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Statistical atomic models with piecewise exponentially decaying electron densities[*†]

Wen-Ping Wang[‡] and Robert G. Parr[§]

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218
and Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514

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If it is assumed that the electron density of an atom in its ground state is piecewise exponentially decreasing as a function of the distance from the nucleus, then it is shown that much improved values for the energy, and electron densities exhibiting shell structure, are obtained from optimization of the density functionals of Thomas-Fermi, Thomas-Fermi-Dirac, and Thomas-Fermi-Dirac with inhomogeneity correction. An inhomogeneity correction which is one-ninth of the original Weizsacker correction is favored. Numerical results are presented for all first-row atoms and selected second-row atoms, and comparisons are made with results of other methods.

I. PREFACE

If the electron density $\rho(\vec{r})$ of the nondegenerate ground state of an atom with atomic number Z is known, the total energy E in principle can be computed from the energy-density functional,

$$E[\rho] = T[\rho] + V_{ne}[\rho] + V_{ee}[\rho], \tag{1}$$

where $T[\rho]$ is the kinetic energy, $V_{ne}[\rho]$ is the nuclear-electron attraction energy,

$$V_{ne}[\rho] = -Z\int \frac{\rho(1)}{r_1}\,dv_1, \tag{2}$$

and $V_{ee}[\rho]$ is the electron-electron repulsion energy. Furthermore, $V_{ee}[\rho]$ can be separated into two parts,

$$V_{ee}[\rho] = J[\rho] + K[\rho], \tag{3}$$

where the quantity,

$$J[\rho] = \frac{1}{2}\int\int \frac{\rho(1)\rho(2)}{r_{12}}\,dv_1\,dv_2, \tag{4}$$

is the classical Coulomb repulsion energy between ρ and itself, and $K[\rho]$ is the rest, the so-called exchange-correlation energy. If only a normalized approximation to ρ is known, say $\tilde{\rho}$, inserted into Eq. (1) it gives a value higher than the true E; Eq. (1) is a minimum for the true density. That is,

$$\delta\{E[\tilde{\rho}] - \mu N[\tilde{\rho}]\} = 0, \quad \text{for } \tilde{\rho} = \rho, \tag{5}$$

where

$$N[\tilde{\rho}] = \int \tilde{\rho}(1)\,dv_1, \tag{6}$$

and μ is a Lagrange multiplier, the chemical potential of the atom.

The foregoing theorems, due to Hohenberg and Kohn,[1] hold for any number of electrons and provide the fundamental basis for the search, now more than half a century old, for the correct energy-density functional. The trouble is that, except for the trivial case of one-electron systems, the correct $T[\rho]$ and $K[\rho]$ are not as yet known.

In the present work, we shall not be concerned with $K[\rho]$. We formally neglect the correlation energy part of $K[\rho]$, and we adopt the homogeneous electron gas approximation of Dirac[2] for the exchange energy,[3]

$$K_0[\rho] = \frac{-3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int \rho^{4/3}(1)\,dv_1 = -\kappa_e\int \rho^{4/3}\,dv. \tag{7}$$

Neither shall we be much concerned with $T[\rho]$. For it, we adopt the first two terms of the gradient expansion,[1,4]

$$T[\rho] = T_0[\rho] + T_2[\rho], \tag{8}$$

where the quantity,

$$T_0[\rho] = \tfrac{3}{10}(3\pi^2)^{2/3}\int \rho^{5/3}\,dv = \kappa_F\int \rho^{5/3}\,dv, \tag{9}$$

is the original kinetic energy formula of Thomas[5(a)] and Fermi,[5(b)] while the quantity,

$$T_2[\rho] = \frac{1}{9}\left(\frac{1}{8}\int \frac{(\nabla\rho)(\nabla\rho)}{\rho}\,dv\right) = \frac{1}{9}T_W, \tag{10}$$

is one-ninth the inhomogeneity correction T_W introduced by Weizsacker.[6] Although some of it is very new, the evidence for Eq. (8) is strong. Not only has it been derived theoretically,[1,4,7] but also it has been shown to give the Hartree-Fock kinetic energy within 1% for many atoms, when ρ is taken to be the Hartree-Fock density.[8,9]

It is commonly thought that the shell structure of atoms is inaccessible through simple energy-density functionals.[10] We shall show that, to the contrary, shell structure can be obtained if we impose a certain constraint on the atomic density, that it is piece wise exponentially decaying.

II. MODEL

Hartree-Fock electron densities[11] for ground state of the atoms He, Ne, Ar, Kr, and Xe are shown in Figs. 1–5. Note the remarkable accuracy of the generalization: The electron density of the ground state of an atom is a monotonically decreasing function of r,[12] well represented as a continuous piecewise exponential function of r with as many different exponential regions as there are principal quantum numbers.

In an actual or Hartree-Fock atom, the transitions from one exponential to the next occur over certain intervals and cannot be associated with single points. However, the minima in the radial density are well-defined and physically meaningful points, which allow one to separate an atom into different exponential regions.[13] This fact about electron densities is our point of departure. We shall see that, when it is imposed as a constraint, approximate energy-density functionals give much improved results.

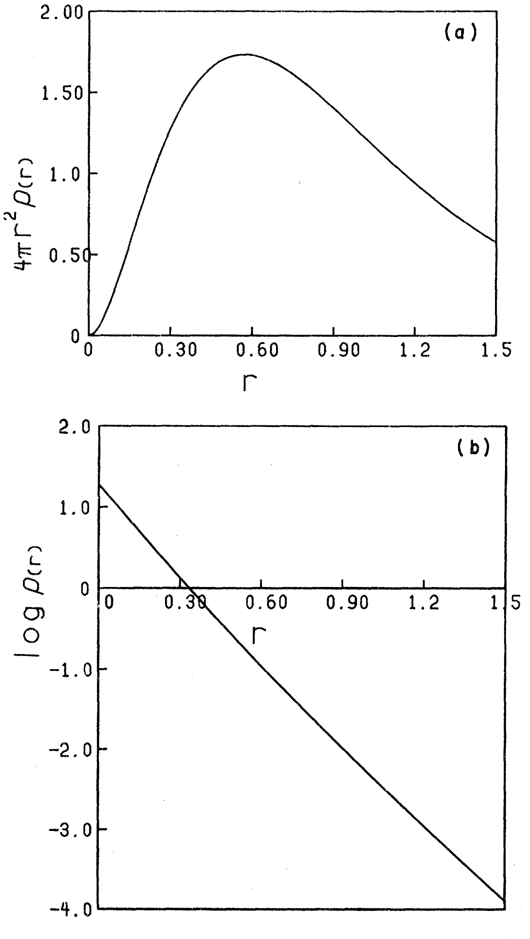

FIG. 1. (a) Radial distribution function for He. (b) Electron density of He.

