The calculation of atomic fields

L. H. Thomas

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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 $V \to 0$ as $r \to \infty$, $Vr \to E$, 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 $\hbar^3$ 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),

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

There are ((3) above) electrons at two for each \( h^2 \) of phase space for which

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

i.e. at

\[ \frac{2}{h^2} \frac{4}{3} \pi (2meV)^{\frac{1}{2}} \]

per unit of ordinary (coordinate) space.

Thus ((4) above)

\[ \nabla^2 V = 4\pi e \cdot \frac{2}{h^2} \frac{4}{3} \pi (2meV)^{\frac{1}{2}} \]

i.e.

\[ \frac{1}{r^2} \frac{d}{dr} r^2 \frac{dV}{dr} = 4\pi e \cdot \frac{2}{h^2} \frac{4}{3} \pi (2me)^{\frac{1}{2}} V^{\frac{1}{2}} \]

……(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,’

\[ a = \frac{h^2}{4\pi^2 me^2} = 5.3 \times 10^{-9} \text{ cms., potential in terms of the potential of an electron at this distance, so} \]

\[ r = \rho \frac{h^2}{4\pi^2 me^2} , \]
\[ V = \psi e \sqrt[4]{\frac{\rho^2}{4\pi^2 me^2}} , \]

and equation 1.1 becomes

\[ \frac{1}{\rho^2} \frac{d}{d\rho} (\rho^2 \frac{d\psi}{d\rho}) = \frac{8\sqrt{2}}{3\pi} \psi^{\frac{3}{2}} \]

……(1.2),

with \( \psi \to 0 \) 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 \( \rho \) is then given by

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

Putting \( \psi = \frac{9\pi^2}{128} \phi \), the equation for \( \phi \) is

\[ \frac{1}{\rho^2} \frac{d}{d\rho} (\rho^2 \frac{d\phi}{d\rho}) = \phi^{\frac{3}{2}} \]

……(1.3).
2. Discussion of the equation.

Write log $\rho = x$, $\rho \phi = w$, and the equation becomes
\[
\frac{d^2w}{dx^2} - 7 \frac{dw}{dx} + 12w = w^\frac{1}{4} \quad \ldots (2'1),
\]
or, if $dw/dx = p$
\[
\frac{dp}{dw} = 7 + \frac{w(w^\frac{1}{4} - 12)}{p} \quad \ldots (2'2).
\]
The maximum and minimum locus of this equation is
\[
p = -\frac{w(w^{\frac{1}{4}} - 12)}{7}
\]
The inflexion locus is
\[
p = -\frac{2w(w^{\frac{1}{4}} - 12)}{7 + (1 + 6w^{\frac{1}{4}})^2} = f(w),
\]
and
\[
\left(\frac{dp}{dw}\right)_{p=f(w)} - f'(w) = \pm 3w^{\frac{1}{4}}(w^{\frac{1}{4}} - 12)[7 + (1 + 6w^{\frac{1}{4}})^2]^{-\frac{3}{2}}(1 + 6w^{\frac{1}{4}})^{-\frac{1}{2}},
\]
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 $w$, $p \to 0$, $(4w - p)^4 \sim c(p - 3w)^6$, $(w > 0)$,
at $w \to 144$, $p \to 0$, $(7.772(w - 144) - p)^{\gamma \alpha} (7.772(w - 144) + p)^{\gamma \alpha} \sim c$,
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,
\[
p = -\frac{4\lambda}{\sqrt{12}} w^{\frac{1}{4}}(w^{\frac{1}{4}} - 12)^{\frac{1}{4}} \quad \ldots (2'21),
\]
\[
w = \frac{144}{(1 + e^{-\lambda x})^4}
\]
which satisfies
\[
\frac{3}{5\lambda} \frac{dp}{dw} = \frac{12}{5} + \frac{3}{\lambda} + \frac{w(w^{\frac{1}{4}} - 12)}{p}.
\]
The solutions of $2'2$ lie roughly as in the sketch (Fig. 1),
the arrows give the direction of increase of $\rho$. 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 $\rho$ becomes infinite.
Mr Thomas, The calculation of atomic fields

545
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.

3. The numerical integration.

For the initial values put

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

in 2-1, obtaining

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

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

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

$$= u \left( \lambda^2 - 7\lambda - 6 \right) + u^2 \left( -4\lambda^2 - 7\lambda - 3 + a \left( 3\lambda^2 - 7\lambda \right) \right)$$

$$+ u^3 \left( -7\lambda^2 - 7\lambda \right) + 2a^2 \lambda^2) - 3a^2 \lambda^2 u^4$$

$$= \frac{1}{2} u^3 \left[ 35 \sqrt{73} - 292 + a \left( 134 - 14 \sqrt{73} \right) \right]$$

$$+ au^3 \left[ 7 \left( 4 \sqrt{73} - 34 \right) + a \left( 61 - 7 \sqrt{73} \right) \right] - 3a^2 \lambda^2 u^4.$$

Fig. 1
For \( \lambda = - \frac{1}{2} (\sqrt{73} - 7) = -0.77200 \) and \( u > 0 \).

\[ G < 0 \text{ for } a = -(35 \sqrt{73} - 292)/(134 - 14 \sqrt{73}) = -0.0027900, \]
\[ G > 0 \text{ for } a = 0, \]

from which it can be shown that for \( u > 0 \)

\[ -0.77200 u < \frac{du}{dx} < -0.77200 (u - 0.0027900u^2) \quad \text{(3.1)}. \]

For the actual numerical integration it is convenient to put

\[ x = X \log_{10}, \quad w = 144.10^Y, \]

so that (3.1) becomes

\[ \frac{d^2Y}{dx^2} = \log_{10} \left(12.10^Y + 0.25 - \left(3.5 - \frac{dY}{dx}\right)^2\right) \quad \text{(3.2)}, \]

while

\[ \psi = \frac{9n^2}{128} 144.10^Y - 4(X+c) \quad \text{......(3.31)}, \]

\[ Z = \frac{9n^2}{128} (4 - \frac{dY}{dx}) 144.10^Y - 3(X+c) \quad \text{......(3.32)}, \]

\[ \rho = 10^{X+c} \quad \text{......(3.33)}, \]

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

If \( Y = -1, \quad u = 10^Y - 1 = 77828, \)

and \( 1.3515 > \frac{dY}{dx} > 1.3489 \quad \text{(from 3.1)}. \)

Starting with

\[ X = 0, \quad Y = -1, \quad \frac{dY}{dx} = 1.35, \]

numerical integration was carried out by steps of 0.1 to \( X = -3 \) by the aid of the formulae

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

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

For $X = -3$ it appears that

$$3.5 - \frac{dY}{dX} = 0.508, \quad \log_{10} 144 + Y = 7.4385$$

so equation 3.32 gives

$$Z = \frac{9\pi^2}{128} \cdot 1.008 \cdot 10^{2.1335 - 3c},$$

i.e.

$$c = 0.7611 - \frac{1}{3} \log_{10} N,$$

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

e.g.

for $N = 55$ (caesium), $c = 0.1810.$


The following table gives the values of

$$3.5 - \frac{dY}{dX} \quad \text{and} \quad \log_{10} 144 + Y$$

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

For $\rho < 0.006$, the field is sensibly a Coulomb field.

For $\rho > 1.5$, 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

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

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

$$\psi = \psi_0 \left(\frac{N}{55}\right)^{\frac{2}{3}}.$$

The values $Z$, 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.
Mr Thomas, The calculation of atomic fields

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