

The Wave Mechanics of an Atom with a Non-Coulomb Central Field. Part II. Some Results and Discussion. By D. R. HARTREE, Ph.D., St John's College.

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§ 1. *Introduction.*

In the previous paper an account has been given of the theory and methods used for determining the characteristic values and functions of Schrödinger's wave equations for a non-Coulomb central field of force whose potential v is given. In this paper some results of the application of these methods will be given and discussed; references to the previous paper will be prefixed by a I. Atomic units (see I, § 1) will be used throughout this paper.

There are two different objects which one may have in view in doing numerical work of this kind.

First, the object may be to find an empirical field of force for a given atom, for which the characteristic values of the wave equation give as closely as possible the terms of the optical and X-ray spectra of that atom.

Secondly, as suggested in I, § 1, it may be to find a field of force such that the distribution of charge given by the wave functions for the core electrons shall reproduce the field*.

Certainly these are not altogether independent; in the first case, one may hope that the empirical field may be expressible as the sum of contributions from the different core electrons†, and in the second case, one may hope that the characteristic values in the field so found will give approximately the term values of the spectra of that atom. Nevertheless they are distinct in that in one case the atomic field may be chosen without reference to the characteristic functions themselves, and in the other case depends essentially on them, so that they involve rather different procedure in the numerical work. The first would be the more appropriate if the results were to be used to find the relative intensities of lines in the spectrum, and some work from this point of view has already

* Corresponding work for the orbital atomic model has been done from the first point of view by E. Fues, *Zeit. f. Phys.*, Vol. xi, p. 364 (1922); Vol. xii, p. 1; Vol. xiii, p. 211 (1923); Vol. xxi, p. 265 (1924); D. R. Hartree, *Proc. Camb. Phil. Soc.*, Vol. xxi, p. 265 (1923) and Y. Sugiura and H. C. Urey, *Det Kongel. Danske Videnskab. Selskab., Math.-Phys. Medd.*, Vol. vii, No. 13 (1926), and from the second by R. B. Lindsay, *Publ. Mass. Inst. Technology*, Series II, No. 20 (1924).

† For the orbital atomic model the writer has tried to obtain such results, but without success.

been done by Sugiura*, the second, if the distribution of charge were required† and further results were to be based on it (for example X-ray scattering factors F').

The work here described was done with the second as its main object, and this demands consideration of the appropriate field of force to use for the core electrons.

§ 2. *The Field of Force for a Core Electron.*

Consider an atom such as the neutral atom of an alkali metal, consisting of closed n_k groups and a series electron. The potential v for the series electron is that of the field of the centrally symmetrical distribution of charge of the closed groups; but just as in the theory of the hydrogen atom the field acting on the electron is that of the nucleus only, not that of the nucleus and its own distributed charge, so here the field for a core electron is the total field of the nucleus and all the closed groups, less its own contribution to that field. Now except for an electron with $l=0$, its own contribution to the field is not centrally symmetrical, so that it would seem that the assumption of a central field is not applicable to it; on the other hand, the structure of the X-ray terms is that of terms due to a spinning electron in a central field.

It is just here that we meet the most serious doubts concerning the replacement of the actual many-body problem by a one-body problem with a central field for each electron, even as a first approximation.

A doublet term of an X-ray spectrum is due not to the presence of a single definite electron, but to the absence of one from an otherwise complete n_k group; the presence of this last electron gives the single 1S term characteristic of a complete group. Now it is only through operation of Pauli's exclusion principle‡ that an n_k group lacking one electron to make it complete gives only a spectral term of the same type (multiplicity and l -value) as would be given by that electron alone in a central field of other complete groups, and that the complete group gives only a 1S term; this principle is essentially an expression of the behaviour of a number of electrons with the same n_k , whose mutual interactions may be considerable, and this involves developments of quantum mechanics beyond those applied in this paper.

In order to make headway at all without departing from the simple idea of a central field for each electron, a simplifying assump-

* Y. Sugiura, *Phil. Mag.*, Ser. 7, Vol. iv, p. 495 (1927).

† The determination of the distribution of charge directly from a potential or field given as a function of the radius involves numerical differentiation, which is an unsatisfactory process, especially in this case, when it is possible to make a small increase of the field at one radius and a small decrease at another without appreciably affecting the fit between calculated and observed term values.

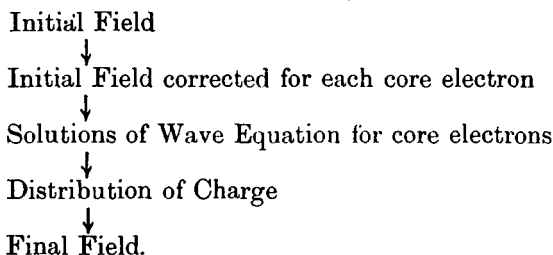
‡ See, for example, F. Hund, *Linienpektren*, p. 114 *et seq.*

tion is necessary here in dealing with core electrons, and in this paper it will be assumed that the appropriate potential to take in working out the characteristic value and function for a core electron is the total potential of the nucleus and of the whole electronic distribution of charge, less the potential of the centrally symmetrical field calculated from the distribution of charge of that electron, *averaged over the sphere for each radius*; the radial density of this averaged distribution of charge is just the normalised value of P^2

(i.e. the charge between radii r and $r + dr$ is $P^2 dr / \int_0^\infty P^2 dr$) or, for a complete n_k group consisting of s electrons, it is $1/s$ of the contribution to the radial density from this whole group.

It would of course be possible in most cases to carry out the work for the core electrons without taking into account at all the fact that the distributed charge of a core electron does not contribute to the field acting on it, but it seems probable that a better approximation to the actual distribution of charge will be obtained by making some correction, even if it is only a crude one. Besides, in treating the outer electrons of negative ions, some such correction is necessary in order to make the work possible at all.

For numerical work we have to start from a field which will be called the 'initial field'; for each n_k corresponding to a group of core electrons the field is corrected, as explained above, for the fact that the distributed charge of an electron must be omitted in finding the field acting on it, and for the field so corrected the part of the solution of the wave equation depending on r is found by the methods given in I; then from the solutions for all groups of core electrons a distribution of charge can be calculated (if the n_k groups are all complete, this distribution of charge will be centrally symmetrical), and then the field of the nucleus and this distribution of charge can be found; this may be called the 'final field.' The process may be expressed briefly in diagrammatic form:



If the final field is the same as the initial field, the field will be called 'self-consistent,' and the determination of self-consistent fields for various atoms is the main object of this paper. The self-consistent field so found is a characteristic of the particular atom

in the particular state of ionisation considered; it involves no arbitrary functions or constants whatever.