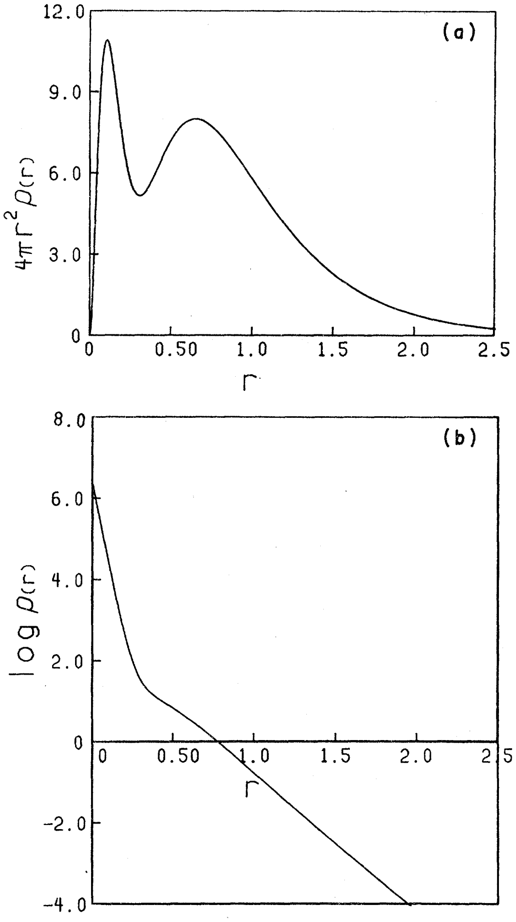

FIG. 2. (a) Radial distribution function for Ne. (b) Electron density of Ne.

The piecewise exponential behavior holds as well for other atoms as for noble gas atoms. While Figs. 1–5 depict Hartree-Fock and not exact densities, we may presume that exact densities will show similar behavior.[14]

In the present paper, we will discuss first-row atoms in detail, and we also will present some results on second-row atoms. Third- and fourth-row atoms will be discussed in a later paper.

Table I gives the Hartree-Fock energies and energy components for the first-row atoms in their ground states. Table II gives the parameters characterizing the electron densities. The latter show that the number of zones in an atom is the number of distinct values of the principal quantum number. A minimum in the radial distribution function defines a good radius for separating the atoms into zones. The number of electrons in the zone near the nucleus is close to the number of electrons in the K shell.

The measure of validity of an approximate ener-

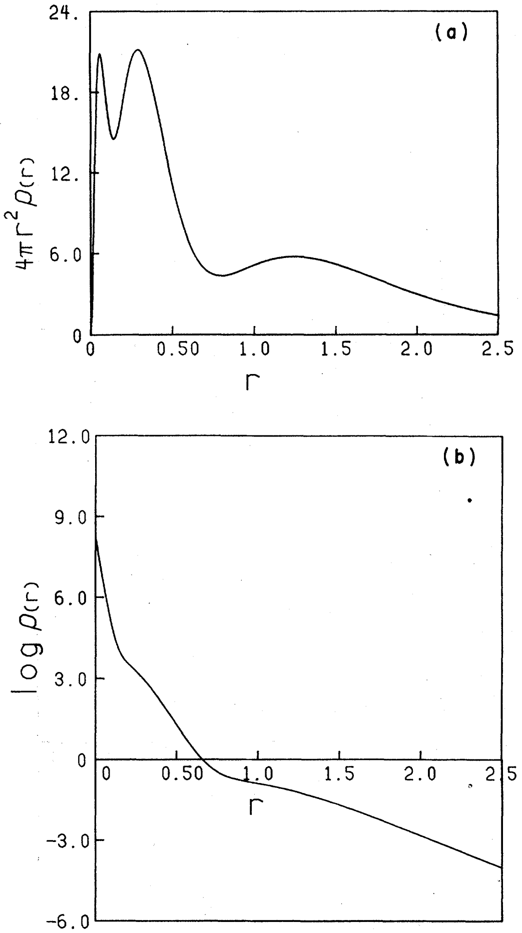

FIG. 3. (a) Radial distribution function for Ar. (b) Electron density of Ar.

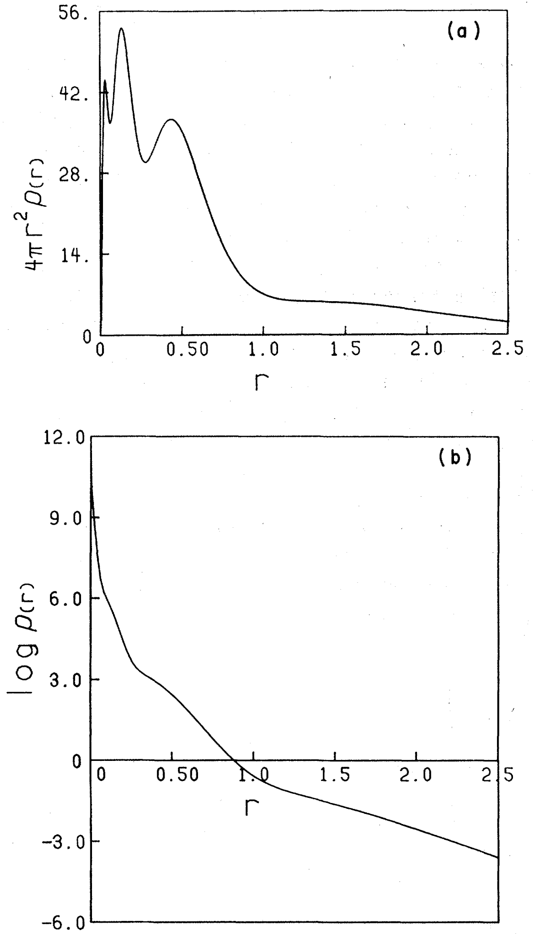

FIG. 4. (a) Radial distribution function for Kr. (b) Electron density of Kr.

