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Validity of Variational Solutions of the Thomas-Fermi Model of a Many electrons atom

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Abstract. Some variational solutions of the Thomas – Fermi equation with different initial slopes are compared. The results show that as far as the binding energies are concerned, one must choose a trial function with its slope very close to the Baker's constant.

Introduction

The Thomas–Fermi (TF) model of many – electrons atom, [1-2], has an unsatisfactory feature in that it leads to a radial electron density which decreases as the inverse fourth power of the distance from the nucleus, whereas the Hartree approximasion [3], the quantum mechanical equivalent of the TF – theory [4], shows that it should decrease exponentially.

Recently there has been considerable renewed interest in calculating leading corrections [5-9] to the binding energy of the TF-atom. By making use of the Z^{-1} expansion theory, the Hellmann-Feynman theorem, and the TF-theory, Tal and Levy [8] derived recursion relations that provid accurate estimates of the total binding energy of the TF-atom.

In this paper, we use the Z^{-1} expansion to reexpress the ionization energy of many-electrons atom to the second order leading corrections, in terms of the initial slope of the trial variational solutions of the variational scheme [10-11] which replaces the TF-theory. We, then compare three types of trial solutions that have been suggested to be suitable for the low [12], medium [13], and high [14] atomic-number atoms. It is concluded that none of these solutions is suitable for the model. 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 only for solutions with a slope very close to $B = -1.588070972$ (the negative of the Baker's constant).

Thomas - Fermi Equation: Variational Approach

The TF - theory leads to the differential Equation [1-2]

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

where the dimensionless variable x is given by:

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

and r/a_o is the distance from the nucleus, in units of the Bohr radius a_o, and Z is the atomic number. For a neutral atom, this equation is to be solved subject to the boundary conditions

$$\phi(o) = 1, \qquad \phi(\infty) = 0, \qquad \phi'(\infty) = 0 \tag{3}$$

with normalization conditions

$$\int \rho \, dv = N \tag{4}$$

where N is the number of electrons, dv is the volume element, and ρ is the electron density which is related to $\phi(x)$ by:

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

with

$$a = \frac{1}{4}\left(\frac{9\pi^2}{2Z}\right)^{1/3} a_o \tag{5}$$

Choosing [12]

$$\mathscr{L}(\phi, \phi', x) = \frac{1}{2}\left(\frac{d\phi}{dx}\right)^2 + \frac{2}{5}\left(\frac{\phi^5}{x}\right)^{1/2} \tag{6}$$

the variational principle

$$L(\phi) = \int_0^\infty \mathscr{L} \, dx \tag{7}$$

is the equivalent of Eq. (1), since substitution of Eq. (6) into the Euler – Lagrange equation

$$\frac{\partial \mathscr{L}}{\partial \phi} - \frac{\partial}{\partial x}\left[\frac{\partial \mathscr{L}}{\partial \phi'}\right] = 0 \tag{8}$$

results in the TF– equation.

In this variational scheme, the function ϕ (x) is a trial function that depends on a number of appropriately chosen parameters [12]

$$\phi = \phi\,(C_1, C_2, \ldots\ldots, C_i) \tag{9}$$

Once a trial function is chosen, the optimal values of L (ϕ) is determined by finding those values of the parameters which satisfy the following set of simultaneous equations

$$\frac{\partial\, L\,(C_1, C_2, \ldots, C_i)}{\partial C_j} = 0 \qquad \text{for } j = 1,2,\ldots,i \tag{10}$$

In the next section, the binding energy for neutral atoms will be expressed in terms of these functions and their validity will be discussed.

TF– Binding Energies: Leading Corrections

The zero – order correction to the total binding energy E is calculated from [1,15 pp.42-55].

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

where ϕ' (o) is the initial slope of ϕ (x):

$$\phi'\,(o) = \left(\frac{d\phi(x)}{dx}\right)_{x=o} \tag{12}$$

Numerical calculations give [1,15 pp.42-55]

$$\phi'\,(o) = -B = -1.588070972 \tag{13}$$

where B is the Baker's constant [16]. The corresponding binding energy then takes the form

$$E_{TF} = -0.768745124 \quad Z^{7/3}\,[\frac{e^2}{a_o}] \tag{14}$$

In the variational scheme $\phi(x)$ is a trial function occuring in Eq. (6), and Eq. (8). For the leading corrections, we use the Z^{-1} expansion techniques introduced [17] and applied to the TF– model [8] to find the asymptotic TF– energy. The binding energy of a many-electrons atom, having Z protons and N electrons, can be written, in units of $[\frac{e^2}{a_o}]$, as

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

where the expansion coefficients $\varepsilon_n(N)$ for $n > 1$ are generally not known, and for $n = 0$, the zero - order coefficients $\varepsilon_o(N)$ has the asymptotic form [18].

$$\varepsilon_o(N) \simeq a_{oo}\, N^{1/3} + a_{o1} \tag{16}$$

where

$$a_{oo} = -(\frac{3}{2})^{1/3},$$

and

$$a_{o1} = \frac{1}{2}$$

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 theorm

$$-R(Z, N) = (\frac{\partial E}{\partial Z}) = \sum_{n=o}^{\infty} (2-n)\, \varepsilon_n(N)\, Z^{(1-n)} \tag{17}$$

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

$$E(Z) - E(Z-1) \simeq -R(Z) - \varepsilon_o(Z) \tag{18}$$

where all terms containing $\varepsilon_n(Z)$, $n > 3$ have been neglected. Moreover it can be shown that [19]

$$E(Z) = \frac{R^2(Z)}{4\beta^2(z)\, \varepsilon_o(z)}, \; \beta(Z) \leqslant 1 \tag{19}$$