It is thought that the distribution of charge in the self-consistent field is probably the best approximation to the actual distribution of charge in the atom which can be obtained without very much more elaborate theoretical and numerical work, and so is the most suitable to use in any problems involving this distribution of charge; also it is hoped that when the time is ripe for the practical evaluation of the exact solution of the many-electron problem, the self-consistent fields calculated by the methods given here may be helpful as providing first approximations.

For each solution of the wave equation in the self-consistent field (corrected as already explained) in the case of a core electron there will be a characteristic value of the energy parameter ϵ ; it is a further question whether these values of ϵ are directly related to the optical and X-ray term values by the relation

$$\epsilon = \nu/R.$$

For the core electrons, this again depends on the details of the mutual interaction of the electrons in a closed group, and on the effect of the removal of one on the remainder; the simplest case, that of the normal state of neutral helium, has been worked out, and suggests that this relation may be expected to hold closely for the X-ray terms (see § 4).

§ 3. *Some Practical Details.*

The determination of the self-consistent field for any atom is a matter of successive approximation. Fortunately this process is 'stable' in that change of the initial field, of the same sign throughout, gives a change of the final field of the opposite sign. Consider, for example, an increase in the initial (positive) field; this pulls the whole distribution of charge further in, so that the negative charge inside a given radius is greater and the final field at each radius less than it was without the increase in the initial field.

For the first atom tried the initial field for the first approximation was obtained by Thomas' method*; in this case preliminary solutions of the wave equations have to be found with the same initial field for all core electrons, without the correction referred to above, in order to estimate the correction. It is better to build up an initial field as the sum of estimated contributions from the different groups of core electrons, so that the corrected field for each can be used even in the first approximation; when the calculations for two or three atoms have been completed this building up of the initial field can be done quite satisfactorily by interpolation or extrapolation.

* L. H. Thomas, *Proc Camb. Phil. Soc.*, Vol. xxiii, p. 542 (1927). It is necessary to extrapolate the field empirically beyond the range to which Thomas' results apply.

Since a given change in Z means a smaller *proportional* change in the field at small radii than at large radii, it might be expected that the final field would be more sensitive to changes in Z of the initial field at large radii than at small. This proves to be the case, and, with the stability of the process of successive approximation to a self-consistent field, suggests that the initial field at any stage should be taken between the initial and final fields of the previous approximation, nearer the final field at small r and nearer the initial field at large r . This general rule is justified by experience*.

For a central field of potential v , which is a function of r only,

$$Z = -r^2 dv/dr = dv/d(1/r)$$

is the point charge which, placed at the nucleus, would give the same *field* at radius r as the actual field; it is often called the 'effective nuclear charge' and this name will be used here. The quantity

$$Z_p = rv$$

is the point charge, which, placed at the nucleus, would give the same *potential* at radius r as that of the actual field; it may be called the 'effective nuclear charge for potential†'. It is usually convenient to work with Z and Z_p rather than with the field and the potential themselves, since Z and Z_p vary over a much smaller range. Differentiating $Z_p/r = v$ and substituting for dv/dr we have

$$-\frac{dZ_p}{dr} = \frac{Z - Z_p}{r},$$

and when Z is given as a function of r it has proved more satisfactory to find Z_p by numerical integration of this equation (which is very easy) than by direct integration of $v = -\int Zr^{-2}dr$ ‡.

In the numerical work, two places of decimals have usually been kept in Z in the initial and final fields, and the successive approximations towards a self-consistent field have been continued until the maximum difference in Z between the initial and final fields became less than 0.1.

* The process of successive approximation by taking the initial field always equal to the final field of the previous approximation is not always convergent, though perhaps it usually is. Even when it is, a more rapid convergence to the self-consistent field is obtained by the rule given here.

† The large difference between Z and Z_p is not always realised; for Rb the maximum value of Z/Z_p is over 2 and that of $Z - Z_p$ is over 13, so that Z and Z_p cannot be considered as even approximately equal for a non-Coulomb field.

‡ The reason is that Z is known at equal intervals of r , and for the direct integration unduly small intervals would have to be used in some regions, in order to keep down the higher orders of difference due to the r^{-2} factor; the formula for the mean value \bar{Z} for $dv = \bar{Z}\delta(1/r)$, when Z is known at equal intervals of r not of $1/r$, is more trouble to use than the differential equation.

§ 4. *The Normal State of Neutral Helium.*

The simplest case of an atom with more than one electron to which the idea of the self-consistent field is applicable is that of the normal state of neutral helium. In this case we consider the motion of one electron in the field of the nucleus and the second electron, and try to determine this field so that the 1_s wave function for the first electron gives a charge distribution for which the field is the same as that assumed for the second electron.

The numerical work went so easily that an extra decimal place was kept in Z , and the successive approximation was carried to a point where the maximum difference between the values of Z for the initial and final fields was 0.002.

The value of Z and the radial charge density $-dZ/dr$ for this field are given in Table I.

TABLE I.
*Neutral Helium, Normal State. Self-Consistent Field
and Distribution of Charge*

r atomic units	Z	$-dZ/dr$ electrons per atomic unit	r atomic units	Z	$-dZ/dr$ electrons per atomic unit
0	2.000	0.00	1.6	0.239	0.48
0.1	1.988	0.30	1.8	0.159	0.33
0.2	1.932	0.83	2.0	0.105	0.22
0.3	1.826	1.28	2.2	0.068	0.15
0.4	1.682	1.57	2.4	0.044	0.10
			2.6	0.028	0.06
0.6	1.344	1.73	2.8	0.018	0.04
0.8	1.013	1.55	3.0	0.011	0.026
1.0	0.733	1.25			
1.2	0.515	0.94	3.5	0.003	0.009
1.4	0.354	0.68	4.0	0.001	0.003

The most interesting point about the calculation is the value of the energy parameter ϵ , which was found to be $\epsilon = 1.835$ (24.85 volts), while the observed term value for the normal state of neutral helium gives $\nu/R = 1.81$ (24.6 volts). Now the calculated value of ϵ is found by considering the wave equation for one electron in the field of the nucleus and the distributed charge of the other, without taking into account the effect of the removal of one on the energy or distribution of charge of the other, while in the actual removal of one the change of charge distribution of the other is quite appreciable. Until it can be shown that the calculated energy parameter of the wave equation, for one electron in the self-consistent field

of the nucleus and the other, would be expected to agree well with the energy required to remove one electron, the other adjusting its charge distribution to the change of field caused by that removal, the very close agreement actually found must be taken as an empirical justification of the simple approximations used to represent the interactions of electrons with the same n_k , and of the general idea underlying the work, rather than as a notable success of the method. But it does suggest that in general for core electrons the energy parameter of the wave equation for the self-consistent field, corrected as already explained, may be expected to be a good approximation to the value of ν/R for the corresponding X-ray term*.