gy functional we take to be the extent to which a minimization with respect to ρ, in accord with Eq. (5), gives energy quantities in agreement with Table I and densities in agreement with Table II.[15]

These considerations lead us to postulate, as a constraint on the electron density,

$$\rho(r)=\begin{cases} A_1\exp(-2\lambda_1 r), & 0\le r\le R_1 \quad (K\text{ shell}),\\ A_2\exp(-2\lambda_2 r), & R_1\le r\le R_2 \quad (L\text{ shell}),\\ A_3\exp(-2\lambda_3 r), & R_2\le r\le R_3 \quad (M\text{ shell}),\end{cases} \tag{11}$$

etc., with $0<R_1<R_2<$etc. and $\lambda_1\ge\lambda_2\ge\lambda_3\ge$etc. We assume that ρ is continuous but $d\rho/dr$ not necessarily so.

When Eq. (11) is inserted in energy functionals of the form of Eq. (1), we obtain modifications of the customary statistical models for atoms; we call the models so defined Modified Models. Different models are defined by different assumptions on $T[\rho]$ and $K[\rho]$, and also by whether a correction is included for the discontinuity in $d\rho/dr$. One determines the parameters: $A_1, A_2, \ldots$; $\lambda_1, \lambda_2, \ldots; R_1, R_2, \ldots$; by minimization of the approximate functional, subject to continuity and normalization constraints.

If the Weizsacker-type inhomogeneity term of Eq. (10) is regarded as arising from a kinetic energy increment of the form $-(\frac{1}{18})\int \rho^{1/2}\nabla^2(\rho^{1/2})\,dv$, we would expect contributions to the kinetic energy due to discontinuities in $\nabla\rho$, of magnitude

$$T_s[\rho]=\frac{1}{36}\oint\left[\left(\frac{d\rho}{dr}\right)_{r=R^-}-\left(\frac{d\rho}{dr}\right)_{r=R^+}\right]dS. \tag{12}$$

If the proper inhomogeneity term is merely Eq. (10) as it stands, on the other hand, there would be no need for such a contribution. We have made calculations both with and without these singularity contributions.

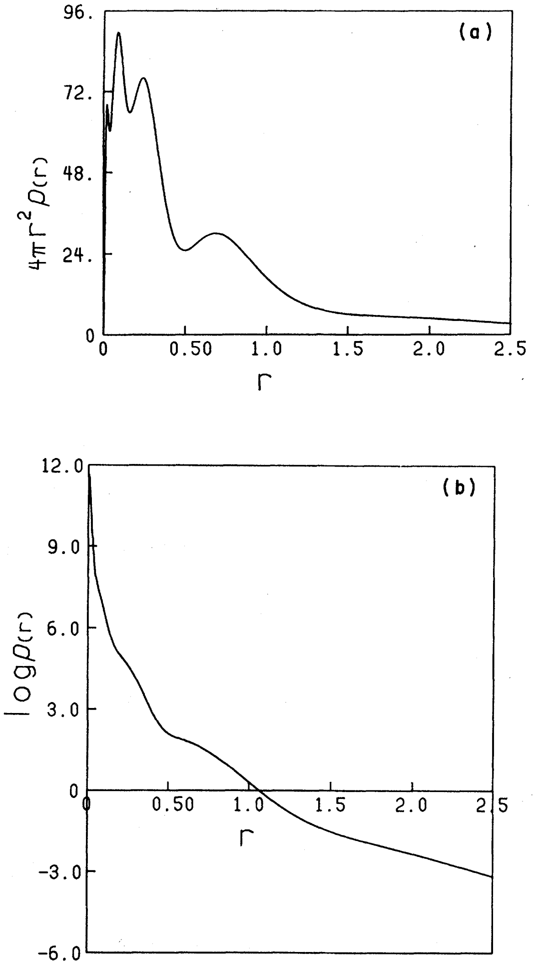

FIG. 5. (a) Radial distribution function for Xe. (b) Electron density of Xe.

TABLE I. Hartree-Fock energy components for ground states of first-row atoms. [a]

Atom (z)	E [b]	V_{ne}	J	K [c]	$\left\lvert \frac{V_{ne}}{J} \right\rvert$
Li (3)	−7.433	−17.15	4.1	−1.8	4.2
Be (4)	−14.57	−33.64	7.2	−2.7	4.7
B (5)	−24.53	−56.89	11.7	−3.8	4.9
C (6)	−37.69	−88.14	17.8	−5.0	5.0
N (7)	−54.40	−128.4	26.2	−6.6	4.9
O (8)	−74.81	−178.1	36.6	−8.1	4.9
F (9)	−99.41	−238.7	50.9	−10.0	4.7
Ne (10)	−128.5	−311.1	66	−12	4.7

[a] Wave functions from Ref. 11(a).

[b] Kinetic energy $T = -E$.

[c] Values of K are taken from Refs. 8(b) and 16.

TABLE II. Hartree-Fock electron-density parameters for the ground states of first-row atoms. [a]

Atoms	λ_1 [b]	λ_2	R	N_1	A_1
Be	3.38	0.59	1.096	2.05	354
C	5.10	0.99	0.621	2.13	128
O	6.56	1.30	0.419	2.19	312
F	7.44	1.43	0.356	2.20	449
Ne	8.16	1.55	0.307	2.21	620

[a] Parameter values from Ref. 13(a).

[b] $2\lambda_1$ is the exponential parameter for $0 \le r \le R$; $2\lambda_2$ is the exponential parameter for $R \le r$. N_1 is the number of electrons in the region $0 \le r \le R$. The number of electrons outside that region is $(Z - N_1)$. A_1 is the electron density at the nucleus.

