The total energy of binding of a heavy atom. By Mr E. A. MILNE, Trinity College.

[*Received* 4 May, *read* 25 July, 1927.]

1. In a recent important paper*, L. H. Thomas has originated a method for calculating approximately the field in the interior of a heavy atom. His main assumption is that the 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 6-volume. On this assumption, Poisson's equation

$$\nabla^2 V = -4\pi\rho$$

is found to lead to an equation of the form

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

where ϕ is proportional to the potential V and ξ is proportional to the radial distance r.

To an astrophysicist, the form of (1) immediately suggests that of Emden's† differential equation

$$\frac{1}{\xi^2}\frac{d}{d\xi}\left(\xi^2\frac{d\phi}{d\xi}\right) = -\phi^n, \quad \text{.....................(2)}$$

which describes the gravitational equilibrium of a spherical mass of perfect gas of polytropic index n. Here ϕ may be considered to be either the gravitational potential or the temperature. Emden's solution of (2) with $n = 3$ is the basis of Eddington's famous theory of the internal constitution of the stars. The methods used by Thomas for discussing (1) are similar to those used by Emden for discussing (2).

Amongst Emden's results, perhaps the most notable is that which shows that once (2) has been solved, the total gravitational potential energy (or the mean temperature)‡ can be calculated without further quadrature. The object of the present note is to apply Emden's method to determine the total electrostatic potential energy of an atom built on Thomas's model, and so the total binding energy of the electrons.

2. *Evaluation of an integral.* We consider first a generalised form of Thomas's equation,

$$\frac{1}{\xi^2}\frac{d}{d\xi}\left(\xi^2\frac{d\phi}{d\xi}\right) = \phi^n: \quad \text{.....................(3)}$$

* "The calculation of atomic fields," *Proc. Camb. Phil. Soc.*, 23, 1927, 542.

† Emden, *Gaskugeln*, Leipzig, 1907.

‡ This adaptation is due to Eddington.

From the mode of derivation of the equation, the charge density ρ is proportional to ϕ^n, whilst $V \propto \phi$, and the total electrostatic energy $\frac{1}{2}\int \rho V d\tau$ thus involves the evaluation of a definite integral

$$I_a{}^b = \int_a^b \phi^{n+1} \xi^2 d\xi.$$

Substituting for $\xi^2 \phi^n$ from (3) and integrating by parts, this gives

$$I_a{}^b = \left[\xi^2 \phi \frac{d\phi}{d\xi}\right]_a^b - \int_a^b \left(\frac{1}{\xi^2}\right)\left(\xi^2 \frac{d\phi}{d\xi}\right)^2 d\xi,$$

where the new integrand has been re-arranged as a product of two factors. Integrating again by parts and then substituting for

$$\frac{d}{d\xi}\left(\xi^2 \frac{d\phi}{d\xi}\right)$$

from (3), we find

$$I_a{}^b = \left[\xi^2 \phi \frac{d\phi}{d\xi} + \xi^3 \left(\frac{d\phi}{d\xi}\right)^2\right]_a^b - 2\int_a^b \xi^3 \left(\phi^n \frac{d\phi}{d\xi}\right) d\xi.$$

On integrating the last integral by parts (treating $\phi^n d\phi/d\xi$ as the perfect differential), we obtain an integrated part together with a multiple of the original integral I_a^b. Re-arranging, we find

$$I_a{}^b = \frac{n+1}{n-5}\left[\xi^2 \phi \frac{d\phi}{d\xi} + \xi^3 \left(\frac{d\phi}{d\xi}\right)^2 - \frac{2}{n+1}\,\xi^3 \phi^{n+1}\right]_a^b.$$

This is, essentially, the analogue for equation (3) of Emden's result for (2).

