The simplest atomic system is the hydrogen atom for which an exhaustive physical description exists. It can be regarded as an electrostatic two-body problem involving one proton and one electron whose quantum-mechanical description, including relativistic effects, is well understood. Problems arise when we consider multi-electron atoms because electrons interact not only with the attractive central electrostatic field of the nucleus, but also experience a mutual repulsion whose strength depends on the mutual distance between the electrons and is, in general, too large to be treated as a perturbation. Several methods of approximation designed to model this interaction are present in the literature.

Here we focus on the theory developed independently by Thomas and Fermi\(^2\) for the ground state of complex atoms (or ions).

The purpose of this model is to provide a method of calculating the electron density \(\rho(r)\) and, from it, the electrostatic potential due to the nucleus and the cloud of electrons. The electrons of the system obey Fermi–Dirac statistics and are confined to a region of space by a central potential \(V(r)\). The volume of this region is assumed to be large enough to contain many electrons but small enough that \(V(r)\) does not vary appreciably over the size of the region. Under these assumptions, the electrons move freely and a statistical approach can be applied. Because the number of electrons is large, many of them have high principal quantum numbers, so that semi-classical methods should be useful.

Let us consider atoms at the absolute zero of temperature. The electron kinetic energy is a minimum, and the electrons are packed in phase space as densely as possible consistent with the exclusion principle. If \(p_0\) is the maximum value for the electron momentum, then because not more than two electrons are allowed (by the exclusion principle) in each volume element (of size \(\hbar^3\)) of phase space, the number \(n\) of electrons per unit volume is

\[
n = \frac{2}{\hbar^3} \frac{4\pi}{3} p_0^3.
\]

The electrostatic potential energy for an electron is denoted by \(-eV\), and it is confined in a neutral atom if its energy is nonpositive:

\[
\frac{p^2}{2m} - eV = 0.
\]

Hence the maximum momentum \(p_0\) is given by:

\[
\frac{p_0^2}{2m} = eV.
\]

By inserting Eq. (3) into Eq. (1), we can express the electron charge density \(\rho = -en\) in terms of the potential \(V\):

\[
\rho = -\frac{1}{3\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} (eV)^{3/2}.
\]

Obviously, from Eq. (2), there is no confined electron for \(V < 0\) and \(p = 0\).

The sources of the electrostatic potential \(V(r)\) are the point charge \(Ze\) of the nucleus (assumed point-like and located at the origin) and the electron distribution around it. By considering the charge density \(\rho(r)\) as continuous, it satisfies the Poisson equation:

\[
\nabla^2 V = -4\pi \rho.
\]

From Eqs. (4) and (5), we then obtain the differential equation for \(V(r)\):

\[
\nabla^2 V = \frac{4e}{3\pi} \left(\frac{2m}{\hbar^2}\right)^{3/2} (eV)^{3/2}.
\]

The boundary conditions to be satisfied by the solution of Eq. (6) are such that when \(r \to 0\), the potential becomes the Coulomb field of the nucleus,

\[
V(r) \to \frac{Ze}{r},
\]

while for \(r \to \infty\):

\[
V(r) \to 0,
\]

which ensures that the atom as a whole is uncharged.

Equation (6) can be cast in a simpler form with a suitable change of variables. Let us set

\[
V(r) = \frac{Ze}{r} \phi(r) = \frac{Ze}{r} \varphi(r)/r
\]

where \(\varphi(r) = Z_{\mathrm{eff}}/Z\), and

\[
r = bx,
\]

with

\[
b = \frac{1}{2} \left(\frac{3\pi}{4}\right)^{2/3} \frac{\hbar^2}{me^2} Z^{-1/3} \approx 0.8853 a_0 Z^{-1/3}.
\]
Then, in terms of the new variables, Eq. (6) becomes (for \( \varphi \geq 0 \)):

\[
\varphi'' = \frac{\varphi^{3/2}}{\sqrt{x}}
\]  

(12)

(a prime denotes differentiation with respect to \( x \)) with the boundary conditions:

\[
\varphi(0) = 1,
\]  

(13a)

\[
\varphi(\infty) = 0.
\]  

(13b)

The Thomas–Fermi equation (12) is a universal equation, which does not depend on \( Z \) or on physical constants (\( \hbar, m, e \)). Its solution gives, from Eq. (9), a screened Coulomb potential with \( Z_{\text{eff}} \) as an effective screened nuclear charge, and its \( Z \) independence indicates that the form of the potential (and, hence, of the electron charge distribution) is the same for all atoms in the Thomas–Fermi approximation.

