Results of Calculations of Atomic Wave Functions. I.—*Survey, and Self-consistent Fields for* Cl⁻ *and* Cu⁺.

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1. *Introduction.*

An approximation to the structure of a many-electron atom can be obtained by considering each electron to be a stationary state in the field of the nucleus and the Schrödinger charge distribution of the other electrons, and rather more than five years ago I gave a method of working out atomic structures based on this idea, and called the field of the nucleus and distribution of charge so obtained the " self-consistent field."*

The method of working out the self-consistent field for any particular atom involves essentially (*a*) the estimation of the contributions to the field from the various electron groups constituting the atom in question ; (*b*) the solution of the radial wave equation for an electron in the field of the nucleus and other electrons, this solution being carried out for each of the wave functions supposed occupied by electrons in the atomic state considered ; and (*c*) the calculation of the contribution to the field from the Schrödinger charge distribution of an electron group with each radial wave function. The estimates of the contributions to the field have to be adjusted by trial until the agreement between the contributions finally calculated and those estimated is considered satisfactory.

In the paper in which the method was first suggested, some results were also given, and since then, results for a number of atoms have been worked out by myself and others, and some of these have been published. But the results published have usually been results for the whole atom, such as the total charge distribution or field ; detailed results such as individual wave functions, and contributions to the field from the different electron groups have not been given except for O, O⁺, O⁺⁺, O⁺⁺⁺, and Si⁺⁴.† These individual wave functions and contributions to the field, however, are often the quantities

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* Hartree, ' Proc. Camb. Phil. Soc.,' vol. 24, pp. 89, 111 (1928).

† Oxygen : Hartree and Black, ' Proc. Roy. Soc.,' vol. 139, p. 311 (1933). Silicon McDougall, ' Proc. Roy. Soc.,' vol. 138, p. 550 (1932).

required in applications. A considerable amount of information of this kind is available, and has been supplied privately to anyone who knew of its existence and asked for it, but for some time it has seemed desirable to publish it so as to make it more widely available.

There were, however, some objections to publishing it as it stood. As experience of working out atomic structures has increased, several improvements have been made in numerical technique, and also the standard of what is considered a " satisfactory " agreement between estimated and calculated contributions to the field has gone up considerably. A good deal of the available information was based on old work in which neither the degree of agreement between estimated and calculated fields, nor the numerical accuracy to which the work was carried out, now seem adequate. It seemed desirable therefore to carry out a revision of the work, using the improved methods and working to a higher numerical accuracy (principally in order to lessen the effect of possible cumulative integration errors), and also aiming at a higher standard of agreement between estimated and calculated contributions to the field, before publishing the detailed results. That such revision is desirable is shown by appreciable differences in some cases between the revised and earlier results.

The method of carrying out the numerical work is now fairly well standardised, and the revision of the calculations is largely a matter of expert computing. A grant was made by the Government Grants Committee of the Royal Society for the purpose of employing the professional assistance of expert computers in connection with this work, and I wish to acknowledge my thanks to the committee for its assistance, to Miss D. S. Greene,* for undertaking the arrangements for getting the work done, and to Dr. L. J. Comrie and Mr. D. S. Sadler who actually did the calculations, for the very satisfactory way they have carried out the computing work which is of rather unusual and not altogether straightforward kind.

With this assistance available, the work of improving the earlier results of any particular atom is being carried out as follows. From the earlier work, I make revised estimates of the contributions to the field from the various electron groups, and the computing work carried out professionally is concerned with the calculation of wave functions in the field so constructed, regarded as *given*, and of charge distributions from these wave functions. For reference I will call these calculations the " standard calculations." Unless estimates of

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the contributions to the field have been unusually fortunate, the results of these standard calculations are not yet near enough to the self-consistent field to be quite satisfactory, but they should be near enough for the effect of any variation of the estimates to be treated as a first order variation from the results of the standard calculations.

A further revision of the estimates is made if necessary and the *variations* in the wave functions, etc., due to the *variations* in the estimates from those used in the standard calculations, are calculated, and the variations of wave functions, etc., added to the results of the standard calculations; the variations are so small that this variation calculation is very much shorter and easier than the main calculation. If necessary, further revisions of the estimates are made and corresponding variations from the results of the standard calculations are worked out, until a satisfactory approximation to the self-consistent field is obtained. For the atoms for which results are given here, I have myself been responsible for carrying out these final stages of the work.

This paper presents the results of this work for two atoms, Cl^- and Cu^+; the earlier work for both of these atoms was done by myself, and some results for Cl^- were published in my first paper. Some results of the earlier work on Cu^+ have been published by Slater in connection with his approximations to the wave functions by analytical formulæ.* Other atoms for which such work is in progress are Al^{+3}, K^+, Rb^+, Cs^+.

The results for Cu^+ here given are interesting, as they are the first which have been obtained for an atom with an outer shell of 18 electrons; the other atoms for which calculations have so far been carried out are atoms for which the outer shell is a complete or incomplete 8-shell. Comparison of the results for Cu^+ and the alkali metal ions may throw light on the characteristic difference of properties of the two sub-groups of the first column of the periodic table.

Since the method of obtaining approximate wave functions for a many-electron atom by means of the " self-consistent field " was suggested, a better approximation has been indicated independently by Slater† and Fock‡, and the equations obtained by the latter; but the numerical application of Fock's approximation involves difficult problems of numerical technique for any but the lightest atoms, and as far as I know, no case has yet been worked out quantitatively. Slater and Fock have shown that the approximation made in the " self-consistent field " method is the best for its simplicity that could be

* Slater, ' Phys. Rev.,' vol. 42, p. 33 (1932).
† ' Phys. Rev.,' vol. 35, p. 210 (1929).
‡ ' Z. Physik,' vol. 61, p. 126 (1930).

obtained ; also it is probable that in the solution of Fock's equations for any atom the first step would be the approximate solution of the equations of the self-consistent field, so that as well as being the best results at present available, the results, of which those presented here form a part, are also steps on the way to better approximations.

