



Contents lists available at ScienceDirect

Journal of King Saud University – Science

journal homepage: www.sciencedirect.com



Variational relativistic correction to the Thomas-Fermi model of atoms

O.H. Mobarek^a, Ibrahim Al-lehyani^{a,b,*}^a Department of Physics, Faculty of Science, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia^b King Abdulaziz City for Science and Technology, Riyadh, Saudi Arabia

ARTICLE INFO

Article history:

Received 19 February 2019

Revised 18 April 2019

Accepted 21 May 2019

Available online 23 May 2019

ABSTRACT

A relativistic correction to the Thomas-Fermi model of atoms is obtained by utilizing the variational solutions proposed by Csavinszky [Phys. Rev. **166** (1968) 53]. The relativistic effect appears important for heavier elements, and our correction improves the ionization energies more noticeably with an increasing atomic number. The radial expectation values are calculated and compared with Hartree-Fock values. The non-relativistic results for $\langle r^2 \rangle$ are slightly better, and our relativistic correction enhanced the expectation value of the potential energy $\langle 1/r \rangle$.

© 2019 The Authors. Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

The Thomas-Fermi [TF] statistical model (Fermi, 1927; Thomas, 1927) of the atom provides a method to describe the ground state potentials and densities of large atoms, molecules, metals, and even neutron stars (Englert and Schwinger, 1984). This model is a crude approximation to the N-electron Schrödinger equation and is exact in the case of infinite nuclear charge. It does not account for the exchange effect, and it assumes that the electron gas is in its ground state. The use of electronic density to describe many-electron systems was an inception of several approaches in physics, including Density Functional Theory (DFT); and the simplicity of TF model formulation made it suitable to produce initial potentials in self-consistent field methods. Several trials were proposed to improve the theory (Lehtomäki and Lopez-Acevedo, 2017) but our aim here is to improve it while keeping it as simple as possible to produce pseudopotentials. In this work, the solution proposed by Csavinszky (1968, 1972, 1976, 1979) is corrected for relativistic effects. In Section 2, the variation solution is summarized to pave the way for the relativistic correction in Section 3. Our results are presented and discussed in Section 4.

2. Theory

The theory is detailed in references (Fermi, 1927; Thomas, 1927) and reviewed in many others (Spruch, 1981; Lieb, 1981). It leads to a differential equation of the form

$$\frac{d^2\phi}{dx^2} = \frac{\phi^{3/2}(x)}{\sqrt{x}} \quad (1)$$

The dimensionless variable x is related to the distance from the nucleus r by

$$x = \frac{r}{q} \quad (2)$$

the proportionality constant q is defined as

$$q = \frac{(3\pi)^{2/3}}{2^{7/3}} \frac{\hbar^2}{m_e e^2} Z^{-1/3} = 0.885 a_0 Z^{-1/3} \quad (3)$$

where m_e and e are the mass the charge of an electron, a_0 is the Bohr radius (=1 in atomic units), and Z is the atomic number.

For a neutral atom, Eq. (1) is to be solved with the boundary conditions

$$\phi(0) = 1, \quad \phi(\infty) = 0, \quad \phi'(\infty) = 0 \quad (4)$$

One of the shortcomings of this equation is that electron density decreases as the inverse fourth power of r , while it should decrease exponentially (Gombas, 1949). This shortcoming can be eliminated when the TF equation is replaced by its equivalent variational solution starting with the Lagrangian

$$L(\phi) = \int_0^\infty F(\phi, \phi', x) dx, \quad (5)$$

where

* Corresponding author.

E-mail address: iallehyani@kau.edu.sa (I. Al-lehyani).

Peer review under responsibility of King Saud University.



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

Substituting Eq. (6) into the Euler-Lagrange equation

$$\frac{\partial F}{\partial \phi} - \frac{\partial}{\partial x} \frac{\partial F}{\partial \phi'} = 0 \tag{7}$$

results in the TF Eq. (1).

