

*The Wave Mechanics of an Atom with a Non-Coulomb Central Field. Part I. Theory and Methods.* By D. R. HARTREE, Ph.D., St John's College.

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### § 1. Introduction.

On the theory of atomic structure proposed by Bohr, in which the electrons are considered as point charges revolving in orbits about the nucleus, the orbits being specified by quantum conditions, it is well known that both a qualitative and an approximate quantitative explanation of many features of the simpler optical spectra and of X-ray spectra of atoms with many electrons (e.g. Rydberg sequences in optical spectra, term magnitudes in both X-ray and optical spectra) can be given, if the assumption is made that the effects of the electrons on one another can be represented by supposing each to move in a central non-Coulomb field of force\*; further, the additional concept of a spinning electron provides a similar explanation of other features of these spectra† (e.g. doublet structure of terms and magnitude of doublet separation, anomalous Zeeman effect). This assumption of a central field was admittedly a rough approximation made in the absence of any detailed ideas about the interaction between the different electrons in an atom, but in view of its success as a first approximation for the orbital atom model, the question arises whether the same simple approximations may not give useful results when applied to the new formulation of the quantum theory which has been developed in the last two years.

The wave mechanics of Schrödinger‡ appears to be the most suitable form of the new quantum theory to use for this purpose, and will be adopted throughout. Further, if  $\psi$  is a solution of the wave equation (suitably normalised), the suggestion has been made by Schrödinger, and developed by Klein§, that  $|\psi|^2$  gives the volume density of charge in the state described by this  $\psi$ ; whether this interpretation is always applicable may be doubtful, but for the wave functions corresponding to closed orbits of electrons in an atom, with which alone this paper will be concerned, it has the advantage that it gives something of a model both of the stationary states (if  $\psi$  only contains one of the characteristic functions) and of the process of radiation (if  $\psi$  is the sum of

\* See, for example, M. Born, *Vorlesungen über Atommechanik* (or the English translation, *The Mechanics of the Atom*), Ch. III.

† For a general review, see R. H. Fowler, *Nature*, Vol. cxix, p. 90 (1927); for a more detailed treatment, F. Hund, *Linienpektren*, Ch. III.

‡ E. Schrödinger, *Ann. der Phys.*, Vol. LXXIX, pp. 361, 489; Vol. LXXX, p. 437; Vol. LXXXI, p. 109 (1926); *Phys. Rev.*, Vol. xxviii, p. 1049 (1926).

§ F. Klein; *Zeit. f. Phys.*, Vol. xli, p. 432 (1927).

a number of characteristic functions), and gives a simple interpretation of the formula of the perturbation theory, namely, that the change in the energy is the perturbing potential averaged over the distribution of charge. Also in considering the scattering of radiation of wave length not large compared to atomic dimensions, the coherent radiation scattered by a hydrogen atom is given by treating the scattering as classical scattering by the distribution of charge given by Schrödinger's suggestion (if the wave length is not too short)\*, and this is probably true for any atom. For the purpose of this paper the suggestion will be adopted literally; the charge distribution for an atom in a stationary state is then static (it does not necessarily follow that the charge itself is static).

Further, the distribution of charge for a closed  $n_k$  group of electrons is centrally symmetrical†, which suggests that on the wave mechanics the assumption of a central field may give results more satisfactory in detail than could be expected on the older form of quantum theory.

Schrödinger's suggestion concerning the interpretation of  $\psi$  affords a hope that it may be possible to consider the internal field of the atom as being due to the distribution of charge given by the characteristic functions for the core electrons; we may, in fact, attempt to find a field of force such that the total distribution of charge, given by the characteristic functions in this field (taken in suitable multiples corresponding to the numbers of electrons in different  $n_k$  groups), reproduces the field. The solution of this problem, or rather a refinement of it, is, indeed, the main object of the quantitative work to be considered here.

One point of contrast between the old 'orbital' mechanics and the new wave mechanics may be emphasised here at once. On the orbital mechanics the motion of an electron in an orbit lies wholly between two radii (the potential energy and so the total energy depends on the field at distances greater than the maximum radius, but this does not affect the motion); on the wave mechanics the solution of the wave equation is different from zero at all but a finite number of values of the radius, and depends on the field at all distances (though certainly the solution is very small, and depends on the field to an extent negligible in practice, at very large radii and usually at very small radii).

It will be seen later (§ 2) that, for a given characteristic function, it is possible to specify two points which may to a certain extent be considered to mark the apses of the corresponding orbit in the orbital atom model, but the characteristic function is not zero

\* I. Waller, *Nature*, Vol. cxx, p. 155 (1927); *Phil. Mag.* Nov. 1927 (Supplement).

† See A. Unsöld, *Ann. der Phys.*, Vol. lxxxii, p. 355, §§ 5 and 6. Unsöld proves this by considering the energy of an indefinitely small charge in the field of a closed group; it also follows directly for the charge distribution from Unsöld's formulae '67), (69).

outside them; as a consequence, it is not possible to make a strict separation between 'penetrating' and 'non-penetrating' solutions of the wave equation as it was possible to divide orbits into two such classes. This suggests that it would be interesting to enquire what occurs in the wave mechanics in cases when on the orbital mechanics an atom may have a 'penetrating' and a 'non-penetrating' orbit with the same quantum numbers\*  $n_k$ , and also whether the comparatively large doublet separations of some terms corresponding to orbits classed as 'non-penetrating' can be explained by the non-zero fraction of the total charge which must, on the wave mechanics, lie inside the core.

Associated with this question is that of the assignment of the principal quantum number  $n$  to a solution of the wave equation in a non-Coulomb field; in the orbital mechanics this was assigned in a perfectly definite way, to which there is no direct analogy on the wave mechanics. In this paper  $l$  will be written for the subsidiary quantum number, taking integer values from zero upwards, which is less by unity than Bohr's azimuthal quantum number  $k$ ; this follows the practice adopted by various writers†; to avoid altering a notation which has become familiar,  $k$  will be retained as a suffix in referring to the quantum numbers of an electron, so that  $l=k-1$ . It seems best to define  $n$  such that  $n-k=n-l+1$  is the number of values of the radius  $r$  for which  $\psi=0$ , excluding  $r=0$  (if it is a root) and  $r=\infty$ ;  $n-l$  is then the number of values of  $r$  for which  $|\psi|^2$  is a maximum. This agrees with Bohr's principal quantum number  $n$  for the hydrogen atom.

Both in order to eliminate various universal constants from the equations and also to avoid high powers of 10 in numerical work, it is convenient to express quantities in terms of units, which may be called 'atomic units,' defined as follows:

*Unit of length*,  $a_H = h^2/4\pi^2me^2$ , on the orbital mechanics the radius of the 1-quantum circular orbit of the H-atom with fixed nucleus.

*Unit of charge*,  $e$ , the magnitude of the charge on the electron.

*Unit of mass*,  $m$ , the mass of the electron.

Consistent with these are:

*Unit of action*,  $h/2\pi$ .

*Unit of energy*,  $e^2/a =$  potential energy of charge  $e$  at distance  $a$  from an equal charge  $= 2hcR =$  twice the ionisation energy of the hydrogen atom with fixed nucleus.

*Unit of time*,  $1/4\pi cR$ .