§ 5. *Rubidium.*

These methods were first applied to the Rb atom, and more extensive work has been done for it than for any other atom. This choice was made because it seemed interesting to examine what happened on the wave mechanics when on the orbital model an internal and an external orbit of the same n_k were possible, and this does not occur for elements of too low atomic number [Cu ($N = 29$) is the first such atom which also gives an optical spectrum which can be dealt with by a central field]; for Rb it does occur, and at the same time the atomic number is small enough for the effects of the relativity variation of mass and of the spinning electron to be dealt with adequately as independent first order perturbations (except perhaps for $l = 0$); also for Rb, the writer had fairly extensive results worked out for the orbital model, and it seemed likely that these would be interesting for comparison.

The work for the core electrons was carried out for the ion Rb^+ . For the first approximation the initial field was calculated by Thomas' method already mentioned, without the correction for the fact that a core electron is not acted on by its own distribution of charge; the final field for the first approximation was taken as the initial field for the second, and the correction was applied. Some trial changes in the field were then made to give an idea of the sensitivity of the final field to a change in the initial field, and a third initial field was built up from estimates of the contributions to Z from the different groups of core electrons. The maximum difference between this initial field and the final field calculated from it was 0.08 in Z ; this was within the limit of disagreement (0.1 in Z) which had been previously laid down, so that the process

* Actually the work was done in the inverse order; the application of the method to helium as an experiment was suggested by the good agreement between values of ϵ so calculated and the observed X-ray term values for more complicated atoms.

of approximation was not carried further. Fig. 1* shows the process of successive approximation to a self-consistent field; for the three approximations the difference between the values of Z for the initial and the final field is plotted as a function of r .

The effective nuclear charge Z and the radial charge density $-dZ/dr$ of the final field† of the third approximation is given in Table II: the values of Z probably differ from those of the self-consistent field by less than 0.05 throughout.

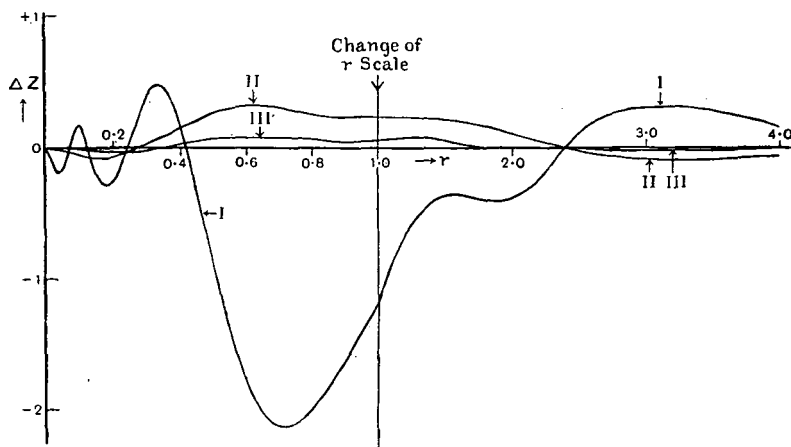


Fig. 1. Showing successive approximations to self-consistent field. Difference ΔZ between effective nuclear charge of initial and final field plotted against r for the three approximations (Curves I, II, III) made in the calculations for Rb.

§6. Rubidium. Comparison of Charge Distribution Calculated by Different Methods.

In Fig. 2* the separate contributions to the radial charge density from the different groups of core electrons are shown, also the total radial density; the regions of maximum charge density corresponding to the K , L , M 'shells' will be noticed, but there is no peak, only a flattening out of the curve, for the N 'shell,' as the contribution from the M electrons is still appreciable and decreases more quickly than the contribution from the N electrons increases. In Fig. 3 the charge distribution curve (Curve I) thus calculated is compared with those calculated by other methods, viz.:

* In Figs. 1, 2, 3 a different scale of r is used for $r < 1$ and $r > 1$. A scale open enough to show the detail of the curves for large r is unnecessarily open for larger r ; the use of two uniform scales has seemed preferable to the continuous distortion introduced, for example, by a logarithmic scale of r .

† The charge density is calculated from the wave functions from which the final field is built up, not by numerical differentiation of Z .

(1) By the general method of Thomas* (Curve II). In effect, Thomas' work deals with the solution in classical mechanics of the problem investigated here on the basis of the wave mechanics. In the notation of this paper, Thomas' equation (1.2) gives

$$-dZ/dr = (8\sqrt{2/3\pi}) r^2 v^{\frac{1}{2}} = (8\sqrt{2/3\pi}) \sqrt{(rZ_p)^3}.$$

The potential v (or preferably $Z_p = rv$, which varies more slowly and thus is easier to interpolate) can be calculated from the table at the end of Thomas' paper and the radial charge density follows directly from this equation.

TABLE II.
*Rubidium⁺. Approximate Self-Consistent Field
and Distribution of Charge.*

r atomic units	Z	$-dZ/dr$ electrons per atomic unit	r atomic units	Z	$-dZ/dr$ electrons per atomic unit
0	37.00	0	0.40	21.56	37.3
0.005	36.99	7.6	0.45	19.68	37.5
0.01	36.92	21.0	0.50	17.85	35.2
0.02	36.60	40.8	0.6	14.71	26.9
0.03	36.16	45.6	0.7	12.45	18.5
0.04	35.71	42.6	0.8	10.93	12.5
0.05	35.30	39.0	0.9	9.89	8.9
0.06	34.92	37.5	1.0	9.09	7.05
0.07	34.53	38.9			
0.08	34.14	41.8	1.2	7.81	6.08
			1.4	6.60	5.90
0.10	33.23	49.3	1.6	5.44	5.47
0.12	32.20	54.0	1.8	4.43	4.69
0.14	31.12	54.1	2.0	3.60	3.82
0.16	30.06	50.2			
0.18	29.11	44.6	2.5	2.21	2.08
0.20	28.29	39.2	3.0	1.52	0.90
			3.5	1.21	0.38
0.25	26.52	31.0	4.0	1.09	0.16
0.30	25.02	31.2	4.5	1.04	0.06
0.35	23.36	34.8	5.0	1.01	0.02

(2) From the orbital atomic model, with half integer values of k (Curve III). This curve is approximate only†.