This independence simplifies many problems in atomic physics which, otherwise, could not be treated directly owing to mathematical complexities. Furthermore, the simple and general assumptions underlying the Thomas–Fermi approximation make this method a very useful approach to a great variety of physical problems not limited to atomic physics.\(^3\)

In particular, the Thomas–Fermi model is widely used in nuclear physics, for example, to answer questions related to nuclear matter in neutron stars.\(^4\)

In spite of its generality, the application of the Thomas–Fermi method is based on the solution \( \varphi(x) \) of the second-order nonlinear differential equation (12). Unfortunately a general analytical (or even sufficiently good approximate) solution of Eq. (12) satisfying the boundary conditions (13) does not exist. However, an exact particular solution of Eq. (12) satisfying only condition (13b), was discovered by Sommerfeld:\(^5\)

\[
\varphi = \frac{144}{x^3}.
\]  

(14)

This solution can be regarded as an asymptotic expression of the desired solution, and Sommerfeld considered a “correction” to Eq. (14) that takes into account the condition (13a). However, this corrected approximate solution has a divergent first derivative at \( x = 0 \).\(^6\)

In 1928 Majorana found an interesting semi-analytical solution of the Thomas–Fermi equation,\(^7\) which, unfortunately, remained unpublished and unknown until now (see Ref. 6). As will be clear below, the Majorana solution can be considered as a modification of Eq. (14), but the method followed by him is extremely original and very different from the one used by Sommerfeld in Ref. 5.

Let us consider solutions of the Thomas–Fermi equation (12) which are expressed in the parametric form:

\[
x = x(t),
\]  

(15a)

\[
\varphi = \varphi(t).
\]  

(15b)

We will use a dot \( \cdot \) to denote derivatives with respect to \( t \).

The strategy adopted by Majorana is to perform a double change of variables:

\[
x, \varphi(x) \rightarrow t, u(t),
\]  

(16)

where the new unknown function is \( u(t) \). The relation connecting the two sets of variables (assumed to be invertible) has a differential nature, that is

\[
t = t(x, \varphi),
\]  

(17a)

\[
u = u(\varphi, \varphi').
\]  

(17b)

Using Eqs. (17a) and (17b) the second-order differential equation (12) for \( \varphi \) is transformed into a first-order equation for \( u \). Note, however, that in general Eqs. (17a) and (17b) are implicit equations for \( t \) and \( u \), because \( x \) and \( \varphi \) depend on them (one is looking for parametric solutions in terms of the parameter \( t \) and the unknown function \( u \)). For the specific case of the Thomas–Fermi equation, Majorana introduced the following transformation:

\[
t = 144^{-1/6} x^{1/2} \varphi^{1/6},
\]  

(18)

\[
u = - \left( \frac{16}{3} \right)^{1/3} \varphi^{-4/3} \varphi'.
\]  

(19)

Observe that Eq. (18) is reminiscent of the Sommerfeld solution, because it can be cast into the form:

\[
\varphi = \frac{144}{x^3} t^6.
\]  

(20)

The differential equation for \( u(t) \) is obtained by taking the \( t \)-derivative of Eq. (19):

\[
\frac{du}{dt} = - \left( \frac{16}{3} \right)^{1/3} x^{-4/3} \left[ - \frac{4}{3} \varphi' + \varphi'' \right],
\]  

(21)

and inserting Eq. (12):

\[
\frac{du}{dt} = - \left( \frac{16}{3} \right)^{1/3} x^{-4/3} \left[ - \frac{4}{3} \varphi' + \frac{\varphi^{3/2}}{x^{1/2}} \right].
\]  

