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ATOMIC ENERGY CALCULATION BY A MODIFIED STATISTICAL THEORY

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A modified Thomas—Fermi equation proposed by GOMBÁS is solved. The total energies calculated for representative atoms of the periodic system are in good agreement with the experimental values. The role of the modifying term is illustrated.

In a recent paper [2], GOMBÁS suggested a new basic equation for calculation of electron number density of the Thomas—Fermi atom or ion. He also showed that a good approximate solution to this could be obtained with a method based on the Fermi—Amaldi correction. The present work demonstrates how a direct solution to the same equation can be performed. The solutions obtained enable us to calculate such characteristic quantities of the atoms as the total energy, diagmagnetic susceptibility, etc. A striking feature of the calculated data — especially in view of the semi-empirical treatment of the problem (see Appendix) — is their excellent agreement over a wide range with the experimentally determined energy values.

Method of calculation

The equation suggested is

$$\varrho = \sigma_0 \left(V - V_0 - \frac{e a_0}{8} \frac{1}{r^2} \right)^{3/2} . \tag{1}$$

where $\varrho(r)$ is the number density of electrons, the potential $V(r)$ is

$$V(r) = -\frac{Ze}{r} + \int \frac{e\varrho(r')}{|\mathbf{r}-\mathbf{r}'|} dv' , \tag{2}$$

r is the distance from the centre of the atom (or ion), and the constants appearing elsewhere have their usual meaning [3].

With the Poisson equation we obtain

$$\nabla^2 (V - V_0) = 4\pi e \sigma_0 \left(V - V_0 - \frac{e a_0}{8} \frac{1}{r^2} \right)^{3/2} . \tag{3}$$

This nonlinear, inhomogeneous, second order, ordinary differential equation can be solved *by the Adams—Störmer method* if one knows the boundary conditions, i.e. the initial conditions for V.

The density must be real, therefore we shall suppose that

$$\varrho(r) = 0, \quad \text{if} \quad r \leqslant r_1 . \tag{4}$$

In this range Eq. (1) yields

$$\nabla^2(V - V_0) = 0, \quad \text{if} \quad r \leqslant r_1 . \tag{5}$$

The boundary conditions are

and

$$\left.\begin{aligned} &\lim_{r\to 0} rV = Ze \\ &\lim_{r\to r_1} r(V-V_0) = \frac{ea_0}{8r_1} \end{aligned}\right\} \quad \text{if} \quad r \leqslant r_1 . \tag{6}$$

The solution of Eq. (5), using (6), is

$$V-V_0 = Ze\left(\frac{1}{r} - \frac{1}{r_1}\right) + \frac{ea_0}{8r_1^2}, \quad \text{if } r \leq r_1. \tag{7}$$

Performing the following generally used transformations into dimensionless variables

$$\varphi = \frac{r}{Ze}(V-V_0) \quad \text{and} \quad r = \mu x, \tag{8}$$

we obtain for (3)

$$\varphi'' = \left(\varphi - \frac{\gamma}{x}\right)^{3/2} x^{-1/2}, \quad \text{if } x \geq x_1, \tag{9}$$

where

$$\gamma = \frac{a_0}{8}\,\frac{1}{Z\mu} = 0.1412\, Z^{-2/3}. \tag{10}$$

By requiring the inner ($x \leqslant x_1$) and outer ($x \geqslant x_1$) solutions and their derivatives to be continuous at the point x_1, we get

$$\varphi(x_1) = \frac{\gamma}{x_1} \tag{11}$$

and

$$\varphi'(x_1) = \frac{\gamma}{x_1^2} - \frac{1}{x_1} . \tag{12}$$

Moreover, it can be seen from (9) that

$$\varphi''(x_1) = 0, \tag{13}$$

$$\varphi'''(x_1) = 0, \tag{14}$$

$$\varphi^{(IV)}(x_1) = 0. \tag{15}$$

Therefore the initial function according to (11)—(15) is:

$$\varphi(x) = \frac{\gamma}{x_1} + \varphi'(x_1)(x-x_1) + (x-x_1)^{7/2}, \quad \text{if } x \sim x_1. \tag{16}$$

With the aid of this initial function as well as the mesh-point technique we are able to solve Eq. (9). The electron number density of a statistical atom is given by

$$\varrho = \frac{Z}{4\pi\mu^3}\left(\frac{\varphi}{x} - \frac{\gamma}{x^2}\right)^{3/2}, \tag{17}$$

and the fact that the electron number is N, i.e.

