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2000 J. Phys. A: Math. Gen. 33 5913

(http://iopscience.iop.org/0305-4470/33/33/309)

J. Phys. A: Math. Gen. **33** (2000) 5913–5918. Printed in the UK PII: S0305-4470(00)13177-4

# Electrons in a shell: the Thomas–Fermi solution

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Received 12 April 2000, in final form 30 June 2000

**Abstract.** The spatial distribution of electrons inside an empty spherical shell with an impenetrable wall is studied by means of the Thomas–Fermi model. The general solution is expanded in a perturbative series and the explicit analytic solution for the first three terms of the series is provided.

## 1. Introduction

Due to its simplicity and elegance, the Thomas–Fermi (TF) model is an almost obligatory first step in atomic physics courses prior to more accurate descriptions of the atomic structure. In addition to the standard TF solutions for the neutral atom and the positive ions, the TF model may also be used to study related problems, of academic interest, involving electron density profiles with spherical symmetry. In this context, in [1], the spatial distribution of $N \gg 1$ non-relativistic electrons placed inside an empty spherical impenetrable shell of radius $a$, at zero temperature, was analysed. In that work, using arguments of balance of pressures, it was concluded that the electron density is concentrated in a thin layer of characteristic thickness $\delta$ near the wall. The estimate for $\delta$ is

$$\delta \approx a_{\mathrm{B}}^{3/5} a^{2/5} N^{-1/5} \tag{1}$$

where $a_{\mathrm{B}}$ is the Bohr radius.

Here we analyse the fully fledged TF problem and provide an explicit analytical solution for the resulting differential equation. In section 2 we set the TF equation in the appropriate form for this problem, expand the solution in a perturbative series and obtain the specific differential equation for each order. In section 3, the explicit solutions are obtained. Finally, in section 4 the results are shown and commented on.

## 2. The Thomas–Fermi equation

The usual TF equation for the neutral atom is derived from three assumptions (see [2]):

(a) the electron density, $n$, and the electrostatic potential, $\phi$, are related by Poisson's equation;
(b) the equation of state of the electron cloud is that of a Fermi gas at zero temperature; and
(c) the condition of hydrostatic equilibrium is fulfilled throughout the electron distribution.

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The resulting equation is

$$\ddot{\chi}(x) = \chi^{3/2}(x)/x^{1/2} \tag{2}$$

where $x$ is the distance from the origin, $r$, measured in $b$ units

$$r = bx \qquad b = \kappa a_{\mathrm{B}} N^{-1/3} \tag{3}$$

with $\kappa = (3\pi)^{2/3}/2^{7/3}$ and $\chi(x)$ is a function related to $n$ by

$$n = \kappa'(N^2/a_{\mathrm{B}}^3)(\chi/x)^{3/2} \tag{4}$$

with $\kappa' = 32/9\pi^3$. In our notation, a dot over a function indicates a derivative with respect to the argument.

In the neutral atomic case, the existence of the pointlike positive charge at the origin forces $\chi(0) = 1$ as a first boundary condition. The second boundary condition can be obtained by imposing the neutrality of the system, i.e. the total number of electrons, $N$, is equal to the nuclear charge.

Here, the description of $N$ electrons inside the empty shell of radius $a$ leads obviously to a TF equation equal to equation (2), with equations (3) and (4) having exactly the same meaning. The boundary conditions are, however, different. Here, as $n(0)$ is finite, we have

$$\chi(0) = 0. \tag{5}$$

The normalization condition extends only to the radius $a$ of the shell, i.e. $\int_0^a n(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r} = N$. In dimensionless units this relation adopts the form

$$\int_0^{x_a} \chi^{3/2}(x)\, x^{1/2}\,\mathrm{d}x = 1.$$

Using equation (2) and integrating by parts, we obtain

$$x_a\dot{\chi}(x_a) - \chi(x_a) = 1. \tag{6}$$

Note that

$$x_a \equiv a/b = \kappa^{-1}(a/a_{\mathrm{B}})N^{1/3} \tag{7}$$

is the value of $a$ expressed in $b$ units.