\* For example, on the orbital mechanics, Rb, Cu, Ag, Au, have  $3_3$  X-ray orbits, and for the neutral atoms of these elements the first  $d$  term corresponds to a non-penetrating  $3_3$  orbit.

† See, for example, F. Hund, *op. cit.*, *passim*.

These units being consistent, the ordinary equations of classical and wave mechanics hold in them; in particular Schrödinger's wave equation for the motion of a point electron with total energy  $E$ , in a static field in which its potential energy is  $V$ , becomes

$$\nabla^2 \psi + 2(E - V) \psi = 0. \quad \dots(1.1)$$

For an attractive field,  $V$  is always negative; it is convenient to write

$$V = -v, \quad \dots(1.2)$$

so that the quantity  $v$  calculated in numerical work is usually positive.

For terms of optical and X-ray spectra,  $E$  is always negative. It is convenient to write

$$E = -\frac{1}{2}\epsilon, \quad \dots(1.3)$$

the factor  $\frac{1}{2}$  being introduced in order that  $\epsilon$  shall be the energy as a multiple of the ionisation energy of the hydrogen atom; if a characteristic value of the solution of the wave equation gives directly a spectral term, of wave number  $\nu$ , then

$$\epsilon = \nu/R. \quad \dots(1.4)$$

The wave equation in terms of  $v$  and  $\epsilon$  is

$$\nabla^2 \psi + (2v - \epsilon) \psi = 0. \quad \dots(1.5)$$

The present paper is divided into two parts; this, the first, deals with the methods used for solving this equation for a given non-Coulomb central field, and with the relevant theory; the second with the question of the determination of the potential  $v$ , and with an account and discussion of the results for some actual atoms.

## § 2. *Theory.*

When the field is spherically symmetrical so that  $v$  is a function of the radius  $r$  only, and spherical polar coordinates  $r, \theta, \phi$  are used,  $\psi$  separates into a product of a function  $\chi(r)$  of  $r$  only, and a surface spherical harmonic  $S(\theta, \phi)$ ; if  $l$  is the order of the spherical harmonic, the function  $\chi$  satisfies the equation

$$\frac{d^2 \chi}{dr^2} + \frac{2}{r} \frac{d\chi}{dr} + \left[ 2v - \epsilon - \frac{l(l+1)}{r^2} \right] \chi = 0 \quad \dots(2.1)$$

or, writing

$$P = r\chi \quad \dots(2.2)$$

and using dashes to denote differentiation with respect to  $r$ ,

$$P'' + [2v - \epsilon - l(l+1)/r^2] P = 0. \quad \dots(2.3)$$

This is the form in which the wave equation is used in the greater part of this paper.

There are three advantages in working with  $P$  rather than with  $\chi$ ; first, the differential equation is simpler, secondly,  $P^2$  gives the *radial* density of charge if  $P$  is suitably normalised (i.e.  $P^2 dr / \int_0^\infty P^2 dr$  is the charge lying between radii  $r$  and  $r + dr$ )\*, and this is the quantity often required in applications, thirdly, as a consequence of this,  $P^2$  is the weighting function for the perturbing potential at different radii, in the case of a perturbation which is centrally symmetrical.

If we recall that the wave equation is derived from the classical Hamiltonian equation of the problem by the substitution

$$p_x = i \frac{\partial}{\partial x}, \text{ etc.}$$

(in atomic units), and also that on the orbital mechanics the radial momentum  $p_r$  in an orbit of angular momentum  $k$  (in atomic units  $\hbar/2\pi$ ) is given by

$$p_r^2 = 2v - \epsilon - k^2/r^2,$$

equation (2.3) suggests that as far as we can picture an orbit corresponding to a given solution of the wave equation, its angular momentum in atomic units is given by  $k^2 = l(l+1)$  ( $l$  integral), and that its apses are given by the roots of

$$2v - \epsilon - l(l+1)/r^2 = 0, \quad \dots (2.4)$$

i.e. by the points of inflexion of  $P$  other than those which occur at the points where  $P = 0$ . Usually this expression has two roots, between which it is positive; between them  $P$  has an oscillatory character, outside them it has an exponential character; it may have one root only (in the case  $l = 0$ ) or four (for  $l > 0$  only). On the orbit model of the atom, when four roots occur they give the apses of an internal and an external orbit with the same energy†; what then happens on the wave mechanics will be discussed in the second part of this paper.

The first requirement is a method for finding values of  $\epsilon$  for which, given  $v$  as a function of  $r$ , the solution  $P$  of (2.3) is zero at  $r = 0$  and  $\infty$  (Schrödinger's condition is that  $\psi$  should be finite

\* According to Schrödinger's interpretation of  $\psi$  (§ 1) the charge lying in an element of volume defined by  $dr d\theta d\phi$  is  $\psi^2 r^2 \sin^2 \theta dr d\theta d\phi / \int \psi^2 r^2 \sin^2 \theta dr d\theta d\phi$ , the integral being over all space, so that the charge lying between radii  $r$  and  $r + dr$  is

$$\psi^2 r^2 dr / \int_0^\infty \psi^2 r^2 dr = P^2 dr / \int_0^\infty P^2 dr,$$

the integration of the spherical harmonic factor cancelling out.

† In general the internal and external orbits with the same energy will not both be quantum orbits, but when they occur it is usually possible (always if integral quantum numbers are used) to obtain an internal and an external quantum orbit with the same quantum numbers.

everywhere; since  $P = r\chi$ ,  $P$  must be 0, not only finite, at  $r = 0$ ), and the solution for each value of  $\epsilon$ . The value of  $\epsilon$  then gives a spectral term for the motion of an electron in the field  $v$ , and, with the arbitrary multiplying constant adjusted so that  $\int_0^\infty P^2 dr = 1$ ,  $P^2$  gives the radial density of charge. In this part of the paper we shall consider the solution of (2.3) for a given  $v$  subject to the necessary boundary conditions, and in the second consider how  $v$  may itself be related to the solutions of (2.3).

For any value of  $\epsilon$ , we can find a solution of (2.3) which is zero at  $r = 0$  and a solution which is zero at  $r = \infty$ . Except for certain values of  $\epsilon$ , these solutions are independent, and the one zero at  $r = 0$  is infinite at  $r = \infty$  and vice versa, but for certain values of  $\epsilon$  the two solutions (apart from an arbitrary multiplying constant in each) are the same. These are the values of  $\epsilon$  and the solutions required, and this aspect of them suggests the following method of determining them, viz. integrate the equation\* outwards from  $P = 0$  at  $r = 0$ , and inwards from  $P = 0$  at  $r = \infty$ , and by trial find a value of  $\epsilon$  for which these solutions meet at some convenient intermediate radius  $r$ ; since each solution contains an arbitrary multiplying constant,  $P'/P$  rather than  $P$  itself has to be the same in both solutions. This is in effect the method adopted in the numerical work (for an example see § 10), and it has proved very satisfactory in practice. In finding the required value of  $\epsilon$ , it is not necessary to integrate from the beginning for each value of  $\epsilon$ ; it is possible to calculate directly (and accurately, not only to the first order) the variation in the solution for a variation in the value of  $\epsilon$ , and this can be used to shorten the numerical work considerably. A general variation equation of which this is a special case will be given in § 4.