$$\int \varrho \, dv = N, \tag{18}$$

yields the unknown value of the initial derivative $\varphi'(x_1)$. The kinetic and potential energy terms are the known equations

$$E_{\text{kin}} = \varkappa_k \int \varrho^{5/3} \, dv, \tag{19}$$

$$E_{\text{pot}} = -\int \frac{Ze^2}{r} \varrho \, dv + \frac{1}{2}\iint \frac{e^2 \varrho(r)\, \varrho(r')}{|\mathbf{r}-\mathbf{r}'|} dv \, dv'. \tag{20}$$

Although the above treatment is based on the Thomas—Fermi theory, the exchange energy will be calculated here as a first order perturbation:

$$E_{\text{ex}} = -\varkappa_a \int \varrho^{4/3} \, dv. \tag{21}$$

Thus, using dimensionless variables and e^2/a_0 units, the total energy has the form

$$E_{\text{tot}} = E_{\text{kin}} + E_{\text{pot}} + E_{\text{ex}} = -\frac{(2Z)^{7/3}}{(3\pi)^{2/3}} \times$$

$$\times \int_{x_1}^{x_2} \left[-\frac{3}{5} u^{5/2} x^2 + u^{3/2} x - u^{3/2} x \int_{x_1}^{x>x'} u^{3/2}(x') \cdot x'^2 \cdot dx' + ku^2 \right] dx, \tag{22}$$

where

$$u = \frac{\varphi}{x} - \frac{\gamma}{x^2}$$

and

$$k = 3^{4/3}\,(16\pi Z)^{-2/3}.$$

The upper limit x_2 corresponds to a value $x > x_1$ at which u becomes zero again. (Negative ions, whose φ function runs upwards, were not considered.) The φ functions of the neutral atoms or the positively charged ions exhibit the same behaviour as in the usual Thomas–Fermi theory. On examining the dependence of the energy value upon the computational range only a slight (1–2 per cent) difference was found in the results by changing x_2 from 15 to 25. The computational limit was therefore chosen so that x_2 should be 25.

Calculations were also performed to examine the stability of the numerical method. In Tables I and II the convergence of the initial derivative and

Table I

Stability of the method with $\varepsilon = 0.01$ for argon

h	$-E_{\text{tot}}$ [e^2/a^0]	$-\varphi'$	mesh-points	x_2	$-\chi$ [10^{-6} cm^3]
0.0312	523.4	0.870101	800	25	43.2
0.0208	523.4	0.922374	1200	25	38.2
0.0156	522.8	0.955814	1600	25	44.6
0.0125	522.2	0.977982	2000	25	49.7

Table II

Convergence of the total energy and of the initial derivative for argon if $h = 0.0125$ and $x_2 = 25$. Diamagnetic susceptibility (χ) is very sensitive to change in ε

ε	$-E_{\text{tot}}$ [e^2/a^0]	$-\varphi'$	$-\chi$ [10^{-6} cm^3]
0.1	521.97	0.978008	18.7
0.05	522.23	0.977983	39.0
0.01	522.24	0.977982	49.7
0.005	522.24	0.977983	44.9
0.001	522.24	0.977983	47.1

of the energy value are seen for argon changing the step (h) and the accuracy of the norm (ε), defined as

$$|N^{-1}\int \varrho\, dv - 1| < \varepsilon\,. \tag{23}$$

The convergences and hence the stability of the numerical method are satisfactory. From these data it was judged sufficient to take 2000 mesh-points during the computational time (thereby exhausting the memory of an ICT-1900 computer).

It is interesting to note that the function φ is, at least initially, in the vicinity of the Thomas—Fermi φ_0. This fact can give us, as GOMBÁS suggested, a first approximation x_1' to the exact initial point x_1; from value x_1 the suitable initial derivative can be calculated by means of (12). All this is illustrated in Table III.

