J. King Saud Univ., Vol. 2, *Science (2)*, pp. 185-194 (1410/1990)

Electronic Potentials of Neutral Atoms

Ahmed Alharkan and Hamad Alhendi
Department of Physics, College of Science, King Saud University, P.O. Box 2455,
Riyadh, 11451, Saudi Arabia

(Received 25 September 1988; accepted for publication 17 January 1989)

Abstract. The variational techniques, the Z^{-1} expansion and the Hellmann-Feynman theorem are applied to the Thomas-Fermi model to calculate the electronic potentials of neutral atoms to second leading order correction. It is shown that the obtained electronic potentials are in agreement with the Hartree Fock approximation with an average error less than 0.5% for $2 \leqslant Z \leqslant 86$. Also the ratio of the binding energy to the electronic potential tends to the constant value 3/7.

Introduction

Although the Thomas-Fermi theory(TF) [1,2] of many electron systems is an exact model at large nuclear charge limit ($Z \rightarrow \infty$) [2], it is in poor agreement with the Hartree approximation [3], the quantum mechanical equivalent of the TF-theory [4]. However, there are indications that this model could provide an accurate quantum description of atoms, molecules, and solids [5] and has thus given rise to many practical calculation schemes [6].

Recently, there has been a renewed interest in the TF-model and related theories. Of particular interest is the calculation of the leading corrections to the binding energies and the electronic potentials of many-electron atoms [7-13].

In two previous paper [12,13], by making use of the Z^{-1} expansion theory [9-11], the TF- model, and the variational techniques [14], we have expressed the ionization energy of many electrons atom to the second order corrections, in terms of just the initial slope of the solutions of the TF- model and the atomic number Z. We have obtained a new energy formula for the ground state ionization energy of neutral atoms, which is in remarkable agreement with Hartree-Fock (HF) calculations (with an average error less than 0.25 %).

In the present paper, using the new energy formula for the ground state ionization energy [12], we calculate the expectation values of the inverse of the radial distance from the nucleus ($< r^{-1} >$), and the electronic potential at the atomic nucleus. Our calculations show that the electronic potential of an atom is in excellent agreement, for all Z, with the HF-values. We also find that the ratio (Q) of the binding energy (E) to the electronic potential (V_{ne}) tends, as in the corresponding HF- ratio, to the universal constant 3/7 [9]. For completeness, using the expectation values $< r^{-1} >$, we compare three types of trial solutions that, in the zero order corrections, have been suggested in the literature to be suitable for the low [16], medium [17], and higher [18] atomic number atoms. We again find that, as in previous calculations [12], only a trial function with its slope close to the (negative) Baker's costant (B) [19] is acceptable for the model.

Thomas-Fermi Electronic Potential: Leading Corrections

To calculate the electronic potential, through the use of Hellmann- Feynman theorem, one needs to know the total binding energy. The zero order binding energy of the TF-model is calculated from [1] (in units of $[\frac{e^2}{a_0}]$)

$$E(Z) = C_o Z^{7/3} \tag{1}$$

where

$$C_o = (\frac{12}{7}) (\frac{2}{9\pi^2})^{1/3} \phi'(0) \tag{2}$$

and $\phi'(0)$ is the initial slope of an acceptable solution of the TF- equation. In particular, for the Baker's solution, numerical calculations give [1]

$$\phi_B'(0) = - B = - 1.588070972 \tag{3}$$

where B is the Baker's constant [19].

The binding energy to the second leading correction has been calculated in ref. [12], and is given by

$$E(Z) = C_o F(Z) Z^{7/3}$$

where

$$F(Z) = 1 - 0.6504 Z^{-1/3} + 0.364 Z^{-2/3} \tag{4}$$

We now consider the calculation of the electronic potentials. The partial derivative of E(Z,N) with respect to Z is related to the expectation values of r^{-1} (the inverse of the radial distance from the nucleus), denoted by $< r^{-1} >$, through the Hellmann – Feynmann theorem by

$$- < r^{-1}(Z, N) > = (\frac{\partial E}{\partial Z})_N \tag{5}$$

using Eqs. (1) and (5), one then obtains the zero order expectation values of $< r^{-1} >_o$

