Comparison of Variational Solutions of the Thomas-Fermi Model in Terms of the Corrected Ionization Energy

I. Agil, A. Alharkan, H. Alhendi, and A. Alnaghmoosh

King Saud University, College of Science, Physics Department, Riyadh, Saudi Arabia

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It is shown that leading corrections, to the ionization energy, of many-electrons atom, can be expressed as leading corrections of initial slope of trial variational solutions of the Thomas-Fermi equation. Some variational solutions with different initial slopes are compared. A comparison of the results shows, that as far as the binding energies are concerned a trial function with its slope not close to the (negative) Baker's constant may not be suited.

I. Introduction

It is well known that the Thomas-Fermi (TF) model [1] of many electrons atom, as it stands, shows poor predictions if compared to the Hartree approximation [2], the quantum mechanical equivalent of the TF theory [3].

Quite recently there has been a considerable renewed interest in calculating leading corrections [4], to the binding energy of the TF-atom. The problem of incorporating the first leading correction in the TF-model, was predicted by Scott [5], the values for the second and the third corrections were suggested by March and Paskett [6] and Schwinger [7]. It has been suggested by Tal and Levy [8] that a Z^{-1} expansion could lead to a better fit for the total binding energy of the TF-atom.

In this paper we use the Z^{-1} expansion to re-expresse the ionization energy of many-electrons atom to the second leading corrections, in term of the initial slope of the trial variational solutions of the TF-equation, where no attention has been paid to the calculation of these nonzero order corrections in terms of trial variational functions of the variational scheme [9] which replaces the TF theory. By restoring to the variational scheme many physical quantities such as the electric potential, the electron density within the atom, and the interaction energies between two TF-atoms can be calculated in terms of trial variational functions [9].

Finally, we compare three types of trial solutions that have, in the zero order corrections, been suggested in the literature to be suited for the low [10], medium [11] and higher [12] atomic-number atoms. It is concluded that multiparameter solutions are more suitable for the model and our calculations show that the total ground-state binding energy of an atom is in excellent agreement, for all Z, with the Hartree-Fock (HF) method.

Reprint requests to Dr. Ahmed M. Alharkan, King Saud University College of Science, Physics Department, P.O. Box 2455, Riyadh 11451, Saudi Arabia.

II. Thomas-Fermi Equation: Variational Approach

Introducing the dimensionless variable x by

$$x = 4\left(\frac{2Z}{9\pi^2}\right)^{1/3}\left(\frac{r}{a_0}\right),$$

where r is the distance from the nucleus, in units of the Bohr radius a_0, and Z the atomic number, the TF-theory leads to the differential equation [1]

$$\frac{d^2\phi}{dx^2} = \frac{\phi^{3/2}}{x^{1/2}} \tag{1}$$

which, for a neutral atom, is to be solved with the boundary and subsidiary (normalization) conditions

$$\phi(0) = 1\,, \quad \phi(\infty) = 0\,, \quad \phi'(\infty) = 0 \tag{2}$$

and

$$\int \varrho\, dv = N\,, \tag{3}$$

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where N is the number of electrons, $\mathrm{d}v$ is the volume element, and ϱ is the electron density, which is related to $\phi(x)$ by

$$\varrho = \frac{Z}{4\pi a^3}\left(\frac{\phi}{x}\right)^{3/2}$$

with (4)

$$a = \frac{1}{4}\left(\frac{9\pi^2}{2Z}\right)^{1/3} a_0 .$$

Choosing [10]

$$\mathscr{L}(\phi, \phi', x) = \frac{1}{2}\left(\frac{\mathrm{d}\phi}{\mathrm{d}x}\right)^2 + \frac{2}{5}\left(\frac{\phi^5}{x}\right)^{1/2}, \quad (5)$$

the variational principle

$$L(\phi) = \int_0^\infty \mathscr{L}\,\mathrm{d}x \quad (6)$$

is the equivalent of (1) since substitution of (5) into the Euler-Lagrange equation

$$\frac{\partial \mathscr{L}}{\partial \phi} - \frac{\partial}{\partial x}\left(\frac{\partial \mathscr{L}}{\partial \phi'}\right) = 0 \quad (7)$$

results in the TF-equation.