§ 2. *Summary of Notation and Nomenclature.*

All quantities are supposed measured in natural atomic units, that is units such that the measures of the mass of the electron, of the magnitude of the charge on the electron, and of $h/2\pi$, are all 1 ; the unit of length is

$$h^2/4\pi^2 me^2 = 0 \cdot 532 \text{ A.U.}$$

If, in spherical polar co-ordinates with origin at the nucleus, the wave function of a single electron in a central field of potential v is written

$$\psi (r, \theta, \phi) = \frac{\text{P} (r)}{r} \, \text{S}_l (\theta, p), \qquad (1)$$

where S_l is a spherical harmonic of degree l, $\text{P} (r)$ is called the radial wave function, and satisfies the equation*

$$d^2\text{P}/dr^2 + [2v - \varepsilon - l (l + 1)/r^2] \, \text{P} = 0, \qquad (2)$$

where ε is the negative energy parameter reckoned with the ionization energy of the hydrogen atom as unit, so that if ν is the corresponding wave number, $\varepsilon = \nu/\text{R}$. It is sometimes convenient to write the quantum numbers n, l of the wave function of which $\text{P} (r)/r$ is the radial part as suffixes [viz., $\text{P}_{n, l} (r)$], or alternatively in the form $\text{P} (nl \,|\, r)$; and for specifying the value of l it is best to adopt the usual conventional letter according to the scheme

	s	p	d	f	g	h	...
for $l =$	0	1	2	3	4	5	...

If $\text{P} (r)$ is normalized so that $\int_0^\infty \text{P}^2 \, dr = 1$, then $\text{P}^2 \, dr$ is the charge lying in a spherical shell between radii r and $r + dr$, on Schrödinger's interpretation of the wave function, and P^2 may conveniently be called the " radial density " of the charge distribution of the electron concerned ; if P is not normalized the radial density is $\text{P}^2 \Big/ \int_0^\infty \text{P}^2 \, dr.$

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* *Cf.* Hartree, *loc. cit.*

If we write*

$$Z_0 (nl, nl \,|\, r) = \int_0^r [P \,(nl \,|\, r)]^2 \, dr \Big/ \int_0^\infty [P \,(nl \,|\, r)]^2 \, dr, \qquad (3)$$

then $Z_0(nl, nl \,|\, r)$ is the total charge lying inside radius r, for an electron in an (n, l) wave function. If the field of the atom is considered to be spherically symmetrical, and Z is the " effective nuclear charge " at radius r, defined so that the field† at radius r is Z/r^2, then for an atom of nuclear charge N

$$Z = N - \Sigma \, Z_0 \,(nl, nl \,|\, r)$$

the sum being over all occupied wave functions. There may be a number of wave functions with the same values of (nl); if there are N_{nl} wave functions‡ with given values of n and l, then

$$Z = N - \Sigma_{nl} N_{nl} Z_0 \,(nl, nl \,|\, r) \qquad (4)$$

the sum being now over all values of n and l; if the (nl) group is complete, $N_{nl} = 2 \,(2l + 1)$.

If C is the total charge on the atom,

$$C = N - \Sigma_{nl} N_{nl},$$

so (4) can be written alternatively

$$Z = C + \Sigma_{nl} N_{nl} \,[1 - Z_0 \,(nl, nl \,|\, r)]. \qquad (5)$$

For an electron occupying an (nl) wave function, $[1 - Z_0 \,(nl, nl \,|\, r)]$ is the charge lying outside radius r, and tends to 0 for large r; $[1 - Z_0 \,(nl, nl \,|\, r)]$ may be described as the contribution to Z at radius r from an electron occupying an (nl) wave function, and unit charge on the nucleus; it is in terms of these contributions to Z that work on the self-consistent field is usually done, and the extent of the agreement between estimated and calculated contributions expressed.

* This notation is unnecessarily elaborate for consideration of the self-consistent field alone, but is used for consistency with the notation which is necessary in some applications of the results (see Hartree and Black, *loc. cit.*), and which is also convenient for the extension to Fock's equations.

† It is important to remember that when Z varies with r, the potential at radius r is not even approximately Z/r, in general.

‡ If the (nl) group is not complete, its contribution to the field is not spherically symmetrical and for the purpose of the self-consistent field we take a spherical average. Slater has shown that the approximation involved in taking this average is of the same order as that involved in omitting the interchange terms which form the difference between Fock's equations and the equations of the self-consistent field.

In the results of which this paper gives a first instalment, the agreement will be considered " satisfactory " if the difference between the estimated and calculated contributions $N_{nl} [1 — Z_0 (nl, nl | r)]$ to Z from each whole group does not exceed 0·02 at any radius, and the difference between the sums of the contributions for the whole atom does not exceed 0·03 at any radius, and probably the actual results presented will usually be well within these limits.

For the standard calculations and subsequent work based on them, the contributions to Z have been estimated to 0·005, and the calculated values have been calculated to three decimals, the last not always certain to 1 or 2. For all but the outermost groups, it has been quite practicable to estimate the contributions to Z so that the difference between estimated and calculated values is nowhere greater than 0·005, and for the outermost group it has been possible to attain a maximum difference of 0·01 or only slightly over. The atoms for which results are given here are the two most troublesome of all for which calculations have been carried out, on account in each case of the sensitiveness of the outer groups to the estimated contributions to the field, and the order of agreement of estimated and calculated contributions to Z, and so of approximation to the self-consistent field, attained for them should always be attainable for others with less trouble.

