Fixed-shell statistical atomic models with piecewise exponentially decaying electron densities*

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Various versions of a statistical model of atoms are developed in which the numbers of electrons in different regions of an atom are fixed by certain postulates. It is assumed that the electron density can be represented by a sum of exponentially decreasing functions. The electronic energies and electronic densities of these new models are found to be comparable to the corresponding Hartree-Fock results and are substantial improvements over the original Thomas-Fermi statistical model and its various extensions. Densities of the new models are improvements over the modified statistical models of Wang and Par [Phys. Rev. A 16, 891 (1977)]. Some corrections to this reference are included.

I. INTRODUCTION

Most statistical treatments of atoms[1] have concentrated on obtaining the electronic density by minimizing the total statistical energy; these densities and energies may then be compared with the experimental or the Hartree-Fock (HF) results. Some workers[2–4] have used HF and other highly accurate densities to calculate the statistical energies. A combination of these approaches, in which one imposes certain constraints on electron density while minimizing the total energy, can provide information about both the validity of the statistical treatment and the correctness of energy-density functionals.

Wang and Parr[5,6] have developed a new statistical model of atoms, in which the total one-electron density in an atom is represented by a sum of decaying exponential functions. Energies of this model are comparable to HF values and are big improvements over the original Thomas-Fermi (TF) (Ref. 7) and Thomas-Fermi-Dirac (TFD) (Ref. 8) models. Nevertheless, the densities of some atoms are in poor agreement with HF results, and errors were made in these calculations.[9] In the present work, we propose a modified model, the fixed-shell model, in which we impose the constraint that the number of electrons in each "exponential region" is fixed by a postulate, and we compare this model with the model of Wang and Parr.[5,6] Henceforth we call Ref. 6 paper I.

Following paper I, we express the total energy E of the nondegenerate ground state of an atom with atomic number Z in terms of the exact density ρ

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

where $T[\rho]$ is the kinetic energy, $V_{ne}[\rho]$ is the nuclear-electron attraction energy, and $V_{ee}[\rho]$ is the electron-electron repulsion energy. $V_{ee}[\rho]$ can be separated into two parts

$$V_{ee}[\rho]=J[\rho]+K[\rho]\ , \tag{2}$$

where $J[\rho]$ is the classical Coulomb repulsion energy between ρ and itself, and $K[\rho]$ the exchange-correlation energy. We neglect the correlation energy part of $K[\rho]$, and adopt the homogeneous electron-gas approximation of Dirac[8] for the exchange energy[10]

$$\begin{aligned}K_0[\rho]&=-\tfrac{3}{4}(\tfrac{3}{4})^{1/3}\int\rho^{4/3}(1)dv_1\\&=-\kappa_e\int\rho^{4/3}dv\ .\end{aligned} \tag{3}$$

For $T[\rho]$, we adopt the first two terms of the gradient expansion[11,12,13]

$$T[\rho]=T_0[\rho]+T_2[\rho]\ , \tag{4}$$

where the quantity

$$\begin{aligned}T_0[\rho]&=\tfrac{3}{10}(3\pi^2)^{2/3}\int\rho^{5/3}dv\\&=\kappa_F\int\rho^{5/3}dv\end{aligned} \tag{5}$$

is the original formula of Thomas[7(a)] and Fermi,[7(b)] while the quantity

$$T_2[\rho]=\tfrac{1}{9}\left[\tfrac{1}{8}\int\frac{(\nabla\rho)(\nabla\rho)}{\rho}dv\right]=\tfrac{1}{9}T_W \tag{6}$$

is one-ninth the inhomogeneity correction T_W introduced by Weizsacker.[14]

II. MODEL

We now propose a rule for separating electrons into regions[15]: The number of different exponential regions or shells is the same as the maximum occupied principal quantum number of the atom. The region nearest the nucleus is called the K shell. Similarly, $L,M,N,\ldots$ shells are labeled according to their relative positions with respect to the nucleus. Each region can have as many electrons as allowed by the corresponding principal quantum number. Thus for the K shell, the maximum number is two, and for the L shell the maximum number is eight. In paper I, we did not set an upper limit on the number of electrons in each shell.