(22)

By using Eq. (18) and Eq. (19) to eliminate \( x^{1/2} \) and \( \varphi^{1/2} \), respectively, we obtain:

\[
\frac{du}{dt} = \frac{4}{9} \frac{tu^2 - 1}{t} x^{1/3} \varphi^{1/3}.
\]  

(23)

We now express the quantity \( \dot{x} \varphi^{1/3} \) in terms of \( t, u \). From Eq. (18),

\[
x = 144^{1/3} t^2 \varphi^{-1/3}.
\]  

(24)

By taking the explicit \( t \)-derivative of both sides, we have

\[
\dot{x} = 144^{1/3} [2 t \varphi^{-1/3} + t^2 \varphi (\varphi^{-4/3} \varphi')],
\]  

(25)

and after some algebra we find:

\[
\dot{x} \varphi^{1/3} = 144^{1/3} \frac{2t}{1 - t^2 u}.
\]  

(26)

By inserting this result into Eq. (23), we finally obtain the differential equation for \( u(t) \):

\[
\frac{du}{dt} = \frac{4}{9} \frac{tu^2 - 1}{1 - t^2 u}.
\]  

(27)

Condition (13a) implies, from Eqs. (18) and (19), that \( x = 0 \) at \( t = 0 \), and

\[
u(0) = - \left( \frac{16}{3} \right)^{1/3} \varphi_0',
\]  

(28)

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where \( \varphi_0' = \varphi'(x = 0) \). The initial condition to be satisfied by \( u(t) \) for the unique solution of Eq. (27) is obtained from the boundary condition (13b) by inserting the Sommerfeld asymptotic expansion (14) into Eqs. (18) and (19). For \( x \to \infty \), we have \( t = 1 \), and

\[
u(1) = 1.
\]

We then easily recognize that the branch of \( u(t) \) that gives the Thomas–Fermi function (in parametric form) is the one between \( t = 0 \) and \( t = 1 \). In this interval we look for the solution of Eq. (27) by using a series expansion in powers of the variable \( \tau = 1 - t \):

\[
u = a_0 + a_1 \tau + a_2 \tau^2 + a_3 \tau^3 + \cdots.
\]

From condition (29) we immediately have

\[
d_0 = 1.
\]

The other coefficients are obtained by an iterative formula coming from the substitution of Eq. (30) into Eq. (27):

\[
\sum_{k=0}^{\infty} \sum_{l=0}^{\infty} A(k, l) \varphi^{k+l} = 0,
\]

where

\[
A(k, l) = a_{l+1}[(l+1)(l+2)(l+3) + 2(l+4)a_{l+1} + (l+7)a_{l-1} - (k+l+1) \delta_{l0}a_{l+1} + \delta_{k0} \delta_{l0}. \]

(33)

We define \( a_{-1} = 0 \). Equation (32) can also be cast in the form \( k + l = m, l = n \):

\[
\sum_{m=0}^{\infty} \sum_{n=0}^{m} A(m-n, n) \varphi^{m} = 0,
\]

so that, for fixed \( m \), the relation determining the series coefficients is the following:

\[
\sum_{n=0}^{m} a_{m-n}[(n+1)a_{n+1} - 2(n+4)a_{n} + (n+7)(1 - \delta_{n0})a_{n-1}] + \delta_{m0} \delta_{n0} = 0,
\]

with \( m = 0, 1, 2, 3, \ldots \). [We have explicitly used that \( a_{-1} = 0 \). Equation (35) for \( m = 0 \), \( a_0 - 1 \) \( a_1 - 8a_0 + 1 = 0 \), is satisfied identically due to Eq. (31).] For \( m = 1 \) we have a second-degree algebraic equation for \( a_1 \):

\[
a_1^2 - 18a_1 + 8 = 0
\]

of which we have to choose the smallest root (we are performing a perturbative expansion):

\[
a_1 = 9 - \sqrt{73}.
\]

The remaining coefficients are determined using Eqs. (31) and (37). Excluding the cases \( m = 0, 1 \), Eq. (35) can be written after some algebra as:

\[
a_m = \frac{1}{2(m+8)-(m+1)a_1} \left( \sum_{n=1}^{m-2} a_{m-n}(n+1)a_{n+1} + 2(n+4)a_{n} + (n+7)a_{n-1} + a_{m-1}(m+7) - 2(m+3)a_1 + a_{m-2}(m+6)a_1 \right).
\]

Table I. Numerical values for the first 20 coefficients for the series expansion of the function \( u(t) \) in Eq. (30).