The contributions to Z may be called " stable," in the sense that if the estimated contributions from any group is increased over a range of r, the effect of this is to decrease the calculated contribution from this group (and from others also) ; for an increase of Z means that the attractive field on an electron towards the nucleus is increased, the wave functions of electrons in the field become more compact, and the proportion of the electron distribution lying inside any given radius is increased ; that is Z_0 for that group is increased, and $1 — Z_0$ is decreased ; and $1 — Z_0$ occurs with a positive sign in (S).

For all but the groups of the outermost shell, it is usually if not always the case that the change in the calculated contributions is smaller than the change in the estimated contributions. If this were so for all groups, an iterative process, taking the calculated contributions from one approximation as the estimates for the next, would give a series of calculations with results converging to those for the self-consistent field ; though this process would be unnecessarily lengthy, as with experience it is usually possible to make revised estimates better than those obtained by simply taking the calculated contributions of the previous approximation. But for the groups of the outer shell, and particularly the most loosely bound group, there sometimes occurs a phenomena which may be

termed over-stability, in which a change of estimated contribution to Z causes a change in the calculated contribution larger than a change in the estimate. When a group is over-stable in this sense, an iterative process would not con-verge, but, for small variations, would oscilllate and diverge, and it is then quite necessary to choose, as revised estimates of contributions to Z, values better than the calculated contributions of the previous approximation; it is also unusually difficult to make satisfactory estimates and adjustments to them, so the process of approximation to the self-consistent field is most troublesome in such cases.

A numerical example of over-stability is given in the discussion of the results for Cu$^+$ in § 4.

§ 3. *Description and Explanation of the Tables.*

It is proposed to give the following results for each atom for which calculations on these lines are carried out :—

(a) A table of the radial wave functions $P(nl|r)$, not normalized, and also P/r^{l+1} for small r.

(b) A subsidiary table giving for each wave function the value of the energy parameter ε in the radial wave equation (2), and the value of the normalizing integrals $\int_0^\infty P^2 \, dr$.

(c) A table of the contributions $2 \, (2l + 1) \, [1 - Z_0 \, (nl, \, nl \,|\, r)]$ to Z at radius r. [The atoms for which calculations are at present in progress all consist of complete groups so that $N_{nl} = 2 \, (2l + 1)$.]

(a) *and* (b).—The radial wave functions are tabulated unnormalized for several reasons.

In applications of the results, integrals of the form $\int_0^\infty P \, (\alpha \,|\, r) \, F \, (r) \, P \, (\beta \,|\, r) \, dr$, with normalized wave functions, often occur; but in evaluating them it is at least as easy to use unnormalized wave functions and divide by

$$\left[\int_0^\infty P^2 \, (\alpha \,|\, r) \, dr \right]^{\frac{1}{2}} \left[\int_0^\infty P^2 \, (\beta \,|\, r) \, dr \right]^{\frac{1}{2}}$$

at the end, as to use normalized wave functions throughout. The values of the normalization integrals $\int_0^\infty P^2 \, dr$ are given in the subsidiary table.

Also as $r \to 0$, P/r^{l+1} tends to a finite and non-zero value, and for numerical reasons it is convenient in the integration of the wave equation to keep this limit the same for different wave functions with the same l. When this is done, these different wave functions are nearly the same for r small, and advantage can often be taken of this in applications; this advantage is lost when normalized wave functions are used.

Also in dividing each calculated value of P by the square root of the normalizing integral, and rounding off to the number of places retained in the table, there is some loss of accuracy and the resulting rounded-off values may not be quite normalized.

It has therefore seemed best to tabulate actual calculated values of P in most cases. In almost all cases the tabulated values are rounded off from the values obtained on the calculation sheets, on which usually one, and occasionally two, more significant figures appear than in the tables; so that it is hoped that the divergence from the correct solution of the equations with the field actually used in the final calculations is generally not more than 1 in the last figure tabulated. The field actually used was not of course exactly the self-consistent field, and it is rather difficult to estimate the variation in the calculated values which would result from replacing the actual field used by the self-consistent field, but in the results here given this variation would probably not be more than 1 or 2, in the last figure tabulated, for a wave function of an inner group, and might be rather more for a wave function of one of the outer groups (especially for $(3p)$ in Cl^- and $(3d)$ in Cu^+) but should not usually be more than 5.

The calculations generally provide values of P at about twice as many values of r as those shown in the table, the intervals used in the numerical integration being usually half those used in the tabulation; the tables here given should be adequate for all ordinary applications, but the intermediate values of P can be supplied as required.

For some applications, P may be required for small r to greater accuracy, or at smaller intervals of r, than it is given in the main table; for such purpose it is best to work in terms of P/r^{l+1}, as this is finite and non-zero at $r = 0$, and is nearly linear in r for r small, and so is easy to interpolate; and a small table of this function for small r is given at the head of the main table.

A table is also given of the energy parameters ε for the different wave functions. Each of these is formally the negative energy of an electron in a wave function in the field of the nucles and the rest of the atom, or the energy required to remove this electron from the corresponding wave function to rest

at infinity, the rest of the atom being considered as providing a static field ; this is not the same as the X-ray ionization energy of the atom, for the rest of the atom is not a static field but an electronic system whose configuration and energy changes when one electron is removed. But empirically there is a close quantitative correspondence between these ε's and the X-ray ionization energies, which has not been fully explained as far as I am aware.

(c) For each atom the contributions to Z are tabulated, partly because they will be useful as a starting-point for a better approximation to the self-consistent field if one is ever required, and also for the first steps in the solution of Fock's equations,* but more particularly because they are probably the most useful quantities in terms of which to carry out the interpolation between different atoms. Slater has suggested a method of interpolation of wave functions based on the approximate representation of the wave functions by analytical formulæ, and interpolation of the constants in these formulæ, but hardly enough atoms have been yet worked out to provide enough values of the constants between which to interpolate accurately ; the change of atomic structure with atomic number is rather irregular (cf. the occurrence of " transition groups ") so that the relations between the atomic number and the constants defining a wave function would not be expected to be very easy functions to interpolate accurately. If fairly accurate wave functions are required, it seems best at present not to try to interpolate the wave functions themselves, but to interpolate the contributions to Z, which are probably much less sensitive to details of atomic structure, and calculate wave functions in the field so constructed. This must in any case be the process in beginning the calculation of the self-consistent field for a new atom, and it is mainly for this purpose that the contributions to Z are tabulated.