In a previous work (Mobarek, 1991), $\phi(x)$ was proposed to take the form

$$\phi(x) = \left(ae^{-\alpha x} + be^{-\beta x} \right)^m, \tag{8}$$

where a, b, α, β are unknown parameters and the power $m = 1, 2, \text{ and } 4$. The original proposal of this form adopted the value $m = 2$ (Csavinsky, 1968). In this paper, we propose an improvement of the equivalent variational solution by taking the relativistic correction into consideration for the original proposed power. The first boundary condition of Eq. (4) requires that

$$a + b = 1. \tag{9}$$

and the solution must satisfy the normalization condition

$$\int_0^\infty n(r) d\tau = N \tag{10}$$

where N is the number of electrons, which equals the atomic number for neutral atoms, and the integration is over the entire space. The proper parameters are those that minimize the Lagrangian of Eq. (5).

The electron density $n(r)$ within the atom is related to $\phi(x)$ by Gombas (1949)

$$n(r) = \frac{Z}{4\pi q^3} \left(\frac{\phi(x)}{x} \right)^{3/2}. \tag{11}$$

3. Relativistic correction

To account for the relativistic effect, Hamiltonian must be written in its relativistic form and used to generate the electron density. Then, following the same procedure of the original TF equation will produce the relativistic form of the TF equation (Vallarta and Rosen, 1932)

$$\frac{d^2 \phi}{dx^2} = \frac{\phi^{3/2}(x)}{x^{1/2}} \left(1 + \lambda \frac{\phi(x)}{x} \right)^{3/2} \tag{12}$$

where $\lambda = \left(\frac{4}{3\pi} \right)^{2/3} \alpha^2 Z^{4/3}$ and α is the fine structure constant.

When $1 > \lambda \frac{\phi(x)}{x}$ the equation can be approximated by

$$\frac{d^2 \phi}{dx^2} = \frac{\phi^{3/2}(x)}{x^{1/2}} + \frac{3}{2} \lambda \frac{\phi^{5/2}(x)}{x^{3/2}} + \frac{3}{8} \lambda^2 \frac{\phi^{7/2}(x)}{x^{5/2}}. \tag{13}$$

The non-relativistic form of TF Eq. (1) is obtained as $\lambda \rightarrow 0$.

After the relativistic consideration, the variational solution of Eq. (6) becomes

$$F_{rel}(\phi, \phi', x) = \frac{1}{2} \left(\frac{d\phi}{dx} \right)^2 + \frac{2}{5} \frac{\phi^{5/2}}{x^{1/2}} + \frac{3}{7} \lambda \frac{\phi^{7/2}}{x^{3/2}} + \frac{1}{12} \lambda^2 \frac{\phi^{9/2}}{x^{5/2}}. \tag{14}$$

Eq. (13) can be deduced if the variational principle is applied to Eq. (14). The Lagrangian L can be written as

$$L = L_1 + L_2 + L_3 + L_4, \tag{15}$$

using the notation

$$L_1 = \int \frac{1}{2} \left(\frac{d\phi}{dx} \right)^2 dx, \tag{16}$$

$$L_2 = \int \frac{2}{5} \frac{\phi^{5/2}}{x^{1/2}} dx, \tag{17}$$

$$L_3 = \int \frac{3}{7} \lambda \frac{\phi^{7/2}}{x^{3/2}} dx, \tag{18}$$

$$L_4 = \int \frac{1}{12} \lambda^2 \frac{\phi^{9/2}}{x^{5/2}} dx. \tag{19}$$

Using the variable n defined as

$$n = \frac{\beta}{\alpha} \tag{20}$$

then substituting ϕ in Eq. (16) gives

$$L_1 = \alpha \left[\frac{a^4}{2} + 4a^3b \left(\frac{1+n}{3+n} \right) + a^2b^2 \left(\frac{1+4n+n^2}{1+n} \right) + 4ab^3 \left(\frac{n+n^2}{1+3n} \right) + \frac{b^4n}{2} \right], \tag{21}$$

$$L_2 = \frac{2}{5} \sqrt{\frac{\pi}{\alpha}} \left[\frac{a^5}{\sqrt{5}} + \frac{5a^4b}{\sqrt{4+n}} + \frac{10a^3b^2}{\sqrt{3+2n}} + \frac{10a^2b^3}{\sqrt{2+3n}} + \frac{5ab^4}{\sqrt{1+4n}} + \frac{b^5}{\sqrt{5n}} \right], \tag{22}$$