As in paper I, we assume that the density is spherically symmetric and can be represented in the form

$$\rho(r)=\begin{cases} A_1\exp(-2\lambda_1 r), & 0\le r\le R_1 \quad (K \text{ shell}) \\ A_2\exp(-2\lambda_2 r), & R_1\le r\le R_2 \quad (L \text{ shell}) \\ A_3\exp(-2\lambda_3 r), & R_2\le r\le R_3 \quad (M \text{ shell}) \\ \text{etc.}, \end{cases} \tag{7}$$

with $0\le R_1\le R_2$, etc., and $\lambda_1\ge\lambda_2\ge\lambda_3$, etc. We require that $\rho(r)$ but not $d\rho/dr$ be continuous. The parameters λ_i are constants. The resulting fixed-shell models of Thomas-Fermi (FTF), Thomas-Fermi-Dirac (FTFD), Thomas-Fermi-Dirac-$\frac{1}{9}$-Weizsacker (FTFD $\frac{1}{9}$W), and Thomas-Fermi-Dirac-$\frac{1}{9}$ Singular-Weizsacker (FTFD$\frac{1}{9}$SW) models are defined by different assumptions for $T[\rho]$ and $K[\rho]$, and by whether or not corrections[16] for the discontinuity in $d\rho/dr$ at $r=R_i$ are included, where R_i is the radius separating the regions. The energy expressions are minimized with respect to the parameters in the density, subject to continuity and normalization conditions. The final energy satisfies the virial theorem.

The corresponding "modified" models, MTF, MTFD, etc., are the models of paper I, in which numbers of electrons in different shells are treated as variational parameters.

For first-row atoms, our model is a two-shell one with a single $R_i\equiv R$. Given the total number of electrons N, the spatial distinction between K and L shells allows us to write the normalization condition as

$$\int\rho(r)dv=N=N_1+N_2\ , \tag{8}$$

in which

$$N_1=\int_0^R\rho(r)4\pi r^2dr=2 \tag{9}$$

is the number of electrons in the K shell, and

$$N_2=\int_R^\infty\rho(r)4\pi r^2dr \tag{10}$$

is the number of electrons in the L shell. The calculational parameters are λ_1 and λ_2. We first discuss first-row atoms in detail and subsequently present detailed results for second- and third-row atoms.

III. RESULTS

A. First-row atoms

1. *Thomas-Fermi model*

As shown in Table I, for the "two-shell" atoms Li through Ne, the FTF energies are higher and

TABLE I. Fixed-shell (FTF) and modified (MTF) Thomas-Fermi models[a] for first-row atoms: energies and energy components.[b]

Atom	$E_{\rm HF}$[c]	V_{ne}	J	$\left\lvert\frac{V_{ne}}{J}\right\rvert$	$E_{\rm FTF}$(% error)[c]	$E_{\rm MTF}$(% error)[c]	$E_{\rm TF}$[d](% error)[c]
Li	−7.433	−16.38	3.889	4.213	−6.248(15.9)	−7.926(−6.63)	−9.978(−34.2)
Be	−14.57	−33.48	7.233	4.628	−13.12(9.95)	−15.51(−6.45)	−19.52(−34.0)
C	−37.69	−90.94	18.44	4.932	−36.25(3.82)	−39.94(−5.97)	−50.29(−33.4)
O	−74.81	−183.5	36.57	5.020	−73.49(1.76)	−78.16(−4.48)	−98.39(−31.5)
Ne	−128.5	−315.2	62.58	5.037	−126.3(1.71)	−131.5(−2.33)	−165.6(−28.9)

[a]Models defined in Sec. II of text.
[b]Energy components defined in Sec. I of text, $T=-E$. Energies are in hartrees.
[c]Errors are deviations relative to $E_{\rm HF}$, which are from Ref. 17(a).
[d]$E_{\rm TF}$ is calculated from $E_{\rm TF}=-0.7687Z^{7/3}$, Ref. 18.