The contribution from each (nl) group is tabulated, not the contribution from one electron, as these contributions from each whole group are the quantities usually required. Three decimals are given, as although only two decimals and sometimes a 5 in the third place were used in the estimates, the variations of the calculated values with the variations in the estimates show that the third decimal in the calculated values is probably within 2 or 3

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* The functions occurring in Fock's equations, corresponding to the P's in the equations of the self-consistent field, are orthogonal functions, which the solutions of the self-consistent field equations are not ; but the changes in contributions to Z due to making the P's orthogonal are probably smaller than those due to the resonance terms in Fock's equations, and as a first step the $Z_0 (\alpha\alpha|r)$ functions which occur in Fock's equations can be taken as those of the self-consistent field.

of its value for the self-consistent field in most cases, and almost certainly for the inner groups; so that the third decimal is of some value, although not certain to a unit.

§ 4. *Results for* Cl⁻.

The maximum difference between estimated and calculated contributions to Z from any group, for the standard calculations, was $0 \cdot 03$; revised estimates, were made for all groups on the basis of the results of the standard calculations, and a second set of revised estimates was made for the $(3p)^6$ group only, and was used for the calculations giving the results tabulated. The maximum difference between estimated and calculated contributions to Z for the field used to give these results is less than $0 \cdot 01$ for each group, and the difference between estimated and calculated Z for the whole atom is also nowhere larger than $0 \cdot 01$; for the earlier calculations of which some results were given in my first paper, the maximum difference in the total Z was $0 \cdot 08$.

The wave function for the outermost (nl) group of a negative ion is very sensitive to the estimated field. Analytically this arises from the smallness of the energy parameter ε for such a wave function; it is related to the looseness of binding of this electron, although, as already emphasized, ε cannot be taken directly as a measure of the ionization energy. For large r, the behaviour of the wave function is chiefly determined by the value of ε; when the estimated field is changed, then ε for each wave function is changed, and if ε is small, a small change in ε may be a considerable *proportional* change and so affect considerably the behaviour of the wave function for large r. The $(3p)^6$ group is in fact over-stable in the sense explained at the end of § 2, and it is satisfactory that such a good agreement between estimated and calculated contributions was reached at the second revision of the estimates used in the standard calculations.

Table I.—Cl⁻ Wave Functions.

Tables of P/r^{l+1} for small r.

r.	(1s).	(2s).	(2p).	(2s).	(3p).
0·000	100	100	400	100	400
0·005	91·86	91·79	383·4	91·79	383·4
0·010	84·38	84·14	367·6	84·12	367·5
0·015	77·52	77·01	352·5	76·97	352·2
0·020	71·23	70·36	338·2	70·30	337·6

Table of P.

r.	(1s).	(2s).	(2p).	(3s).	(3p).
0·000	0·000	0·000	0·000	0·000	0·000
0·005	0·459	0·459	0·010	0·459	0·010
0·010	0·844	0·841	0·037	0·841	0·037
0·015	1·163	1·155	0·079	1·155	0·079
0·020	1·425	1·407	0·135	1·406	0·135
0·03	1·805	1·752	0·280	1·749	0·280
0·04	2·034	1·921	0·460	1·913	0·458
0·05	2·150	1·951	0·664	1·937	0·661
0·06	2·183	1·872	0·884	1·850	0·878
0·07	2·156	1·709	1·113	1·678	1·105
0·08	2·087	1·483	1·346	1·441	1·335
0·09	1·989	1·210	1·579	1·158	1·563
0·10	1·873	0·906	1·808	0·842	1·785
0·12	1·616	0·241	2·244	0·157	2·203
0·14	1·357	−0·442	2·639	−0·542	2·572
0·16	1·117	−1·102	2·984	−1·208	2·884
0·18	0·905	−1·710	3·276	−1·812	3·133
0·20	0·725	−2·252	3·516	−2·336	3·320
0·22	0·576	−2·722	3·704	−2·771	3·446
0·24	0·455	−3·117	3·845	−3·115	3·514
0·26	0·357	−3·439	3·942	−3·368	3·528
0·28	0·278	−3·693	4·001	−3·537	3·494
0·30	0·216	−3·884	4·026	−3·625	3·416
0·35	0·113	−4·130	3·968	−3·543	3·058
0·40	0·058	−4·122	3·786	−3·116	2·523
0·45	0·030	−3·944	3·528	−2·447	1·868
0·50	0·015	−3·662	3·228	−1·622	1·137
0·55	0·008	−3·326	2·912	−0·711	0·367
0·60	0·004	−2·969	2·598	+0·231	−0·414
0·7	0·001	−2·276	2·014	2·065	−1·928
0·8		−1·681	1·519	3·673	−3·296
0·9		−1·209	1·123	4·966	−4·460
1·0		−0·852	0·817	5·924	−5·403
1·1		−0·591	0·587	6·571	−6·133
1·2		−0·405	0·418	6·946	−6·669
1·4		−0·186	0·207	7·076	−7·266
1·6		−0·079	0·101	6·674	−7·403
1·8		−0·035	0·048	6·006	−7·251
2·0		−0·015	0·023	5·244	−6·932
2·2		−0·006	0·011	4·488	−6·529
2·4		−0·002	0·005	3·788	−6·089
2·6		−0·001	0·002	3·167	−5·646
2·8			0·001	2·628	−5·213
3·0				2·170	−4·803
3·2				1·785	−4·419
3·4				1·464	−4·061
3·6				1·198	−3·733
3·8				0·979	−3·431
4·0				0·799	−3·154
4·5				0·479	−2·562
5·0				0·286	−2·089
5·5				0·171	−1·710
6·0				0·102	−1·403