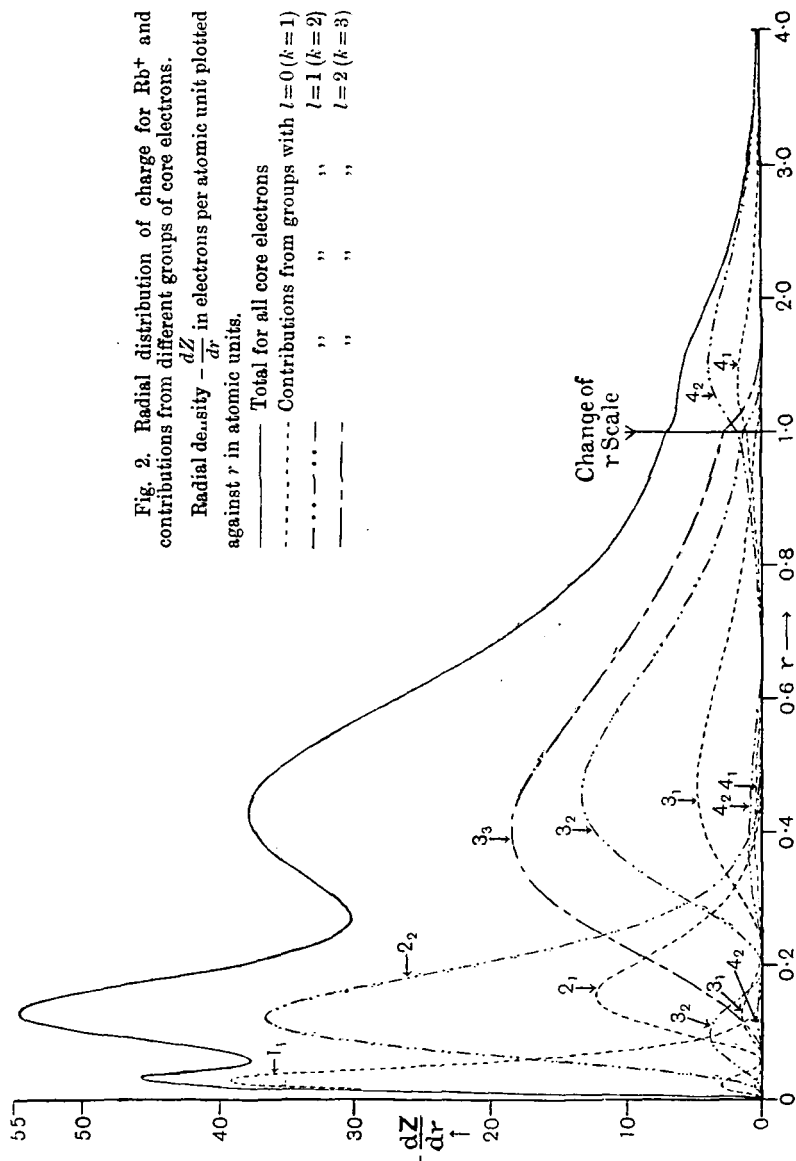
* *loc. cit.*

† For simplicity it has been assumed that all orbits of the same n have the same inner apsidal distance and that all of the same k have the same outer apsidal distance, both of which assumptions are approximately but not accurately true. The orbital model has not been worked out completely for half integer values of k , but the curve is drawn from data estimated from the work with integer values.

(3) From the approximate application of the wave mechanics suggested by Pauling* (Curve IV), in which the radial distribution

Fig. 2. Radial distribution of charge for Rb^+ and contributions from different groups of core electrons.

Radial density $\frac{dZ}{dr}$ in electrons per atomic unit plotted against r in atomic units.

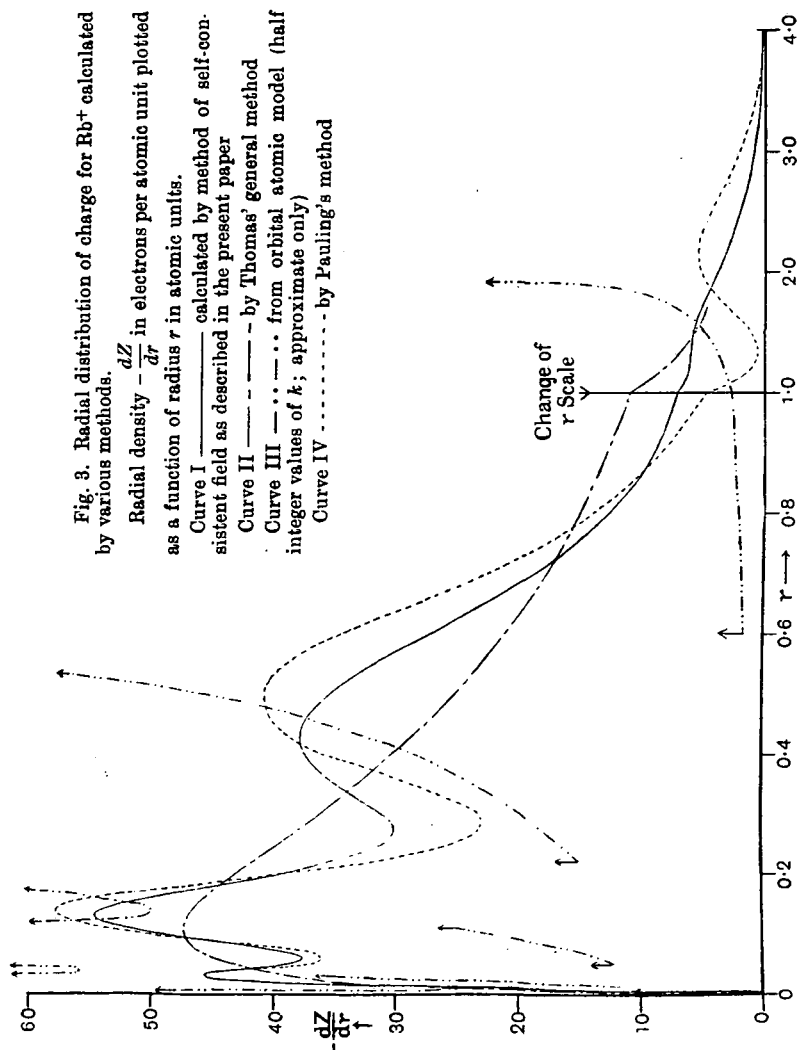


of charge for an electron is taken to be that for an electron with the same n_k in a certain Coulomb field, the nuclear charge for this

* L. Pauling, *Proc. Roy. Soc.*, Vol. cxiv, p. 181 (1927).