TABLE II. Fixed-shell (FTF) and modified (MTF) Thomas-Fermi models for first-row atoms: electron densities.[a,b]

Model	Atom	λ_1	λ_2	R	N_1	A_1
FTF	Li	2.570	0.3215	1.527	2	10.98
	Be	3.611	0.5735	0.9009	2	31.32
	C	5.675	0.9518	0.4950	2	126.7
	O	7.748	1.241	0.3417	2	329.7
	Ne	9.836	1.481	0.2614	2	683.1
MTF	Li	14.22	1.341	0.1782	0.2056	213.5
	Be	15.65	1.476	0.1619	0.2741	379.6
	C	17.91	1.689	0.1414	0.4111	854.1
	O	19.72	1.859	0.1285	0.5482	1518.0
	Ne	21.24	2.003	0.1193	0.6852	2372.0

[a]See text for definitions of models and parameters, especially Eq. (7).
[b]For corresponding parameters for the HF electron density, see paper I.

the corrected MTF energies are lower than the corresponding HF energies. For the MTF model, the revised values for the energy and the scaled density parameters defined in the Appendix of paper I, are

$$E_{\mathrm{MTF}}=-0.6106Z^{7/3}\,,$$
$$\xi_1=9.858\,,$$
$$\xi_2=0.9295\,, \tag{11}$$
$$M_1=0.0685\,,$$
$$M_2=0.9315\,,$$

and

$$S=0.2570\,. \tag{12}$$

Both FTF and MTF energies are definite improvements (vis-à-vis Hartree-Fock) over the original TF values.

Comparing the exponential parameters and radii in Table II with the HF results in Table II of paper I, we see that the FTF densities are improvements over the MTF model of paper I.

No general solution valid for all atomic numbers can be found for the FTF model. Each atomic problem has to be solved separately. Consequently, the ratio $|V_{ne}/J|$ is no longer atom independent, as it was in the MTF and original TF models.[20]

2. *Thomas-Fermi-Dirac models*

The energies of the FTFD model, as shown in Table III, are within 9% of the HF values and are remarkable improvements over the original TFD model. These E_{FTFD} values are also improvements over the corrected E_{MTFD} values, which exhibit deviations of up to 28.7%. A good approximation for the E_{MTFD} values of first-row atoms is

$$E_{\mathrm{MTFD}}=-0.606Z^{7/3}-0.273Z^{5/3}\,. \tag{13}$$

TABLE III. Fixed-shell Thomas-Fermi-Dirac model[a] for first-row atoms: energies and energy components.[b]

Atom	V_{ne}	J	K_0	E_{FTFD}(% error)[c]	E_{MTFD}(% error)[c]	E_{TFD}[d](% error)[c]
Li	−18.57	4.604	−1.680	−7.821(−5.22)	−9.569(−28.7)	−11.64(−56.6)
Be	−36.97	8.406	−2.609	−15.59(−7.00)	−18.13(−24.4)	−22.20(−52.4)
C	−97.78	20.72	−4.991	−41.03(−8.86)	−45.03(−19.5)	−55.56(−47.4)
O	−194.6	40.22	−8.002	−81.20(−8.54)	−86.31(−15.4)	−106.9(−42.9)
Ne	−331.3	67.82	−11.59	−137.5(−7.00)	−143.3(−11.5)	−177.9(−38.4)

[a]Model defined in Sec. II of text.
[b]Energy components defined in Sec. I of text, $T=-E$. Energies are in hartrees.
[c]Errors are relative to E_{HF}, which are given in Table I.
[d]E_{TFD} is calculated from $E_{\mathrm{TFD}}=-0.7687Z^{7/3}-0.266Z^{5/3}$, Ref. 19.

TABLE IV. Fixed-shell and modified Thomas-Fermi-Dirac models for first-row atoms: electron densities.[a,b]

Model	Atom	λ_1	λ_2	R	N_1	A_1
FTFD	Li	2.830	0.5293	1.218	2	14.90
	Be	3.843	0.7792	0.7713	2	38.65
	C	5.879	1.135	0.4492	2	144.2
	O	7.939	1.408	0.3180	2	362.2
	Ne	10.02	1.636	0.2468	2	735.8
MTFD	Li	15.95	1.609	0.1493	0.1811	274.1
	Be	17.21	1.719	0.1397	0.2470	466.9
	C	19.27	1.901	0.1263	0.3798	1001.0
	O	20.94	2.052	0.1170	0.5136	1732.0
	Ne	22.37	2.181	0.1100	0.6478	2658.0

[a]See text for definitions of models and parameters.
[b]For corresponding parameters for the HF electron density, see paper I.

Densities of the FTFD model and the revised results for the MTFD model are given in Table IV.