Table I—(continued).

r.	(1s).	(2s).	(2p).	(2s).	(3p).
7				0·036	−0·954
8				0·013	−0·654
9				0·004₅	−0·451
10				0·001₅	−0·313
12					−0·152
14					−0·075
16					−0·037
18					−0·019
20					−0·009
22					−0·004
24					−0·002
26					−0·001

	ϵ.	$\int_0^\infty \mathrm{P}^2\, dr.$		ϵ.	$\int_0^\infty \mathrm{P}^2\, dr.$
(1s)	209·0	0·5346	(3s)	1·079	67·89
(2s)	18·35	7·252	(3p)	0·114	119·90
(2p)	14·37	7·232			

Table II.—Cl⁻ Contributions to Z.
Table of $2(2l+1)[1 - Z_0(nl, nl\,|\,r)]$.

r.	(1s).	(2s).	(2p).	(3s).	(3p).
0·000	2·000	2·000	6·000	2·000	6·000
0·005	1·999	2·000	6·000	2·000	6·000
0·010	1·990	1·999	6·000	2·000	6·000
0·015	1·971	1·998	6·000	2·000	6·000
0·020	1·940	1·996	6·000	1·999	6·000
0·03	1·840	1·988	5·999	1·999	6·000
0·04	1·700	1·979	5·998	1·998	6·000
0·05	1·535	1·969	5·995	1·997	6·000
0·06	1·358	1·958	5·990	1·996	5·999
0·07	1·181	1·949	5·982	1·995	5·999
0·08	1·013	1·942	5·969	1·994	5·998
0·10	0·717	1·934	5·928	1·993	5·995
0·12	0·488	1·932	5·859	1·992	5·991
0·14	0·323	1·931	5·760	1·992	5·985
0·16	0·208	1·927	5·628	1·992	5·978
0·18	0·132	1·916	5·464	1·991	5·969
0·20	0·082	1·894	5·273	1·988	5·959
0·22	0·051	1·859	5·056	1·984	5·948
0·24	0·031	1·812	4·820	1·979	5·935
0·26	0·018	1·753	4·568	1·973	5·923
0·28	0·010	1·682	4·305	1·966	5·910
0·30	0·006	1·603	4·037	1·958	5·899

Table II—(continued).

r.	(1s).	(2s).	(2p).	(3s).	(3p).
0·35	0·002	1·379	3·370	1·939	5·873
0·40		1·142	2·743	1·922	5·853
0·45		0·917	2·187	1·911	5·840
0·50		0·716	1·712	1·905	5·835
0·55		0·548	1·321	1·903	5·833
0·60		0·411	1·005	1·902	5·833
0·7		0·221	0·564	1·898	5·825
0·8		0·114	0·305	1·872	5·791
0·9		0·056	0·161	1·816	5·713
1·0		0·027	0·083	1·728	5·591
1·1		0·013	0·042	1·612	5·423
1·2		0·006	0·021	1·476	5·217
1·4		0·001	0·004	1·182	4·725
1·6			0·001	0·900	4·180
1·8				0·662	3·641
2·0				0·476	3·137
2·2				0·336	2·682
2·4				0·236	2·284
2·6				0·164	1·940
2·8				0·114	1·644
3·0				0·080	1·394
3·2				0·058	1·181
3·4				0·042	1·002
3·6				0·032	0·850
3·8				0·025	0·721
4·0				0·019	0·613
4·5				0·006	0·409
5·0				0·002	0·275
5·5				0·001	0·185
6·0					0·125
7					0·057
8					0·024
9					0·010
10					0·003
11					0·001

§ 5. *Results for* Cu$^+$.

For Cu$^+$ the (3d) wave function is very sensitive to the estimated field, the reason being rather different from the case of the (3p) wave function of Cl$^-$. Here the value of ε is not inconveniently small, but there is a considerable range over which the attractive field is only slightly larger than the centrifugal field (whose potential energy is represented by the term $l(l+1)/r^2$ in the radial wave equation (2)) so that a small change in the attractive field makes

a large proportional change in the resultant field and so in the wave function. Analytically, in the wave equation

$$\mathrm{P}'' + [2v - \varepsilon - l(l+1)/r^2]\,\mathrm{P} = 0.$$

the coefficient of P remains small over a considerable range.

This feature is closely related to the position of Cu in the periodic table. The occurrence of the " transition group " of elements to Sc to Ni in the periodic table is associated with the transition of the $(3d)$ wave function from that of potassium, where it is nearly hydrogen-like and is an excited state of the series electron, to the much more compact $(3d)$ wave function, forming part of the core, of the copper atom. This transition, which is just completed in copper, is due, roughly speaking, to the variation with atomic number of the range over which the attractive force exerted on an electron by the rest of the atom is greater than the centrifugal force on an electron with angular momentum specified by $l = 2$; for potassium the centrifugal force is greatest except at distances well outside the atom; for copper the atomic field is enough, but not much more than just enough, to hold an electron with $l = 2$ in the core against the centrifugal force.
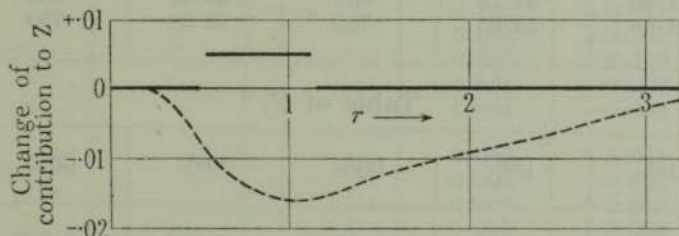

Fig. 1.—To illustrate overstability of $(3d)^{10}$ group. ——— Full-line curve shows change of estimated contribution to Z; — — — broken curve shows consequent change of calculated contribution to Z.