Applying to Thomas's case and extending the integration from 0 to ∞ we find

$$\int_0^\infty \phi^{\frac{5}{2}} \xi^2 d\xi = \frac{5}{7} \lim_{\xi \to 0} \xi^2 \frac{d\phi}{d\xi}\left(\phi + \xi \frac{d\phi}{d\xi}\right).$$

For an atomic field, ϕ has a singularity at the origin, its behaviour being of the form

$$\phi \sim \frac{a_0}{\xi} + a_1$$

for ξ small. We find then

$$\int_0^\infty \phi^{\frac{5}{2}} \xi^2 d\xi = -\frac{5}{7} a_0 a_1. \quad \text{.................(4)}$$

3. *The electrostatic potential energy.* Thomas's equation for the atomic field V at distance r is

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{dV}{dr}\right) = -4\pi\rho, \quad \text{.................(5)}$$

with

$$\rho = -e\,\frac{2}{h^3}\,\frac{4\pi}{3}(2me)^{\frac{3}{2}} V^{\frac{3}{2}} \quad \text{.................(6)}$$

and the solution V for r small behaves like

$$V \sim \frac{Ne}{r} + v_0,$$

where N is the atomic number and v_0 is the self-potential at the origin of the distribution ρ. Now the system of charges consists of $+Ne$ at $r = 0$ together with the distribution ρ. Let the latter give rise to a field of potential $v(r)$. Then

$$V = \frac{Ne}{r} + v(r).$$

The electrostatic energy is then $W = \frac{1}{2}\Sigma eV$

or $$W = \tfrac{1}{2}\int \rho V d\tau + \tfrac{1}{2} Nev_0. \qquad \text{.....................(7)}$$

Thomas makes the substitutions

$$v = \xi \frac{h^2}{4\pi^2 me^2},$$

$$V = \frac{9\pi^2}{128} \frac{4\pi^2 me^3}{h^2} \phi,$$

so that for ξ small, the behaviour of ϕ is

$$\phi \sim \frac{128}{9\pi^3} \frac{N}{\xi} + \omega_0, \qquad \text{........................(8)}$$

say. With these substitutions, (5) reduces to (1), the integral in (7) reduces to a multiple of (4), and (7) itself reduces to

$$W = \frac{9\pi^2}{128} \frac{2\pi^2 me^4 N}{h^2} \omega_0 \left[\frac{5}{7} + 1\right], \qquad \text{...............(9)}$$

where in the [] we have shown separately the contributions corresponding to the two terms in (7).

We shall put

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

the ionisation potential of the normal hydrogen atom.

By the theorem of the virial, since the atomic cluster of electrons is in a steady state, the average kinetic energy is equal to one-half the average potential energy taken with negative sign. Consequently the total energy E of the system of moving charged masses —itself a negative quantity—is one-half expression (9), or

$$E = \frac{6}{7} \cdot \frac{9\pi^2}{128} \chi N \omega_0. \qquad \text{.....................(10)}$$

It remains to evaluate ω_0.

4. *Value of ω_0.* Suppose that by any means whatever we have found a solution of (1) which near $\xi = 0$ is of the form

$$\phi \sim \frac{b_0}{\xi} + b_1. \qquad \text{.......................(11)}$$

Make the substitution $\xi = \alpha\xi_1$, $\phi = \beta\phi_1$. Then

$$\frac{1}{\xi_1^2}\frac{d}{d\xi_1}\left(\xi_1^2 \frac{d\phi_1}{d\xi_1}\right) = \alpha^2\beta^{\frac{1}{2}}\phi_1^{\frac{3}{2}}$$

and, near $\xi = 0$,

$$\phi_1 \sim \frac{b_0}{\alpha\beta\xi} + \frac{b_1}{\beta}.$$

It follows that if we choose α and β so that

$$\alpha^2\beta^{\frac{1}{2}} = 1,$$

$$\frac{b_0}{\alpha\beta} = \frac{128}{9\pi^2}N,$$

then ϕ_1 is precisely the ϕ of equation (8), and accordingly

$$\omega_0 = \frac{b_1}{\beta}.$$

Solving for α and β we find

$$\omega_0 = b_1\left(\frac{128}{9\pi^2}\frac{N}{b_0}\right)^{\frac{4}{3}}. \qquad \text{.....................(12)}$$