Over most of the range of  $r$  for which  $P$  is appreciable, equation (2.3) as it stands is in a suitable form for numerical integration; but for small values of  $r$  (out to or a little beyond the first maximum of  $|P|$ ) and for large values (from about the last maximum of  $|P|$  outwards) other forms are more suitable, and will now be considered.

If we write  $\eta = -P'/P$ , .....(2.5)  
equation (2.3) reduces to a non-linear first order equation in  $\eta$ , viz.

$$\eta' = \eta^2 + 2v - \epsilon - l(l+1)/r^2, \quad \text{.....(2.6)}$$

and it might seem that this equation, being of the first order so that one of the integrations for  $P$  is reduced to a simple quadrature, would be more suitable for numerical work than the equation for  $P$

\* An outline of the method used for the practical numerical integration of the equation for  $P$  is given in § 9.

itself, but the zeros of  $P$  give rise to infinities in  $\eta$  and  $\eta'$  which make numerical work with this equation impracticable except in certain regions. For large values of  $r$  (as specified above) it is, however, very suitable.

### § 3. Form of Solution for Small Values of $r$ .

When  $r$  is small the substitution of

$$P = r^c(1 + a_1 r + \dots) \quad \dots\dots(3.1)$$

provides the indicial equation

$$c(c-1) - l(l+1) = 0,$$

of which the positive root is  $c = l + 1$ , so that for small  $r$  the solution remaining finite at  $r = 0$  behaves as  $r^{l+1}$ .

In the neighbourhood of  $r = 0$  it is therefore convenient to work with

$$Q = Pr^{-(l+1)} \quad \dots\dots(3.2)$$

rather than with  $P$ , or with

$$-Q'/Q = \xi = \eta + (l+1)/r \quad \dots\dots(3.3)$$

rather than with  $\eta$ . The equation for  $\xi$  is

$$\xi' = \xi^2 - 2(l+1)\xi/r + 2v - \epsilon, \quad \dots\dots(3.4)$$

and is the most convenient one to use up to or a little beyond the first maximum of  $|P|$ ; the only difficulty is at  $r = 0$  itself, where the second and third terms of this expression for  $\xi'$  become infinite. This difficulty is avoided by the use of the solution in series to give values of  $\xi$  and  $\xi'$  at  $r = 0$ .

For an atom of atomic number  $N$  we certainly have, in the neighbourhood of  $r = 0$ ,

$$v = N/r + v_0 + o(1) \quad \dots\dots(3.5)$$

( $v_0$  is the potential at the nucleus of the negative distribution of charge due to the outer electrons, and is of course negative), and the series solution of the equation for  $\xi$  (or of that for  $P$ ) gives

$$\xi = N/(l+1), \quad \xi' = [N^2/(l+1)^2 + 2v_0 - \epsilon]/(2l+3), \text{ at } r = 0. \quad \dots\dots(3.6)$$

With these initial values, the numerical integration can be begun without difficulty.

### § 4. Variation Equations.

It may happen that for a certain range of  $r$  a solution of the equation for  $P$  has been found for a certain potential function  $v$  and a certain value of  $\epsilon$ , and that the solution for a different function  $v$  or a different value of  $\epsilon$ , or both, is required. [This is more general than the 'perturbation theory' of wave mechanics, for which the

original solution must be a characteristic solution of the differential equation, and the variation of  $\epsilon$  is connected in a definite way with the variation of  $v$ .] The difference in the solution for a change of value of  $\epsilon$  is required, for example, in the process of finding by trial a value of  $\epsilon$  which is a characteristic value for any particular field.

Let  $P$  be the solution of

$$P'' + [2v - \epsilon - l(l+1)/r^2] P = 0, \quad \dots\dots(4.1)$$

which has already been found, and let the solution be required of

$$P_1'' + [2v_1 - \epsilon_1 - l(l+1)/r^2] P_1 = 0. \quad \dots\dots(4.2)$$

Writing  $\Delta$  for the variation of a quantity at given  $r$ , i.e.

$$v_1 - v = \Delta v, \quad \epsilon_1 - \epsilon = \Delta \epsilon, \quad P_1 - P = \Delta P,$$

and subtracting, we have

$$(\Delta P)'' + [2v_1 - \epsilon_1 - l(l+1)/r^2] \Delta P + [2\Delta v - \Delta \epsilon] P = 0, \quad \dots\dots(4.3)$$

which is an exact (not only first order) equation for  $\Delta P$ , and it is usually easier to solve this equation numerically than to work through a solution of (4.2) independent of the solution of (4.1).

In the particular case  $\Delta v = 0$ ,  $\Delta \epsilon \rightarrow 0$ , we have

$$\left(\frac{\partial P}{\partial \epsilon}\right)'' + [2v - \epsilon - l(l+1)/r^2] \left(\frac{\partial P}{\partial \epsilon}\right) - P = 0 \quad \dots\dots(4.4)$$

(the differentiation with respect to  $\epsilon$  being for  $r$  constant), for which a formal solution in quadratures can be found, but on account of the zeros of  $P$  this formal solution is more trouble for numerical work than the integration of the equation as it stands.

It is interesting to note that a simple derivation of the formula for the first order perturbation in  $\epsilon$  for a central perturbing field can be found from (4.3).

For this purpose, suppose the value of  $\epsilon$  in (4.1) to be a characteristic value for the field  $v$ , and  $P$  to be the corresponding characteristic function. Consider first order variations only, i.e. write  $v$  and  $\epsilon$  for  $v_1$  and  $\epsilon_1$  in the coefficient of  $\Delta P$  in (4.3), giving

$$(\Delta P)'' + [2v - \epsilon - l(l+1)/r^2] \Delta P + [2\Delta v - \Delta \epsilon] P = 0. \quad \dots\dots(4.5)$$

Knowing the solution  $P$  of (4.1), adopt the standard method for the solution of (4.5), i.e. write

$$\Delta P = PR; \quad \dots\dots(4.6)$$

the terms in  $R$  disappear on substituting, leaving

$$PR'' + 2P'R' + [2\Delta v - \Delta \epsilon] P = 0$$



whence, multiplying by  $P$  and integrating,

$$\left[ P^2 R' \right]_0^\infty + \int_0^\infty [2\Delta v - \Delta\epsilon] P^2 dr = 0.$$

Also from (4.6)  $P^2 R' = P(\Delta P)' - P'(\Delta P)$ .

Now if  $P$  and  $P_1$  are characteristic solutions of (4.1) and (4.2) respectively,  $P, P', P_1$  and  $P'_1$  (and so  $\Delta P$  and  $\Delta P'$ ) must all be zero at  $r = \infty$ , and also at  $r = 0$  except for  $l = 0$ , while, for  $l = 0$ ,  $P$  and  $P_1$  (and so  $\Delta P$ ) are zero at  $r = 0$  and  $P', \Delta P'$  are finite. Thus in all cases  $P^2 R'$  is zero at both limits, whence

$$\int_0^\infty [2\Delta v - \Delta\epsilon] P^2 dr = 0,$$

$$\Delta\epsilon = \left[ \int_0^\infty 2\Delta v P^2 dr \right] / \left[ \int_0^\infty P^2 dr \right] \quad \dots\dots(4.7)$$

which is the form Schrödinger's perturbation equation\* takes for a central perturbation of a central field (it must be remembered that  $\epsilon$  is defined as *twice* the negative energy in atomic units).