$$< r^{-1} >_o = -\frac{7}{3} C_o Z^{4/3} \tag{6}$$

The zero-order electronic potential $V_{ne}^{(o)}$ is calculated from:

$$V_{ne}^{(o)} = - Z < r^{-1} >_o \tag{7}$$

Similarly, using Eqs. (4) and (5) one obtains the corrected $< r^{-1} >$ to the second leading correction:

$$< r^{-1} > = -\frac{7}{3} C_o G(Z) Z^{4/3}$$

where

$$G(Z) = 1 - 0.5574857 \ Z^{-1/3} + 0.26 \ Z^{-2/3} \tag{8}$$

The corrected electronic potential V_{ne} to the second leading correction is, now, calculated from:

$$V_{ne} = - Z < r^{-1} > \tag{9}$$

which upon using Eq. (6) becomes

$$V_{ne} = \frac{7}{3} C_o Z^{7/3} G(Z) \tag{10}$$

As can be easily seen the resulting Eq. (10) for the electronic potential reduces to the zero order TF-potential for $\phi'(o) = \phi_B'(o)$ and large Z (see Eq. (7)). It can also be seen that Eq. (10) produces, almost, the same values as in the HF-approximation [20, pp. 28-88] for the case in which $\phi'(o) = \phi_B'(o)$. In general this formula could be applied to various possible suitable trial functions of the TF-model.

Results and Conclusion

It is well known that atomic energies, as well as electronic potentials computed from Eqs. (1) and (7) are rather inaccurate with high average error exceeding 20%

for the first and 18% for the later (see Table 1). We have found, however, that accurate predictions can be obtained using Eqs. (4) and (10) (see Table 2). The average errors calculated from these equations are dramatically reduced to 0.21% and 0.41%, respectively, when the initial slope equals to -1.588070972 the negative of Baker's constant. In Tables 1 and 2, we also calculate, $Q = E/V_{ne}$, the ratio of the atomic energy E and electronic potential V_{ne}.

Table 1. Uncorrected binding energies, electronic potentials, and their ratio $Q = E / V_{ne}$.

Z	$-E^a$(HF)	$-E^b(\phi_B')$	$-V^a_{ne}$(HF)	$-V^b_{ne}(\phi_B')$	Q(HF)^a	Q^b
2	2.8617	3.8742	6.7491	9.0399	0.42401	0.42857
4	14.5730	19.5249	33.6352	45.5581	0.43327	0.42857
6	37.6876	50.2885	88.1369	117.340	0.42760	0.42857
9	99.4093	129.523	238.667	302.221	0.41652	0.42857
12	199.615	253.438	479.046	591.356	0.41669	0.42857
15	340.718	426.575	812.221	995.342	0.41949	0.42857
19	599.165	740.527	1422.96	1727.90	0.42107	0.42857
24	1043.31	1277.25	2478.43	2980.25	0.42096	0.42857
29	1638.95	1986.30	3922.24	4634.70	0.41786	0.42857
34	2399.87	2878.94	5743.30	6717.54	0.41786	0.42857
36	2752.05	3289.69	6582.58	7675.94	0.41808	0.42857
42	3975.44	4713.72	9466.19	10998.7	0.41996	0.42857
46	4937.78	5828.42	11755.8	13599.6	0.42003	0.42857
50	6022.93	7080.20	14325.4	16520.5	0.42044	0.42857
54	7232.14	8472.94	17165.2	19770.2	0.42133	0.42857
58	8566.92	10010.3	20299.5	23357.4	0.42203	0.42857
66	11641.5	13532.7	27675.8	31576.3	0.42064	0.42857
72	14321.3	16579.0	34118.7	38684.3	0.41975	0.42857
77	16806.1	19390.7	40032.4	45245.0	0.41981	0.42857
84	20676.5	23755.7	49181.1	55429.9	0.42042	0.42857
85	21266.9	24420.8	50568.1	56981.9	0.42056	0.42857
86	21866.8	25096.4	51977.6	58558.4	0.42070	0.42857
	Average Error$^{(c)}$	20.264%		18.006%		1.996%

a : Obtained from E(HF) and $< r^{-1}$ (HF) $>$ values Ref. [20].