<table>
<thead>
<tr>
<th>( n )</th>
<th>( a_n )</th>
<th>( a_{n+1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.455996</td>
<td>0.0316498</td>
</tr>
<tr>
<td>2</td>
<td>0.304455</td>
<td>0.0252839</td>
</tr>
<tr>
<td>3</td>
<td>0.222180</td>
<td>0.0202322</td>
</tr>
<tr>
<td>4</td>
<td>0.168213</td>
<td>0.0162136</td>
</tr>
<tr>
<td>5</td>
<td>0.129804</td>
<td>0.0130101</td>
</tr>
<tr>
<td>6</td>
<td>0.101300</td>
<td>0.0104518</td>
</tr>
<tr>
<td>7</td>
<td>0.0796352</td>
<td>0.00840559</td>
</tr>
<tr>
<td>8</td>
<td>0.0629230</td>
<td>0.00676661</td>
</tr>
<tr>
<td>9</td>
<td>0.0499053</td>
<td>0.00545216</td>
</tr>
<tr>
<td>10</td>
<td>0.0396962</td>
<td>0.00439678</td>
</tr>
</tbody>
</table>

Note that the sum on the right-hand side involves coefficient \( a_i \) with \( i \leq m - 1 \), so that the relation in Eq. (38) gives explicitly the value of \( a_m \) once the previous \( m - 1 \) coefficients \( a_{m-1}, a_{m-2}, \ldots, a_2, a_1 \) (and \( a_0 \)) are known.

The series expansion in Eq. (30) is uniformly convergent in the interval \([0, 1]\) for \( \tau \), because the series \( \sum_{n=0}^{\infty} a_n \) is convergent. In fact, by letting \( \tau = 1 \) (\( t = 0 \)) in Eq. (30), we have from Eq. (28):

\[
-\varphi_0' = \left[ \frac{3}{16} \right]^{1/3} \sum_{n=0}^{\infty} a_n \varphi,
\]

which shows that the sum of such a series is determined by the (finite) value of \( \varphi_0' \) (\( \varphi_0' = 1.588 \) and thus \( \sum_{n=0}^{\infty} a_n \approx 2.7746 \)). Note also that the \( a_n \) are positive definite and that the series in Eq. (39) exhibits geometrical convergence with \( a_n / a_{n-1} \approx 4/5 \) for \( n \to \infty \). The numerical values of the first 20 coefficients are given in Table I.

Given the function \( u(t) \), we now have to look for the parametric solution \( x = x(t) \), \( \varphi = \varphi(t) \) of the Thomas–Fermi equation. To this end let us write

\[
\varphi(t) = \exp \left[ \int_0^t w(t) dt \right],
\]

where \( w(t) \) is an auxiliary function to be determined in terms of \( u(t) \), and condition (13a) [\( \varphi(t = 0) = 1 \)] is automatically satisfied. By substituting Eq. (40) into Eq. (19) and using Eq. (26), we immediately find that

\[
w = -\frac{6ut}{1 - r^2u}.
\]

In summary, the parametric solution of Eq. (12), with the boundary conditions (13), takes the form:

\[
x(t) = \sqrt{\frac{4t}{7}} e^{2\delta(t)},
\]

\[
\varphi(t) = e^{-6\delta(t)},
\]

where

\[
\delta(t) = \int_0^t \frac{ut}{1 - r^2u} dt.
\]

and \( u(t) \) is given by the series expansion in Eq. (30) with the coefficients determined by Eqs. (31), (37), and (38). Equation (42) represents the celebrated Majorana solution of the Thomas–Fermi equation; it is given in terms of only one quadrature.\(^8\)

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We have performed numerically the integration in Eq. (43) stopping the series expansion in Eq. (30) at $n = 10$ and $n = 20$, respectively, and compared the parametric solutions thus obtained from Eq. (42) with the exact (numerical) solution of the Thomas–Fermi equation. We found that the two Majorana solutions approximate the exact solution with relative errors of the order of 0.1% and 0.01%, respectively.