$$L_3 = -\lambda \frac{6\sqrt{\pi\alpha}}{7} \left[\sqrt{7a^7 + 7a^6b\sqrt{6+n} + 21a^5b^2\sqrt{5+2n} + 35a^4b^3\sqrt{4+3n} + 35a^3b^4\sqrt{3+4n} + 21a^2b^5\sqrt{2+5n} + 7ab^6\sqrt{1+6n} + \sqrt{7nb^7} \right], \tag{23}$$

$$L_4 = \lambda^2 \frac{\sqrt{\pi\alpha^2}}{9} \left[a^9 9^{3/2} + 9a^8b(8+n)^{3/2} + 36a^7b^2(7+2n)^{3/2} + 84a^6b^3(6+3n)^{3/2} + 126a^5b^4(5+4n)^{3/2} + 126a^4b^5(4+5n)^{3/2} + 84a^3b^6(3+6n)^{3/2} + 36a^2b^7(2+7n)^{3/2} + 9ab^8(1+8n)^{3/2} + b^9(9n)^{3/2} \right], \tag{24}$$

The normalization condition Eq. (10), using our form of ϕ and the electron density in Eq. (11), becomes

$$N = Z \frac{\sqrt{\pi}}{2\alpha^{3/2}} \left[\frac{a^3}{3^{3/2}} + \frac{3a^2b}{(2+n)^{3/2}} + \frac{3ab^2}{(1+2n)^{3/2}} + \frac{b^3}{(3n)^{3/2}} \right]. \tag{25}$$

For a neutral atom $Z = N$, Eq. (25) can be rearranged to write β in terms of the other parameters

$$\alpha = \left(\frac{\sqrt{\pi}}{2} \left[\frac{a^3}{3^{3/2}} + \frac{3a^2b}{(2+n)^{3/2}} + \frac{3ab^2}{(1+2n)^{3/2}} + \frac{b^3}{(3n)^{3/2}} \right] \right)^{2/3}. \tag{26}$$

Using this form of α and the boundary condition of Eq. (9), the Lagrangian depends on two parameters only, a and n besides its dependence on the atomic number Z . Now, $L(a, n)$ can be minimized with respect to these parameters for a specific element.

The limited-memory Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm was used for calculating the optimized values of the parameters. With an accuracy of 10^{-7} in the Lagrangian, the parameters were iterated until an optimized set is reached for each element. The minimization process is quick and does not need many computer resources.

4. Results and discussion

Table 1 shows the values of the optimizing parameters for selected elements. The total energy (energy necessary to remove

Table 1
The values of the parameters of Eq. (8) for neutral atoms for different elements.

Element	Z	a	b	α	β
H	1	0.722	0.278	0.178	1.760
He	2	0.722	0.278	0.178	1.762
Be	4	0.722	0.278	0.178	1.766
C	6	0.723	0.277	0.179	1.771
Ne	10	0.724	0.276	0.179	1.783
Ar	18	0.727	0.273	0.180	1.811
Kr	36	0.733	0.267	0.182	1.893
Xe	54	0.741	0.259	0.184	1.995
Hg	80	0.753	0.247	0.188	2.173
Rn	86	0.756	0.244	0.189	2.219
U	92	0.759	0.241	0.190	2.267

all electrons of an atom) is calculated from the relation (March, 1975)

$$E = \left(\frac{12}{7}\right) \left(\frac{2}{9\pi^2}\right) Z^{7/3} \phi'(0), \quad (27)$$

where $\phi'(0)$ is the slope of $\phi(x)$ at origin. The calculated energies are shown in Table 2 and compared with non-relativistic and empirical values, which are calculated using experimental parameters. The improvement due to the correction is apparent from the comparison with the empirical energies, especially for heavier elements. This is understandable because the relativistic effect is more pronounced with an increasing atomic number. For such a simple model, the accuracy is excellent.