III. CALCULATIONS

We label as follows the various modified statistical model calculations which we here report. All models make use of Eq. (11) for the density.

$$\mathrm{TF}: E[\rho] = T_0[\rho] + V_{ne}[\rho] + J[\rho], \tag{13}$$

$$\mathrm{TFD}: E[\rho] = T_0[\rho] + V_{ne}[\rho] + J[\rho] + K_0[\rho], \tag{14}$$

$$\mathrm{TFD}\tfrac{1}{9}\mathrm{W}: E[\rho] = T_0[\rho] + T_2[\rho] + V_{ne}[\rho] + J[\rho] + K_0[\rho], \tag{15}$$

$$\mathrm{TFD}\tfrac{1}{9}\mathrm{SW}: E[\rho] = T_0[\rho] + T_2[\rho] + T_s[\rho] + V_{ne}[\rho] + J[\rho] + K_0[\rho]. \tag{16}$$

In all cases, the energy expression is minimized with respect to the parameters in the density, subject to continuity and normalization constraints. The virial theorem is always satisfied for the final energy, as one can prove by Fock's method.[17]

For Ne and other first-row atoms, our model is a two-shell model. The parameters determining the density are A_1, A_2, λ_1, λ_2 and $R (R = R_1$ here). Given the total number of electrons, N, the continuity condition and the normalization condition leave three independent parameters. The orthogonality between the first and the second shell allows us to rewrite the normalization condition of Eq. (6) as

$$N = N_1 + N_2, \tag{17}$$

in which

$$N_1 = \int_0^R \rho(r) 4\pi r^2 \, dr \tag{18}$$

is the number of electrons in the first shell, and

$$N_2 = \int_R^\infty \rho(r) 4\pi r^2 \, dr \tag{19}$$

is the number of electrons in the second shell. In actual calculations, we take the independent param-

TABLE III. Modified statistical models for the ground state of Ne.[a]

Model	λ_1	λ_2	N_1	R	V_{ne}	J	K	E^{e}	(% error)
Accurate Hartree-Fock[b]	8.16	1.55	2.205	0.307	−311.1	66.64	−12.60[c]	−128.5	
TF	14.65	1.69	1.145	0.175	−317.6	68.61	none	−124.5	(3.1)
TFD	15.10	1.86	1.119	0.163	−334.2	74.44	−11.46	−135.6	(−5.5)
TFD$\frac{1}{9}$W	9.67	1.67	1.719	0.239	−304.5	69.08	−10.81	−123.1	(4.2)
TFD$\frac{1}{9}$SW[d]	9.11	1.56	1.890	0.262	−298.4	66.25	−10.54	−121.4	(5.5)

[a] See text for definitions of parameters and models.

[b] See Table I and II.

[c] From Ref. 16.

[d] The contribution of the singularity to T is 1.64.

[e] $T=-E$.

eters to be N_1, λ_1 and λ_2. In certain calculations, we have set $N_1=2$ or its values as determined from Hartree-Fock calculations, and we have only two independent parameters.[18]

For the modified TF model, a general solution valid for all atomic number can be found. This is presented in the Appendix, together with a corresponding analysis for the TFD and TFD$\frac{1}{9}$W cases.

A. Neon atom

Results for the Ne atom are presented in Table III. The modified TF energy −124.5 agrees with the Hartree-Fock energy −128.5 well and is considerably better than the original TF value −165.8.[19] The energy of the modified TFD model, −135.6, is lower than the Hartree-Fock value. However, this value is much better than the original TFD value of −178.[20]

As soon as the inhomogeneity correction is added, the results become very encouraging. The energies are above the Hartree-Fock energy, and the electron densities approximate well the Hartree-Fock density, indicating that the functional (with imposed boundary conditions) is beginning to be a remarkable approximation to the true energy functional for the system. There is little difference between the TFD$\frac{1}{9}$W and TFD$\frac{1}{9}$SW descriptions.

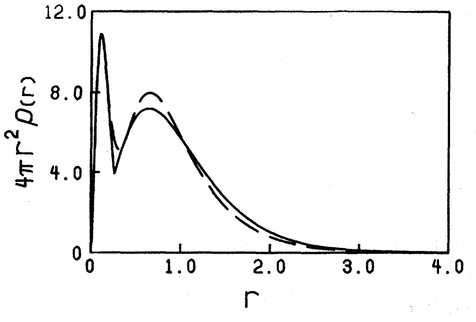

FIG. 6. Radial distribution functions for Ne. Dashed line, Hartree-Fock density; solid line, modified Thomas-Fermi-Dirac-$\frac{1}{9}$ Weizsacker model density.

Figure 6 shows the radial distribution function obtained from the TFD$\frac{1}{9}$W model, compared with the Hartree-Fock density. The shell structure is well represented and the minimum in the radial distribution function is well predicted.

B. First-row atoms

For the "two zone" atoms Li through Ne, the results are presented in Tables IV through XI. These results show a generally considerable improvement over the original TF and TFD models, for both energies and electron densities. Detailed trends are discussed in Sec. IV below.

C. Second-row atoms

The natural model for a second-row atom is a three-zone one. It is known that the radial distri-

TABLE IV. Modified and original Thomas-Fermi models for first-row atoms: energies.

Atom	Modified TF energy[a] (% error)[b]	Original TF energy[c] (% error)[b]
Li	−7.502(−0.93)	−9.978(−34.2)
Be	−14.68(−0.76)	−19.52(−34.0)
B	−24.71(−0.73)	−32.86(−34.0)
C	−37.81(−0.32)	−50.29(−33.4)
N	−54.17(+0.42)	−72.05(−32.4)
O	−73.98(+1.1)	−98.39(−31.5)
F	−97.37(+2.1)	−129.5(−30.3)
Ne	−124.5(+3.1)	−165.6(−28.9)

[a] Model defined by Eqs. (11) and (13) of text. See Appendix Eq. (A7).

[b] Errors are relative to Hartree-Fock, for which energies are given in Table I.

[c] E_{TF} is calculated from $E_{\mathrm{TF}}=-0.7687\,Z^{7/3}$, Ref. 19.

TABLE V. Modified Thomas-Fermi model for first-row atoms: electron densities.[a,b]

Atom	λ_1	λ_2	R	N_1	A_1
Li	9.807	1.133	0.2610	0.3435	116.5
Be	10.79	1.247	0.2371	0.4580	207.2
B	11.63	1.344	0.2201	0.5725	323.7
C	12.36	1.428	0.2072	0.6870	466.1
N	13.01	1.503	0.1968	0.8015	634.4
O	13.60	1.572	0.1882	0.9159	828.7
F	14.15	1.635	0.1809	1.030	104.9
Ne	14.65	1.693	0.1747	1.145	129.5

[a] Model defined by Eqs. (11) and (13) of text.