We can also obtain an approximate analytical solution by inserting the series expansion (30) into expression (43):

$$ I(t) = \int_{1-t}^{1} \frac{u(1-\tau)}{1-(1-\tau)^2 u} d\tau $$

$$ = \int_{1-t}^{1} \frac{1}{1-t} \frac{1}{1-\tau} \frac{1}{1} d\tau, $$

with

$$ b_n = a_n - a_{n-1}, $$

$$ c_n = b_{n-1} - b_n $$

for $n \geq 1$, while $b_0 = 1$ and $c_0 = 0$. Note that

$$ b_n < 0 \quad \text{for} \quad n \geq 1, $$

$$ c_n < 0 \quad \text{for} \quad n > 1 $$

and $b_0, c_1 > 0$. If we neglect $O(\tau^2)$ terms in Eq. (44), the quantity $I(t)$ is approximated by:

$$ I(t) = \frac{b_1}{c_1} t - \frac{1}{c_1} \log(1-t). $$

and, in terms of the original $a_n$ coefficients, the approximate parametric solution of the Thomas–Fermi equation is

$$ x(t) = \sqrt{1444 \tau^2(1-t)} - 2(a_2 - a_0) \tau \left[ 2(1-a_1)-(1-a_1)^2 \right], $$

$$ \varphi(t) = (1-t)^{6(2-a_1)} \left[ (1-a_1)^2 \right]. $$

In Fig. 1 we compare the above solution with the exact (numerical) one.

In general, we can truncate the series in Eq. (44) at a certain power $\tau$ and thus approximate the integrand function by a rational function:

$$ F(\tau) = \frac{1 + b_1 \tau + b_2 \tau^2 + \ldots + b_k \tau^k}{c_1 \tau + c_2 \tau^2 + \ldots + c_k \tau^k} \equiv \frac{P(\tau)}{Q(\tau)}. $$

Let us then assume that the roots $\tau_i$ ($i = 1, 2, \ldots, k$) of the polynomial in the denominator,

$$ Q(\tau_i) = 0, $$

are known, so that we can decompose the function $F(\tau)$ into a sum of simple rational functions:

$$ \frac{1}{Q(\tau)} = \frac{1}{c_k} \left( \frac{f_1}{\tau - \tau_1} + \frac{f_2}{\tau - \tau_2} + \ldots + \frac{f_k}{\tau - \tau_k} \right), $$

and

$$ F(\tau) = \frac{1}{c_k} (1 + b_1 \tau + b_2 \tau^2 + \ldots + b_k \tau^k) $$

$$ \times \left( \frac{f_1}{\tau - \tau_1} + \frac{f_2}{\tau - \tau_2} + \ldots + \frac{f_k}{\tau - \tau_k} \right). $$

The expressions for the coefficients $f_i$ ($i = 1, 2, \ldots, k$) in terms of the roots $\tau_i$ are as follows:

$$ f_i = \prod_{l=1, l \neq i}^{k} \frac{1}{\tau_i - \tau_l}. $$

If we insert the decomposition (52) into Eq. (44), the integral $I(t)$ is thus given by a (double) sum whose generic element has the following form:

$$ \int_{1-t}^{1} \frac{\tau^n}{\tau - \tau_i} \log(1-t) d\tau = -\tau_i^n \log(1-t) + \sum_{l=1}^{n} \frac{n}{l} \tau_i^{n-l} $$

$$ \times [(1-\tau_i)^l - (1-\tau_i)^l]. $$

Then, in general, the parametric solution of Eq. (12) can be formally written as:

