Comparison of solutions to the Thomas-Fermi equation by a direct method and variational calculus

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In this paper we perform a comparison between two solutions of the Thomas-Fermi equation. One of these solutions is the one recently found by Bougoffa (2014) which makes use of a direct method to solve the differential equation. The other solution found uses a variational method. The first method uses approximations of the residual conditions after assuming a trial function, inspired by the Sommerfeld solution. Our solution does not require approximations and we found that it reproduces more conveniently the corresponding numerical solution in terms of relative error.

Keywords: Thomas-Fermi equation; approximate solution; variational calculus.

1. Introduction

From the earliest days of quantum mechanics, it has been clear that one could not hope to solve most of the physically interesting systems exactly, especially those with more particles. Thus, by 1930 (only three years after the first works of Thomas [1] and Fermi [2], and five years after the advent of the "new" quantum theory), a large variety of approximate methods had been developed to construct approximate analytical solutions for nonlinear differential equations. There has been a great deal of work on rigorous mathematical problems in quantum theory, most of it on the fundamentals and relevant operator theory.

The Thomas-Fermi equation is a nonlinear ordinary differential equation for modeling electrons of an atom. In particular, the Thomas-Fermi model is widely used in nuclear physics, for example, to answer questions related to nuclear matter in neutron stars [3]. In spite of its generality, the application of the Thomas-Fermi method is based on the solution $u(x)$ of the second-order nonlinear differential equation which is difficult to determine.

The purpose of this model is give a expression for the electron density $\rho(r)$, and of course, the electrostatic potential between the nucleus and the cloud of electrons at a distance r for this. This central potential $V(r)$ dominates the interaction of electrons obeying Fermi-Dirac statistics in a volume region considered to be large enough so that $V(r)$ does not vary appreciably over the size of the region. In this case the electrons move freely. Under these conditions, 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 $p_{\max}$ is the maximum value for the electron momentum

$$n = \frac{8\pi}{3h^3} p_{\max}^3, \tag{1}$$

where n is the number of electrons per unit volume. The potential energy is $-eV$, and it is confined in a neutral atom if its energy is non-positive, *i.e.*

$$\frac{p^2}{2m} = eV. \tag{2}$$

Using the expression (2) into (1), we can express the electron charge density in terms of the potential V,

$$\rho(r) = -en = -\frac{1}{3\pi^2}\sqrt{\left(\frac{2meV}{\hbar^2}\right)^3}. \tag{3}$$

Now the electronic charge density $\rho(r)$ and the potential $V(r)$ are related via the Poisson equation:

$$\nabla^2 V(r) + 4\pi\rho(r) = 0, \tag{4}$$

Taking into account the solution of (4), the boundary conditions are such that $V(r)$ tends to Ze/r when $r \to 0$ (Coulomb field), and $V(r)$ tends to zero when r tends to infinity.

The Thomas-Fermi equation in its usual form is presented when performing a change of variable

$$x = \frac{r}{a}, \quad V(r) = \frac{eZu(r)}{r}, \quad a = a_0 \left(\frac{9\pi^2}{128Z}\right)^{1/3}, \tag{5}$$

where

$$a_0 = \frac{h^2}{4\pi^2 m_e e^2} = 5.2917721092.10^{-11}\,m \approx 0.53\ \text{Å},$$

is the first Bohr radius of the hydrogen atom, at a distance r from the nucleus, m_e and e are the mass and charge of electron.

This change is also convenient because it eliminates all numerical constants in Eq. (4) leading to an universal non-linear second-order ordinary differential equation which describes all atoms without distinguishing their composition or number of electrons. Substituting the changes described in (5) into Eq. (4), we find the Thomas-Fermi equation

$$\frac{d^2u}{dx^2} - \frac{u^{3/2}}{x^{1/2}} = 0. \tag{6}$$

This new equation (6) satisfies

$$u(0) = 1, \quad u(\infty) = 0. \tag{7}$$

An important parameter is the magnitude of the initial slope

$$B = -\frac{du(r)}{dr}\Big|_{x=0}, \tag{8}$$

such as under numerical integration yields $B = 0.5055\pi = -1.588$ [4].

There have been many attempts to construct an approximate analytical solution of the Thomas-Fermi equation for atoms [5, 6] in these cases using variational principles, trying to solve the equation by proposing a one-parameter trial function:

$$u_1(x) = (1 + \eta x)e^{-\eta x}, \tag{9}$$

where $\eta = 1.905$ and Csavinsky [7] has proposed a two-parameters trial function:

$$u_2(x) = \left(a_0 e^{-\alpha_0 x} + b_0 e^{-\beta_0 x}\right)^2, \tag{10}$$

where a_0=0.7218337, α_0=0.1782559, b_0=0.2781663 and β_0=1.759339. Later, Kesarwani and Varshni [8] suggested:

$$u_3(x) = \left(ae^{-\alpha x} + be^{-\beta x} + ce^{-\gamma x}\right)^2, \tag{11}$$

where a=0.52495, α=0.12062, b=0.43505, β=0.84795, $c = 0.04$ and $\gamma = 6.7469$.