[b] For corresponding parameters for the Hartree-Fock electron density, see Table II.

bution function $r^2\rho$ has two minima (Fig. 3). Therefore, we separate the density into three zones by these two minima. Results are given in Tables XII and XIII for TFD$\frac{1}{9}$W and TFD$\frac{1}{9}$SW models of selected second-row atoms. The numerical techniques for obtaining these results are straightforward extensions of those used for the two-zone model.

IV. DISCUSSION

A. Other forms for the electron density

An assumption on electron density alternative to Eq. (11), suggested by angular momentum consideration, would be

$$\rho(r)=\begin{cases} A_1\exp(-2\lambda_1 r), & 0\le r\le R_1,\\ A_2 r^2\exp(-2\lambda_2 r), & R_1\le r\le R_2,\\ A_3 r^4\exp(-2\lambda_3 r), & R_2\le r\le R_3,\end{cases} \tag{20}$$

etc., with $0<R_1<R_2<$ etc. and $\lambda_1\ge\lambda_2\ge\lambda_3\ge$ etc. We have carried out a number of calculations[18] with this constraint. The results for two-shell models are in fact generally better than those obtained from Eq. (11). The energy for the modified two-shell TF model with density given by Eq. (20) is

$$E_{\mathrm{MTF}}=-0.5788\,Z^{7/3}, \tag{21}$$

while the energy for the model with Eq. (11) is $-0.5779\,Z^{7/3}$ (see Appendix). The electron densities of the model with Eq. (20) are in better agreement with the Hartree-Fock densities near the nucleus while in worse agreement as $r\to\infty$, as compared with the model with Eq. (11). However, for three-shell cases, the energies obtained from Eq. (20) are generally higher than those obtained from Eq. (11). A functional form which is a mixture of Eq. (11) and Eq. (20) for some purposes might be preferable to either.

TABLE VI. Modified and original Thomas-Fermi-Dirac models for first-row atoms: energies.

Atom	Modified TFD energy[a] (% error)[b]	Original TFD energy[c] (% error)[b]
Li	−9.054 (−21.8)	−11.64 (−56.6)
Be	−17.16 (−17.8)	−22.20 (−52.4)
B	−28.27 (−15.2)	−36.75 (−49.8)
C	−42.61 (−13.1)	−55.56 (−47.4)
N	−60.35 (−10.9)	−78.86 (−45.0)
O	−81.67 (−9.17)	−106.9 (−42.9)
F	−106.71 (−7.34)	−139.86 (−40.7)
Ne	−135.61 (−5.49)	−177.95 (−38.4)

[a] Model defined by Eqs. (11) and (14) of text. Also see Appendix.

[b] Errors are relative to Hartree-Fock, for which energies are given in Table I.

[c] E_{TFD} is calculated from $E_{\mathrm{TFD}}=-0.7687Z^{7/3}-0.266Z^{5/3}$, Ref. 20.

TABLE VII. Modified Thomas-Fermi-Dirac model for first-row atoms: electron densities.[a,b]

Atom	λ_1	λ_2	R	N_1	A_1
Li	10.48	1.385	0.2255	0.3260	140.6
Be	11.40	1.476	0.2100	0.4389	242.1
B	12.20	1.556	0.1981	0.5520	370.4
C	12.89	1.627	0.1887	0.6653	525.3
N	13.51	1.692	0.1808	0.7787	706.8
O	14.08	1.752	0.1742	0.8922	914.9
F	14.61	1.808	0.1684	1.006	1149
Ne	15.10	1.860	0.1634	1.119	1410

[a] Model defined by Eqs. (11) and (14) of text.

[b] For corresponding parameters for the Hartree-Fock density, see Table II.

B. Stability of neutral atoms and negative ions

It is known that negative ions are unstable in the original TF model of atoms and ions because the classical electrostatic self-interaction of electrons is included in the energy functional.[21] For the modified statistical models in this work, we find all negative ions to be unstable with respect to the corresponding neutral atoms with the same number of shells. For the Ne atom and the positive ions Ne^{+} and Ne^{+2}, we also obtain negative ionization potentials. The results are shown in Table XIV. This means that these atoms and ions are incorrectly predicted to be unstable with respect to ionization processes. Similar results are found for other first-row atoms. These are undesirable results; nevertheless, we note a favorable trend, that the better the energy functional used, the better the ionization potential obtained.

TABLE VIII. Modified TFD$\frac{1}{9}$W model for first-row atoms: energies and energy components.[a,b]

Atom	T_0	T_2	V_{ne}	J	K_0	E [c]	(% error) [d]
Li	6.492	1.072	−17.98	4.341	−1.492	−7.565	(−1.78)
Be	12.82	1.848	−35.33	8.371	−2.387	−14.67	(−0.69)
B	21.77	2.813	−59.68	13.96	−3.444	−24.58	(−0.20)
C	33.56	3.958	−91.62	21.23	−4.649	−37.52	(0.451)
N	48.39	5.278	−131.6	30.29	−5.994	−53.67	(1.34)
O	66.45	6.765	−180.2	41.23	−7.473	−73.21	(2.14)
F	87.89	8.415	−237.7	54.13	−9.080	−96.31	(3.12)
Ne	112.9	10.22	−304.5	69.08	−10.81	−123.1	(4.24)

[a] Model defined by Eqs. (11) and (15) of text.
[b] For corresponding components for the Hartree-Fock energy, see Table I.
[c] The total kinetic energy $T = T_0 + T_2 = -E$.
[d] Errors are relative to Hartree-Fock, for which energies are given in Table I.