This sensitiveness of the $(3d)$ wave function, and the comparatively large number of electrons with this radial wave function, makes the $(3d)^{10}$ group seriously over-stable in the sense defined at the end of § 2. Fig. 1 shows quantitatively an example; the full curve shows a variation made in the estimated contribution to Z from the $(3d)^{10}$ group, and the broken curve the consequent variation in the calculated contribution, which can be seen at once to be considerably greater than the variation in the estimated contribution.

This pronounced overstability of the $(3d)^{10}$ group makes the process of approximation to the self-consistent field very troublesome; altogether, nine steps of approximation were made in order to obtain the results here given; most of these steps were mainly concerned with revision of the estimated

contribution from the $(3d)^{10}$ group. In the final approximation, for which the results are tabulated, the differences between estimated and calculated contributions to Z from each group are less than $0\cdot01$ throughout ; the $(3d)$ wave function, and contribution of the $(3d)^{10}$ group to Z, are the best that can be obtained without doing the calculation throughout with an accuracy corresponding to three full decimals in the estimated contributions to Z.

Observed values of ν/R for the X-ray levels are given in the same table as the values of the energy parameter ε of the central field wave functions ; although the values of ε cannot be regarded as calculated values of the X-ray levels, as already mentioned, they agree very closely with the observed values for the X-ray levels ; a similar close agreement was also found for Rb$^+$.*

Table III.—Cu$^+$ Wave Functions.
Table of P/r^{l+1} for small r.

r.	$(1s)$.	$(2s)$.	$(2p)$.	$(3s)$.	$(3p)$.	$(3d)$.
0·000	100·0	100·0	1000	100	1000	1000
0·005	86·51	86·31	930	86·29	930	953
0·010	74·87	74·12	866	74·04	866	909
0·015	64·80	63·29	807	63·12	806	868
0·020	56·60	53·65	752	53·38	750	828

Table of P.

r.	$(1s)$.	$(2s)$.	$(2p)$.	$(3s)$.	$(3p)$.	$(3d)$.
0·000	0·000	0·000	0·000	0·000	0·000	0·000
0·005	0·433	0·432	0·023	0·431	0·023	0·000
0·010	0·749	0·741	0·087	0·740	0·087	0·001
0·015	0·972	0·948	0·182	0·947	0·181	0·003
0·020	1·122	1·073	0·301	1·068	0·300	0·007
0·025	1·215	1·127	0·438	1·118	0·436	0·012
0·03	1·263	1·125	0·589	1·110	0·585	0·020
0·035	1·276	1·077	0·748	1·055	0·742	0·031
0·04	1·264	0·992	0·912	0·963	0·902	0·044
0·05	1·187	0·742	1·243	0·697	1·223	0·079
0·06	1·071	0·427	1·565	0·365	1·527	0·126
0·07	0·940	0·081	1·864	0·004	1·800	0·184
0·08	0·809	−0·270	2·132	−0·357	2·034	0·253
0·09	0·686	−0·609	2·367	−0·700	2·225	0·332
0·10	0·574	−0·925	2·565	−1·013	2·369	0·420
0·12	0·392	−1·462	2·855	−1·513	2·518	0·621
0·14	0·261	−1·858	3·013	−1·830	2·495	0·847
0·16	0·170	−2·119	3·063	−1·968	2·326	1·091
0·18	0·110	−2·263	3·027	−1·946	2·038	1·346
0·20	0·070	−2·311	2·925	−1·793	1·659	1·605

* Hartree, *loc. cit.*

Table III—(continued).

r.	(1s).	(2s).	(2p).	(3s).	(3p).	(3d).
0·22	0·044	−2·286	2·779	−1·536	1·216	1·863
0·24	0·027	−2·206	2·602	−1·202	0·731	2·117
0·26	0·017	−2·089	2·409	−0·817	0·223	2·362
0·28	0·010	−1·948	2·208	−0·400	−0·290	2·595
0·30	0·006	−1·795	2·007	+0·030	−0·797	2·815
0·35	0·002	−1·400	1·534	+1·079	−1·974	3·296
0·40		−1·044	1·136	1·988	−2·953	3·671
0·45		−0·754	0·821	2·694	−3·701	3·944
0·50		−0·533	0·583	3·190	−4·222	4·126
0·55		−0·369	0·408	3·494	−4·545	4·231
0·60		−0·253	0·282	3·637	−4·702	4·276
0·7		−0·115	0·132	3·578	−4·654	4·236
0·8		−0·051	0·061	3·247	−4·314	4·089
0·9		−0·022	0·028	2·804	−3·839	3·888
1·0		−0·009	0·012	2·349	−3·328	3·666
1·1		−0·004	0·005$_5$	1·925	−2·834	3·439
1·2		−0·002	0·002$_5$	1·553	−2·382	3·217
1·3		−0·001	0·001	1·238	−1·984	3·004
1·4				0·978	−1·640	2·803
1·6				0·599	−1·103	2·437
1·8				0·359	−0·731	2·117
2·0				0·213	−0·479	1·838
2·2				0·125	−0·311	1·594
2·4				0·073	−0·201	1·381
2·6				0·042	−0·129	1·196
2·8				0·024	−0·083	1·034
3·0				0·014	−0·053	0·892
3·2				0·008	−0·034	0·769
3·4				0·004	−0·021	0·662
3·6				0·002	−0·014	0·568
3·8				0·001	−0·009	0·487
4·0					−0·005	0·417
4·5					−0·001	0·281
5·0						0·188
5·5						0·124
6·0						0·081
7						0·034
8						0·014
9						0·006
10						0·002$_5$
11						0·001
12						

	ϵ.	ν/R obs. X-ray term.	$\int_0^\infty P^2\, dr$.		ϵ.	ν/R obs. X-ray term.	$\int_0^\infty P^2\, dr$
(1s)	658·0	661·6	0·10589	(3s)	8·968	8·9	7·905
(2s)	78·45	81·0	1·1568	(3p)	6·078	5·7	14·913
(2p)	69·86	68·9	2·0621	(3d)	1·195	0·4	21·296

Table IV.—Cu$^+$ Contributions to Z.