The last two equations are obtained using an equivalent Firsov's variational principle [9]. The first equation has been modified by Wu [10] in the following form:

$$u_4(x) = (1 + m\sqrt{x} + nx)^2 e^{-2m\sqrt{x}}, \tag{12}$$

where $m = 1.14837$ and $n = 4.0187 \times 10^{-6}$.

Recently, M. Desaix et al. [12] proposed the following expression:

$$u_5(x) := \frac{1}{[1 + (kx)^a]^b}, \tag{13}$$

where $a = 0.9237797117$, $b = 2.097976638$ and $k = 0.4834685937$. Moreover, other attempts have been carried out to solve this problem [13, 14]. But, all of these proposed trial functions do not reproduce appropriately the numerical solution of the Thomas-Fermi equation [15] and its derivative at $x = 0$. They did not prove to be efficient when used to calculate the total ionization energy of heavy atoms.

Oulne [16], proposed a trial function which depends on three parameters α, β and γ:

$$u_6(x) = (1 + \alpha\sqrt{x} + \beta x e^{-\gamma\sqrt{x}})^2 e^{-2\alpha\sqrt{x}}, \tag{14}$$

The optimum values of the variational parameters α, β and γ, obtained by minimizing the Lagrangian, are respectively equal to 0.7280642371, -0.5430794693 and 0.3612163121.

From other methods Marinca et al. [17], solve the Thomas-Fermi equation in this case using OHAM (Optimal Homotopy Asymptotic Method), finding a pair of approximate solutions with good accuracy. These solutions are somewhat complicated, introducing many parameters in a combination (or rather a generalization) of solutions found previously by other authors using simpler functions.

A solution has recently been tested which is based in the trial function of Wu [10], in which we add other terms given account for a solution more closer to the numerical solution obtaining good results adjusted to the semi-analytic solution of other works In the area. The solution is of type Wu such that [11] $u_{\text{our}}(x) = (1 + a\sqrt{x} + bx + cx\sqrt{x})^2 \exp(-2a\sqrt{x})$ with $a = 0.9614236887819619$, $b = -0.3442527917822383$, and $c = 0.08703140640977791$. Our solution has shown to have relative errors below 4% with respect to other solutions and to the numerical solution.

More recently Bougoffa [18] inspired in the Sommerfeld solution found a solution to Thomas-Fermi equation by a direct method to solve the differential equation. The idea is new and very simple but powerfully motivational. Their method consists in the reduction of the original differential equation (6) into an equivalent equation, so that the solution can then be expressed in a logarithmic form. In the process, once the solution is proposed, it is an algebraic subsidiary condition that cannot be solved unless it approximates certain terms to simpler expressions, such as a function expansion. The result is that one can make several approximations and obtain almost two distinct solutions.

In the present work, we propose a new trial function, constructed on the basis of the Bougoffa [18] function, which reproduces correctly the numerical solution of the Thomas-Fermi equation [15]. It also gives more precise results for the total ionization energies of heavy atoms in comparison with the previously proposed approximate solutions.

2. The system

We use variational techniques and optimization to find analytical solutions. In this case, the idea is that the Thomas-Fermi differential equation, can be described by the following Lagrangian

$$L(u) = \frac{1}{2}\left(\frac{du}{dx}\right)^2 + \frac{2}{5}\frac{u^{5/2}}{x^{1/2}}. \tag{15}$$

This Lagrangian is equivalent to equation (6) when one uses the Euler-Lagrange equation

$$\frac{d}{dx}\frac{\partial L}{\partial u'} = \frac{\partial L}{\partial u}, \tag{16}$$

where the prime symbol denotes derivative respect to the x variable. Finally, the total Lagrangian will be

$$L_t = \int_0^\infty L dx, \tag{17}$$

thus, when a solution is fixed, $u = u(x, \alpha_i)$, $i = 1, 2, 3...$, in terms of some coefficients, it can be optimized using a total Lagrangian minimum condition to find the value of arbitrary constant

$$\frac{\partial L_t}{\partial \alpha_i} = 0. \tag{18}$$

3. Solutions

The first solution proposed in [18], is

$$u_{p1}(x) = (1 + ax)^{-2}. \tag{19}$$

This solution is achieved from a direct method to solve the associated differential equation and making approximations in terms of a subsidiary condition. We propose the same function but in this case solved through variational method leading to $a = 0.569270441723403$ (fully analytical) in comparison with the value found by Bougoffa $a = 9^{-1/3}$. When this is calculated, however, the solution may also be achieved

analytically obtaining the corresponding Lagrangian

$$L = \frac{2\left(5a^2 + \frac{1+ax}{\sqrt{x}}\right)}{2(1 + ax)^6}, \tag{20}$$

Now integrating over the interval $x \in (0, \infty)$,

$$Lt = \frac{2a}{5} + \frac{7\pi}{64\sqrt{a}}, \tag{21}$$

and optimizing

$$\frac{\partial Lt}{\partial a} = \frac{2}{5} + \frac{7\pi}{128\sqrt{a^3}} = 0. \tag{22}$$