C. Unconstrained TFD$\frac{1}{9}$W and TFD$\frac{1}{5}$W models

One may ask whether a completely free functional form in the TFD$\frac{1}{9}$W model would not be best. Comprehensive calculations on atoms with this functional (and no constraints) would be desirable to carry out; they seem not to have been done heretofore. We have done some calculations using our multizone technique to anticipate what the results of such unconstrained TFD$\frac{1}{9}$W calculations would be, however. If we calculate Ne with two zones and three zones, the results for the TFD$\frac{1}{9}$W energy are −123.10 and −131.4; for TFD$\frac{1}{9}$SW models, the results are −121.4 and −126.7. The Hartree-Fock energy is −128.5. As we go to an infinite number of zones, the limit for the modified TFD$\frac{1}{9}$W model would be the unconstrained TFD$\frac{1}{9}$W result. While this result would be much better than the original TF and TFD results, it would be below the Hartree-Fock and exact energies. Hence, the TFD$\frac{1}{9}$W energy functional must be deficient in some sense.

The residual deficiency is at least in part associated with the nuclear cusp condition. Unconstrained TFDW calculation would produce the correct cusp; the factor $\frac{1}{9}$ with the Weizsacker inhomogeneity correction ruins that. From this point of view, the TFD$\frac{1}{5}$W functional as proposed and tested by Tomishima and Yonei[22] is somewhat superior, although still lacking. These authors in fact have obtained very good energies with this functional, but it must itself be deficient because it gives kinetic energies too high by about 10 percent if Hartree-Fock densities are put into it.[8,9] Also this functional has not been derived theoretically, although a result close to it has been obtained.[23]

TABLE IX. Modified TFD$\frac{1}{9}$W model for first-row atoms: electron densities.[a,b]

Atom	λ_1	λ_2	R	N_1	A_1
Li	4.962	1.174	0.4224	0.6525	32.17
Be	5.863	1.267	0.3683	0.8191	65.27
B	6.653	1.349	0.3312	0.9785	112.4
C	7.361	1.424	0.3037	1.133	174.7
N	8.007	1.492	0.2824	1.283	253.0
O	8.603	1.555	0.2652	1.431	348.0
F	9.157	1.613	0.2410	1.576	460.2
Ne	9.677	1.668	0.2390	1.719	590.3

[a] Model defined by Eqs. (11) and (15) of text.
[b] For corresponding parameters for the Hartree-Fock density, see Table II.

For the unconstrained TFD$\frac{1}{9}$W model, neutral atoms would be expected to be stable with respect to ionization, and the asymptotic behavior of the electron density should be quite good.

D. Z-dependence of atomic energy

The simplicity of our modified models and the good atomic energies they give allow us to discuss the interesting problem of Z dependence of atomic energies.

The original TF energy for a neutral atom with atomic number Z is given by[19,24,25]

$$E_{\mathrm{TF}} = -0.7687\, Z^{7/3}. \tag{22}$$

The modified TF model energy for a two-shell atom is, from the Appendix

$$E_{\mathrm{MTF}} = -0.5779\, Z^{7/3}, \tag{23}$$

while for a three-shell atom is, from the Appendix,

$$E_{\mathrm{MTF}} = -0.6599\, Z^{7/3}. \tag{24}$$

From the results in Table IV, for first-row atoms the errors in Eq. (22) are of the order of 30% while the errors in Eq. (23) are less than 3.1%. For second-row atoms, the errors in Eq. (22) are of the

TABLE X. Modified TFD$\frac{1}{9}$SW model for first-row atoms: energies and energy components.[a,b]

Atom	T_0	T_2	T_s	V_{ne}	J	K_0	E [c]	(% error) [d]
Li	6.190	0.9927	0.1780	−17.34	4.046	−1.430	−7.361	(0.969)
Be	12.30	1.728	0.3056	−34.22	7.854	−2.297	−14.33	(1.65)
B	20.96	2.649	0.4623	−57.99	13.17	−3.324	−24.07	(1.88)
C	32.42	3.748	0.6468	−89.25	20.12	−4.500	−36.81	(2.33)
N	46.87	5.018	0.8576	−128.5	28.81	−5.815	−52.74	(3.05)
O	64.49	6.453	1.094	−176.2	39.34	−7.264	−72.04	(3.70)
F	85.46	8.049	1.354	−232.7	51.80	−8.840	−94.86	(4.58)
Ne	109.9	9.801	1.638	−298.3	64.63	−10.84	−121.4	(5.92)

[a] Model defined by Eqs. (11) and (16) of text.

[b] For corresponding components for the Hartree-Fock energy, see Table I.

[c] The total kinetic energy $T = T + T_2 + T_s = -E$.

[d] Errors are relative to Hartree-Fock, for which energies are given in Table I.

order of 25%, while the errors in Eq. (24) are less than 10%, as shown in Table XV. Modified TF energies for four-shell atoms will be lower than Eq. (24) yet higher than Eq. (22).

Csavinszky[26] has obtained the approximate (one-zone) solution of the Thomas-Fermi equation for atoms which decreases exponentially with r and finds

$$E = -0.5855\, Z^{7/3}. \tag{25}$$

This formula gives values lower than does Eq. (23) yet higher than does Eq. (24). Politzer and Parr[27] gave as an empirical formula,

$$E = -0.6000\, Z^{7/3}, \tag{26}$$

which gives good agreement with Hartree-Fock results for first and second-row atoms. Our Eqs. (23) and (24) are better, however.

For the TFD$\frac{1}{9}$W model, we cannot say that the inhomogeneity correction has $Z^{2/3}$ dependence, as some authors claim[4(a),7(a)] because the exponential parameter λ_1 in the inner region of an atom strongly depends on Z. Because of this, the prediction that the inhomogeneity correction is far less important than the Fermi energy or the exchange energy may not be valid. From our modified TFD$\frac{1}{9}$W model calculations, we in fact find that the inhomogeneity correction to kinetic energy is more important than the exchange energy as Z becomes large. The calculation by Kim and Gordon[16] and by Shih[8] support these results.

TABLE XI. Modified TFD$\frac{1}{9}$SW model for first-row atoms: electron densities.[a,b]

Atom	λ_1	λ_2	R	N_1	A_1
Li	4.403	1.020	0.5138	0.8039	26.34
Be	5.296	1.124	0.4333	0.9729	55.00
B	6.081	1.215	0.3812	1.135	96.60
C	6.788	1.296	0.3442	1.293	152.3
N	7.433	1.369	0.3162	1.446	223.0
O	8.030	1.437	0.2942	1.596	309.4
F	8.586	1.499	0.2764	1.744	412.3
Ne	9.107	1.558	0.2615	1.890	532.1

[a] Model defined by Eqs. (11) and (16) of text.