In this variational scheme the function $\phi(x)$ is a trial function that depends on a number of appropriately chosen parameters [10],

$$\phi = \phi(C_1, C_2, \ldots, C_i) . \quad (8)$$

Once a trial function is chosen which satisfies the boundary conditions (2) and the normalization condition (3), and the integral in the variational principle (6) is performed, the quantity $L(\phi)$ becomes a function of the parameters in ϕ, i.e.

$$L(\phi) = L(C_1, C_2, \ldots, C_i) , \quad (9)$$

from (9) the optimal values of $L(\phi)$ is determined by finding those values of the parameters which satisfy the set of simultaneous equations

$$\left.\begin{array}{c} \dfrac{\partial L(C_1, C_2, \ldots, C_i)}{\partial C_1} = 0 , \\ \vdots \\ \dfrac{\partial L(C_1, C_2, \ldots, C_i)}{\partial C_i} = 0 . \end{array}\right\} \quad (10)$$

III. TF-Binding Energies: Leading Corrections

The zero-order correction to the total binding energy E is calculated from [1]

$$E = \left(\frac{12}{7}\right)\left(\frac{2}{9\pi^2}\right)^{1/3} Z^{1/3}\phi'(0)\left[\frac{e^2}{a_0}\right], \quad (11)$$

where $\phi'(0)$ is the initial slope of $\phi(x)$:

$$\phi'(0) = \left(\frac{\mathrm{d}\phi(x)}{\mathrm{d}x}\right)_{x=0} . \quad (12)$$

Numerical calculations give [1]

$$\phi'(0) = -B = -1.588070972 , \quad (13)$$

where B is the Baker's constant [13]. The corresponding binding energy then takes the form

$$E_{\mathrm{TF}} = -0.768745124\, Z^{7/3}[e^2/a_0] . \quad (14)$$

In the variational scheme, $\phi(x)$ is a trial function occuring in (6) and (8). For the leading corrections we use the Z^{-1} expansion techniques introduced in [14] and applied to the TF-model in [8] to find the asymptotic TF-energy. The binding energy of the many-electrons atom, having Z protons and N electrons, can be written, in units of $[e^2/a_0]$, as

$$E(Z, N) = \sum_{n=0}^{\infty} \varepsilon_n(N) Z^{(2-n)} , \quad (15)$$

where the expansion coefficients $\varepsilon_n(N)$ for $n>1$ are generally not known, and for $n = 0$, the zero-order coefficients $\varepsilon_0(N)$ has the asymptotic form [15]

$$\varepsilon_0(N) \simeq a_\infty N^{1/3} + a_{01} , \quad (16)$$

where

$$a_{00} = -(3/2)^{1/3} \quad \text{and} \quad a_{01} = 1/2 .$$

The partial derivative of $E(Z, N)$, with respect to Z, can be related to the expectation value $R(Z, N)$ of r through the Hellmann-Feynman theorem

$$-R(Z, N) = \left(\frac{\partial E}{\partial Z}\right)_N = \sum_{n=0}^{\infty} (2-n)\varepsilon_n(N) Z^{(1-n)} . \quad (17)$$

For a neutral atom ($N = Z$), (15) and (16) yield the following approximate recursion relation [8]:

$$E(Z) - E(Z-1) \simeq -R(Z) - \varepsilon_0(Z) \ , \qquad (18)$$

where all terms containing $\varepsilon_n(Z)$, $n > 3$ have been neglected. Moreover it can be shown that [16]

$$E(Z) = \frac{R^2(Z)}{4\beta^2(Z)\,\varepsilon_0(Z)} \ , \quad \beta(Z) \leqslant 1 \ . \qquad (19)$$

For the hydrogen atom one has $\beta^2(1) = 1$, whereas for the original TF-model $\beta^2(Z) = \left(\frac{7}{6}\right)^2 \frac{C_0}{a_{00}}$, where $C_0 = \left(\frac{12}{7}\right)\left(\frac{2}{9\pi^2}\right)^{1/3} \phi_\beta'(0)$ and $\phi_\beta'(0) = -1.588070972$, the (negative) of Baker's constants. By combining (17) and (19) it is possible to express (minus) the right handside of (18) as follows:

$$\begin{aligned} R(Z) + \varepsilon_0(Z) = \varepsilon_0(Z)\{[1-\beta^2(Z)]^2 - \beta^4(Z)\} \\ + 2\beta(Z)[\langle \beta^2(Z) - 1\rangle \varepsilon_0^2(Z) \\ + E(Z-1)\,\varepsilon_0(Z)] \ . \qquad (20) \end{aligned}$$