Table III

Values of $\varphi'(x_1)$. x_1' means the approximate value of x_1 calculated using the Thomas—Fermi φ_0

Z	γ	$\varphi_0(x_1')$	x_1'	φ_1	x_1	$-\varphi'(x_1)$
6	0.042762	0.941	0.045	0.961960	0.044453	0.855815
10	0.030419	0.956	0.032	0.971232	0.031320	0.918313
18	0.020557	0.971	0.021	0.979464	0.020988	0.977982
26	0.016088	0.977	0.016	0.983494	0.016358	1.008689
36	0.012950	0.981	0.013	0.986366	0.013129	1.031882
54	0.009883	0.987	0.010	0.989487	0.009988	1.056026
80	0.007605	0.989	0.0076	0.991784	0.007668	1.074997
86	0.007247	0.9893	0.0073	0.992196	0.007304	1.078064
92	0.006928	0.9896	0.0070	0.992408	0.006981	1.080815

Results

All terms of the total energy are represented in Fig. 1 and in Table IV. The agreement with the experimental values is very good, though not that with the virial theorem, from which the differences are about 15—20 per cent. The results for the diamagnetic susceptibility expression are less satisfactory (see Table IV). This expression, which includes the product $\varphi \cdot x^4$ in its integrand is very sensitive for the numerical accuracy, as can be seen from Tables I and II.

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Table IV

Energy and diamagnetic susceptibility for atoms and ions in e^2/a_0 and 10^{-6} cm^3 units, respectively. The Thomas—Fermi values for susceptibility χ_{TF} are taken from [3]. The agreement for hydrogen is especially noteworthy

Element	Z	N	$-E_{pot}$	E_{kin}	$-E_{ex}$	$-E_{tot}$	$-E_{experimental}$	$-\chi_{TF}$	$-\chi$	$-\chi_{experimental}$
H	1	1	0.4965	0.1291	0.1225	0.4900	0.5000	—	26.9	—
He	2	2	3.075	0.9121	0.4496	2.612	2.904	—	30.7	—
Be	4	4	18.44	6.091	1.600	13.95	14.68	—	32.8	—
C	6	6	51.88	18.07	3.323	37.13	37.86	—	33.8	—
Ne	10	10	188.5	69.55	8.258	127.2	129.5	67.0	40.7	6.8
Ar	18	18	818.4	319.4	23.20	522.2	525.4	81.0	49.7	19.5
Fe	26	26	2 034	818.2	44.1	1 260	1 249	—	44.7	—
Kr	36	36	4 534	1 868	77.4	2 743	2 704	102	53.9	28.0
X	54	54	12 235	5 177	156	7 214	7 079	117	64.0	42.4
Hg	80	80	31 850	13 790	305	18 360	18 680	—	—	—
Ra	86	86	37 950	16 500	345	21 790	—	—	—	—
U	92	92	44 690	19 500	388	25 570	25 520	—	—	—
Ca^+	20	19	1 063	418.4	27.8	672.1	—	—	—	—
Rb^+	37	36	4 849	2 001	81.1	2 929	2 885	—	—	—
Ba^{++}	56	54	13 370	5 670	165	7 865	—	—	—	—
Hg^{++}	80	78	31 840	13 790	305	18 360	—	—	—	—

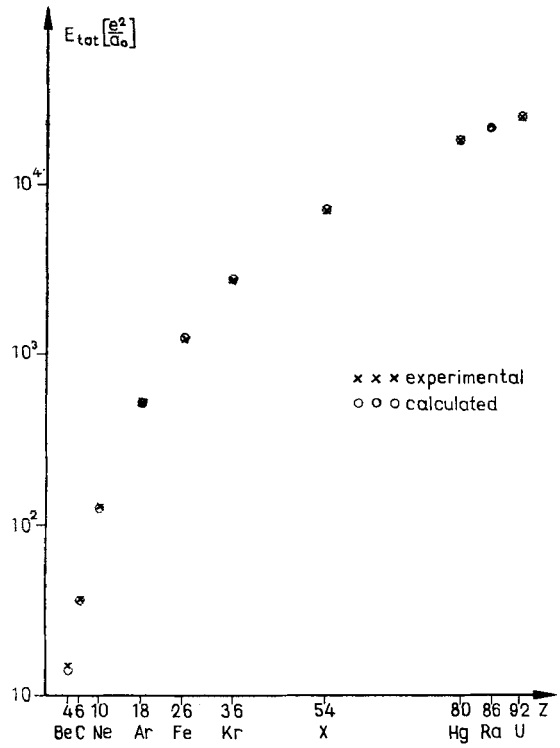

Fig. 1. Experimental and calculated total energy values for various atoms of the periodic system

Appendix

The Thomas—Fermi formula (1) originates from a model in which the electrons are grouped according to their azimuthal quantum numbers, namely

$$\varrho = \sum_{l=0}^{\infty} \varrho_l \sim \int_0^{l_\mu} \varrho_l \, dl. \tag{24}$$

Here $l_\mu = l_\mu(r)$ means the maximum "quantum number" for which ϱ_l is real.