It is physically clear that for a large $N$, almost the whole volume of the cavity will be empty and the electron distribution will be concentrated in the vicinity of the wall. For this reason, it is more convenient to move our coordinate frame, up to now on the origin, to the shell radius, i.e. to $r = a$. Thus we define the $y$ coordinate as

$$x \equiv x_a - y. \tag{8}$$

Thus $y$ is the radial distance from the wall towards the centre measured in $b$ units. In terms of $y$ equation (2) is

$$\ddot{\chi}(y) = (\chi^{3/2}(y)/x_a^{1/2})(1 - y/x_a)^{-1/2} \tag{9}$$

and the two boundary conditions read

$$\chi(y = x_a) = 0 \tag{10a}$$

$$-x_a\dot{\chi}(y = 0) - \chi(y = 0) = 1. \tag{10b}$$

Now it is convenient to perform the following change of scale:

$$y \equiv x_a^{2/5} z \tag{11a}$$

$$\chi(y) \equiv \frac{\psi(z)}{x_a^{3/5}} \tag{11b}$$

which converts equation (9) into

$$\ddot{\psi}(z) = \psi^{3/2}(z)/(1 - z/x_a^{3/5})^{1/2} \tag{12}$$

and converts equations (10*a*) and (10*b*) into

$$\psi(z = x_a^{3/5}) = 0 \tag{13a}$$

$$-\dot{\psi}(z = 0) - \psi(z = 0)/x_a^{3/5} = 1. \tag{13b}$$

Note that after the rescaling performed in equations (11*a*) and (11*b*), the actual length unit one is working with, $d$, is given by

$$a - r \equiv \mathrm{d}z \qquad d = b x_a^{2/5} = \kappa^{3/5} a_{\mathrm{B}}^{3/5} a^{2/5} N^{-1/5}. \tag{14}$$

In the limit of $x_a \gg 1$, we define the 'small' parameter $\varepsilon$ as

$$\varepsilon = 1/x_a^{3/5}. \tag{15}$$

In terms of $\varepsilon$, we expand $\psi(z)$,

$$\psi(z) = \psi_0(z) + \varepsilon\psi_1(z) + \varepsilon^2\psi_2(z) + \cdots. \tag{16}$$

Formally speaking, this development is meaningful for $\varepsilon \ll 1$ and for $z < x_a^{3/5}$. When this expansion is inserted into equation (12), and the terms of the same order in powers of $\varepsilon$ are compared, we obtain the following equations:

$$\ddot{\psi}_0 = \psi_0^{3/2} \tag{17}$$

$$\ddot{\psi}_1 = \psi_0^{3/2}\left[\frac{3}{2}\frac{\psi_1}{\psi_0} + \frac{z}{2}\right] \tag{18}$$

$$\ddot{\psi}_2 = \psi_0^{3/2}\left[\frac{3}{2}\frac{\psi_2}{\psi_0} + \frac{3}{8}\frac{\psi_1^2}{\psi_0} + \frac{3}{4}\frac{\psi_1}{\psi_0}z + \frac{3}{8}z^2\right]. \tag{19}$$

With respect to the first boundary conditions, equation (13*a*) leads to

$$\psi(z = x_a^{3/5}) = \psi_0(z = x_a^{3/5}) + \varepsilon\psi_1(z = x_a^{3/5}) + \varepsilon^2\psi_2(z = x_a^{3/5}) + \cdots = 0$$

which implies that

$$\psi_0(z = x_a^{3/5}) = \psi_1(z = x_a^{3/5}) = \psi_2(z = x_a^{3/5}) = \cdots = 0. \tag{20a}$$

With respect to the second boundary condition, equation (13*b*) leads to

$$-[\dot{\psi}_0(0) + \varepsilon\dot{\psi}_1(0) + \varepsilon^2\dot{\psi}_2(0) + \cdots] - \varepsilon[\psi_0(0) + \varepsilon\psi_1(0) + \varepsilon^2\psi_2(0) + \cdots] = 1$$

which, to be fulfilled at all orders, implies

$$-\dot{\psi}_0(0) = 1 \qquad -\dot{\psi}_1(0) - \psi_0(0) = 0 \qquad -\dot{\psi}_2(0) - \psi_1(0) = 0 \qquad \ldots. \tag{20b}$$