In Table 3, the expectation values $\langle r^2 \rangle$ are presented and compared to Hartree-Fock (HF) values. In general, the non-relativistic calculation looks slightly better compared to HF, but the deviation from HF is quite large for both. In the case of $\langle r^2 \rangle$, there is a way to check the results further with the molar diamagnetic susceptibil-

ity, which is related to the mean value of the squared radii of the electron cloud by Gombas (1949)

$$\chi_m = -4.75 \times 10^{-6} \frac{N}{6} \langle r^2 \rangle. \quad (28)$$

This quantity is measured experimentally, and its values are tabulated in reference (Saito, 2009). The current calculation is much better compared to the experiment, especially for heavy ions.

To complete the comparison, we list in Table 4 the mean values of the reciprocal of the electron cloud radii $\langle 1/r \rangle$ and the mean values of the radii $\langle r \rangle$. The improvement in the relativistic calculation over the non-relativistic ones is small but clear.

Our calculation accounted for the minimization of the Lagrangian of the system. This could be the reason for generating the best results with the ionization energy, and -though small- in the values of $\langle 1/r \rangle$ because it represents the potential energy.

Pseudopotentials are approximated potentials that have proven to be highly useful in calculating different types of properties.

Table 2
Total ionization energies (in atomic units) of the non-relativistic calculation in reference (Mobarek, 1991) E_0 and the current work E_{rel} compared to the empirical values E_{emp} from reference (Gombas, 1949).

Element	Z	E_{emp}	E_0	err. (%)	E_{rel}	err. (%)
H	1	0.500	0.5984	19.68	0.5985	19.7
He	2	2.904	3.0156	3.84	3.0176	3.91
Be	4	14.68	15.198	3.53	15.223	3.70
C	6	37.86	39.143	3.39	39.256	3.69
Ne	10	129.5	128.96	0.42	129.65	0.12
Ar	18	525.4	508.09	3.29	514.47	2.08
Kr	36	2704	2560.6	5.30	2642.8	2.26
Xe	54	7079	6595.2	6.83	6964.1	1.62
Hg	80	18680	16501	11.66	18098	3.12
Rn	86	21866 ^a	19535	10.66	21628	1.09
U	92	25520	22864	10.41	25560	0.16

^a Empirical value is not available, HF value is used instead.

Table 3
Comparison (similar to Table 2) of the radial expectation value $\langle r^2 \rangle$ in atomic units. The third column is the Hartree-Fock (HF) values $\langle r^2 \rangle_{HF}$ (Saito, 2009), the fourth column is the non-relativistic values $\langle r^2 \rangle_0$ (Mobarek, 1991), and the sixth column is the current work $\langle r^2 \rangle_{rel}$. The last three columns are the molar magnetic Susceptibilities (in units of $10^{-6} \text{ cm}^3 \text{ mol}^{-1}$) of the current work χ_{rel} , the experimental values χ_{exp} from reference (Haynes, 2017), and the percentage deviation from the experimental values.

Element	Z	$\langle r^2 \rangle_{HF}$	$\langle r^2 \rangle_0$	err. (%)	$\langle r^2 \rangle_{rel}$	err. (%)	χ_{rel}	χ_{exp}	err. (%)
H	1	3.00	8.85	194.9	8.85	194.9	3.98	7.01	76.13
He	2	2.37	11.15	370.4	11.14	370.2	1.88	8.82	369.15
Be	4	17.32	14.04	18.9	14.03	19.0	9.0	11.11	23.44
C	6	13.79	16.08	16.6	16.05	16.3	6.0	12.71	111.83
Ne	10	9.37	19.06	103.4	18.99	102.6	6.74	15.04	123.15
Ar	18	26.03	23.19	10.9	22.99	11.7	19.6	18.21	7.09
Kr	36	39.53	29.21	26.1	28.59	27.7	28.8	22.65	21.35
Xe	54	62.65	33.44	46.6	32.24	48.5	43.9	25.54	41.82
Hg	80	68.63	38.12	44.5	35.89	47.7	33.4	28.42	14.91
Rn	86	81.24	39.05	51.9	36.55	55.0	-	28.95	-
U	92	123.59	39.94	67.7	37.17	69.9	28.0	29.44	5.14

Table 4Comparison of the expectation values of $\langle 1/r \rangle$ in (atomic units)⁻¹ among the HF (Saito, 2009), non-relativistic (Mobarek, 1991), and relativistic correction results.