b : Obtained from E ($\phi_B'(0)$) Eq. (1) and $< r^{-1} (\phi_B' (o)) >$ Eq. (7)

c : The average error is calculated for All Atoms in the range $2 \leqslant Z \leqslant 86$ with respect to the corresponding Hartree-Fock values. The average error of a set (X_i) with respect to (Y_i), i = 1, 2, ..., n, is defined by

$$(\frac{1}{n}) \sum_{i=1}^{n} \left| \frac{x_i - y_i}{y_i} \right| .$$

Table 2. Corrected binding energies, electronic potentials, and their ratio $Q = E / V_{ne}$.

Z	$-E^a$(HF)	$-E^b(\phi_B')$	$-V^a_{ne}$(HF)	$-V^b_{ne}(\phi_B')$	Q(HF)^a	Q^b
2	2.8617	2.7626	6.7492	6.5206	0.42401	0.42368
4	14.5730	14.3455	33.6352	34.2591	0.43327	0.41873
6	37.6876	37.8325	88.1369	90.5800	0.42760	0.41767
9	99.4093	99.9206	238.667	239.383	0.41652	0.41741
12	199.615	199.040	479.046	476.692	0.41669	0.41754
15	340.718	339.606	812.221	812.894	0.41949	0.41777
19	599.165	597.886	1422.96	1430.00	0.42107	0.41810
24	1043.31	1045.13	2478.43	2497.38	0.42096	0.41849
29	1638.95	1642.40	3922.24	3921.37	0.41786	0.41883
34	2399.87	2400.80	5743.30	5727.97	0.41786	0.41914
36	2752.05	2751.53	6582.58	6563.01	0.41808	0.41925
42	3975.44	3973.74	9466.19	9471.39	0.41996	0.41955
46	4937.78	4935.69	11755.8	11759.1	0.42003	0.41973
50	6022.93	6020.11	14325.4	14337.0	0.42044	0.41990
54	7232.14	7230.85	17165.2	17214.1	0.42133	0.42005
58	8566.92	8571.52	20299.5	20398.8	0.42203	0.42020
66	11641.5	11656.4	27675.8	27723.1	0.42064	0.42046
72	14321.3	14335.7	34118.7	34081.6	0.41975	0.42063
77	16806.1	16816.2	40032.4	39966.1	0.41981	0.42076
84	20676.5	20678.6	49181.1	49125.4	0.42042	0.42093
85	21266.9	21268.2	50568.1	50523.3	0.42056	0.42096
86	21866.8	21867.4	51977.6	51943.9	0.42070	0.42098
	Average Error$^{(c)}$	0.212%		0.409%		0.417%

a : Obtained from E(HF) and $< r^{-1}$ (HF) $>$ values Ref. [20].

b : Obtained from E $(\phi_B'(0))$ Eq. (4) and $< r^{-1} (\phi_B'(o)) >$ Eq. (8)

c : The average error is calculated for All Atoms in the range $2 \leq Z \leq 86$ with respect to the corresponding Hartree-Fock values. The average error of a set (X_i) with respect to (Y_i), $i = 1, 2, \ldots, n$, is defined by $(\frac{1}{n}) \sum_{i=1}^{n} \left| \frac{x_i - y_i}{y_i} \right|$.

In Fig. 1, the ratio Q is ploted versus Z for both the hartree- Fock values and the present calculations Eqs. (4,10). In both calculations the ratio Q oscillates about the Thomas-Fermi ratio $3/7 \simeq 0.42857$, and tends to it for large Z. However, our calculations oscillate about $Q_{TF} = 3/7$ smoothly in contrast to the sharp oscillation of the Hartree-Fock. It is to be noticed that, in our formulation, the ratio Q is independent of the initial slope $\phi'_{\pm}$ (o), and thus independents of the solutions of the TF-equation.

Table 3. Uncorrected expectation values of r^{-1}.