Coulomb field, different for each group of core electrons, being given by an empirical table.

It will be seen that the distribution given by Thomas' method is a good smoothed-out approximation to the distribution



giving the self-consistent field; the curves intersect several times, as do also the curves for Z , the integrated charge density, as can be seen roughly from the curve in Fig. 1 for the first approximation, for which the initial field was calculated by Thomas' method. The

maximum difference in Z between the self-consistent field and Thomas' field is just less than 2.

If the details of the field or charge distribution are unimportant for any application, it seems very possible that Thomas' field or distribution might very well be accurate enough. If it is used, however, one point should be kept in mind, namely that it gives a radial charge density which for small r is proportional to $r^{\frac{1}{2}}$, while on the wave mechanics the radial density for small r is proportional to r^2 ; this may cause apparently large divergences in results involving, for example, $r^{-1}dZ/dr$, such as arise in calculating the charge distribution in plane sheets.

A glance at Fig. 3 shows that the charge distribution calculated from the wave mechanics and from the orbit model of the atom are entirely different in character. For the orbit model the contribution from a group of core orbits to the radial density near the outer apse, of radius r_0 , becomes infinite like $(r_0 - r)^{\frac{1}{2}}$ as $r \rightarrow r_0$ from below, and falls discontinuously to zero as r passes through r_0 , and there is similar distribution outside the inner apse, so that the radial density curve for the whole atom has infinite discontinuities at the apsidal distances of all the orbits*. The distribution according to the wave mechanics remains always finite and continuous; a particular point to notice about it is that it tends asymptotically to zero (roughly exponentially) as r increases, so that it is not possible to assign a definite size to the atom. Another point is that the successive maxima in the radial density curve (for $n > l + 1$) calculated by the wave mechanics have no analogy whatever on the orbital model.

For small radii the distribution calculated by Pauling's method agrees well with that calculated from the self-consistent field, as would be expected, since Pauling's method is based on the wave functions in a Coulomb field, and for small radii the main contribution to the radial density is from electrons for which the proportional deviation of the field from a Coulomb field is small over the range where the wave function is appreciable. For large radii, however, the difference between the two distributions increases, till for the outermost electrons there is little agreement between them.

There are two reasons for this. First, the scale of the distribution of charge as given by Pauling is too large (i.e. the 'size screening constant' given by Pauling's Table VIII is too large†), the error in scale increasing with n (the principal quantum number) and being quite large for the outermost groups of core electrons

* With the half integer values of k there are no circular orbits. The curve for the orbital model is really much more broken than as shown in Fig. 3 (see second footnote on page 119).

† The effect of Pauling's correcting factor ΔS_s is small in this case, so that the errors lie in the values of S_{s_0} .

($n = 4$ in this case). Secondly, Pauling takes the radial distribution for any one group of electrons to be proportional to that of an electron in a certain Coulomb field; the actual deviation from a Coulomb field is always such that the effective nuclear charge decreases with increasing r , and the effect of this is to make the peaks of the radial density curve lower and less sharp than they are for a Coulomb field, and particularly to decrease the rate at which the radial density beyond the outermost maximum falls off with increasing r . These two effects combine to make the maxima and minima of the radial distribution curve calculated by Pauling's method too pronounced; in particular with Pauling's distribution of charge the contribution to the radial density from the M electrons has become small before that due to the N electrons has begun to increase up to its outermost maximum, so that the radial density drops to a very small value at about $r = 1.3$; with the self-consistent distribution of charge the contribution from the M electrons falls off more slowly, and the increase of that from the N electrons begins at a smaller radius, so that there is actually no minimum between the M and N 'shells'.

The comparison between the distribution of charge calculated in different ways has been based on the results for Rb, but, with appropriate alterations in details, most of it would apply to any atom.

§7. Rubidium. Comparison of Calculated and Observed Term Values.

The characteristic values of the energy parameter ϵ for the different solutions of the wave equation in the self-consistent field may be compared with the terms of the X-ray and optical spectra.

We consider first the X-ray terms; for these, the removal of one electron is presumably accompanied by some readjustment of the remainder of the atom, but the results for helium suggest that without taking this into account, the values of ϵ so calculated from the self-consistent field (corrected for the fact that the distributed charge of a core electron does not contribute to the field on itself) may be in good agreement with the X-ray term values. A comparison is given in Table III; the effects of the relativity variations of mass and of the spinning electron were calculated as first order perturbations by the formulae given in I, § 8. The agreement is strikingly good, especially when it is remembered that there is no arbitrary function or constant available to be adjusted to bring calculated results into agreement with the observations. The calculated term values refer to the Rb^+ ion; those for the neutral atom would probably be smaller by about 0.4 on account of the effect of the distributed charge of the series electron in decreasing the potential inside the core; the field and so the distribution of charge of the core electrons would not be altered appreciably. The observed

4_1 and 4_2 terms are probably somewhat uncertain apart from this effect, which is relatively largest for them.

TABLE III.
*Rubidium. Comparison of Observed X-Ray Term Values and Energy
Parameters for Core Electrons.*

n_k	ν/R obs.*	ϵ calc. for Rb^+ ion				ν/R obs. - ϵ calc.	ν/R obs. - ϵ calc. for orbit model
		Final approxi- mation to self- consistent field	Spin Correction	Relativity Correction	Total		
$1_1 K$	1119.1	1103	-100	+113	1116	-3	0
$2_1 L_1$	152.3	144.5	-9.8	+15.1	149.8	-2.4	-0.6
$2_2 \begin{Bmatrix} L_{II} \\ L_{III} \end{Bmatrix}$	137.6	132.3	+2.8	+2.4	137.5	-0.1	0
	133.2		-1.4		133.3	+0.1	
$3_1 M_1$	24.1	21.24	-1.56	+2.51	22.19	-1.9	-0.0
$3_2 \begin{Bmatrix} M_{II} \\ M_{III} \end{Bmatrix}$	18.2	16.55	+0.44	+0.44	17.43	-0.8	-0.1
	17.6		-0.22		16.77	-0.8	
$3_3 \begin{Bmatrix} M_V \\ M_V \end{Bmatrix}$	8.4	8.28	+0.12	+0.08	8.48	(0)	0
	unresolved		-0.08		8.28		
$4_1 N_1$	(2.4)	2.964	-0.198	+0.322	3.088	(+0.7)	
$4_2 \begin{Bmatrix} N_{II} \\ N_{III} \end{Bmatrix}$	(1.3)	1.557	+0.040	+0.041	1.638	(+0.3)	
			-0.020		1.578		

* The observed values for all terms but the K term have been taken from a paper by D. Coster and F. P. Mulder, *Zeit. f. Phys.*, Vol. xxxviii, p. 264 (1926). The value for the K term is from M. Siegbahn, *Spectroscopy of X-rays*.