A first approximation to (20) is to make $\beta(Z)$ independent of Z and require correct behavior at the limits $Z \to 1$ and $Z \to \infty$, thus with $\beta^2(Z) \to 1$ and $\beta(Z) = \beta$ for any Z [8]

$$\begin{aligned} E(Z) \simeq E(Z-1) + \beta^2 \varepsilon_0(Z) \\ - 2\beta[E(Z-1)\,\varepsilon_0(Z)]^{1/2} \ , \qquad (21) \end{aligned}$$

which can be summed to yield

$$E(Z) \simeq \beta^2 \left\{ \sum_{n=0}^{Z} [\varepsilon_0(n)]^{1/2} \right\}^2 \ . \qquad (22)$$

Taking n in (22) to be a continuous variable as $Z \to \infty$ and replacing the summation by integration, one obtains the following asymptotic binding energy:

$$E(Z) \simeq C_0 Z^{7/3} + C_1 Z^{6/8} + O(Z^{5/3}) \ , \qquad (23)$$

where

$$\begin{aligned} C_1 &\simeq -\frac{7}{10}\left(\frac{2}{3}\right)^{1/3} C_0 \ , \\ C_0 &= \left(\frac{12}{7}\right)\left(\frac{2}{9\pi^2}\right)^{1/3} \phi'(0) \ . \end{aligned} \qquad (24)$$

Table 1. Comparison of total uncorrected ionization energies (in units of $[e^2/a_0]$).

Z	$-E^{a}$ (HF)	$-E^{b}$ (ϕ_β')	$-E^{b}$ (ϕ_1')	$-E^{b}$ (ϕ_2')	$-E^{b}$ (ϕ_3')
2	2.8617	3.8742	3.4256	3.2172	3.0156
4	14.5730	19.5249	17.2642	16.2136	15.1977
6	37.6876	50.2885	44.4658	41.7599	39.1434
8	74.8094	98.3994	87.0061	81.7115	76.5918
10	128.5471	165.6211	146.4444	137.5329	128.9156
12	199.6146	253.4381	224.0934	210.4568	197.2704
16	397.5049	495.9016	438.4830	411.8003	385.9984
20	676.7582	834.6779	738.0336	694.1226	649.6941
28	1 506.8708	1 830.1400	1 618.2346	1 519.7615	1 424.5389
36	2 752.0549	3 289.6880	2 908.7871	2 731.7808	2 560.6177
48	5 465.1333	6 436.9248	5 691.6167	5 345.2690	5 010.3545
54	7 232.1382	8 472.9943	7 491.8926	7 035.9937	6 595.1450
66	11 641.4531	13 532.7080	11 965.8047	11 237.6582	10 533.5488
72	14 321.2500	16 578.9883	14 659.3672	13 767.3115	12 904.7031
80	18 408.9902	21 199.4941	18 744.8809	17 604.2129	16 501.1992
86	21 866.7715	25 096.4277	22 190.6035	20 840.2559	19 534.4824
Average Error		20.653%	6.683%	3.822%	7.230%

[a] Hartree-Fock values from [17].
[b] Values corresponding to uncorrected Thomas-Fermi energies, Eq. (14).
[1] Trial solution proposed by Kesarwani and Varshni [12].
[2] Trial solution proposed by Mu-Shiang [11].
[3] Trial solution proposed by Csavinszky [10].
The average error is calculated for ALL ATOMS in the range $1 \leqslant Z \leqslant 86$ with respect to the corresponding Hartree-Fock values.
The average error of a set (X) with respect to (Y), $i = 1, 2, \ldots, n$, is defined by $\left(\frac{1}{n}\right) \sum_{i=1}^{n} \left| \frac{x_i - y_i}{y_i} \right|$.