Z	$< r^{-1}(HF) >^a$	$< r^{-1}(\phi_B') >^b$	$< r^{-1}(\phi_1') >^b$	$< r^{-1}(\phi_2') >^b$	$< r^{-1}(\phi_3') >^b$
2	3.37456	4.51994	3.51822	3.99659	3.75339
4	8.40880	11.38953	8.86535	10.07078	9.45795
6	14.68948	19.55664	15.22244	17.29224	16.23997
9	26.51857	33.58014	26.13801	29.69202	27.88519
12	39.92046	49.27964	38.35814	43.57373	40.92217
15	54.14805	66.35610	51.65007	58.67297	55.10259
19	74.89268	90.94189	70.78708	80.41206	75.51881
24	103.26781	124.17691	96.65646	109.79892	103.11741
29	135.24973	159.81708	124.39794	141.31244	132.71326
34	168.92065	197.57460	153.78752	174.69815	164.06737
36	182.84938	213.22063	165.96603	188.53258	177.05995
42	225.38559	261.87350	203.83632	231.55212	217.46165
46	255.56064	295.64438	230.12279	261.41278	245.50523
50	286.50723	330.40952	257.18317	292.15259	274.37445
54	317.87408	366.11502	284.97552	323.72388	304.02457
58	349.99045	402.71381	313.46320	356.08505	334.41647
66	419.33029	478.42935	372.39841	423.03375	397.29117
72	473.87115	537.28235	418.20822	475.07236	446.16315
77	519.90076	587.59784	457.37265	519.56201	487.94550
84	585.48950	659.87994	513.63538	583.47485	547.96906
85	594.91925	670.37494	521.80444	592.75470	556.68420
86	604.39032	680.91119	530.00562	602.07098	565.43359
Average Error(c)		18.006%	8.764%	4.405%	4.383%

a : Hartree - Fock values from Ref. [20]

b : Values corresponding to uncorrected $< r^{-1} (\phi') >$ Eq. (6),

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

$$(\frac{1}{n}) \sum_{i=1}^{n} \left| \frac{x_i - y_i}{y_i} \right| .$$

1,2, and 3 : correspond to initial slopes of trial solutions proposed by Csavinsky [16], Kesarwani et al. [18], Wu [17], respectively.

Table 4. Corrected expectation values of r^{-1}

Z	$<r^{-1}(HF)>^a$	$<r^{-1}(\phi_B')>^b$	$<r^{-1}(\phi_1')>^b$	$<r^{-1}(\phi_2')>^b$	$<r^{-1}(\phi_3')>^b$
2	3.37456	3.26029	2.53773	2.88279	2.70737
4	8.40880	8.56478	6.66663	7.57309	7.11225
6	14.68948	15.09666	11.75089	13.34867	12.53648
9	26.51867	26.59817	20.70340	23.51846	22.08731
12	39.92046	39.72432	30.92050	35.12478	32.98736
15	54.14805	54.19292	42.18252	47.91812	45.00219
19	74.89268	75.26295	58.58295	66.54852	62.49889
24	103.26781	104.05768	80.99610	92.00922	86.41025
29	135.24973	135.21973	105.25191	119.56310	112.28741
34	168.92065	168.46976	131.13300	148.96326	139.89851
36	182.84938	182.30592	141.90274	161.19739	151.38815
42	225.38559	225.50926	175.53122	199.39836	187.26451
46	255.56064	255.63252	198.97847	226.03375	212.27908
50	286.50723	286.73996	223.19180	253.53938	238.11093
54	317.87408	318.77878	248.13007	281.86853	264.71619
58	349.99045	351.70273	273.75732	310.98035	292.05649
66	419.33029	420.04703	326.95496	371.41132	348.81009
72	473.87115	473.35501	368.44867	418.54697	393.07742
77	519.90076	519.04010	404.00888	458.94232	431.01465
84	585.48950	584.82642	455.21542	517.11145	485.64407
85	594.91925	594.39227	462.66132	525.56976	493.58765
86	604.39032	603.99915	470.13907	534.06427	501.56525
Average Error$^{(c)}$		0.409%	22.033%	11.431%	16.821%

a : Hartree - Fock values from Ref. [21]

b : Values corresponding to uncorrected $< r^{-1} (\phi')$ Eq. $>$ (8),

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

$$(\frac{1}{n}) \sum_{i=1}^{n} \left| \frac{x_i - y_i}{y_i} \right| .$$

1,2, and 3 : correspond to initial slopes of trial solutions proposed by Csavinsky [16], Kesarwani et al. [18], Wu [17], respectively.