For comparison, the differences between the observed and calculated term values on the orbital model are also given, the field used in these calculations being chosen to give as good a fit as possible. Compared with these differences, those between term values observed and calculated by the methods of this paper look rather large, but it must be remembered the latter calculated values

depend on the self-consistent field and do not involve even one adjustable constant, so that they could be calculated without knowledge of the observed term values, while for the orbit model the calculated values depend on a whole adjustable function, the field, which is chosen empirically to give the best fit to the observed terms. When we come to consider the optical term, it will be seen that even so the advantage lies with the wave mechanics.

The agreement between the calculated and observed spin doublets is very satisfactory; for the L spin doublet the separation deduced from direct observations is 4.4, the value calculated from the general empirical (first order) formula $(\alpha^2/16)(N-3.5)^4$ is 4.19, and the value calculated by the perturbation formula (also first order) is 4.20. The calculated M doublet separation agrees with that observed within the limits of observational error. It seems possible that first order relativity and spin corrections may not be adequate for the terms with $l=0$ ($k=1$), for which the first order corrections separately are about 10 per cent. of the total term value; for these terms also the difference between observed and calculated term values is largest.

As an example of the magnitude of the correction for the fact that the distributed charge of a core electron does not contribute to the field acting on itself, it may be mentioned that for the 2_s term this correction is about 12, so that if it were not taken into account the agreement between observed and calculated term values would be entirely lost.

For the optical terms, the quantum defect $q = n - n^*$, i.e. the difference between the principal and effective quantum numbers, is the most suitable quantity to use in making a comparison of the results of calculation with observation. Such a comparison is given in Table IV, in which the calculated values are for the final approximation to a self-consistent field, the observed values are calculated from the terms given in Fowler's table†, and for comparison the differences between observed and calculated values of the quantum defect are given for the orbital atomic model, with the field found to give about the best general agreement between the calculated and observed optical and X-ray terms‡. The differences of quantum defect between observation and calculation on the wave mechanics appear at first sight rather large, but they are all positive and of about the same magnitude, which is very satisfactory as will be seen shortly. The corresponding differences on the orbit model show a very much wider range of variation and the largest is

† A. Fowler, *Report on the Series in Line Spectra*, p. 104. The first d term has been given the principal quantum number $n=4$ in accordance with §8 of the present paper. The doublet separation for this term has not been observed and the value given is estimated from the value observed for the second d term.

‡ Integer values of k were used in these calculations. The writer has tried some work with half integral values of k , but without any very marked improvement in the general agreement between observed and calculated values.

greater than the largest with the wave mechanics; moreover, this is the best agreement attained with a whole arbitrary function available for adjustment.

It was one of the unsatisfactory points about the results for the orbit model that the calculated variation of the quantum defect within a sequence of terms of the same k (i.e. the deviation from a simple Rydberg formula) was very much larger than the observed variation (larger by a factor from 2 to 3 for the s terms and from $1\frac{1}{2}$ to $2\frac{1}{2}$ for p terms, the error for the first term being relatively the largest). This was found to be the case for all atoms for which calculation was done, and could not be avoided by using half-integer values of k . For the results according to the wave mechanics

TABLE IV.

Rubidium. Comparison of Observed and Calculated values of Quantum Defect for Optical Terms.

n_k	$q = n^* - n_{\text{obs.}}$	q calculated				q obs. - q calc.	q obs. - q calc. orbit model
		Calc. final approx.	Spin Correction	Relativity Correction	Total		
5 ₁	3.195	2.986	- .034	.056	3.008	+ .187	- .224
6 ₁	3.153	2.964	- .034	.057	2.987	.166	- .160
7 ₁	3.146	2.960	- .034	.057	2.983	.163	- .130
5 ₂	{ 2.707	2.519	- .007	.015	2.527	.180	- .010
	{ 2.720		+ .014		2.548	.172	
6 ₂	{ 2.670	2.494	- .007	.015	2.502	.168	+ .058
	{ 2.683		+ .014		2.523	.160	
4 ₃	{ 0.233 $\Delta\nu = (7)$	0.028	Doublet $\Delta\nu = 3.3$.000	0.028	.205	

considered here the calculated variation is actually less than the observed, and this is satisfactory as will appear shortly.

The reasons why the differences between the observed quantum defect and that calculated on the wave mechanics are more satisfactory than they appear at first sight is this. The series electron when outside the core presumably polarises it, and the resultant polarisation gives rise to an attractive force on the series electron, always central, in addition to the field due to the unperturbed distribution of charge†. The additional field would act on the series

† In the case of He (terms other than s terms) the core consists of a hydrogen-like system, for which the second order Stark effect, on which the polarisability depends, can be worked out exactly for a uniform perturbing field. This has already been treated on the wave mechanics by I. Waller, *Zeit. f. Phys.*, Vol. xxxviii, p. 635 (1926); see particularly § 3.

electron as a central perturbing field having an inverse fourth power potential at large distances. It would certainly increase all calculated values of the quantum defect, and from the effect of such a perturbing field on the orbit model it may be expected that for the s and p terms it would increase the calculated quantum defect somewhat more for the first term or two of each sequence than for the rest, and would affect the two sequences about equally; this is just what is required to improve the agreement between calculated and observed values, both for the individual terms and for the variation of quantum defect within each sequence. How the d terms would be affected is not so easy to say.

This effect has not been calculated as it is not yet clear how the perturbing field may be expected to vary when the distance of the series electron from the core is not large compared with the dimensions of the latter, and this is the important part of the range for application to these terms. It would seem necessary at present to use an empirical perturbing field with a potential proportional to r^{-4} for large r , the behaviour for small r being chosen to give—in combination with the self-consistent field due to the unperturbed core—the best fit for the observed terms.