Equations for the variation of  $\xi$  or  $\eta$  due to difference of potential function or of  $\epsilon$  can be obtained in the same way as (4.3) for the variation of  $P$ . The equation for  $\Delta\eta$  is

$$(\Delta\eta)' = 2\eta\Delta\eta + (\Delta\eta)^2 + 2\Delta v - \Delta\epsilon, \quad \dots\dots(4.8)$$

and since  $\Delta$  indicates a variation for a given value of  $r$ , it follows from the definition of  $\xi$  (3.4) that  $\Delta\xi = \Delta\eta$ .

To find  $\Delta P$ , we have by definition of  $\eta$

$$\eta = -d(\log P)/dr,$$

so that  $\Delta\eta = -d(\Delta \log P)/dr = -d[\log(P_1/P)]/dr$ .

For the solution  $P$  which is zero at the origin, it is most convenient to choose the arbitrary multiplying constants so that  $P_1/P = 1$  at  $r = 0$ ; if this is done, then

$$P_1/P = \exp \left[ - \int_0^r \Delta\eta dr \right]$$

(exactly, not only to the first order).

### § 5. Form of Solution in Region where Deviation from Coulomb Field is Inappreciable.

As already explained, for large values of  $r$  the solution used in the numerical work is that which is zero at  $r = \infty$ ; in the region where the field can be taken to be that of a point charge equal to the core charge  $C$ , certain relations between different solutions can be used to shorten the numerical work by avoiding the numerical integration in each particular case.

\* *Ann. der Phys.*, Vol. LXXX, p. 443, equation (7').

It is most convenient for work with these solutions to use as independent variable not  $r$  but

$$\rho = Cr/n^*, \quad \dots\dots(5.1)$$

the 'effective quantum number'  $n^*$  of a term being defined in the usual way,

$$\epsilon = C^2/(n^*)^2. \quad \dots\dots(5.2)$$

For the field of a point charge  $C$ , for which  $v = C/r$ , the equation (2.3) for  $P$  becomes, with  $\rho$  as independent variable,

$$\frac{d^2P}{d\rho^2} + \left[ \frac{2n^*}{\rho} - 1 - \frac{l(l+1)}{\rho^2} \right] P = 0, \quad \dots\dots(5.3)$$

for which the solution is a confluent hypergeometric function†

$$P = W_{n^*, l+\frac{1}{2}}(2\rho),$$

as pointed out by Eddington‡ and Sugiura§. From the asymptotic formula for the confluent hypergeometric function|| it follows that for large  $\rho$  the solution of (5.3) which is zero at  $\rho = \infty$  behaves like  $\rho^{n^*} e^{-\rho}$  as  $\rho \rightarrow \infty$ , so, in order to work with a function which remains finite, we define  $M$  by

$$P = \rho^{n^*} e^{-\rho} M \quad \dots\dots(5.4)$$

(apart from an arbitrary multiplying constant); an asymptotic series for  $M$  in inverse powers of  $\rho$  can be written down from that for the confluent hypergeometric function, but for values of  $\rho$  which are practically interesting the series diverges too early to be of much value, and  $M$  is best found by numerical integration of the appropriate equation (except of course for integral values of  $n^*$ , for which  $M$  is a polynomial of degree  $n^* - l - 1$  in  $1/\rho$ ).

In integration inwards from  $r = \infty$ ,  $r$  is clearly an unsuitable independent variable; the most suitable one appears to be  $1/\rho$  (rather than  $1/r$ ), and with this independent variable  $M$  satisfies

$$u^2 \frac{d^2M}{du^2} - 2[(n^* - 1)u - 1] \frac{dM}{du} + (n^* - l - 1)(n^* + l)M = 0; \quad \dots\dots(5.5)$$

we will write  $M(n^*, l)$  for the solution of this equation with given values of  $n^*$  and  $l$ , and take the dependent variable  $u$  as understood.

† E. T. Whittaker and G. N. Watson, *Modern Analysis*, Ch. xvi.

‡ A. S. Eddington, *Nature*, Vol. cxx, p. 117 (1927).

§ Y. Sugiura, *Phil. Mag.*, Ser. 7, Vol. iv, p. 498 (1927).

|| Whittaker and Watson, *op. cit.*, § 16.3.

As with the equation for  $P$ , it is convenient to work with the logarithmic derivative of  $M$  when  $u$  is much smaller than the first zero of  $M$ . The equation for

$$\zeta = -d(\log M)/du \quad \dots\dots(5.6)$$

is found to be

$$u^2 \frac{d\zeta}{du} = (n^* + l)(n^* - l - 1) - 2\zeta[1 - (n^* - 1)u] + \zeta^2 u^2. \quad \dots\dots(5.7)$$

A solution in series provides the initial values

$$\zeta = \frac{1}{2}(n^* + l)(n^* - l - 1), \quad \frac{d\zeta}{du} = (n^* - l)\zeta, \quad \text{at } u = 0. \quad \dots\dots(5.8)$$

The relations referred to between different solutions of the wave equation take the form of recurrence relations between the values for a given  $u$  (or  $\rho$ , not  $r$ ) of the functions  $M$  for values of  $n^*$  and  $l$  differing by integers.

Epstein† has given such recurrence relations for the function  $\rho^{n^*} M$ , using the fact that the series for this function, for the solution of the wave equation finite at  $r = 0$ , is a limiting form of the hypergeometric series; recurrence formulae for  $M$  can be derived from the formulae given by Epstein, but in the present case we are interested in the solutions for which  $M$  is finite at  $r = \infty$ , and it is most convenient to choose the arbitrary constants in the solutions for different  $n^*$ ,  $l$  so that

$$M(n^*, l) = 1 \text{ at } u = 0 \text{ for all } n^*, l, \quad \dots\dots(5.9)$$

which is a different choice from that adopted in the relations given by Epstein, so that the coefficients in the relations used here and in those derived from Epstein's are not the same; the relations will here be derived direct from the differential equation.

§ 6. *Recurrence Relations between functions  $M$  for values of  $n^*$  and  $l$  differing by integers.*

Using  $D$  to denote differentiation with respect to  $u$  and writing for shortness

$$F(n^*, l, D) = u^2 D^2 - 2[(n^* - 1)u - 1]D + (n^* - l - 1)(n^* + l), \quad \dots\dots(6.1)$$

equation (5.4) for  $M(n^*, l)$  becomes

$$F(n^*, l, D)M(n^*, l) = 0. \quad \dots\dots(6.2)$$

† P. Epstein, *Proc. Nat. Acad. Sci.*, Vol. XII, p. 629 (1926).

Since the function  $F$  contains  $u$  as well as the operator  $D$ , it is not commutative with  $D$ , but it is easily verified that

$$D \cdot F(n^*, l, D) = F(n^* - 1, l, D) \cdot D,$$

so that, differentiating (6.2),

$$D \cdot F(n^*, l, D) M(n^*, l) = F(n^* - 1, l, D) \cdot DM(n^*, l) = 0,$$

i.e.  $DM(n^*, l)$  satisfies the differential equation for  $M(n^* - 1, l)$ . Since, apart from an arbitrary multiplying constant, this equation has only one solution finite at  $u = 0$ , it follows that

$$DM(n^*, l) = aM(n^* - 1, l), \quad \dots\dots(6.3)$$

$a$  being a constant for a given  $n^*, l$  which must be determined to fit the initial condition (5.9).