$$ x(t) = \sqrt{1444 \tau^2 \epsilon^2(t)}, $$

$$ \varphi(t) = e^{\epsilon(t)}, $$

where $\epsilon(t) = e^{I(t)}$ is approximated by:

$$ \epsilon(t) = \prod_{i=1}^{k} \left( 1 - \frac{\tau_i - t}{1 - \tau_i} \right)^{-(1+c_i)S_i} \left( 1 - \frac{\tau_i - t}{1 - \tau_i} \right)^{\frac{n}{l} \tau_i^{n-l}} $$

$$ \times \prod_{i=1}^{k} \prod_{l=1}^{n} \prod_{j=1}^{l} \exp\left( \frac{1}{c_k} f_i \left( \frac{n}{l} b_i \tau_i^{n-l} \right) \right). $$

Obviously, using this method, the exact result is recovered in the limit $k \to \infty$. However, this procedure can be employed to obtain approximate but accurate solutions of the Thomas–Fermi equation because, as is clear from the above, we have converted a numerical integration problem [see Eq. (43)] into a numerical search for the roots of the polynomial $Q(\tau)$. Note also that we already know one of these roots (namely, $\tau_i = 0$) given the particular form of $Q(\tau)$. The knowledge of such a root implies that, because the general solution of a fourth-degree polynomial equation in terms of radicals is known, we can obtain an analytical approximate solution from Eqs. (55) and (56) by considering terms in the series in
Eq. (44) up to order $O(\tau^5)$, thus obtaining a much better approximation to Eq. (42) than Eq. (48). We do not report here the explicit form of such a solution because of its very long expression.

In summary, we have discussed an original method due to Majorana that yields a semi-analytical solution of the Thomas–Fermi equation (12) with boundary conditions given by Eqs. (13). The procedure applies as well to different boundary conditions, although the constraint in Eq. (13a) is always automatically satisfied. However, such a constraint is realized in all physical situations in atomic as well as in nuclear physics. We have further studied the Majorana series solution thus obtaining a general formula whose degree of approximation is limited only by the numerical algorithm for searching the roots of a given polynomial rather than the approximation for integrating a rational function. It is interesting to compare our method with the one used recently in Ref. 7 based on a Padé approximant approach. The method used by Majorana for solving the Thomas–Fermi equation can be generalized in order to study a large class of ordinary differential equations, but this generalization will be discussed elsewhere.

Problem 1. The normalization condition for the Thomas–Fermi function $\varphi(x)$ is obtained by the constraint that the total charge of the electron cloud (for a neutral atom) is $-Ze$:

$$\int \rho(r) d^3r = -Ze. \quad (57)$$

Express this condition in terms of the Thomas–Fermi function and, by using only Eq. (12) and the boundary conditions (13), show that the Majorana function $u(t)$ defined by Eqs. (18) and (19) takes finite values for $t=0$ and $t=1$, that is, $u(0), u(1) < \infty$.

Problem 2. How are Eqs. (2)–(13) modified for an overall positively charged atom (positive ion)? Could the Majorana method be applied in such a case?

Problem 3. Apply the Majorana method to solve the Thomas–Fermi equation (12) with the following transformation:

$$t = 1 - \frac{1}{\pi} \int \sqrt{x} \varphi, \quad (58)$$

$$\varphi = e^{\int u(t) dt}. \quad (59)$$

In particular, show that, with this transformation, the Thomas–Fermi equation for $\varphi(x)$ is transformed into an Abel equation for $u(t)$:

$$\frac{du}{dt} = \alpha(t) + \beta(t)u + \gamma(t)u^2 + \delta(t)u^3, \quad (60)$$

and deduce the expressions for the functions $\alpha(t), \beta(t), \gamma(t), \delta(t)$.

Problem 4. Consider second-order terms in the expansion in Eq. (44) and evaluate the function $\varepsilon(t)$ in Eq. (56). Then deduce the corresponding approximate expression for the Thomas–Fermi function using Eqs. (55).

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