One unsatisfactory point about the results for the optical terms is the magnitude of the p spin doublet, the calculated separation being about $1\frac{1}{2}$ times that observed. A numerical mistake is a possible explanation, but the work has been thoroughly checked and it seems very unlikely that a mistake anything like big enough to explain the discrepancy could have escaped detection. Another possible explanation is this. The magnitude of the spin doublet on the new quantum mechanics was worked out by Heisenberg and Jordan for a Coulomb field using the matrix method. It seems just possible, though unlikely, that the formula is not applicable to an electron in a field differing widely from a Coulomb field and that in such cases the scalar product ls which occurs in the formula has a value different from $\frac{1}{2}[j(j-1) + l(l+1) - s(s+1)]$, which it has in a Coulomb field. If this were the case, the central field result would be expected to apply still to the core electrons (especially to the L doublet) for which the proportional deviation from a Coulomb field is not large, but not to the series electron.

Apart from this point, the general agreement of X-ray and optical term values calculated by the methods here given with those observed is very satisfactory.

§8. *Solution on Wave Mechanics for the Case when the Equation for Apical Distances has four Roots.*

As already mentioned, Rb was chosen as the first atom for which to do numerical work, partly in order to examine what happened on the wave mechanics in the case in which the equation

$$2v - \epsilon - l(l+1)/r^2 = 0$$

(I, 2.4), giving the apses for the orbital atomic model, has four roots, which for Rb occurs when $l = 2$.

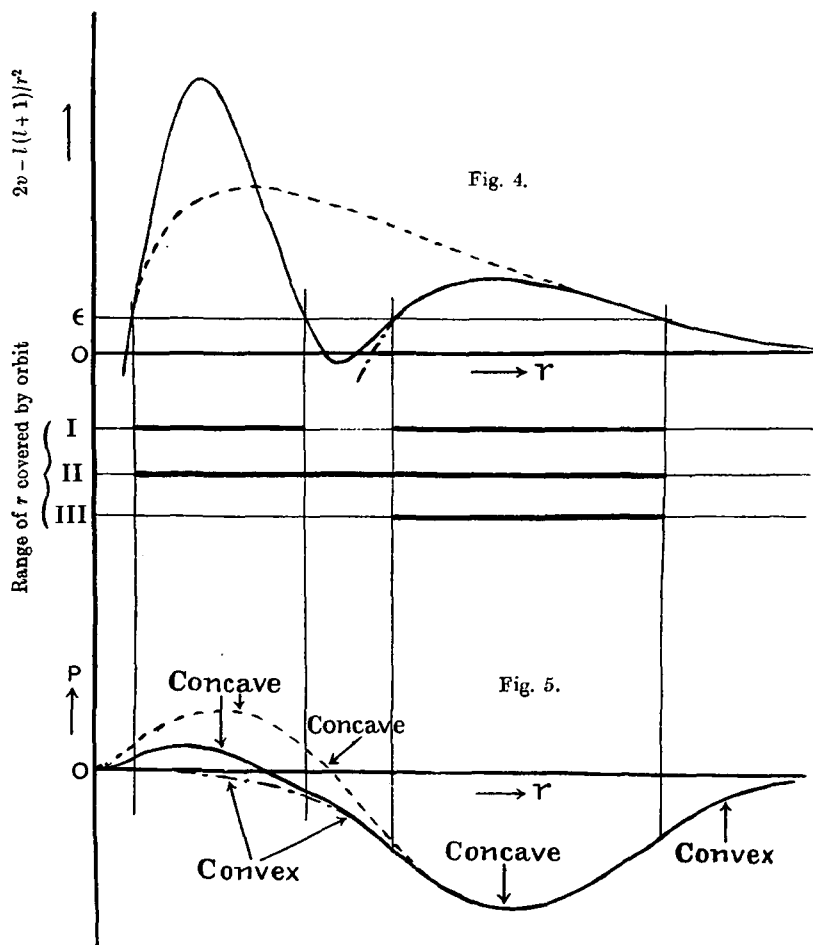


Fig. 4. Curves of $2v - l(l+1)/r^2$ as function of r .

Case I (Internal and external orbit of same energy) —————

Case II (Penetrating orbit) - - - - -

Case III (Non-penetrating orbit) — · — · —

Fig. 5. Wave function corresponding to curves in Fig. 4 above. 'Convex' and 'concave' refer to curvature with respect to r axis.

Figs. 4 and 5 to illustrate behaviour of wave function for field which gives separate internal and external orbits of same energy on orbital atomic model.

In Fig. 4 are shown three curves of $2v - l(l+1)/r^2$ as a function of r for different possible fields, a horizontal line being drawn at

height ϵ , which is supposed to be a characteristic value for all three fields.

The usual curve of $2v - l(l+1)/r^2$ has one maximum, which may lie inside or outside the core; a horizontal line can then only cut it at two points, giving the apses of the corresponding orbit which is penetrating or non-penetrating respectively in the two cases. But the curve may have two maxima, in which case a horizontal line can cut it in four places, giving the apses of an internal and external orbit of the same energy. The curve for this case is drawn full, that for a penetrating orbit is drawn broken, and that for a non-penetrating orbit dot-and-dash. The ranges covered by the orbits in the various cases are marked below.

In Fig. 5 the curves of P against r are drawn to correspond with the curves in Fig. 4, the arbitrary constant being chosen so that the outer part of the curve in Fig. 5 is the same in all three cases. (The curves are diagrammatic only.)

From the differential equation for P (I, 2.3),

$$P'' + [2v - \epsilon - l(l+1)/r^2]P = 0,$$

it follows that when $2v - \epsilon - l(l+1)/r^2$ (i.e. the ordinate of the curve of $2v - l(l+1)/r^2$ above the line at height ϵ in Fig. 4) is positive, which is the case when r lies between the apses of the corresponding orbit, then the (P, r) curve is concave to the r axis, and when $2v - \epsilon - l(l+1)/r^2$ is negative the (P, r) curve is convex to the r axis.

In the case of four roots, the internal and external orbits with the same energy are quite separate mechanically possible orbits (they would in general not both be quantum orbits), whereas on the wave mechanics both are included in a single solution of the wave equation, the complete separation being replaced by a range for r for which the (P, r) curve is convex to the r axis. The effect of this convex piece is that, for the same outer part, P inside—and so the fraction of the total charge lying inside—is smaller than it is when the two intermediate roots of the equation for the apses are absent, so that the corresponding orbit penetrates. On the other hand, when only a non-penetrating orbit is possible, the (P, r) curve must always be convex to the r axis for r smaller than the inner apse of the corresponding orbit, so that P^2 can have no maximum inside the core such as it has in the case of four roots.

