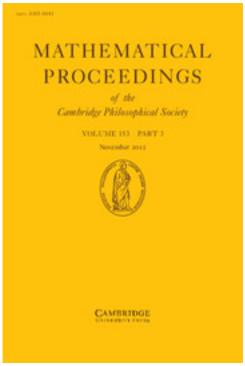

The calculation of atomic fields

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The calculation of atomic fields. By L. H. THOMAS, B.A., Trinity College.

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The theoretical calculation of observable atomic constants is often only possible if the effective electric field inside the atom is known. Some fields have been calculated to fit observed data* but for many elements no such fields are available. In the following paper a method is given by which approximate fields can easily be determined for heavy atoms from theoretical considerations alone.

1. *Assumptions and the deduction from them of an equation.*

The following assumptions are made.

(1) Relativity corrections can be neglected.

(2) In the atom there is an effective field given by potential V, depending only on the distance r from the nucleus, such that

$$V \to 0 \text{ as } r \to \infty,$$

$$Vr \to E, \text{ the nuclear charge, as } r \to 0.$$

(3) Electrons are distributed uniformly in the six-dimensional phase space for the motion of an electron at the rate of two for each h^3 of (six) volume. (This means one for each unit cell in the phase space of translation and rotation of a spinning electron.) The part of the phase space containing electrons is limited to that for which the orbits are closed.

(4) The potential V is itself determined by the nuclear charge and this distribution of electrons.

In reality the effective field at any point depends on whether the point is empty or occupied by a foreign electron or one or another atomic electron and on the circumstances of that occupation. These fields can only be expected to be sensibly the same or approximately calculable from the above assumptions if the density of electrons is large, that is, in the interior of heavy atoms.

If e, m, p are the charge, mass and momentum of an electron, the Hamiltonian function for the electronic motion is ((1) and (2) above),

$$\frac{1}{2m}p^2 - eV.$$

* D. R. Hartree, *Proc. Camb. Phil. Soc.*, **21**, p. 625; E. Fues, *Zeit. für. Phys.*, **11**, p. 369.

There are ((3) above) electrons at two for each h^3 of phase space for which

$$p < (2meV)^{\frac{1}{2}}$$

i.e. at

$$\frac{2}{h^3}\frac{4}{3}\pi(2meV)^{\frac{3}{2}}$$

per unit of ordinary (coordinate) space.

Thus ((4) above)

$$\nabla^2 V = 4\pi e \,.\, \frac{2}{h^3}\frac{4}{3}\pi(2meV)^{\frac{3}{2}}$$

i.e.

$$\frac{1}{r^2}\frac{d}{dr}r^2\frac{dV}{dr} = 4\pi e\frac{2}{h^3}\frac{4}{3}\pi(2me)^{\frac{3}{2}}V^{\frac{3}{2}} \quad \text{......(1·1)},$$

with ((2) above)

$$V \to 0 \text{ as } r \to \infty,$$
$$Vr \to E \text{ as } r \to 0.$$

Now express distance in terms of the 'radius of the normal orbit of the hydrogen atom,' $a = h^2/4\pi^2 me^2 = 5{\cdot}3 \,.\, 10^{-9}$ cms., potential in terms of the potential of an electron at this distance, so

$$r = \rho\,\frac{h^2}{4\pi^2 me^2},$$

$$V = \psi e\Big/\frac{h^2}{4\pi^2 me^2},$$

and equation 1·1 becomes

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{d\psi}{d\rho}\right) = \frac{8\sqrt{2}}{3\pi}\psi^{\frac{3}{2}} \quad \text{......(1·2)},$$

with

$$\psi \to 0 \text{ as } \rho \to \infty,$$
$$\rho\psi \to N, \text{ the atomic number, as } \rho \to 0.$$

(It is useful to note that with 'a' as unit of length, the charge and mass of the electron as units of charge and mass, $h = 2\pi$, whence 1·2 is at once verified.)