The algebraic solution to the above equation is found directly

$$a = \frac{(35\pi)^{2/3}}{32 \times 2^{1/3}}. \tag{23}$$

Bougoffa also proposes another solution such that

$$u_{p2}(x) = (1 + ax)^{-3}. \tag{24}$$

In this case , the result is

$$L = \frac{9a^2}{2(1 + ax)^8} + \frac{2}{5\sqrt{x}(1 + ax)^{15/2}}. \tag{25}$$

TABLE I. The values of the functions proposed by Bougoffa by direct method (DM), our solutions via variational method (VM), and numerical solution using a Runge-Kutta method.

x	Numerical	u_{p1}^a	u_{p2}^a	u_{p1}^b	u_{p2}^b
0	1	1	1	1	1
0.005	0.9925	0.995209	0.997143	0.994331	0.994683
0.01	0.9854	0.990453	0.994298	0.988711	0.989403
0.05	0.9352	0.953604	0.971919	0.945414	0.948483
0.1	0.8818	0.910364	0.944880	0.895179	0.900445
0.5	0.607	0.649971	0.760834	0.605955	0.611942
1	0.424	0.456075	0.592241	0.406073	0.401305
2	0.243	0.259910	0.379210	0.218657	0.199476
5	7.88E-2	0.086314	0.134052	0.067593	0.046610
10	2.43E-2	0.029649	0.040670	0.022325	0.010564
12	1.71E-2	0.021824	0.028095	0.016305	0.006836
15	1.08E-2	0.014831	0.017363	0.010989	0.003931
20	5.78E-3	0.008874	0.008954	0.006518	0.001871
25	3.47E-3	0.005900	0.005206	0.004310	0.001032
30	2.26E-3	0.004204	0.003290	0.003059	0.000628
35	1.55E-3	0.003146	0.002209	0.002283	0.000410
40	1.11E-3	0.002443	0.001555	0.001769	0.000283
45	8.28E-4	0.001952	0.001135	0.001411	0.000203
50	6.32E-4	0.001595	0.000854	0.001151	0.000150

Superscript ^{a} correspond to the Eq. (19) and (24) for direct method, respectively, that is, the original solutions found by Bougoffa. Superscript ^{b} correspond to the Eq. (19) and (24) variational calculus, respectively, that is, our solutions.

TABLE II. Comparison of the relative error (%) of the functions respect of numerical solution. In this case
$Er(y_{Num}, y_i) = (y_{Num} - y_i)/y_{Num} \times 100$

x	$Er(Num, u_{p1}^a)$	$Er(Num, u_{p2}^a)$	$Er(Num, u_{p1}^b)$	$Er(Num, u_{p2}^b)$
0	0	0	0	0
0.005	-0.2730	-0.4678	-0.1845	-0.2199
0.01	-0.5128	-0.9030	-0.3360	-0.4062
0.05	-1.9679	-3.9263	-1.0922	-1.4203
0.1	-3.2393	-7.1536	-1.5172	-2.1144
0.5	-7.0792	-25.3434	0.1721	-0.8142
1	-7.5649	-39.6797	4.2279	5.3523
2	-6.9589	-56.0535	10.0173	17.9108
5	-9.5364	-70.1170	14.2219	40.8492
10	-22.0156	-67.3688	8.1263	56.5232
12	-27.6306	-64.3018	4.6451	60.0180
15	-37.3276	-60.7725	-1.7573	63.5979
20	-53.5438	-54.9137	-12.7851	67.6216
25	-70.0325	-50.0457	-24.2141	70.2397
30	-86.0296	-45.5765	-35.3898	72.1740
35	-103.0245	-42.5636	-47.3534	73.4886
40	-120.1331	-40.0970	-59.4371	74.4948
45	-135.7528	-37.1338	-70.4694	75.4526
50	-152.4069	-35.1603	-82.2696	76.1368

TABLE III. Comparison of total ionization energies in units (e^2/a_0) from HF and solutions by direct method and variational calculus.