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

$$R(Z) + \varepsilon_o(Z) = \varepsilon_o(Z)\{[1-\beta^2(Z)]^2 - \beta^4(Z)\} + 2\beta(Z)[(\beta^2(Z)-1)\varepsilon_o^2(Z) + E(Z-1)\varepsilon_o(z)]^{1/2} \tag{20}$$

As a first approximation to Eq. (20) one can make $\beta(z)$ independent of Z, and maintain correct behavior at the limits $Z \rightarrow 1$ and $Z \rightarrow \infty$. Thus with $\beta^2(Z) \rightarrow 1$ and $\beta(Z) = \beta$ for any Z [8].

$$E(Z) = E(Z-1) + \beta^2 \varepsilon_o(Z) - 2\beta[E(Z-1)\varepsilon_o(Z)]^{1/2} \tag{21}$$

can be summed to yield,

$$E(Z) = -\beta^2 \left\{ \sum_{n=o}^{Z} [\varepsilon_o(n)]^{1/2} \right\}^2 \tag{22}$$

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

$$E(z) \simeq C_o Z^{7/3} + C_1 Z^{6/3} + O(Z^{5/3}) \tag{23}$$

where

$$\begin{aligned} C_1 &= -\frac{7}{10}(\frac{2}{3})^{1/3} V_{o}, \\ C_o &= (\frac{12}{7})(\frac{2}{9\pi^2})^{1/3} \phi'(o) \end{aligned} \tag{24}$$

thus with a correct choice of $\varepsilon_o(z)$ [18] and $\beta(z)$ [8], the resulting energy to the second leading correction can be written as

$$E(Z) = (\frac{12}{7})(\frac{2}{9\pi^2})^{1/3} Z^{7/3} \Phi'(o)[\frac{e^2}{a_o}] \tag{25}$$

where

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

and

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

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

Results and Conclusion

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

$\phi'_1(o) = -1.404194$ for the trial solution proposed by Kesarwani et al. [14],

$\phi'_2(o) = -1.3187456$ for the trial solution proposed by Wu [13],

$\phi'_3(o) = -1.2361179$ for the trial solution proposed by Csavinszky [12].

The result is listed in Table 1 together with the corresponding Hartree – Fock values.

Table 1. Comparison of total corrected ionization energies, in units of (e^2/a_o)

Z	$-E^a$ (HF)	$-E^b(\phi'_B)$	$-E^b(\phi'_1)$	$-E^b(\phi'_2)$	$-E^b(\phi'_3)$
2	2.862	2.763	2.443	2.294	2.150
4	14.573	14.346	12.685	11.959	11.166
6	37.688	37.833	33.452	31.416	29.488
8	74.81	75.35	66.63	62.58	58.65
10	128.55	128.61	113.72	106.80	100.11
12	199.62	199.04	175.99	165.28	154.93
18	526.8	525.4	464.5	436.3	408.9
22	848.4	848.9	750.6	704.9	660.8
26	1262.4	1265.4	1118.9	1050.8	984.9
30	1777.9	1780.9	1574.7	1478.8	1386.2
36	2752.1	2751.5	2432.9	2284.9	2141.7
40	3539.0	3537.4	3127.9	2937.5	2753.5
44	4441.5	4439.7	3925.6	3686.7	3455.7
48	5465.1	5462.3	4829.9	4536.0	4251.8
54	7232.1	7230.9	6393.6	6004.6	5628.3
72	14321.0	14336.0	12676.0	11904.0	11159.0
74	15287.0	15301.0	13529.0	12706.0	11910.0

Table 1. *Continued.*

Z	$-E^a$ (HF)	$-E^b(\phi'_B)$	$-E^b(\phi'_1)$	$-E^b(\phi'_2)$	$-E^b(\phi'_3)$
76	16291.0	16302.0	14414.0	13737.0	12689.0
80	18409.0	18415.0	16283.0	15292.0	14334.0
82	19524.0	19528.0	17267.0	16216.0	15200.0
84	20677.0	20679.0	18284.0	17172.0	16096.0
86	21867.0	21867.0	19335.0	18159.0	17021.0
Average Error^C		0.32%	11.53%	16.91%	22.12%

a : **Hartree – Fock values from Fischer [20, pp.28-88].**

b : Values corresponding to corrected Thomas–Fermi energies, Eq. (25).

c : The average error is calculated for All Atoms in the range $1 \leq Z \leq 86$ with respect to the corresponding Hartree–Fock values. The average error of the set $[X_i]$ with respect to $[Y_i, i = 1, 2, \ldots, n$, is defined by

$$\left(\frac{1}{n}\right) \sum_{i=1}^{n} \left| \frac{X_i - Y_i}{Y_i} \right|$$

1, 2, and 3: Correspond to trial solutions proposed by Kesarwani and Varshni [14], Wu [13] and Csavinsky [12], respectively.

It is seen from Table 1 that solutions with initial slope close to the Baker's constant give better results for the total ionization energy with an average error 0.323%. It is concluded that none of these variational solutions is suitable for the model. One, therefore, should impose the condition $\phi'(o) = \phi'_B(o)$, in addition to the boundary ones, in order to get an agreement with the Hartree-Fock results.

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التحقق من صحة الحلول التغايرية لنموذج توماس - فرمي للذرة متعددة الإلكترونات

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(أُستلِم في ١٣ رمضان ١٤٠٧هـ، قُبِل للنشر في ٣ ربيع الآخر ١٤٠٨هـ)

ملخص البحث. لقد تمت مقارنة حلول تغايرية مختلفة الميل لمعادلة توماس - فيرمي. وتبين النتائج أنه فيما يتعلق بطاقات الربط، يجب اختيار دالة محاولة ميلها قريب جدًا من ثابت بيكر.