Element	Z	$\langle 1/r \rangle_{HF}$	$\langle 1/r \rangle_0$	err. (%)	$\langle 1/r \rangle_{rel}$	err. (%)
H	1	1.00	1.82	82.1	1.82	82.1
He	2	3.37	4.59	36.0	4.59	36.0
Be	4	8.41	11.57	37.5	11.56	37.5
C	6	14.69	19.86	35.2	19.85	35.1
Ne	10	31.11	39.24	26.1	39.21	26.1
Ar	18	69.73	85.92	23.2	85.82	23.1
Kr	36	182.85	216.50	18.4	215.89	18.1
Xe	54	317.87	371.74	16.9	369.99	16.4
Hg	80	548.13	627.83	14.5	623.03	13.7
Rn	86	604.39	691.38	14.4	685.61	13.4
U	92	661.82	756.43	14.3	749.60	13.7

The TF equation can be used as a starting point to produce them and the parameterization process can be built into the generating codes. Moreover, the codes can use multi-condition processes (minimization that takes into account different values other than the Lagrangian) according to the calculation needed from the pseudopotentials.

Acknowledgment

The authors acknowledge the financial support for this work from King Abdulaziz City for Science and Technology Grant No. 31-105.

References

- Csavinszky, P., 1968. Approximate variational solution of the Thomas-Fermi equation for atoms. *Phys. Rev.* 166, 53–56.
- Csavinszky, P., 1972. Complementary variational principles in the Thomas-Fermi theory. *Phys. Rev. A* 5, 2198–2204.
- Csavinszky, P., 1976. Theory of the screening of impurity ions in semiconductors with spatially-variable dielectric constants. *Phys. Rev. B* 14, 1649–1659.
- Csavinszky, P., 1979. Approximate variational solution of the Thomas-Fermi-Amaldi equation for singly charged negative ions. *Int. J. Qual. Chem.* 13, 115–120.
- Englert, B.-G., Schwinger, J., 1984. Statistical atom: handling the strongly bound electrons. *Phys. Rev. A* 29, 2331–2363.
- Fermi, E., 1927. A statistical method for the determination of some properties of the atom. *Rend. Accad. Naz. Lincei* 6, 602–607.
- Gombas, P., 1949. *Die statistische Theorie des Atoms und ihre Anwendungen*. Springer-Verlag, Wien.
- Haynes, W.M., 2017. *CRC Handbook of Chemistry and Physics*. CRC Press, New York.
- Lehtomäki, J., Lopez-Acevedo, O., 2017. Self-consistent assessment of Englert-Schwinger model on atomic properties. *J. Chem. Phys.* 147, 234102.
- Lieb, E.H., 1981. Thomas-Fermi and related theories of atoms and molecules. *Rev. Mod. Phys.* 53, 603–641.
- March, N.H., 1975. *Self-Consistent Fields in Atoms: Hartree and Thomas-Fermi Atoms*. Pergamon Press, New York.
- Mobarek, O.H., 1991. Variational correction of the Thomas-Fermi model of atoms. *Arab Gulf J. Scient. Res.* 9, 63–78.
- Saito, S.I., 2009. Hartree-Fock-Roothaan energies and expectation values for the neutral atoms He to Uuo: the B-spline expansion method. *Atom. Data Nucl. Data Tables* 95, 836–870.
- Spruch, L., 1981. Pedagogic notes on Thomas-Fermi theory (and on some improvements): atoms, stars, and the stability of bulk matter. *Rev. Mod. Phys.* 63, 151–209.
- Thomas, L.H., 1927. The calculation of atomic fields. *Proc. Camb. Philos. Soc.* 23, 542–548.
- Vallarta, M.S., Rosen, N., 1932. The relativistic Thomas-Fermi atom. *Phys. Rev.* 41, 708–712.