Table of $2(2l+1)[1 - Z_0(nl, nl|r)]$.

r.	$(1s)^2$.	$(2s)^2$.	$(2p)^6$.	$(3s)^2$.	$(3p)^6$.	$(3d)^{10}$.
0·000	2·000	2·000	6·000	2·000	6·000	10·000
0·005	1·993	1·999	6·000	2·000	6·000	10·000
0·010	1·958	1·996	6·000	1·999	6·000	10·000
0·015	1·887	1·990	6·000	1·998	6·000	10·000
0·020	1·782	1·981	5·999	1·997	6·000	10·000
0·025	1·652	1·970	5·997	1·996	6·000	10·000
0·030	1·506	1·959	5·993	1·994	5·999	10·000
0·035	1·354	1·949	5·987	1·992	5·998	10·000
0·040	1·201	1·940	5·977	1·991	5·997	10·000
0·05	0·915	1·926	5·942	1·990	5·992	10·000
0·06	0·674	1·920	5·884	1·989	5·984	10·000
0·07	0·482	1·919	5·798	1·989	5·973	10·000
0·08	0·338	1·918	5·681	1·989	5·958	10·000
0·09	0·232	1·915	5·533	1·988	5·940	10·000
0·10	0·157	1·904	5·355	1·986	5·919	9·999
0·12	0·069	1·854	4·923	1·977	5·870	9·996
0·14	0·029	1·757	4·418	1·963	5·819	9·991
0·16	0·012	1·618	3·878	1·945	5·772	9·982
0·18		1·451	3·336	1·925	5·733	9·968
0·20		1·268	2·819	1·907	5·705	9·947
0·22		1·085	2·345	1·893	5·688	9·919
0·24		0·910	1·922	1·883	5·680	9·882
0·26		0·750	1·558	1·878	5·678	9·835
0·28		0·609	1·248	1·876	5·678	9·776
0·30		0·487	0·990	1·876	5·675	9·708
0·35		0·266	0·534	1·871	5·633	9·487
0·40		0·137	0·277	1·839	5·507	9·200
0·45		0·068	0·138	1·768	5·282	8·858
0·50		0·032	0·067	1·657	4·963	8·474
0·55		0·015	0·032	1·514	4·573	8·062
0·60		0·007	0·015	1·353	4·141	7·637
0·7		0·001	0·002	1·018	3·249	6·781
0·8				0·721	2·433	5·965
0·9				0·488	1·762	5·217
1·0				0·320	1·243	4·547
1·1				0·204	0·861	3·953
1·2				0·128	0·587	3·433
1·3				0·079	0·396	2·980
1·4				0·047	0·265	2·584
1·6				0·016	0·115	1·939
1·8				0·005	0·048	1·454
2·0				0·001	0·019	1·087
2·2					0·006	0·811
2·4					0·002	0·604
2·6						0·448
2·8						0·330
3·0						0·243
3·2						0·179
3·4						0·130
3·6						0·095
3·8						0·068
4·0						0·050

Table IV—(continued).

r.	$(1s)^2$.	$(2s)^2$.	$(2p)^6$.	$(3s)^2$.	$(3p)^6$.	$(3d)^{10}$.
4·5						0·022
5·0						0·008
5·5						0·003
6·0						0·001

It is interesting to compare the distribution of charge for Cu^+, with an outer shell of 18 electrons, with that for inert-gas-like ions which have outer shells of 8 electrons; and for this purpose the total charge density for Cu^+ and contributions to it from the groups of the outer shell† are shown as functions of r in fig. 2, and corresponding diagrams for K^+ and Rb^+ are shown in figs. 3 and 4 respectively.‡

The Cu^+ ion is more compact than K^+ or Rb^+; although the outer shell of Cu^+ consists of 18 electrons while those of K^+ and Rb^+ consist of 8, the charge density in Cu^+ is smaller than in K^+ or Rb^+ outside a radius of about 1·2 atomic units; and it is necessary to pass right inside the outer shell of K^+ or Rb^+ to the next inner shell before coming to a region of charge density as high as that in the outermost shell of Cu^+. This agrees with the much smaller observed packing radius for a Cu^+ or Cu^{++} ion than of a K^+ or Rb^+ ion in crystals (the effect of a second ionization of the copper atom would be to contract the " tail " of the $(3d)$ wave function for large r, but it would not greatly alter the distribution).

It should be pointed out here that the total volume density, which is $1/4\pi r^2$ times the radial density, increases steadily as r decreases, and does not show the maxima and minima shown by the radial density curve.

Another interesting comparison between Cu and the alkali metal atoms is that of the series electron wave function and its relation to the interatomic distance in metals. This comparison will be given here although it depends on some results not given in this paper. Slater's theory of cohesion in metals§ suggests that the interatomic distance in the crystal of a metallic element

† To avoid crowding the diagram, the contributions from the individual groups of the inner shell are not shown; the point of interest in the comparison is the structure of the outer shell.

‡ These diagrams are based on results of old work, but the alteration in the results due to revision based on the standard calculations is not likely to be appreciable on the scale of these diagrams.