Thus the solution on the wave mechanics in the case of four roots is intermediate between those corresponding to penetrating and non-penetrating orbits on the orbital model, and may be expected to give some properties of both. e.g. approximately hydrogen-like terms and at the same time comparatively large doublet separations (as shown, for example, by the d terms of Cu I, Ag I, Au I), the latter being due to the maximum of P inside the core. According to the convention already mentioned (I, § 1), the

principal quantum number must be assigned as if the corresponding orbits penetrated.

On the orbital mechanics, if $2v - l(l+1)/r^2$ had two maxima and the intermediate minimum were positive, then the orbits of the series electron whose energy was greater than this minimum would correspond to non-penetrating orbits, and those whose energy was less would correspond to penetrating orbits, and quite a sharp break in the progression of the quantum defect along the sequence of terms would be expected in such a case*. On the wave mechanics, where

TABLE V.

*Sodium⁺. Approximate Self-Consistent Field
and Distribution of Charge.*

r atomic units	Z	$-dZ/dr$ electrons per atomic unit	r atomic units	Z	$-dZ/dr$ electrons per atomic unit
0.00	11.00	0.0	0.5	7.15	8.8
0.02	10.98	2.8	0.6	6.26	9.0
0.04	10.90	7.0	0.7	5.37	8.5
0.06	10.72	10.2	0.8	4.55	7.6
0.08	10.49	11.9	0.9	3.84	6.5
0.10	10.25	12.1	1.0	3.25	5.39
0.12	10.02	11.4	1.2	2.39	3.47
0.14	9.80	10.5	1.4	1.82	2.16
0.16	9.61	9.3	1.6	1.47	1.31
0.18	9.43	8.2	1.8	1.27	0.77
0.20	9.27	7.3	2.0	1.16	0.45
0.25	8.94	6.0	2.5	1.04	0.12
0.30	8.64	6.0	3.0	1.01	0.03
0.35	8.33	6.6			
0.40	7.98	7.4			

the sharp separation between internal and external orbits of the same energy in the case of four roots has disappeared, no such sharp break in a sequence of terms would be expected. As the energy decreased, the range of r for which (P, r) curve is convex to the P axis would shrink and disappear, but that is all; an abnormal increase in quantum defect throughout the sequence, and possibly in doublet separation for the first few terms, would be expected, just as observed, for example, in the d terms of Al I, but no sharp break.

* See G. Wentzel, *Zeit. f. Phys.*, Vol. xix, p. 52 (1923).

§ 9. Sodium and Chlorine.

Approximations to the self-consistent field have been worked out for the ions Na^+ and Cl^- in a similar way to that for Rb^+ , the immediate object being to determine the charge distribution, from which to calculate the functions F' entering in the formula for the intensity of reflection of X-rays from crystals, in connection with recent experimental work on rocksalt. A comparison of the results

TABLE VI.

*Chlorine-. Approximate Self-Consistent Field
and Distribution of Charge.*

r atomic units	Z	$-dZ/dr$ electrons per atomic unit	r atomic units	Z	$-dZ/dr$ electrons per atomic unit
0.00	17.00	0.0	0.5	9.16	12.5
0.01	16.99	2.8	0.6	8.15	8.0
0.02	16.95	8.0	0.7	7.50	5.1
0.03	16.84	13.2	0.8	7.08	3.6
0.04	16.69	16.7	0.9	6.76	3.2
			1.0	6.43	3.27
0.06	16.32	19.6	1.2	5.72	3.90
0.08	15.93	18.7	1.4	4.91	4.21
0.10	15.58	16.2	1.6	4.08	4.06
0.12	15.28	14.0	1.8	3.30	3.72
0.14	15.01	12.9	2.0	2.61	3.25
0.16	14.76	12.7			
0.18	14.47	13.3	2.5	1.30	2.05
0.20	14.19	14.3	3.0	0.50	1.26
			3.5	0.00	0.80
			4.0	-0.33	0.52
0.25	13.42	17.0			
0.30	12.51	18.8	5	-0.69	0.23
0.35	11.57	18.7	6	-0.85	0.11
0.40	10.67	17.2	7	-0.93	0.05
			8	-0.97	0.02

of this work with the results of calculation, using the charge distribution found by the method discussed in this paper, will be given elsewhere, but it may be mentioned here that the result of the comparison is very satisfactory indeed.

In Tables V and VI the values of Z and the radial charge density $-dZ/dr$ for Na^+ and Cl^- are given for the final field of the last approximation made, for which the maximum difference between initial and final field was 0.05 for Na^+ and 0.08 for Cl^- . The values

for Cl^- for $r > 1$ are somewhat uncertain, as the main contribution is from the outermost group of electrons, which is very sensitive to the changes in the initial field. This sensitiveness is a result of the negative charge on the ion, and made the work much more troublesome than for neutral atoms or positive ions. For a multiply charged negative ion, for which there is a repulsive field on one electron when far enough removed from the rest, the distribution of charge for the outer electrons would be still more sensitive to the initial field, and the calculations would probably become unmanageable.

§ 10. *Summary.*

The methods of solution of the wave equation for a central field given in the previous paper are applied to various atoms. For the core electrons, the details of the interaction of the electrons in a single n_k group are neglected, but an approximate correction is made for the fact that the distributed charge of an electron does not contribute to the field acting on itself (§ 2).

For a given atom the object of the work is to find a field such that the solutions of the wave equation for the core electrons in this field (corrected as just mentioned for each core electron) give a distribution of charge which reproduces the field. This is called the self-consistent field, and the process of finding it is one of successive approximation (§ 3).

Approximations to the self-consistent field have been found for He (§ 4), Rb^+ (§ 5), Na^+ , Cl^- (§ 9). For He the energy parameter for the solution of the wave equation for one electron in the self-consistent field of the nucleus and the other corresponds to an ionisation potential of 24.85 volts (observed 24.6 volts); this agreement suggests that for other atoms the values of the energy parameter in the self-consistent field (corrected for each core electron) will probably give good approximations to the X-ray terms (§ 4).

The most extensive work has been carried out for Rb^+ . The distribution of charge given by the wave functions in the self-consistent field is compared with the distribution calculated by other methods (§ 6). The values of X-ray and optical terms calculated from the self-consistent field show satisfactory agreement with those observed (§ 7).

The wave mechanical analogue of the case in which on the orbital model an internal and an external orbit of the same energy are possible is discussed (§ 8).