## 3. The Thomas–Fermi solutions

### *3.1. Zeroth order*

In the lowest order, we have

$$\ddot{\psi}_0 = \psi_0^{3/2} \tag{21}$$

$$\dot{\psi}_0(0) = -1 \qquad \psi_0(z \gg 1) = 0. \tag{22}$$

Equation (21) is a nonlinear second-order differential equation. Its solution is obtained by multiplying both sides by $\dot{\psi}_0$. Thus equation (21) adopts the form

$$\frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}z}[\dot{\psi}_0^2] = \frac{2}{5}\frac{\mathrm{d}}{\mathrm{d}z}[\psi_0^{5/2}]$$

which is readily integrated giving

$$\tfrac{1}{2}[\dot{\psi}_0^2 - \dot{\psi}_0^2(0)] = \tfrac{2}{5}[\psi_0^{5/2} - \psi_0^{5/2}(0)].$$

Now, inserting $\dot{\psi}_0(0) = -1$, and choosing the negative root (the positive root is meaningless), we have

$$\dot{\psi}_0 = -\left[\tfrac{4}{5}\psi_0^{5/2} + 1 - \tfrac{4}{5}\psi_0^{5/2}(0)\right]^{1/2}.$$

By separating variables, $\psi_0$ and $z$, we obtain

$$\int_{\psi_0}^{\psi_0(0)} \frac{\mathrm{d}\psi_0}{\sqrt{\frac{4}{5}\psi_0^{5/2} + 1 - \frac{4}{5}\psi_0^{5/2}(0)}} = z.$$

Finally, imposing the second condition, $\psi_0 \to 0$ for $z \to \infty$, we find $\psi_0(0) = (\frac{5}{4})^{2/5}$. This fixes the solution of equation (21) as

$$\psi_0(z) = \frac{C_0}{(q_0 + z)^4} \tag{23}$$

with $C_0 = 400$, $q_0 = (1600)^{1/5}$.

### *3.2. First order*

Having obtained $\psi_0(z)$, and inserting it into equation (18), we observe that $\psi_1(z)$ fulfils a linear second-order differential equation of Legendre type. The general solution is the sum of the solution of the homogeneous part of the equation and a particular solution of the inhomogeneous part. Imposing the fulfilment of the two boundary conditions, we obtain

$$\psi_1(z) = \frac{-\frac{5}{9}C_0}{(q_0 + z)^3} + \frac{q_0 C_0}{(q_0 + z)^4} + \frac{B_1}{(q_0 + z)^5} \tag{24}$$

with

$$B_1 = -\tfrac{16}{3}\left(\tfrac{4}{5}\right)^{1/5} C_0.$$

The value of $\psi_1$ at the origin is

$$\psi_1(0) = \tfrac{8}{9}\left(\tfrac{4}{5}\right)^{1/5}. \tag{25}$$

### *3.3. Second order*

Now it is necessary to solve equation (19). This is again a linear second-order differential equation of Legendre type; the solution that fulfils equations (20*a*) and (20*b*) is

$$\psi_2(z) = \frac{C_2}{(q_0+z)^2} + \frac{C_4}{(q_0+z)^4} + \frac{B_2}{(q_0+z)^5} + \frac{C_6}{(q_0+z)^6} \tag{26}$$

where

$$C_2 = -\tfrac{5}{81}C_0 \qquad C_4 = \tfrac{32}{9}(\tfrac{4}{5})^{1/5}C_0$$
$$C_6 = \tfrac{160}{9}(\tfrac{4}{5})^{2/5}C_0 \qquad \text{and} \qquad B_2 = -\tfrac{173}{9}\left[\tfrac{32}{45}\right](\tfrac{5}{4})^{1/5}C_0.$$

## 4. Results and conclusion

Using equations (4) and (11) we obtain the electron density profile

$$n(z) = \kappa' N^2 a_{\mathrm{B}}^{-3} x_a^{-12/5}\psi^{3/2}(z) = (72\pi^7)^{-1/5} a_{\mathrm{B}}^{-3/5} a^{-12/5} N^{6/5}\psi^{3/2}(z) \tag{27}$$

where $z$ is the radial distance to the impenetrable shell measured in $d$ units. The solution obtained perturbatively is

$$\psi(z) = \psi_0(z) + \varepsilon\psi_1(z) + \varepsilon^2\psi_2(z) + \cdots.$$

