, and the integration was carried out again. The resulting un-normalized wave functions of the second

approximation and the one-electron contributions to the field are not tabulated here, but are available on application to the author. The energy parameters E are presented in Table I, with the nonrelativistic values and the corresponding observed levels for comparison. In Table II is a comparison of the total probability charge density with the values predicted by the nonrelativistic calculations. The comparison is indicated at intervals of r much greater than those used in calculation, and is carried out only as far as the uncertainty in the slowly increasing $3d$ density can be considered negligible. Outside this point, exchange corrections will completely overshadow the relativistic ones.

IV. DISCUSSION OF RESULTS

The values of E are seen to be in neither better nor worse agreement with experimental values than were the nonrelativistic ones. This is to be expected, since these E 's are not exactly the energy levels of the atom, as Fock¹¹ and others have shown. However, the differences between the energy parameters of two electrons

TABLE II. Total radial charge density $\sum_{nlj} N_{nlj} (P^2_{nlj} + Q^2_{nlj})$ (possible uncertainty of several units in the second decimal place).

r	REL.	NONREL. ⁶	NONREL. EXCH. ⁶
0.005	4.33	3.91	3.91
0.010	12.54	11.71	11.71
0.020	27.38	26.36	26.38
0.030	34.44	33.77	33.76
0.040	35.16	34.85	34.87
0.06	30.08	30.08	30.21
0.09	28.23	27.99	28.38
0.12	34.01	33.61	34.20
0.18	39.13	39.23	39.59
0.24	30.21	30.81	30.97
0.30	20.42	21.26	21.67
0.45	16.51	17.61	19.13
0.60	20.00	21.16	22.74
0.8	17.17	18.02	18.89
1.0	11.76	12.17	12.39

in the same shell but with opposite spin agree well with the few experimental data. It should be noted that because of the oscillating approach to self-consistency the magnitudes of the E 's presented here are less than the completely self-consistent ones (only very slightly so in the 1- and 2-shells).

¹⁰ A. A. Bennett, W. E. Milne and H. Bateman, Bull. Nat. Research. Council No. 92, pp. 76, 77 (1933).

¹¹ V. Fock, Zeits. f. Physik **61**, 126 (1930).

The total probability charge density is seen to differ considerably from both exchange and nonexchange values, in the region close to the nucleus. The charge density for each single electron turns out to resemble that for the nonrelativistic case, but with all maxima "pulled in" and raised. These effects are blurred by the addition of the separate electron densities, but traces of such behavior remain in the total charge density. The size of the relativistic corrections appear to be just too small to produce important corrections in atomic form factors and other secondary characteristics of the whole atom. However, it must be noted that copper is a relatively light ion, and the corrections for such an ion as mercury would be enormously greater.

The energy parameters for the $3d$ electrons given in Table I, but not their separation, are probably much in error, because of their extreme sensitivity to slight corrections in wave functions and fields ("over-stability," as Hartree calls it). Further work on them is in progress. The other 3-shell electrons may be slightly affected, but in any case exchange corrections are far more important here.

A comparison of the total charge density relativistic corrections with those predicted by the relativistic Thomas-Fermi method of Vallarta and Rosen¹² shows fairly good agreement close to the nucleus (out to $r \sim 0.05$), but definite disagreement further out.

V. SMALL SIZE OF MAGNETIC EFFECTS

Bethe and Fermi⁵ have derived expressions for the electrostatic and magnetic interactions between two electrons. The electrostatic interaction energies turn out to be just those introduced into the Hartree equation by the method

¹² M. S. Vallarta and N. Rosen, Phys. Rev. **41**, 708 (1932).

of calculating the one-electron potential function, and so need no further consideration.

The integrals representing the magnetic interaction of electrons can be calculated explicitly with the wave functions just tabulated. The work is simplified by the fact, shown by Hartree,⁹ that in any closed shell the electrons may be paired in such a way that the net current of each pair is zero. The Cu^+ ion containing only closed shells, each electron thus interacts magnetically only with its partner in such a pair.

The integration over the angular portion of the energy integrals is readily carried out after the $1/|r-r'|$ factor of Bethe and Fermi's derivation is expanded in spherical harmonics. Certain formulas for the integral of the product of three spherical harmonics, derived by Gaunt,¹³ are very useful in this procedure. The integration over the radial portion is more complicated, but for the present purpose it sufficed to calculate a very strongly dominating integral. The following values are the upper bounds actually found for the contribution to the energy of each electron, arising from its magnetic interaction with its paired partner. The units are those of Table I. The values found were: (1s), 0.3; (2s), 0.015; $(2p)_{\frac{3}{2}}$, 0.01; $(2p)_{\frac{1}{2}}$, 0.01; (3s), 0.001; $(3p)_{\frac{3}{2}}$, 0.0005; $(3p)_{\frac{1}{2}}$, 0.0008; $(3d)_{\frac{5}{2}}$, 0.0003; $(3d)_{\frac{3}{2}}$, 0.0003. When it is noted that the actual values must be less than these bounds, it is evident that the magnetic interaction energies are negligible beside the usual errors of the self-consistent field method.

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¹³ J. A. Gaunt, Phil. Trans. Roy. Soc. **226**, 151 (1929).