The 'effective nuclear charge' at distance ρ is then given by

$$Z = -\rho^2\frac{d\psi}{d\rho}.$$

Putting $\psi = \dfrac{9\pi^2}{128}\phi$, the equation for ϕ is

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{d\phi}{d\rho}\right) = \phi^{\frac{3}{2}} \quad \text{......(1·3)}.$$

2. *Discussion of the equation.*

Write $\log \rho = x$, $\rho^4 \phi = w$, and the equation becomes

$$\frac{d^2 w}{dx^2} - 7\frac{dw}{dx} + 12w = w^{\frac{3}{2}} \qquad \text{......(2·1)},$$

or, if $dw/dx = p$

$$\frac{dp}{dw} = 7 + \frac{w(w^{\frac{1}{2}} - 12)}{p} \qquad \text{......(2·2)}.$$

The maximum and minimum locus of this equation is

$$p = -\frac{w(w^{\frac{1}{2}} - 12)}{7}$$

The inflexion locus is

$$p = -\frac{2w(w^{\frac{1}{2}} - 12)}{7 \mp (1 + 6w^{\frac{1}{2}})^{\frac{1}{2}}} = f(w),$$

and

$$\left(\frac{dp}{dw}\right)_{p=f(w)} - f'(w) = \pm 3w^{\frac{1}{2}}(w^{\frac{1}{2}} - 12)\{7 \mp (1 + 6w^{\frac{1}{2}})^{\frac{1}{2}}\}^{-2}(1 + 6w^{\frac{1}{2}})^{-\frac{1}{2}},$$

gives the direction in which the solutions cross the inflexion locus.

There are two singular points, $w = 0$, $p = 0$; $w = 144$, $p = 0$.

At $\quad w, p \to 0, \quad (4w - p)^4 \sim c(p - 3w)^3, \quad (w > 0),$

at $w \to 144$, $p \to 0$, $(7{\cdot}772(w - 144) - p)^{7{\cdot}772}({\cdot}772(w - 144) + p)^{{\cdot}772} \sim c$,

give the form of the solutions, c being arbitrary.

The dp/dw discriminant gives $p = 0$, and $w = 144$ or $\phi = 144\rho^{-4}$ as a singular solution.

There is an approximate particular solution,

$$\left.\begin{aligned} p &= -\frac{4\lambda}{\sqrt{12}} w(w^{\frac{1}{4}} - 12^{\frac{1}{2}}) \\ w &= \frac{144}{(1 + e^{-\lambda x})^4} \end{aligned}\right\} \qquad \text{......(2·21)},$$

which satisfies

$$\frac{3}{5\lambda}\frac{dp}{dw} = \frac{12}{5} + \frac{3}{\lambda} + \frac{w(w^{\frac{1}{2}} - 12)}{p}.$$

The solutions of 2·2 lie roughly as in the sketch (Fig. 1), the arrows give the direction of increase of ρ. The only solutions for which $\phi \to 0$ as $\rho \to \infty$ and $\phi = O(1/\rho)$ as $\rho \to 0$ correspond to the solution through O and A in the sketch—2·21 is an approximation to this solution*. Different values of the nuclear charge

* It is only at A that ρ becomes infinite.

correspond to the replacement of x by $x + c$, which does not affect 2·1, so that if the equation is integrated numerically, starting from an initial position with w and p near A and any value of x, all the required solutions can be deduced.