3. *Thomas-Fermi-Dirac-$\frac{1}{9}$ Weizsacker models*

The results for the FTFD$\frac{1}{9}$W model and the corrected results for the MTFD$\frac{1}{9}$W model are given in Tables V and VI. All energies agree well with HF energies and the FTFD$\frac{1}{9}$W model gives much better densities, especially for light atoms.

4. *Thomas-Fermi-Dirac-$\frac{1}{9}$ Singular-Weizsacker models*

As shown in Tables VII and VIII, the results for the FTFD$\frac{1}{9}$SW model and the revised results for the MTFD$\frac{1}{9}$SW model are similar to their corresponding TFD$\frac{1}{9}$W models.

B. Second-row atoms

For the "three-shell" atoms Na through Ar, agreement between the FTF energies and HF ener-

TABLE V. Fixed-shell and modified Thomas-Fermi-Dirac-$\frac{1}{9}$Weizsacker models[a] for first-row atoms: energies and energy components.[b]

Model	Atom	T_0	T_2	V_{ne}	J	K_0	E(% error)[c]
FTFD$\frac{1}{9}$W	Li	6.300	0.7155	−16.78	4.277	−1.530	−7.016(5.61)
	Be	12.72	1.352	−33.68	7.955	−2.409	−14.07(3.43)
	C	34.07	3.280	−89.77	19.95	−4.679	−37.35(0.90)
	O	68.25	6.112	−180.2	39.03	−7.567	−74.36(0.60)
	Ne	116.6	9.871	−308.1	66.13	−11.02	−126.5(1.56)
MTFD$\frac{1}{9}$W	Li	6.618	1.193	−18.44	4.352	−1.539	−7.811(−5.09)
	Be	13.11	2.075	−36.29	8.393	−2.468	−15.18(−4.19)
	C	34.43	4.505	−94.34	21.30	−4.822	−38.93(−3.29)
	O	68.36	7.772	−185.8	41.36	−7.770	−76.13(−1.76)
	Ne	116.4	11.83	−314.4	69.31	−11.26	−128.2(+0.23)

[a]Models defined in Sec. II of text.
[b]Energy components defined in Sec. I of text, $T=-E$. Energies are in hartrees.
[c]Errors are relative to E_{HF}, which are given in Table I.

TABLE VI. Fixed-shell and modified Thomas-Fermi-Dirac-$\frac{1}{9}$Weizsacker models for first-row atoms: electron densities.[a,b]

Model	Atom	λ_1	λ_2	R	N_1	A_1
FTFD$\frac{1}{9}$W	Li	2.504	0.5856	1.275	2	10.48
	Be	3.391	0.8200	0.8142	2	27.18
	C	5.180	1.159	0.4766	2	101.7
	O	6.996	1.422	0.3379	2	256.3
	Ne	8.834	1.643	0.2624	2	521.8
MTFD$\frac{1}{9}$W	Li	6.245	1.343	0.3126	0.4319	44.80
	Be	7.426	1.455	0.2727	0.5447	92.32
	C	9.423	1.643	0.2244	0.7538	253.0
	O	11.10	1.800	0.1953	0.9494	512.6
	Ne	12.57	1.935	0.1754	1.137	881.4

[a]See text for definitions of models and parameters.
[b]For corresponding parameters for the HF electron density, see paper I.

gies is very good, ranging from 1.17% for sodium to −0.76% for argon. These are great improvements over the original TF values, which show deviations of up to −27.8%, and over the corrected MTF energies, which are given by

$$E_{\mathrm{MTF}} = -0.6866 Z^{7/3} . \tag{14}$$

For the FTFD model the energies (Table IX) are lower than the corresponding HF values although the agreements are better than for the first-row atoms. The deviations are within −6.8% as compared with −36.7% for some original TFD values. The densities for the FTFD model are given in Table X.

The results for the FTFD$\frac{1}{9}$SW model and the corrected results for the MTFD$\frac{1}{9}$SW model are given in Tables XI and XII. We notice significant differences between the energy components T_s of these two models.