Now at  $u = 0$

$$\zeta(n^*, l) = -DM(n^*, l)/M(n^*, l) = \frac{1}{2}(n^* + l)(n^* - l - 1)$$

by (5.8), so, to satisfy (5.9), (6.3) must become

$$DM(n^*, l) = -\frac{1}{2}(n^* + l)(n^* - l - 1)M(n^* - 1, l). \quad \dots\dots(6.4)$$

Given  $M(n^* - 1, l)$ ,  $M(n^*, l)$  can thus be found by quadrature from the initial condition  $M(n^*, l) = 1$  at  $u = 0$ ; by further quadratures  $M(n^* + 1, l)$ ,  $M(n^* + 2, l)$  and so on, can be found in succession, but the integration is not necessary as a purely algebraical expression can be found between the functions  $M$  for three values of  $n^*$  increasing by unity.

Substituting  $n^* + 1$  for  $n^*$  in (6.4), we have

$$DM(n^* + 1, l) = -\frac{1}{2}(n^* + l + 1)(n^* - l)M(n^*, l); \quad \dots\dots(6.5)$$

differentiation and substitution of (6.4) gives an expression for  $D^2M(n^* + 1, l)$  and substitution of this and (6.5) in the differentiation equation for  $M(n^* + 1, l)$  gives

$$M(n^* + 1, l) = [1 - n^*u]M(n^*, l) - \frac{1}{4}u^2(n^* + l)(n^* - l - 1)M(n^* - 1, l). \quad \dots\dots(6.6)$$

This, it must be emphasised, is a relation between the different functions  $M$  for the same value of  $u = n^*/Cr$ , not for the same value as  $r$ .

For the relations between solutions for different values of  $l$ , it can be verified by substitution in the differential equation

$$y = [-(n^* - l) + uD]M(n^* + 1, l)$$

satisfies

$$F(n^* + \frac{1}{2}, l + \frac{1}{2}, D)y = 0,$$

and since, apart from an arbitrary multiplying constant, this equation has only one solution  $M(n^* + \frac{1}{2}, l + \frac{1}{2})$  which is finite at  $u = 0$ , we can put

$$M(n^* + \frac{1}{2}, l + \frac{1}{2}) = b[-(n^* - l) + uD]M(n^* + 1, l),$$

or substituting (6.5); and taking  $b = -1/(n^* - l)$  in order to make  $M(n^* + \frac{1}{2}, l + \frac{1}{2}) = 1$  at  $u = 0$  in accordance with (5.9),

$$M(n^* + \frac{1}{2}, l + \frac{1}{2}) = M(n^* + 1, l) + \frac{1}{2}(n^* + l + 1)uM(n^*, l). \quad \dots\dots(6.7)$$

For the purposes of the present paper we are only interested in the solutions for integer values of  $l$ ; by successive use of (6.7) and substitution of (6.6) we obtain

$$M(n^*, l + 1) = [1 + (l + 1)u]M(n^*, l) + \frac{1}{2}(n^* + l)(l + 1)u^2M(n^* - 1, l). \quad \dots\dots(6.8)$$

With these relations between the values of the function  $M$  in a Coulomb field, for values  $n^*$  and  $l$  differing by integers, it is only necessary to find  $M$  by numerical integration of the differential equation for one value of  $l$  and a set of values for  $n^*$  covering a range of unity closely enough to allow of interpolation to the accuracy required; the functions  $M$  for other values of  $n^*$  and  $l$  can then be built up, using first (6.4), then (6.6) and (6.8); the results apply to any atom with a positive core charge.

The numerical integration of equation (5.7) for

$$\zeta = -d(\log M)/du$$

has actually been carried out for  $l = 0$  and  $n^*$  at intervals of 0.1 from 0.6 to 1.5 (for  $l = 0$ , the solution for  $n^* = 1$  is  $\zeta = 0$ , and, for neighbouring values of  $n^*$ ,  $\zeta$  and  $\frac{d\zeta}{du}$  are small over a large range of  $u$ ). The results as immediately obtained are in terms of  $u = n^*/Cr$  as independent variable, for practical application they must be expressed in terms of  $r$ . The method adopted is to find  $\zeta$  for a given value of  $Cr$  for each value of  $l$  and  $n^*$ , and from these values of  $\zeta$  to calculate

$$\frac{\eta}{C} = -\frac{1}{CP} \frac{dP}{dr} = \frac{1}{n^*} - \frac{n^*}{Cr} \left(1 + \frac{\zeta}{Cr}\right), \quad \dots\dots\dots(6.9)$$

which follows by differentiating (5.4) and using (5.1). For each value of  $l$ , the values of  $\eta/C$  so obtained, which refer to the solution zero at  $r = \infty$ , are plotted against  $n^*$ ; the intersection of the curve so obtained with the curve of  $\eta/C$  against  $n^*$  for the solution which is zero at  $r = 0$  then gives the values of  $n^*$  for the characteristic values of the wave equation.

§ 7. *General Formula for the Normalisation Integral for the Series Electron.*

The normalisation integral  $\int_0^\infty P^2 dr$  is required in calculation of perturbations; for the series electron the main contribution to this integral is from values of  $r$  where the field is effectively that of a point charge  $C$ ; using some of the results of the previous section an approximate recurrence formula for this integral can be found, and from it an approximate formula for the integral itself.

We consider the arbitrary constant chosen so that

$$P = e^{-\rho} \rho^{n^*} M; \quad M \rightarrow 1, \quad \rho \rightarrow \infty \quad \dots\dots(7.1)$$

(cf. formula 5.4). Using a dash to indicate differentiation with respect to  $\rho$  (not  $r$ ), as will be done throughout this section, the recurrence formulae (6.4), (6.6) then give respectively

$$\rho P'(n^*, l) = -(\rho - n^*) P(n^*, l) + \frac{1}{2}(n^* + l)(n^* - l - 1) P(n^* - 1, l), \quad \dots\dots(7.2)$$

$$P(n^* + 1, l) = (\rho - n^*) P(n^*, l) - \frac{1}{4}(n^* + l)(n^* - l - 1) P(n^* - 1, l), \quad \dots\dots(7.3)$$

from which elimination of  $P(n^* - 1, l)$  gives

$$P(n^* + 1, l) = \frac{1}{2}[(\rho - n^*) P(n^*, l) - \rho P'(n^*, l)]. \quad \dots\dots(7.4)$$

By subtracting the square of (7.3) from twice the square of (7.4), and then using (7.2) to substitute for  $P(n^* - 1, l)$  in the product term  $P(n^*, l) P(n^* - 1, l)$ , we obtain

$$P^2(n^* + 1, l) = \frac{1}{2}[(\rho - n^*)^2 P^2(n^*, l) + \rho^2 P'(n^*, l)^2] - [\frac{1}{4}(n^* - l - 1)(n^* + l)]^2 P^2(n^* - 1, l).$$