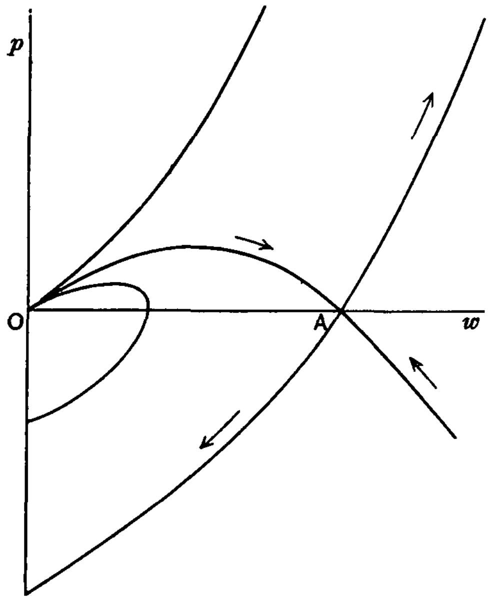

Fig. 1

3. *The numerical integration.*

For the initial values put

$$w = 144\,(u+1)^{-4}, \quad v = \frac{du}{dx},$$

in 2·1, obtaining

$$(u+1)\,v\,\frac{dv}{du} - 5v^2 - 7\,(u+1)\,v - 3u\,(u+2) = 0.$$

If $v' = \lambda\,(u + au^2)$,

$$G \equiv (u+1)\,v'\frac{dv'}{du} - 5v'^2 - 7\,(u+1)\,v' - 3u\,(u+2)$$

$$= u\,(\lambda^2 - 7\lambda - 6) + u^2\,(-4\lambda^2 - 7\lambda - 3 + a\,(3\lambda^2 - 7\lambda))$$
$$+ u^3\,(a\,\{-7\lambda^2 - 7\lambda\} + 2a^2\lambda^2) - 3a^2\lambda^2u^4$$

$$= \tfrac{1}{2}u^2\,\{35\sqrt{73} - 292 + a\,(134 - 14\sqrt{73})\}$$
$$+ au^3\,\{7\,(4\sqrt{73} - 34) + a\,(61 - 7\sqrt{73})\} - 3a^2\lambda^2u^4.$$

For $\lambda = -\frac{1}{2}(\sqrt{73} - 7) = -\cdot77200$ and $u > 0$.

$G < 0$ for $a = -(35\sqrt{73} - 292)/(134 - 14\sqrt{73}) = -\cdot0027900$,

$G > 0$ for $a = 0$,

from which it can be shown that for $u > 0$

$$-\cdot77200u < \frac{du}{dx} < -\cdot77200(u - \cdot0027900u^2) \quad \ldots(3\cdot1).$$

For the actual numerical integration it is convenient to put

$$x = X \log_e 10, \quad w = 144 \,.\, 10^Y,$$

so that 2·1 becomes

$$\frac{d^2Y}{dX^2} = \log_e 10\left\{12 \,.\, 10^{\frac{1}{2}Y} + \cdot25 - \left(3\cdot5 - \frac{dY}{dX}\right)^2\right\} \quad \ldots(3\cdot2),$$

while

$$\psi = \frac{9\pi^2}{128} 144 \,.\, 10^{Y-4(X+c)} \quad \ldots\ldots(3\cdot31),$$

$$Z = \frac{9\pi^2}{128}\left(4 - \frac{dY}{dX}\right) 144 \,.\, 10^{Y-3(X+c)} \quad \ldots\ldots(3\cdot32),$$

$$\rho = 10^{X+c} \quad \ldots\ldots(3\cdot33),$$

where c is to be determined from the atomic number. Z is the effective nuclear charge.

If $\quad Y = -1, \quad u = 10^{\frac{1}{4}} - 1 = \cdot77828$,

and

$$1\cdot3515 > \frac{dY}{dX} > 1\cdot3489 \quad \text{(from 3·1)}.$$

Starting with

$$X = 0, \quad Y = -1, \quad \frac{dY}{dX} = 1\cdot35,$$

numerical integration was carried out by steps of ·1 to $X = -3$ by the aid of the formulae

$$\left(\frac{dy}{dx}\right)_{n+1} - \left(\frac{dy}{dx}\right)_n = \left(\frac{d^2y}{dx^2}\right)_n + \frac{1}{2}\Delta\left(\frac{d^2y}{dx^2}\right)_{n-1} + \frac{5}{12}\Delta^2\left(\frac{d^2y}{dx^2}\right)_{n-2} + \ldots,$$

$$y_{n+1} - y_n = \left(\frac{dy}{dx}\right)_n + \frac{1}{2}\left(\frac{d^2y}{dx^2}\right)_n + \frac{1}{6}\Delta\left(\frac{d^2y}{dx^2}\right)_{n-1} + \frac{1}{8}\Delta^2\left(\frac{d^2y}{dx^2}\right)_{n-2} + \ldots\text{*}.$$

* See Whittaker and Robinson, *The Calculus of Observations*, p. 365.