C. Third-row atoms

For the "four-shell" atoms K through Kr, the results for the FTFD$\frac{1}{9}$SW model are given in

TABLE VII. Fixed-shell and modified Thomas-Fermi-Dirac$\frac{1}{9}$Singular-Weizsacker models[a] for first-row atoms: energies and energy components.[b]

Model	Atom	T_0	T_2	T_s	V_{ne}	J	K_0	E(% error)[c]
FTFD$\frac{1}{9}$SW	Li	6.232	0.7180	0.0311	−16.60	4.147	−1.505	−6.981(6.08)
	Be	12.48	1.351	0.1145	−33.22	7.678	−2.357	−13.95(4.26)
	C	33.21	3.257	0.4309	−88.51	19.27	−4.567	−36.90(2.10)
	O	66.38	6.053	0.9465	−177.2	37.80	−7.388	−73.38(1.91)
	Ne	113.4	9.763	1.656	−303.0	64.19	−10.77	−124.8(2.88)
MTFD$\frac{1}{9}$SW	Li	6.214	1.086	0.2403	−17.67	4.051	−1.457	−7.540(−1.44)
	Be	12.40	1.915	0.4116	−34.98	7.871	−2.352	−14.73(−1.10)
	C	32.90	4.223	0.8698	−91.54	20.19	−4.632	−38.00(−0.82)
	O	65.74	7.355	1.469	−181.1	39.49	−7.505	−74.56(+0.33)
	Ne	112.4	11.27	2.200	−307.3	66.51	−10.92	−125.9(+2.02)

[a]Models defined in Sec. II of text.
[b]Energy components defined in Sec. I of text, $T = -E$. Energies are in hartrees.
[c]Errors are relative to E_{HF}, which are given in Table I.

TABLE VIII. Fixed-shell and modified Thomas-Fermi-Dirac-$\frac{1}{9}$Singular-Weizsacker models for first-row atoms: electron densities.[a,b]

Model	Atom	λ_1	λ_2	R	N_1	A_1
FTFD$\frac{1}{9}$SW	Li	2.517	0.5002	1.341	2	10.53
	Be	3.406	0.7461	0.8439	2	27.17
	C	5.189	1.093	0.4891	2	100.9
	O	6.995	1.374	0.3455	2	253.2
	Ne	8.824	1.582	0.2677	2	514.5
MTFD$\frac{1}{9}$SW	Li	5.360	1.180	0.3885	0.5624	35.12
	Be	6.537	1.304	0.3259	0.6745	75.18
	C	8.534	1.507	0.2568	0.8843	215.2
	O	10.22	1.674	0.2182	1.082	447.3
	Ne	11.70	1.817	0.1929	1.271	782.3

[a]See text for definitions of models and parameters.
[b]For corresponding parameters for the HF electron density, see paper I.

Tables XIII and XIV. As with the first- and second-row atoms, all these energies are higher than the HF energies. A minimum in the percentage error of the total energy occurs for Ni.

IV. DISCUSSION

A. The effects of the fixed-shell postulate on energies and densities

In paper I we did not constrain the maximum number of electrons in each shell and the electronic distributions obtained were, in general, in only fair agreement with the Hartree-Fock results, though the agreements in energies are good. On the other hand, all the present fixed-shell models give good densities though the agreements in energies may not be as good as modified models in some cases, notably for light atoms such as Li.

The exchange energy K of lithium in the HF-density TFD$\frac{1}{9}$W-energy-functional (HF-TFD$\frac{1}{9}$W) calculation is -1.512 a.u.,[2] while the inhomogeneity contribution kinetic energy is 0.753.[4(b)] The error caused by neglecting both of these energy components is 0.759, which is about 10% of the HF Li energy. The Dirac exchange formula always gives an exchange energy less than the HF exchange energy when the HF or near-HF density is used.[2] If we use the actual HF exchange energy -1.851,[2] the error caused by neglecting both exchange and inhomogeneity kinetic energies is 1.098, which is about 15% of the HF Li energy. This makes up most of the 16% discrepancy between FTF energy and HF energy of the Li atom. For neon, the error caused by neglecting both energies is less than 2%. The density deviations between FTF densities and HF densities for first-row atoms are around 2%.