The required recurrence relation for  $\int P^2 d\rho$  is obtained by integrating this. For the second term on the right we have, on integrating by parts,

$$\int \rho^2 (P')^2 d\rho = [\rho^2 P P'] - \int P \frac{d}{d\rho} (\rho^2 P') d\rho;$$

expansion of the differential coefficient under the integral, followed by substitution for  $P''$  from the differential equation for  $P$  (5.3) and integration of the remaining term by parts gives finally

$$\int \rho^2 (P')^2 d\rho = [\rho^2 P P'] - [\rho P^2] - \int [\rho^2 - 2n^* \rho + l(l+1) - 1] P^2 d\rho,$$

so that altogether

$$\begin{aligned} \int P^2(n^* + 1, l) d\rho &= \frac{1}{2} [\rho^2 P P'] - \frac{1}{2} [\rho P^2] \\ &\quad + \frac{1}{2} [(n^*)^2 - l(l+1) + 1] \int P^2(n^*, l) d\rho \\ &\quad - [\frac{1}{4}(n^* - l - 1)(n^* + l)]^2 \int P^2(n^* - 1, l) d\rho, \end{aligned}$$

the function  $P$  in the integrated terms being  $P(n^*, l)$ . These terms vanish at the upper limit  $\rho = \infty$ ; if the field were a Coulomb field for all  $r$ , they would become infinite at the lower limit except for integral values of  $n^*$ . But for the actual wave functions corresponding to optical terms the part which would give the infinite contribution in a Coulomb field is replaced by a part in a non-Coulomb field which gives a contribution small compared to the total value of the integral, so that for an approximate result for these wave functions we may omit the integrated terms and write

$$\int_0^\infty P^2(n^* + 1, l) d\rho = \frac{1}{2} [(n^*)^2 - l(l+1) + 1] \int_0^\infty P^2(n^*, l) d\rho \\ - \left[ \frac{1}{4} (n^* - l - 1)(n^* + l)^2 \right] \int_0^\infty P^2(n^* - 1, l) d\rho. \quad \dots (7.5)$$

For integer values of  $n^*$ , and the choice of the arbitrary constants in the solutions  $P$  for different values of  $n^*$  here made (see 7.1), we have from a formula given by Waller†

$$\int_0^\infty P^2(n, l) d\rho = 2^{-2n} n(n+l)! (n-l-1)!.$$

This satisfies the recurrence relation (7.5), and suggests for a general value of  $n^*$

$$\int_0^\infty P^2(n^*, l) d\rho = 2^{-2n^*} n^* \Gamma(n^* + l + 1) \Gamma(n^* - l), \quad \dots (7.6)$$

which also satisfies it. In applying this result it must be remembered that the integral is taken with respect to  $\rho = Cr/n^*$ , not with respect to  $r$ , and that the arbitrary constant in  $P$  has been chosen according to (7.1), i.e. so that

$$P/\rho^{n^*} e^{-\rho} = M \rightarrow 1, \quad \rho \rightarrow \infty.$$

† I. Waller, *Zeit. f. Phys.*, Vol. xxxviii, p. 635. Using atomic units and the notation of this paper, let  $P$  be defined as  $2C/n$  times Waller's  $rX_{n,l}$ , i.e.

$$P = (2\rho)^{l+1} e^{-\rho} L_{\frac{n+l}{2}}^{(2l+1)}(2\rho) \quad (\rho = Cr/n = \text{half Waller's } \xi);$$

then it follows from Waller's formulae (32'), (33), (34) that

$$\int P^2 d\rho = n[(n+l)!]^2 / (n-l-1)!$$

Now the highest power of  $x$  in  $L_{\frac{n+l}{2}}^{(2l+1)}(x)$  is  $\frac{(n-l-1)!}{(n+l)!} x^{n-l-1}$ , so that, for large  $r$ ,  $P$

as defined behaves like  $\frac{(n-l-1)!}{(n+l)!} (2\rho)^n e^{-\rho}$ . Hence if, instead, the arbitrary constant in  $P$  is to be chosen so that  $P/\rho^n e^{-\rho} \rightarrow 1$  as  $\rho \rightarrow \infty$  (see 7.1),  $\int P^2 d\rho$  must have the value given here.

As explained at the end of the last section, solutions of the equations for  $M$  with different values of  $n^*$  and  $l$  satisfying this condition have been calculated, so that from the values of  $P$  at a comparatively small radius (only large enough for the deviation from a Coulomb field to be inappreciable) the value of the normalisation integral can be found from (7.6), thus avoiding the numerical evaluation of the integral in each particular case.

This formula has been tested on the first  $s$  and the first  $p$  term of Rb, and the errors are about  $2\frac{1}{2}\%$  and  $2\%$  respectively; they would presumably be less for higher terms of the series, since the larger  $n^*$  is, the larger is the proportional contribution to the integral from the range of  $r$  where the field is effectively a Coulomb field.

### § 8. *Perturbations.*

The general first order formula for central perturbations has already been found (see § 4, formula 4.7). If  $\Delta\epsilon$  is the change in characteristic value of the wave equation due to a change  $\Delta v$  in the potential function  $v$ , then

$$\Delta\epsilon = \int_0^\infty 2\Delta v P^2 dr / \int_0^\infty P^2 dr ;$$

this mean value of  $2\Delta v$  weighted by  $P^2$  corresponds to the time average of the perturbing potential in the classical perturbation theory.

Apart from the use of this formula to estimate the alteration in  $\epsilon$  due to a trial change in the field of force, there are two particular perturbations to which it can be applied, viz. the 'relativity' correction and the 'spinning electron' correction.

The relativity perturbation term in the classical Hamiltonian is (in ordinary units)  $-(1/2mc^2)(E - V)^2$ †, or in atomic units

$$\Delta v = \frac{1}{2}\alpha^2(\epsilon/2 - v)^2 \quad [\alpha^2 = (2\pi e^2/ch)^2 = 1/18800],$$

so that 
$$\Delta\epsilon = (\alpha^2/4) \int_0^\infty (\epsilon - 2v)^2 P^2 dr / \int_0^\infty P^2 dr.$$

If  $Z$  is the effective nuclear charge at any radius (the charge which, placed at the nucleus, would give the same *field* as the actual field at that radius), and  $\mathbf{l}$  and  $\mathbf{s}$  are the orbital and spin angular momentum vectors, the spinning electron perturbation term in the classical Hamiltonian is (in ordinary units)  $\frac{1}{2}(eh/2\pi mc)^2 (Z/r^3) \mathbf{l} \cdot \mathbf{s}$ ‡, or in atomic units  $\frac{1}{2}\alpha^2 (Z/r^3) \mathbf{l} \cdot \mathbf{s}$ , so that

$$\Delta\epsilon = \alpha^2 \mathbf{l} \cdot \mathbf{s} \int_0^\infty (Z/r^3) P^2 dr / \int_0^\infty P^2 dr.$$

† See, for example, M. Born, *op. cit.*, p. 234 (English translation, p. 204).

‡ See, for example, F. Hund, *op. cit.*, p. 74, formula (1).



According to Heisenberg and Jordan\*, on the new quantum mechanics the scalar product  $ls$  must, in the case of a Coulomb field, be given the values

$$ls = \frac{1}{2} [j(j+1) - l(l+1) - s(s+1)],$$

$$j = l \pm \frac{1}{2}, \text{ except that } j = \frac{1}{2} \text{ only when } l = 0,$$

$$s = \frac{1}{2}.$$

There is no reference to a Coulomb field in these results, so that, at any rate provisionally, they may be taken to apply also to an atom with a non-Coulomb field.