Now Thomas has tabulated* a function ψ_0 given by

$$\psi_0 = \frac{9\pi^2}{128}\phi,$$

(where ϕ satisfies (1)) and having the behaviour near $\xi = 0$,

$$\psi_0 \sim \frac{55}{\xi} + c_1.$$

Thus we know a solution in which

$$b_0 = \frac{128}{9\pi^2}.55, \quad b_1 = \frac{128}{9\pi^2}c_1.$$

Hence

$$\omega_0 = \frac{128}{9\pi^2}\left(\frac{N}{55}\right)^{\frac{4}{3}} c_1,$$

and thus by (10)

$$E = \frac{6}{7}\frac{\chi N^{\frac{7}{3}}}{55^{\frac{4}{3}}}\lim_{\xi\to 0}\left(\psi_0 - \frac{55}{\xi}\right). \qquad \text{..............(13)}$$

* We have replaced Thomas's ρ throughout by ξ, to avoid confusion with our use ρ for charge-density.

5. *Numerical values.* The last five entries in Thomas's table yield values of $\psi_0 - 55/\xi$ as follows:

ξ	ψ_0	$\psi_0 - 55/\xi$
·003811	14140	− 290
·003027	17870	− 300
·002404	22580	− 300
·001910	28500*	− 300
·001517	35960	− 300

We have a well-defined value $c_1 = \lim (\psi_0 - 55/\xi) = -300$. Inserting this in (13) we get

$$E = -1{\cdot}23\chi N^{7/3} \quad \text{.....................(14)}$$

or in volts, putting $\chi = 13{\cdot}54$, and omitting the minus sign,

$$E = 17N^{7/3} \text{ volts.} \quad \text{.....................(15)}$$

This should be equal to the sum $\sum_1^N \chi_r$ of the successive ionisation potentials of the atom. Estimates of the successive ionisation potentials of oxygen ($N = 8$), iron ($N = 26$) and silver ($N = 47$) have been tabulated by Hartree†. The totals, and the values of E given by (15) are shown in the following table, to which hydrogen ($N = 1$) and helium ($N = 2$) have also been added:

N	$\sum_{r=1}^{N} \chi_r$	$17N^{7/3}$	$\Sigma\chi_r/N^{7/3}$
1	13·5	17	13·5
2	80	86	15·9
8	2000	2200	15·6
26	33600	34000	16·8
47	138000	136000	17·3

The agreement is quite satisfactory. Since Thomas's theory holds only for atoms with a comparatively large number of electrons, we should expect $\Sigma\chi_r/N^{7/3}$ to tend to a limit with increasing N. This appears to be confirmed by the last column in the table.

This constant c_1, which we have determined as the difference between two large numbers, could be found more accurately by

* Corrected value, kindly supplied by Mr Thomas.

† *Proc. Camb. Phil. Soc.*, 22, 473, 1924.

integration if necessary. For the constant b_1 of (11) is proportional to v_0, i.e. to the self-potential of the distribution ρ at the origin, and so must be proportional to

$$\int_0^\infty \frac{\rho}{r} r^2 dr.$$

We readily find in fact that

$$\int_0^\infty \phi^{\frac{3}{2}} \xi d\xi = - \lim_{\xi \to 0} \left(\phi + \xi \frac{d\phi}{d\xi}\right) = - b_1.$$

6. *Summary.* Thomas's differential equation for the average field inside a heavy atom is analogous to Emden's equation for the polytropic equilibrium of a star. Emden's result that the total gravitational potential energy of a star is calculable once the differential equation has been solved is adapted to give the total electrostatic energy, and hence the total energy of binding, of an atom built on Thomas's model. This should be equal to the sum of the successive ionisation potentials. The total energy is found to be proportional to $N^{\frac{7}{3}}$, where N is the atomic number. The values found agree with Hartree's calculations of the successive ionisation potentials of certain atoms.