[b] For corresponding parameters for the Hartree-Fock density, see Table II.

E. Extension to molecular systems

The extension of our modified atomic models to molecules would be of interest. It is known that Thomas-Fermi-Dirac models of molecules cannot lead to binding.[28-30] Several investigators have shown that corrections for inhomogeneity of the Weizsacker type account for the formation of stable molecules in statistical theories.[30,31] It has been shown that the unconstrained TFD$\frac{1}{5}$W model of a diatomic molecule can lead to good binding energy.[31(b)] We encourage studies of both unconstrained and modified statistical models of molecules using inhomogeneity corrections of $\frac{1}{9}\, T_w$ type.

V. SUMMARY

(1) The shell structure of atoms can be obtained from statistical models if the assumption is made that the electron density is a piecewise exponentially decreasing function of the distance from the nucleus.[32]

(2) Energies good to about 5% and electron densities showing semiquantitative agreement with accurate electron densities can be obtained from the modified Thomas-Fermi-Dirac model, with one-ninth of the Weizsacker correction for inhomogeneity added.

(3) There is a compelling evidence favoring the factor $\frac{1}{9}$ in the Weizsacker correction for inhomogeneity.

TABLE XII. Modified TFD$\frac{1}{9}$W and TFD$\frac{1}{9}$SW models for selected second-row atoms: energies and energy components.[a]

Atom (Z)	Model	T_0	T_2	T_s	V_{ne}	J	K_0	E[b]	(% error)[c]
Na(11)	$\frac{1}{9}$W	147.5	17.0	(N.A.)	−397.5	80.81	−12.25	−164.5	(−1.61)
	$\frac{1}{9}$SW	139.2	14.6	5.00	−381.8	76.18	−11.79	−158.7	(1.98)
Cl(17)	$\frac{1}{9}$W	418.2	40.0	(N.A.)	−1112.4	221.2	−25.22	−458.2	(−0.28)
	$\frac{1}{9}$SW	397.6	34.9	12.08	−1075.5	210.5	−24.39	−444.7	(3.22)
Ar(18)	$\frac{1}{9}$W	479.5	44.7	(N.A.)	−1232.0	240.6	−27.73	−524.2	(0.49)
	$\frac{1}{9}$SW	456.4	39.1	13.55	−1273.3	252.6	−27.73	−509	(3.36)

[a] See text for definitions of models, which are three-zone ones.

[b] The total kinetic energy $T=-E$.

[c] Errors are relative to Hartree-Fock, for which energies are $E_{\mathrm{Na}}=-169.9$, $E_{\mathrm{Cl}}=-459.5$, and $E_{\mathrm{Ar}}=526.8$, from Ref. 11b.

(4) Corrections for the effect of the singularity in the derivative of the density can be included, but they do not much affect the numerical predictions.

VI. ACKNOWLEDGMENTS

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APPENDIX. UNIVERSAL SOLUTION FOR THE MODIFIED TF MODEL AND CORRESPONDING ANALYSIS FOR MODIFIED TFD AND TFD $\frac{1}{9}$W MODELS

A. Modified Thomas-Fermi model

For the modified TF model, the dependence on atomic number Z may conveniently be explicitly displayed. For simplicity, we only discuss the two-shell (K and L shell) case in detail; for the three-shell case we just present some results.

We introduce the transformations,

$$\begin{aligned}&s=Z^{1/3}r,\quad S=Z^{1/3}R,\quad \epsilon=Z^{-7/3}E,\\&\zeta_1=Z^{-1/3}\lambda_1,\quad \zeta_2=Z^{-1/3}\lambda_2,\\&Q(s)=Z^{-2}\rho(s).\end{aligned}\tag{A1}$$

Then we find

$$\begin{aligned}\epsilon(Q)=\kappa_F\int Q^{5/3}\,dv_s-\int\frac{Q(s)}{s}\,dv_s\\+\frac{1}{2}\int\int\frac{Q(s_1)Q(s_2)}{s_{12}}\,dv_{s_1}\,dv_{s_2},\end{aligned}\tag{A2}$$

with the constraint

$$Q=\begin{cases}C_1\exp(-2\zeta_1 s), & 0\leqslant s\leqslant S,\\ C_2\exp(-2\zeta_2 s), & S\leqslant s\leqslant\infty.\end{cases}\tag{A3}$$

The normalization condition, Eq. (17), becomes

TABLE XIII. Modified TFD$\frac{1}{9}$W and TFD$\frac{1}{9}$SW models for selected second-row atoms: electron densities.[a,b]

Atom (Z)	Model	λ_1	λ_2	λ_3	R_1	R_2	N_1	N_2	A_1	D_1[c]	D_2[c]
Na(11)	$\frac{1}{9}$W	21.00	5.534	1.410	0.077	0.395	0.464	2.797	2174.2	85.00	2.529
	$\frac{1}{9}$SW	15.88	4.302	1.224	0.110	0.516	0.754	3.310	1421.8	43.58	1.324
Cl(17)	$\frac{1}{9}$W	28.67	6.785	1.615	0.058	0.329	0.601	4.199	6938.1	243.8	6.237
	$\frac{1}{9}$SW	22.58	5.508	1.439	0.078	0.409	0.897	4.876	4814.0	142.5	3.708
Ar(18)	$\frac{1}{9}$W	29.85	6.967	1.645	0.056	0.321	0.623	4.428	8070.1	279.7	7.031
	$\frac{1}{9}$SW	23.63	5.685	1.470	0.075	0.397	0.919	5.128	5641.5	166.0	4.244

[a] See text for definitions of models, which are three-zone ones.

[b] Parameters defined by Eq. (11) in text.

[c] The quantities $D_1=R_1^2\rho_{R_1}$ and $D_2=R_2^2\rho_{R_2}$ are the electron densities at the radii which separate the zones.