Z	HF	$E(u_{p1}^a)$	$E(u_{p2}^a)$	$E(u_{p1}^b)$	$Er(u_{p1}^a)$	$Er(u_{p2}^a)$	$Er(u_{p1}^b)$
92	28070	17790.17	10590.05	21065.86	36.62	62.27	24.95
93	28866	18244.65	10860.58	21604.01	36.80	62.38	25.16
94	29678	18705.68	11135.03	22149.94	36.97	62.48	25.37
95	30506	19173.30	11413.39	22703.67	37.15	62.59	25.58
96	31351	19647.54	11695.69	23265.22	37.33	62.69	25.79
97	32213	20128.40	11981.94	23834.62	37.51	62.80	26.01
98	33093	20615.92	12272.14	24411.91	37.70	62.92	26.23
99	33990	21110.12	12566.33	24997.10	37.89	63.03	26.46
100	34905	21611.02	12864.50	25590.23	38.09	63.14	26.69
101	35839	22118.64	13166.68	26191.32	38.28	63.26	26.92
102	36793	22633.01	13472.87	26800.40	38.49	63.38	27.16
103	37766	23154.15	13783.09	27417.49	38.69	63.50	27.40
104	38758	23682.07	14097.35	28042.63	38.90	63.63	27.65
105	39772	24216.81	14415.66	28675.83	39.11	63.75	27.90
106	40806	24758.38	14738.05	29317.12	39.33	63.88	28.15
107	41862	25306.81	15064.51	29966.52	39.55	64.01	28.42
108	42941	25862.11	15395.07	30624.08	39.77	64.15	28.68
109	44042	26424.31	15729.74	31289.80	40.00	64.28	28.95

Second column is HF numerical solution. The next three columns are ionization energies for Bougoffa and our solutions. In this case, calculus for u_{p1}^b and u_{p2}^b match. The last three columns represents error associated to each solution.

Now integrating over the interval $x \in (0, \infty)$,

$$Lt = \frac{4096}{15015\sqrt{a}} + \frac{9a}{14}, \qquad (26)$$

and optimizing again

$$\frac{\partial Lt}{\partial a} = \frac{9}{14} - \frac{2048}{15015\sqrt{a^3}} = 0, \qquad (27)$$

we find

$$a = \frac{256}{9 \times 725^{2/3}} = 0.35573513495039094, \qquad (28)$$

in comparison with the value found by Bougoffa $a = 144^{-1/3}$.

The values of the functions proposed by Bougoffa (direct method) and our solutions (via variational method) are shown in the Table I. It can be seen that both satisfy the boundary conditions (7), obtaining accurate results. In Table II, the relative error (%) of the solutions are shown in comparison to the numerical solution [15].

To test the efficiency of the different solutions, given by the Eqs. (19) and (24) for direct method and variational calculus respectively, we have calculated the total ionization energy of heavy atoms following the relation [19]

$$E = \frac{12 \times 2^{1/3} \times Z^{7/3}}{7 \times (9\pi^2)^{1/3}} \frac{du}{dx}\Big|_{x=0}, \qquad (29)$$

in hartrees (e^2/a_0) and the obtained results, presented in Table II, are compared with those of Hartree-Fock (HF) [20].

4. Conclusions

In this manuscript a variational method has been used since obtaining the corresponding lagrangian for a Thomas-Fermi system for multielectronic atoms, which is known there is no analytical solution and only an approximate solution is possible. The problem is related to inverse problems to obtain the corresponding lagrangian for systems of differential equations, in this case, non-lineal and the Lagrangian is obtained by direct inspection. The method has been compared with a technique for solving the Thomas-Fermi equation, using direct resolution in terms of ordinary variable changes and series expansions. We show in this manuscript that the variational calculation offers better approximation and a solution closer to the numerical solution.

We proposed a couple of trial functions to find solutions to the Thomas-Fermi equation, based on a solution obtained by Bougoffa through a direct method for solving this differential equation. Comparing the results in Table II, we can see that the Eq. (19) solved by variational methods has a smaller error compared with that obtained by the direct method throughout the measured range. This does not happen to Eq. (24), in which, the error is smaller only in the main interval $0 \leq x \leq 12$. The errors calculated for solutions via direct method are 25.47% and 37.76% for the Eqs. (19) and (24) respectively, compared with the errors for our solutions which are 4.16% and 31.20%, respectively, taking in account 67 points to the x values.

Furthermore, in the test of efficiency in Table III, for various heavy atoms, we can see that our errors are smaller compared with the solutions found by using the direct method. However, we can also see that the errors of ionization energies, by both the direct method or variational method, increase as the atom gets heavier. This, of course, we can say that our solutions are more accurate and can be used to calculate more conveniently some other features for heavy atoms.

The derivative of our function (19) at $x = 0$ is -1.13854 as for function (24) which is closer to the numerical derivative: -1.58807102 [15]. In the case for solution obtained for direct method the derivative of function (19) at $x = 0$ is equal to -0.9615 and for function (24) a value of -0.572357.

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