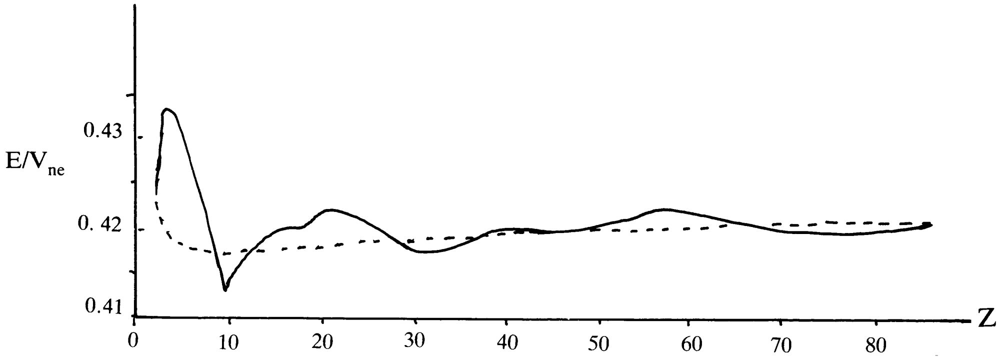

Fig. 1 **E/V$_{ne}$ versus Z for ground state atoms. Solid line: Hartree-Fock ratios. Dashed line: Eqs. (4,10). Data obtained from Ref. [20 p, 28-88].**

Finally in Table 3 and 4, we calculate the uncorrected ad corrected expectation values of the inverse of the radial distance, and compare three variational solutions with different initial slopes. It is shown that the average error is reduced from 18% to 0.41% for the initial slope equals to - 1.588070972. This result is in agreement with our previous calculations. We consider this as another way of justifying the relevance of the new energy formula.

References

[1] Gombas, P. *Encyclopedia of Physics.* Flugge, F. (Ed.) Vol. XXXVI, Berlin: Springer, (1956).

[2] Leib, E.H. and Simon, S. "Thomas - Fermi Theory Revisited." *Phys. Rev. Lett.,* 31 (1973), 681-683; Leib, E.H. "Thomas - Fermi and Related Theories of Atoms and Moleculers." *Rev. Mod. Phys.,* 53 (1981), 603-641.

[3] Hartee, D.R. "The Wave Mechanics of an Atoms with a Non - Columbo Central Field." *Proc. Camb. Phill. Soc.,* 24 (1927), 111-132.

[4] Dirac, P.A. "Note on Exchange Phenomena in Thomas Fermi Atom." *Proc. Camb. Phill. Soc.,* 26 (1930), 376-385.

[5] March, N.H. *Theory of the Inhomogenous Electron Gas,* Lundquist, S. and March, N.H. (Eds.), New York: Plenum (1983) 1; Kohn, W. and Vashisha, P., *ibid,* 79.

[6] Csavinszky, P. "Complementary Variational Principle in the Thomas-Fermi Theory." *Phys. Rev.,* 36 (1972), 2198-2204) Gross, E.K.U. and Dreilzer, R.M. "Thomas-Fermi Approach to Diatomic Systems. I. Solution of the Thomas - Fermi and Thomas - Fermi - Dirac - Weizsacker Equations." *Phys. Rev.,* A20 (1979), 1789-1807. Toepfer, A., Gross, E.K.U. and Dreilzer, R.M. "Thomas - Fermi Approach to Diatomic Systems. II. Correlation Diagrams for N-M and Ne-Ne." *Phys.* Rev. A20 (1979), 1808 - 1815; B rack, M. *Density Functional Methods in Physics,* Dreizler, R.M. and De providencia, J. (Eds.) New York: Plenum, (1985), 331.

[7] Politzer, P., and Parr, R.G. "Some New Energy Formulas for Atoms and Molecules." *J. Chem. Phys.,* 61 (1974), 4258-4262.