Thus with a correct choice of $\varepsilon_0(Z)$ [15] and $\beta(Z)$ [8], the resulting energy to the second leading correction can be written as

$$E(Z) = \left(\frac{12}{7}\right)\left(\frac{2}{9\pi^2}\right)^{1/3} Z^{7/3}\,\Phi'(0)\left[\frac{e^2}{a_0}\right], \tag{25}$$

where

$$\Phi'(0) = F(Z)\,\phi'(0) \tag{26}$$

and

$$F(Z) = 1 - 0.6504\,Z^{-1/3} + 0.364\,Z^{-2/3}\,. \tag{27}$$

As can be easily seen the resulting (25) for the binding energy reduces to the zero-order TF-energy for $\phi'(0) = \phi'_\beta(0)$, and $F(Z) \to 1$ corresponding to large atomic number (see (14)). It can also be shown that this model, (25), reduces to the one given in [8] for the case in which $\phi'(0) = \phi'_\beta(0)$, but $F(Z)$ given by (27). In general, this model could be applied to various possible suitable trial functions.

IV. Results and Conclusion

To test variational solutions, the energy necessary to remove all electrons of an atom is calculated from (25) corresponding to the following initial slopes:

$\phi'_1(0) = -1.404194$ (for the trial solution proposed by Kesarwani & Varshni [12]),

$\phi'_2(0) = -1.3187456$ (for the trial solution proposed by Mu-Shiany [11]),

$\phi'_3(0) = -1.2361179$ (for the trial solution proposed by Csavinszky [10]).

The result is listed in Table 1 and Table 2 together with the corresponding Hartree-Fock values.

It is seen from Table 2 that solutions with initial slope close to Baker's constant give better results for the total ionization energy with an average error 0.323%. This suggests that for corrected energy, one may impose $\phi'(0) \simeq \phi'_\beta(0)$, besides the boundary ones, and this requires a trial solution to be of multiparameter type.

Table 2. Comparison of total corrected ionization energies (in units of $[e^2/a_0]$).

Z	$-E^{a}$ (HF)	$-E^{c}$ (ϕ'_β)	$-E^{c}$ (ϕ'_1)	$-E^{c}$ (ϕ'_2)	$-E^{c}$ (ϕ'_3)
2	2.8617	2.7626	2.4428	2.2941	2.1504
4	14.5730	14.3455	12.6845	11.9591	11.1662
6	37.6876	37.8325	33.4520	31.4164	29.4880
8	74.8094	75.3542	66.6292	62.5747	58.6540
10	128.5471	128.6102	113.7188	106.7988	100.1072
12	199.6146	199.0395	175.9935	165.2838	154.9278
16	397.5049	396.3320	350.4422	329.1170	308.4958
20	676.7582	675.9164	597.6545	561.2858	526.1178
28	1506.8708	1510.3926	1335.5096	1254.2408	1175.6548
36	2752.0549	2751.5291	2432.9395	2284.8894	2141.7268
48	5465.1333	5462.3437	4829.8784	4535.9697	4251.7627
54	7232.1382	7230.8457	6393.6123	6004.5464	5628.3242
66	11641.4531	11656.3613	10306.7139	9679.5264	9073.0439
72	14321.2500	14335.7207	12675.8389	11904.4863	11158.5957
80	18408.9902	18415.1719	16282.9453	15292.0908	14333.9463
86	21866.7715	21867.3555	19335.4141	18158.8105	17021.0469
Average Error		0.323%	11.530%	16.914%	22.120%

[a] Hartree-Fock values from [17].
[c] Values corresponding to corrected Thomas-Fermi energies, Eq. (25).
[1] Trial solution proposed by Kesarwani and Varshni [12].
[2] Trial solution proposed by Mu-Shiang [11].
[3] Trial solution proposed by Csavinszky [10].
The average error is calculated for ALL ATOMS in the range $1 \leqslant Z \leqslant 86$ with respect to the corresponding Hartree-Fock values.
The average error of a set (X) with respect to (Y), $i = 1, 2, \ldots, n$, is defined by $\left(\frac{1}{n}\right)\sum_{i=1}^{n}\left|\frac{x_i - y_i}{y_i}\right|$.

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