§ Slater, ' Phys. Rev.,' vol. 35, p. 509 (1930).
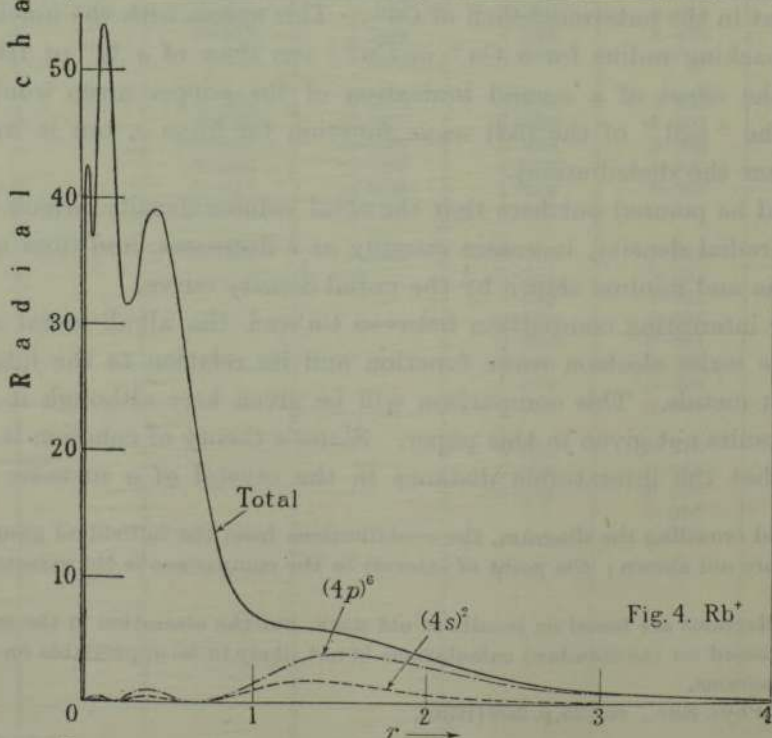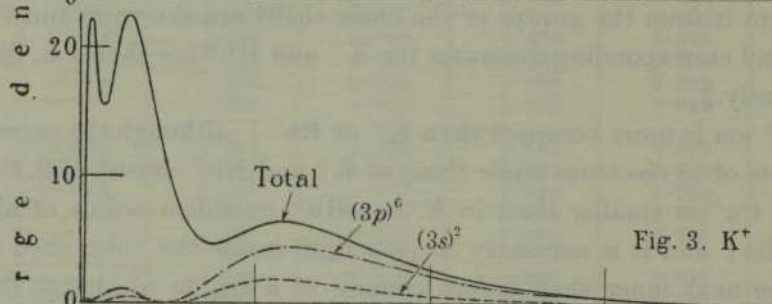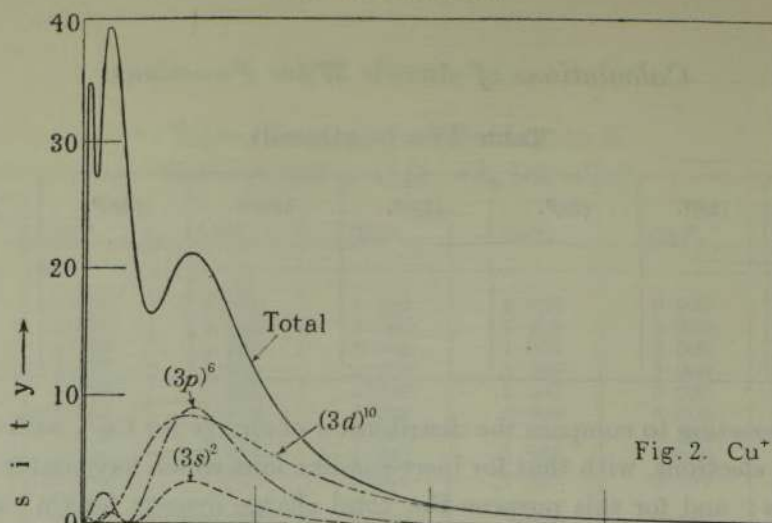
FIGS. 2, 3, 4.—Charge distributions in Cu+, K+, Rb+. Radial charge density in electrons per atomic unit shown as function of radius in atomic units. The full-line curve shows total charge density for the whole atom, the broken curves show the contributions to the total charge density from the groups of the outer shell.

may be given approximately by the condition that the unperturbed series electron wave functions of the two atoms overlap so that their maxima nearly coincide.

If P is the radial function for the series electron, then the wave function itself is P/r (the normal state of the series electron being an *s* state); in Table V the approximate radii of the main maxima of P^2 and of $(P/r)^2$ for the normal series electron wave function are given; and also the observed atomic packing radius (defined as half the interatomic distance) and its ratio to the radii of the maxima of the calculated wave functions.

Table V.

Atom.	Radius of max. $P,^2$ $r_1.$	Radius of max. $(P/r)^2$ $r_2.$	Crystal structure of element.	Packing radius* $r_0.$	$\dfrac{r_0}{r_1}$	$\dfrac{r_0}{r_2}$
K	2·66	2·01	Body centred cubic	2·309	0·87	1·15
Rb	2·84	2·18	,,	2·43	0·86	1·11₅
Cs	3·21	2·53	,,	2·62	0·81	1·04
Cu	1·51	1·04	Face centred cubic	1·275	0·84₅	1·23

(All lengths in A.)
* Taken from Neuberger, ' Z. Krystallog.,' vol. 80, p. 103 (1931).

The results show a relation between series electron wave functions and interatomic distance of the kind suggested by Slater; the atomic radius in all cases lies between the radii at which P and P/r have their maxima, and, except for Cs, about half way between; and the variation of either ratio is considerably less than the variation of the packing radius.

§ 6. *Summary.*

Approximate wave functions for a number of atoms have been calculated by the method of the self-consistent field, but of the available results few have been published in detail. These results for a number of atoms are being revised, and the approximation improved, with a view to' publication so as to make them more generally accessible; this paper presents the results for Cl^- and Cu^+. The results for copper are compared with those for the other alkali metals and characteristic differences noted; and the relation between the interatomic distance in metals and the wave function of the series electron is pointed out.