For $X = -3$ it appears that

$$3\cdot 5 - \frac{dY}{dX} = \cdot 508, \quad \log_{10} 144 + Y = 7\cdot 4385$$

so equation 3·32 gives

$$Z = \frac{9\pi^2}{128} \cdot 1\cdot 008 \cdot 10^{2\cdot 4385 - 3c},$$

i.e. $$c = \cdot 7611 - \tfrac{1}{3} \log_{10} N,$$

since here closely enough $Z = N$ the atomic number.

e.g. for $N = 55$ (caesium), $c = \cdot 1810$.

4. *Numerical results.*

The following table gives the values of

$$3\cdot 5 - \frac{dY}{dX} \text{ and } \log_{10} 144 + Y$$

found by numerical integration and the corresponding values of ρ, Z, ψ for caesium. The former may be in error by about 10 in the last decimal place.

For $\rho_0 < \cdot 006$, the field is sensibly a Coulomb field.

For $\rho_0 > 1\cdot 5$, the approximate formula 2·21 is an accurate enough solution of the differential equation, but this equation is not an accurate representation of the facts.

For the element of atomic number N the corresponding values are given by

$$\rho = \rho_0 \left(\frac{55}{N}\right)^{\frac{1}{3}},$$

$$Z = Z_0 \left(\frac{N}{55}\right),$$

$$\psi = \psi_0 \left(\frac{N}{55}\right)^{\frac{4}{3}}.$$

The values Z_1 are (unpublished) values calculated by Mr Hartree for caesium from the observed levels and which he has very kindly allowed me to include for comparison.

In conclusion, I wish to thank Professor Bohr and Professor Kramers for their encouragement when I was carrying out the numerical integration last March.

$-X$	$3\cdot5-\dfrac{dY}{dX}$	$\log_{10}144+Y$	ρ_0	Z_0	ψ_0	Z_1
0	2·150	1·1584	1·517	7·6	1·887	9·9
·1	2·015	1·0167	1·205	10·4	3·412	12·5
·2	1·880	·8614	·9572	13·7	6·008	16·0
·3	1·746	·6927	·7603	17·5	10·23	19·7
·4	1·615	·5105	·6040	21·6	16·90	24·3
·5	1·489	·3156	·4800	25·8	27·10	29·0
·6	1·371	·1086	·3811	30·1	42·26	33·4
·7	1·261	$\bar{1}$·8901	·3027	34·2	64·18	36·6
·8	1·160	$\bar{1}$·6611	·2404	38·0	95·15	39·5
·9	1·069	$\bar{1}$·4225	·1910	41·3	138·0	42·2
1·0	·987	$\bar{1}$·1752	·1517	44·2	196·1	44·7
1·1	·914	$\bar{2}$·9202	·1205	47·7	273·9	46·6
1·2	·851	$\bar{2}$·6584	·09572	48·7	376·4	47·8
1·3	·795	$\bar{2}$·3906	·07603	50·3	510·4	48·4
1·4	·747	$\bar{2}$·1176	·06040	51·5	683·8	49·3
1·5	·706	$\bar{3}$·8402	·04800	52·5	906·8	50·6
1·6	·671	$\bar{3}$·5590	·03811	53·2	1198	51·6
1·7	·642	$\bar{3}$·2746	·03027	53·8	1556	52·4
1·8	·614	$\bar{4}$·9875	·02404	54·0	2018	53·4
1·9	·595	$\bar{4}$·6979	·01910	54·4	2601	53·9
2·0	·577	$\bar{4}$·4064	·01517	54·6	3340	54·1
2·1	·564	$\bar{4}$·1134	·01205	54·8	4273	54·4
2·2	·552	$\bar{5}$·8191	·009572	54·9	5450	54·6
2·3	·542	$\bar{5}$·5238	·007603	54·9	6936	54·7
2·4	·534	$\bar{5}$·2276	·006040	55·0	8809	54·8
2·5	·527	$\bar{6}$·9306	·004800	55·0	11170	
2·6	·521	$\bar{6}$·6330	·003811	55·0	14140	
2·7	·517	$\bar{6}$·3349	·003027	55·0	17870	
2·8	·513	$\bar{6}$·0364	·002404	55·0	22580	
2·9	·510	$\bar{7}$·7376	·001910	55·0	28570	
3·0	·508	$\bar{7}$·4385	·001517	55·0	35960	