The different expressions given by GOMBÁS for ϱ_l [3], [4], [5] can be summarized as follows

$$\varrho_l = \frac{2l+1}{A}\left[B - C - l(l+1)\right]^{1/2}, \tag{25}$$

where

$$A = 2\pi^2 r^3, \tag{26}$$

$$B = 8me\pi^2 r^2(V - V_0) h^{-2}, \tag{27}$$

$$C = \begin{cases} 0 & \text{in [3]}, \\ \dfrac{1}{2} & \text{in [4]}, \\ \dfrac{1}{4} & \text{in [5]}. \end{cases} \tag{28}$$

The maximum value for l (allowing it to be continuous)

$$l_\mu = \frac{1}{2}\left(\sqrt{1-4C+4B} - 1\right). \tag{29}$$

Performing the quadrature, we get

$$\varrho = \int_0^{l\mu} \varrho_l \, dl = 2\left(\frac{B-C}{3A}\right)^{3/2}. \tag{30}$$

Substituting the values A, B and C, we obtain

$$\varrho = \sigma_0 \left(V - V_0 - \frac{4Ce\,a_0}{8}\,\frac{1}{r^2}\right)^{3/2}, \tag{31}$$

or, in another usual form,

$$\varrho = \frac{8\pi}{3h^3}\left(p_\mu^2 - C\frac{h^2}{4\pi^2 r^2}\right)^{3/2}, \tag{32}$$

with $p_\mu^2 = 2me(V - V_0)$.

PLASKETT [1] also derived Eq. (1) with $C = 1/4$ by applying the B.K.W. approximation. To make the role of the constant C perceptible, we have represented the solutions for the cases $C = 0$, 1/4, 1/2 and 1/8 (see Table V and Fig. 2).

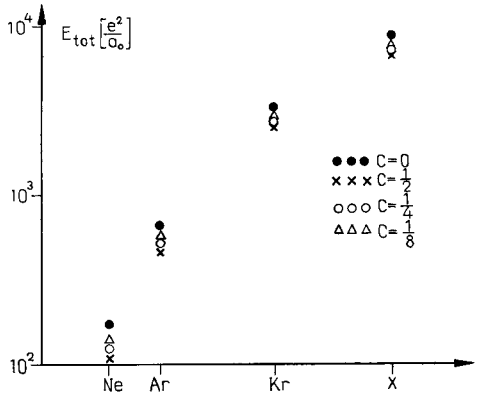

Fig. 2. The role of constant C in the displacement of the energy values. The solutions of $C = 0$ are taken from [6]

Table V

Total energy (e^2/a_0) and diamagnetic susceptibility (10^{-6} cm^3) for various values of C. $Z = N = 18$. Values for $C = 0$ corresponding to the Thomas—Fermi—Dirac solution are taken from [6]

	$C = 0$		$C = 0.5$		$C = 0.25$		$C = 0.125$	
$Z = N$	$-E_{tot}$	$-\chi$	$-E_{tot}$	$-\chi$	$-E_{tot}$	$-\chi$	$-E_{tot}$	$-\chi$
2	—	—	2.050	31.5	2.612	30.7	3.122	23.2
10	176.3	67.0	110.1	42.0	127.2	34.3	140.9	28.7
18	680.7	81.0	463.4	47.7	522.2	49.7	566.6	42.7
36	3378	102	2505	55.3	2743	53.9	2894	42.8
54	8846	117	6670	54.2	7214	64.0	7503	46.0

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РАСЧЕТ ЭНЕРГИИ АТОМОВ В ВИДОИЗМЕНЕННОЙ СТАТИСТИЧЕСКОЙ ТЕОРИИ

Б. АПАДИ

Резюме

Дано решение видоизмененного уравнения Томаса — Ферми, предложенного Гомбашом. Полные энергии, рассчитанные для атомов периодической таблицы хорошо согласуются с экспериментальными данными. Показана роль видоизмененной части уравнения.