[8] Englerts, B.G. and Schwinger, J. "Statistical Atom: Handling the Strongly Bound Electrons." *Phys. Rev.*, A29 (1984), 2331-2338.

[9] Levy, M. and Tal, Y. "Energy Density Relations and Screening Constants in Atoms,"*J. Chem. Phys.*, 61 (1980) 5168-5173, Tal, Y. and Lavy, M. "Recursion Theory for Nonrelativistic Ground - State Atomic Energies and Expectation Values of r." *Phys. Rev.*, A25 (1982), 1838-1845.

[10] Lai, C.S. "The Nonrelativistic Ground - State of a Neutral Atom with Electron Screening Represented by the Hulthen Potential." *Phys. lett.*, A112 (1985), 211-214; "Remarks on the Z Expansion theory and the Z Expansion of the Ground-State Energy of a Neutral Atom." *Cand. J. Phys.* (1985), 1555-1558; Yang, W. "Gradient Correction in Thomas Fermi Theory." *Phys. Rev.*, A34 (1986), 4575-4585.

[11] Shakeshaft, R. and Spruch, L. "Remarks on the Existence and Accuracy of the Z Expansion of the Nonrelativistic Ground-State Energy of a Neutral Atom." *Phys. Rev.*, A23 (1981), 2118-2126.

[12] Agil, I., Alharkan, A., Alhendi, H. and Alnaghmoosh, A. "Comparison of Variation Solutions of The Thomas-Fermi Model in Terms of the Corrected Ionization Energy." "*Z. Naturforsch*, 42a (1987), 943-947.

[13] Alhendi, H. alharkan, A., Alnaghmoosh, A. and alagil, I. "Validity of Variational Solutions of The Thomas-Fermi Model of a Many Electrons Atom." *J. King Saud Univ.*, Vol. 1 *Science (1,2)* (1989), 105-113.

[14] Firsov, O. B. "Interaction Energy of Atoms for Small Nuclear Separations." *Sov. Phys. JEPT*, 5 (1957), 1192-1196.

[15] Sucher, J. "Ground - State Energy of any Atom." *J. Phys.*, B11 (1978), 1515-1520.

[16] Csavinsky, P. "Universal Approximate Analytical Solution of the Thomas - Fermi Equation for Ions." *Phys. Rev.* (1973), 1688-1701.

[17] Wu, M.S. "Modified Variatioal Solution of the Thomas-Fermi Equation for Atoms." *Phys. Rev.*, A26 (1981), 1838-1845.

[18] Kesarwani, R.N. and Varshni, Y.P. "Complementary Variational Principle in the Thomas-Fermi Theory." *Phys. Rev.*, A24 (1981), 1123-1126.

[19] Baker, E. "The Application of the Fermi-Thomas Statistical Model to Calculation of Potential Distribution in Positive Ions." *Phys. Rev.*, 36 (1930), 630-640.

[20] Fischer, C.F., *The Hartree-Fock Methods for Atoms*, New York: Willy and Sons, 1977.

الجهود الالكترونية لذرات متعادلة

أحمد الحركان و حمد الهندي

قسم الفيزياء، كلية العلوم، جامعة الملك سعود، ص.ب ٢٤٥٥، الرياض ١١٤٥١،
المملكة العربية السعودية

(استلم في ١٤ صفر ١٤٠٩هـ، قُبل للنشر في ١٠ جمادي الآخرة ١٤٠٩هـ)

ملخص البحث. في هذه المقالة تم تطبيق الوسائل التغايرية، والنشر من نوع Z^{-1} ، ونظرية هلمان - فاينمان، على نموذج توماس - فيرمي، وذلك لحساب الجهود الأيونية لذرات متعادلة للرتبة الثانية. كما تم تبيان أن الجهود الألكترونية المستحصلة هنا تتوافق مع تقريب هارتري - فوك بمتوسط خطأ لا يتجاوز 0.5% للذرات في المدى $2 < Z < 86$. كما أن النسبة بين طاقة الربط إلى الجهد الأيوني تؤول إلى قيمتها الثابتة 3/7 .