If, as is convenient in the numerical work, the arbitrary constant in  $P$  is taken so that, for small  $r$ ,  $P$  is the same for all solutions with the same  $l$  (strictly, so that the limit of  $P/r^{l+1}$  as  $r \rightarrow 0$  is the same for all solutions), and the main part of the perturbation arises from small values of  $r$  (as is the case for the two special perturbations considered), then  $\int_0^\infty 2vP^2 dr$  will be approximately the same for all solutions with the same  $l$ , so that approximately

$$\Delta\epsilon \propto \left[ \int_0^\infty P^2 dr \right]^{-1}.$$

### § 9. Method of Integrating the Differential Equations.

An outline of the method used for the numerical integration of the differential equations will now be given.

Suppose that a function  $f$  is tabulated at equal intervals  $\delta x$  of the independent variable  $x$ , and the integral  $y = \int f dx$  is required; using central differences†

$$\delta f_{\frac{1}{2}} = f_1 - f_0, \quad \delta f_{1\frac{1}{2}} = f_2 - f_1, \quad \dots,$$

$$\delta^2 f_0 = \delta f_{\frac{1}{2}} - \delta f_{-\frac{1}{2}} = f_1 - 2f_0 + f_{-1}, \quad \dots,$$

the contribution  $\delta y$  to  $y$  from an interval  $\delta x$  is

$$\delta y = \bar{f} \delta x,$$

the mean value  $\bar{f}$  being‡

$$\bar{f} = f_0 + \frac{1}{2}(\delta f)_{\frac{1}{2}} - \frac{1}{12}(\delta^2 f)_0 - \frac{1}{24}(\delta^3 f)_{\frac{1}{2}} + \frac{1}{720}(\delta^4 f)_0 + \dots \quad \dots\dots(9.1)$$

$$= f_0 + \frac{1}{2}(\delta f)_{\frac{1}{2}} - \frac{1}{12}(\delta^2 f)_{\frac{1}{2}} \delta x + \frac{1}{720}(\delta^4 f)_0 + \dots \quad \dots\dots(9.2)$$

$$(f' = df/dx).$$

\* W. Heisenberg and Jordan, *Zeit. f. Phys.*, Vol. **xxvii**, p. 263 (1926).

† See, for example, E. T. Whittaker and G. Robinson, *Calculus of Observations*, p. 35.

‡ For the first formula see Whittaker and Robinson, *op. cit.*, p. 147 (put  $r=1$  and express the result in central differences); the second follows directly from the Euler-Maclaurin formula (Whittaker and Robinson, *op. cit.*, p. 135) on putting  $r=1$  and expressing the differential coefficients in central differences. I am indebted to Mr C. H. Bosanquet for pointing out the advantage of (9.2), involving differences of the derivative of the integrand, with its small fourth order term.

The integration is carried out by one or other of these formulae applied to a series of equal intervals  $\delta x$ , an equation of the second order being reduced to a pair of the first order by the use of the first differential coefficient as a subsidiary dependent variable. Usually the first three orders of difference are taken into account, the fourth order term being an error term.

In the simple evaluation of integrals, the integrand  $f$  is known throughout the whole range of  $x$  before the integration is begun, but in the integration of a differential equation  $f$  for one at least of the first order equations, is an explicit function of the integral of one or more of them, so that the integration has to be carried out by a step-by-step process.

Further, if the integration has been carried out up to the values  $x = x_0$ , only the backward differences  $(\delta f)_{-\frac{1}{2}}, (\delta f)_{-1}, \dots$  are directly available, and in terms of these the formula for  $f$  converges much more slowly than formula (9.1) in the central differences (the coefficient of the fourth order difference is  $-\frac{23}{20}$  instead of  $\frac{11}{20}$ ); if, however, a value of  $f_1$  and hence the differences

$$(\delta f)_{\frac{1}{2}}, (\delta^2 f)_0, (\delta^2 f)_{-\frac{1}{2}}, \dots$$

are available, the use of  $(\delta^3 f)_{-\frac{1}{2}}$  in (9.1) only alters the coefficient of the fourth order term, which is the error term of the method employed, from  $\frac{11}{20}$  to  $-\frac{19}{20}$ . An essential point of the method of integration actually used is the estimation of  $f_1$  when the integration has been carried to the point  $x_0$ ; this estimation depends on the extrapolation, not of  $f_1$  itself, but of the quantities of which it is given as an explicit function, and this estimation is particularly easy to do satisfactorily in the case of the second order equation with the first derivative absent, which is just the type of the equation for  $P$  in the particular problem with which this paper is concerned.

Consider as an example this equation

$$\frac{d^2 P}{dr^2} = - \left[ 2v - \epsilon - \frac{l(l+1)}{r^2} \right] P,$$

already integrated through a series of equal intervals  $\delta r$  up to  $r = r_0$ ; we have the values  $P$  up to  $P_0$  and the backward differences from them.  $dP/dr$ , which is the subsidiary dependent variable used to reduce the second order equation to two first order ones, does not occur, so that the estimation of  $d^2 P/dr^2$  (which is the integrand  $f$  for the evaluation of  $\frac{dP}{dr} = \int f dr$ ) at  $r = r_1$  depends on the estimate of  $P$  only, and this is made as follows.

In terms of  $P''$  and its differences, the second difference of  $P$  is

$$(\delta^2 P)_0 = (\delta r)^2 [P''_0 + \frac{1}{12} (\delta^2 P'')_0 + \dots], \dots \dots (9.3)$$

and by definition of the second difference  $(\delta^2 P)_0$ ,

$$(\delta P)_{\frac{1}{2}} = (\delta P)_{-\frac{1}{2}} + (\delta^2 P)_0.$$

Now at the stage which the calculation is supposed to have reached,  $P_0$  and so  $(\delta P)_{-\frac{1}{2}}$  and  $P_0''$  are known;  $(\delta^2 P')_0$  can be extrapolated from previous values (great accuracy is not needed since its coefficient is small), so that, using (9.3),  $(\delta^2 P)_0$  can be estimated, and from it  $(\delta P)_{\frac{1}{2}}$  and finally  $P_1$ . With this value of  $P_1$ ,  $P_1''$  is calculated from the differential equation, and then  $(\delta P')_{\frac{1}{2}}$  from the integration formula (9.1) with  $f = P''$ ; for the integration of  $P'$  to give  $P$ , the differences of  $P''$ , the derivative of the integrand, are available, so that the formula (9.2), which is the most satisfactory on account of the small coefficient of the fourth order term, can be used.

The differences, tabulated as the work proceeds for use in the integration formulae, also provide a close check on the numerical work, a very important consideration indeed when such work on a large scale is being carried out, especially when a serious mistake at one stage may vitiate all subsequent work.

The intervals  $\delta r$  are kept of such a size that the fourth order difference terms in the integration formulae in any one interval do not affect the last significant figure retained. With intervals of the size so determined, it is only rarely that the method of estimating  $P_1$  described gives a value so different from the value finally obtained by integration that the calculation for the interval has to be repeated with a fresh estimate. The integration formulae depend on the use of a series of intervals of the same size, but it is not necessary to use the same size throughout; the most convenient change is to double the size of interval (in the case of the particular equation considered, the permissible length increases as  $r$  increases), the procedure is then quite straightforward; of the values of  $P''$  and  $P$  already calculated, alternate values are taken to provide a set of differences to give a start to the calculation with intervals of the double length. For numerical reasons, however, it is preferable to take intervals of 1, 2, or 5 times a power of 10; the change of interval length by a factor of  $2\frac{1}{2}$  involves some simple interpolation to provide the initial set of differences, but is otherwise straightforward.