The function $\psi_0(z)$ constitutes the asymptotic solution, and the sum of the other two terms is its finite-size correction up to second order in $\varepsilon$. The three functions obtained, $\psi_0$, $\psi_1$ and $\psi_2$, are finite at the origin, have a negative derivative at the origin and tend asymptotically to zero as functions of $z$. $\psi_0$ is always positive; $\psi_1$ and $\psi_2$, in contrast, become negative at a given point, have one minimum and then tend to zero. The three functions are plotted in figure 1. Note that, strictly speaking, these three functions should fulfil the condition $\psi_0(1/\varepsilon) = \psi_1(1/\varepsilon) = \psi_2(1/\varepsilon) = 0$; therefore, the assumption that they vanish at infinity induces a small error. Examining equations (23), (24) and (26) we realize that from $\psi_0$ there appears a leading error of fourth order in $\varepsilon$, from $\psi_1$ the error is of order three, and from $\psi_2$ the error is of order two. These individual effects inserted in the perturbative expansion given in equation (16) produce a leading effective error of order four in $\varepsilon$. As our calculations stop at the second order in $\varepsilon$ they are not affected by these higher-order corrections.

The value of the energy terms, at the leading order in $\varepsilon$, of the TF solution are

$$V = \frac{1}{2}N^2\frac{e^2}{a} \tag{28}$$

for the electrostatic energy, and

$$T = BN^{9/5}\frac{e^2 a_{\mathrm{B}}^{3/5}}{a^{8/5}} \tag{29}$$

with $\mathrm{B} = \frac{1}{24}(60\pi)^{2/5}$, for the kinetic energy. Note that $V$ is the classical result for a surface charge distribution. For compactness, let us express $V$ and $T$ in Hartree units of energy. Then for the total energy, $E$, we obtain

$$E = V + T = \frac{N^{7/3}}{2\kappa}\varepsilon^{5/3}\left(\frac{e^2}{a_{\mathrm{B}}}\right)\left[1 + \frac{50^{1/5}}{3}\varepsilon\right]. \tag{30}$$

Thus, we observe that $T$ is one order smaller in $\varepsilon$ than $V$. $\kappa$ was defined after equation (3).

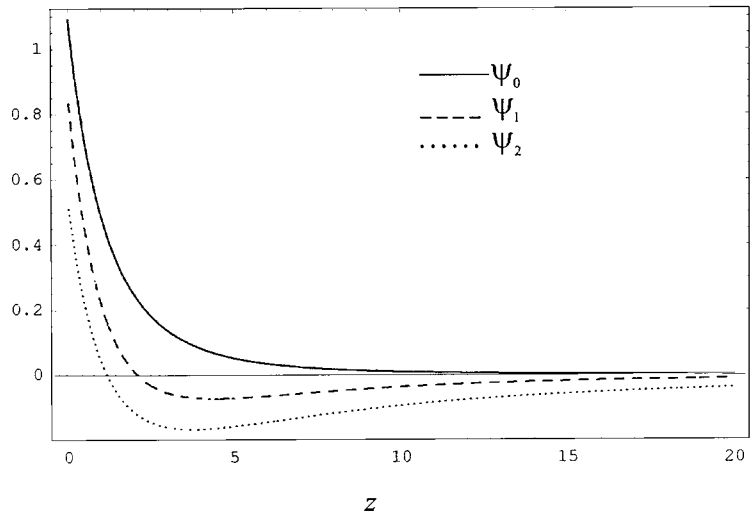


**Figure 1.** Plot of $\psi_0$, $\psi_1$ and $\psi_2$ versus $z$.

Let us now comment on the thickness of the electron cloud near the wall. The characteristic thickness emerging from the TF method is the length $d$ of equation (14). This length is consistent with the $\delta$ of equation (1). In terms of $\varepsilon$, we find the neat result

$$d = a\varepsilon. \tag{31}$$

Thus, as a conclusion we will say that from the TF method for this problem a small, dimensionless, parameter $\varepsilon$ emerges which determines the physics of the electron distribution in the shell, setting a perturbative hierarchy: (a) the leading term of the potential repulsive energy is the classical electrostatic result for a surface charge distribution; (b) the leading term of the kinetic energy is, up to a constant, $\varepsilon$ times the electrostatic energy; and (c) the characteristic thickness of the electron distribution near the wall is exactly $\varepsilon$ times the radius of the cavity.

## Acknowledgments

AFP gratefully acknowledges L Moral for discussions. This work was supported in part by the Spanish DGICYT under Project PB98-1594.

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