TABLE XIV. Energies of modified statistical models for Ne and its ions.[a]

Atom or ion	HF [b]	TF	TFD	TFD$\frac{1}{9}$W	TFD$\frac{1}{9}$SW
Ne	−128.5	−124.5	−135.6	−123.1	−121.4
Ne^+	−127.8	−127.1	−138.0	−124.7	−122.6
Ne^{+2}	−126.4	−129.3	−139.9	−125.6	−123.3
Ne^{+3}	−124.1	−131.0		−125.9	−123.2
Ne^{+4}	−120.5			−125.0	−121.9

[a] See text for definitions of models, which are two-zone ones.

[b] Hartree-Fock energies are from Ref. 11b.

$$N=\int\rho(r)\,dv_r=Z\int Q(s)\,dv_s=N_1+N_2. \tag{A4}$$

For a neutral atom with $N=Z$, we have

$$\int Q(s)\,dv_s=1=M_1+M_2,$$

in which

$$\int_0^S Q(s)4\pi s^2\,ds=M_1,\quad \int_S^\infty Q(s)4\pi s^2\,ds=M_2. \tag{A5}$$

The constrained variation can be carried out and the best values of the parameters obtained numerically. For $N=Z$, the results are as follows:

$$\begin{aligned}&\zeta_1=6.800,\quad \zeta_2=0.7858,\\&M_1=0.1145,\quad M_2=0.8855,\\&S=0.3764.\end{aligned} \tag{A6}$$

For the energy we obtain

$$E_{\text{MTF}}=-0.5779\,Z^{7/3}. \tag{A7}$$

As in the original TF model, we find that the ratio $|V_{ne}/V_{ee}|$ is constant.[24] In the original model, this ratio is 7, which is much higher than most Hartree-Fock values. The modified model gives a ratio of 4.630. For some actual Hartree-Fock values, see Table I.

While the parameters in Eq. (A6) do not provide a particularly good representation of the electron density, this representation is considerable better than that provided by original Thomas Fermi theory (for which $\rho=\infty$ at $r=0$ and ρ falls off as r^{-6}, not exponentially, as $r\rightarrow\infty$, and the shell structure in $r^2\rho$ is missing).

For three-shell models, the modified TF energy is given by

$$E_{\text{MTF}}=-0.6599\,Z^{7/3}, \tag{A8}$$

which agrees within 10% with the Hartree-Fock energies of second row atoms. The parameters for $N=Z$ are as follows:

$$\begin{aligned}&\zeta_1=74.95,\quad \zeta_2=8.040,\quad \zeta_3=1.342,\\&M_1=0.0092,\quad M_2=0.1828,\quad M_3=0.3462,\\&S_1=0.05632,\quad S_2=0.5975.\end{aligned} \tag{A9}$$

The ratio $|V_{ne}/V_{ee}|$ is 5.393.

B. Thomas-Fermi-Dirac model

Again making the transformation of Eq. (A1), we find upon introducing the exchange correction of Eq. (7) is place of Eq. (A2),

$$\begin{aligned}E(Q)=\kappa_F\int Q^{5/3}dv_s-\int\frac{Q(s)}{s}dv_s\\+\frac{1}{2}\int\int\frac{Q(s_1)Q(s_2)}{s_{12}}dv_{s_1}dv_{s_2}\\-Z^{2/3}\kappa_e\int Q^{4/3}dv_s.\end{aligned} \tag{A10}$$

The best Q now depends on Z, and a universal

TABLE XV. Modified and original Thomas-Fermi models for second-row atoms: energies.[a]

Atom	Hartree-Fock energy [b]	Modified TF energy (% error) [c]	Original TF energy [c] (% error) [c]
Na	−161.8	−177.6 (−9.75)	−206.9 (−27.8)
Mg	−199.6	−217.6 (−9.00)	−253.4 (−27.0)
Al	−241.9	−262.2 (−8.40)	−305.5 (−26.3)
Si	−288.8	−311.7 (−7.94)	−363.1 (−25.7)
P	−340.7	−366.2 (−7.48)	−426.5 (−25.2)
S	−397.5	−425.7 (−7.09)	−495.9 (−24.7)
Cl	−459.5	−490.4 (−6.72)	−571.2 (−24.3)
Ar	−526.8	−560.3 (−6.37)	−652.7 (−23.9)

[a] Model defined by Eqs. (11) and (13) of text. See Appendix Eq. (A8).

[b] Hartree-Fock energies are from Ref. 11b.

[c] Errors are relative to Hartree-Fock energies.

[d] E_{TF} is calculated from $E_{\text{TF}}=-0.7687\,Z^{7/3}$, Ref. 19.

solution for all Z is not possible. The total energy as a function of Z may be written in the form

$$E_{\mathrm{MTFD}} = \alpha(Z)Z^{7/3} + \beta(Z)Z^{5/3}, \tag{A11}$$

where $\alpha(Z)$ and $\beta(Z)$ are weakly varying functions of Z. For Z in the range 3 to 10 and $N=Z$, a good approximation is

$$E_{\mathrm{MTFD}} = -0.576Z^{7/3} - 0.248Z^{5/3}. \tag{A12}$$

In the original TFD theory,[20,25] the result is

$$E_{\mathrm{TFD}} = \alpha' Z^{7/3} + \beta' Z^{5/3}, \tag{A13}$$

where the constant α' is equal to -0.7687 and is valid for all Z, and the numerical value of β' varies according to the specific boundary conditions placed on the density.[25] Equation (A12) is a considerably better representation of actual energies than is Eq. (A13), as is shown by the numerical values given in the text.

C. Thomas-Fermi-Dirac-$\frac{1}{9}$ Weizsacker model

If the inhomogeneous correction of Eq. (10) is added, giving the TFD$\frac{1}{9}$W model, there is added to Eq. (A10) a term

$$Z^{2/3}\left(\frac{1}{72}\int \frac{(\nabla_s Q)^2}{Q}\, dv_s\right), \tag{A14}$$

which is explicitly proportional to $Z^{2/3}$. There is a noticeably changed coefficient of $Z^{7/3}$ in the energy expression. Qualitative discussion may be found in Sec. IV of the text.

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‡Present address: Department of Chemistry, Paul M. Gross Chemical Laboratory, Duke University, Durham, N. C. 27706.

§Present address: Department of Chemistry, The University of North Carolina at Chapel Hill, Chapel Hill, N. C. 27514.

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