Doubtless it would be possible to derive formulae for integration over longer intervals with adequate accuracy, but the writer's experience in other similar work is that simple formulae and a large number of intervals are much preferable to complicated formulae and a small number of intervals. Apart from the ease of working with simple formulae, the important question of keeping an adequate check on the numerical work is a difficult one unless the intervals are small, so that the successive differences converge rapidly enough to provide one. From the point of view of

simplicity it may be mentioned that, in the case of the differential equation for  $P$  here considered, only one calculation in each interval requires a slide rule (or logs), namely, that of  $P''$  from the differential equation; the rest involve only additions and subtractions, largely of numbers with one or two significant figures, and multiplications by  $2$ ,  $\frac{1}{2}$ ,  $\frac{1}{4}$ ,  $\frac{1}{12}$ ,  $\frac{1}{24}$  (the last three always of numbers of few significant figures), which can be done mentally.

For the first order equations for  $\xi$ ,  $\eta$  and  $\zeta$  the process is much the same, except that a cruder method has to be used for estimating the value of the integral at the end of the interval in order to obtain a value of the integrand, as the derivative of the integrand is not calculated.

### § 10. *Practical Determination of Characteristic Values and Functions.*

As already explained (see § 2) the characteristic values of  $\epsilon$  are determined by integrating the wave equation (or some equation derived from it) outwards from  $r=0$  and inwards from  $r=\infty$ , and choosing the value of  $\epsilon$  to make the solutions fit at some intermediate radius.

For the electrons with  $n=l+1$  (giving the 'circular orbits' of the Bohr theory)  $P$  has no intermediate zeros, and it is convenient to use the  $\xi$  equation (3.4) for the integration outwards to rather beyond the first maximum of  $P$ , and the  $\eta$  equation (2.6) for the integration inwards. A trial value of  $\epsilon$  is taken and the values of  $\eta$  at the common value of  $r$  for the two solutions are found by numerical integration of the respective equations by the method outlined in the previous section. The solution of the variation equations (see § 4) then gives the changes in these values of  $\eta$  for a given change in  $\epsilon$ , and the value of  $\epsilon$  required to make them the same is found by interpolation (inspection of the square terms in the solution of the variation equations shows whether linear interpolation is valid). An example will make the process clearer.

#### *Example.*

Rb atom with a certain trial field.  $3_s$  electron ( $n=3$ ,  $l=k-1=2$ ).

$$\text{At } r=0.6 \left\{ \begin{array}{l} \text{Integration outwards } \epsilon=7.0, \eta=1.87; \Delta\epsilon=+1.0, \Delta\eta=-0.54 \\ \text{Integration inwards } \epsilon=7.0, \eta=1.35; \Delta\epsilon=+1.0, \Delta\eta=+0.27 \\ \hline \phantom{\text{Integration inwards}} \phantom{\eta=1.35;} 0.52 \phantom{\eta=1.35;} -0.81 \end{array} \right.$$

Linear interpolation for the same value of  $\eta$  at  $r=0.6$  in both integrations gives  $\epsilon=7.64$  (in this case inspection of square terms in the variation equation showed that error of linear interpolation was probably less than 0.03).

It will be noted that  $\Delta\eta$  is of opposite sign for the two integrations; this is always the case, and gives a good intersection for the determination of the characteristic value  $\epsilon$ . This being found,

it is a simple matter to calculate the values of  $\xi$  or  $\eta$  for the other values of  $r$ , and from them to calculate  $P^2$  from either

$$\log_{10} P^2 = 2(l+1) \log_{10} r - 2M \int_0^r \xi dr \quad (M = \log_{10} e),$$

or 
$$\log_{10} P^2 = \log_{10} [P(r_0)]^2 - 2M \int_{r_0}^r \eta dr,$$

according as  $\xi$  or  $\eta$  is given (as  $P^2$  is required to give the charge density and for perturbation calculations, it is usually best to calculate it directly).

For X-ray electrons with  $n > l + 1$  (corresponding to the 'elliptical orbits') it has been found best to integrate equation (3.4) for  $\xi$  from  $r = 0$  out to about the first maximum of  $P$ , and equation (2.3) for  $P$  from there to a point rather beyond the last maximum of  $P$ ; the  $\eta$  equation is integrated inwards to the same point and the estimation of  $\epsilon$  made as already explained.

It is not in practice necessary to integrate the  $\eta$  equation all the way in from  $r = \infty$ . Beyond the 'outer apse' (i.e. the greater root of  $2v - \epsilon - 1(l+1)/r^2 = 0$ , see § 2) the integration outwards is highly unstable\*, so that if we begin an outwards integration of the  $\eta$  equation from a radius outside the range where  $P$  is appreciable (and so well outside the outer apse), the behaviour of the solution is very sensitive to the value of  $\eta$  at this radius chosen to start the integration, and from a very few intervals of integration (2 and 3 in practice) a good estimate can be obtained for the value of  $\eta$  at this radius for the solution required, for which  $\eta$  remains finite at  $r = \infty$ . The integration inwards being correspondingly highly stable, a small error in the value of  $\eta$  at this radius will cancel itself almost entirely in the process of integration inwards to the point where the join is made with the integration outwards from  $r = 0$ . This integration outwards is highly stable as far as the inner apse, and stable as far as the outer apse.

The method of determining the characteristic values for the optical terms has been given at the end of § 6.

In the following paper the results of some calculations on these lines will be given and discussed.

### § 11. Summary.

The paper is concerned with the practical determination of the characteristic values and functions of the wave equation of Schrödinger for a non-Coulomb central field, for which the potential is given as a function of the distance  $r$  from the nucleus.

The method used is to integrate a modification of the equation outwards from initial conditions corresponding to a solution finite

\* It is convenient to speak of the process of the numerical integration of a differential equation as 'stable' if a small change in the solution at one point (for example, a numerical slip) does not produce greater changes in later values as the integration proceeds, and as 'unstable' when the opposite is the case.

at  $r=0$ , and inwards from initial conditions corresponding to a solution zero at  $r=\infty$ , with a trial value of the parameter (the energy) whose characteristic values are to be determined; the values of this parameter for which the two solutions fit at some convenient intermediate radius are the characteristic values required, and the solutions which so fit are the characteristic functions (§§ 2, 10).

Modifications of the wave equation suitable for numerical work in different parts of the range of  $r$  are given (§§ 2, 3, 5), also exact equations for the variation of a solution with a variation in the potential or of the trial value of the energy (§ 4); the use of these variation equations in preference to a complete new integration of the equation for every trial change of field or of the energy parameter avoids a great deal of numerical work.

For the range of  $r$  where the deviation from a Coulomb field is inappreciable, recurrence relations between different solutions of the wave equations which are zero at  $r=\infty$ , and correspond to terms with different values of the effective and subsidiary quantum numbers, are given and can be used to avoid carrying out the integration in each particular case (§§ 6, 7).

Formulae for the calculation of first order perturbations due to the relativity variation of mass and to the spinning electron are given (§ 8).

The method used for integrating the equations numerically is outlined (§ 9).

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