TABLE IX. Fixed-shell Thomas-Fermi-Dirac model[a] for second-row atoms: energies and energy components.[b]

Atom	E_{HF}[c]	V_{ne}	J	K_0	E_{FTFD}(% error)[c]	E_{TFD}[d](% error)[c]
Na	−161.9	−413.4	80.94	−13.30	−172.9(−6.79)	−221.3(−36.7)
Mg	−199.6	−507.7	97.04	−15.19	−212.9(−6.66)	−270.1(−35.3)
Si	−288.9	−731.9	136.2	−19.38	−307.6(−6.47)	−384.7(−33.2)
S	−397.5	−1006.0	184.3	−24.05	−422.7(−6.34)	−522.9(−31.5)
Ar	−526.8	−1331.0	241.6	−29.16	−559.3(−6.17)	−685.5(−30.1)

[a]See text for definition of this three-shell model.
[b]Energy components are defined in Sec. I of text, $T=-E$. Energies are in hartrees.
[c]Errors are relative to E_{HF}, which are from Ref. 17(a).
[d]E_{TFD} is calculated from $E_{TFD}=-0.7687Z^{7/3}-0.266Z^{5/3}$, Ref. 19.

TABLE X. Fixed-shell Thomas-Fermi-Dirac model for second-row atoms: electron densities.[a]

Atom	λ_1	λ_2	λ_3	R_1	R_2	A_1	D_1[b]	D_2[b]
Na	11.00	1.906	0.3345	0.2180	2.273	989.0	9.174	0.0032
Mg	11.98	2.159	0.5313	0.1953	1.652	1295.0	12.00	0.0222
Si	13.95	2.644	0.8065	0.1618	1.109	2087.0	22.84	0.1521
S	15.91	3.121	1.010	0.1380	0.8448	3151.0	38.94	0.4726
Ar	17.87	3.597	1.179	0.1203	0.6839	4529.0	61.50	1.066

[a]Model and parameters are defined in text. This is a three-shell model.
[b]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 shells.

For the other fixed-shell models for first-row atoms as well as for all fixed-shell models for second- and third-row atoms, similar arguments can be applied to explain most of the deviations from the HF results. A minimum exists in the deviation curve of each fixed-shell model for first- and third-row atoms and is always located at an atom with incomplete p- and d-subshell electrons.[21]

The plots in Figs. 1 and 2 show the FTFD, FTFD$\frac{1}{9}$W, and HF densities for Ne and Be. In Fig. 3, the plots of the Kr atom show that the agreements between the FTFD$\frac{1}{9}$W and HF densities are very good only in the regions near the nucleus.

The fixed-shell models not only have fewer variational parameters (which reduces calculational effort) than the corresponding modified models developed in paper I, they also yield very good densities near the nuclei. They give total energies in reasonable agreement with HF results and the discrepancies that remain can be explained in a systematic way.

B. Relative importance of the inhomogeneity correction to kinetic energy and the exchange energy

Define the quantities

$$\alpha=T_2/T_0\ , \tag{15a}$$

where T_2 and T_0 are the total inhomogeneity energy and total Fermi kinetic energy, respectively, and

$$\alpha_1=\frac{T_2^1}{T_0^1},\ \alpha_2=\frac{T_2^2}{T_0^2},\ \alpha_3=\frac{T_2^3}{T_0^3}\ , \tag{15b}$$

etc., where $T_0^1, T_0^2, T_0^3, \ldots$ are the Fermi kinetic energies in $K,L,M,\ldots$ shells, respectively, while

TABLE XI. Fixed-shell and modified Thomas-Fermi-Dirac-$\frac{1}{9}$Singular-Weizsacker models for second-row atoms: energies and energy components.[a,b]

Model	Atom	T_0	T_2	T_s	V_{ne}	J	K_0	E(% error)[c]
FTFD$\frac{1}{9}$SW	Na	143.1	11.97	2.202	−378.6	76.7	−12.39	−157.2(2.90)
	Mg	176.7	14.27	2.841	−465.6	92.1	−14.17	−193.8(2.91)
	Si	256.8	19.64	4.388	−673.3	129.9	−18.16	−280.8(2.80)
	S	386.9	25.90	6.298	−927.5	176.4	−22.61	−386.9(2.67)
	Ar	471.4	33.04	8.578	−1230	232.0	−27.50	−513.0(2.62)
MTFD$\frac{1}{9}$SW	Na	141.4	15.55	5.787	−389.3	75.9	−12.12	−162.7(−0.49)
	Mg	174.6	18.56	6.907	−479.0	92.9	−14.03	−200.0(−0.20)
	Si	288.3	25.36	9.434	−691.5	133.0	−18.16	−288.3(0.21)
	S	395.8	33.21	12.33	−950.4	181.6	−22.73	−395.8(0.43)
	Ar	465.6	42.11	15.60	−1258	239.0	−27.70	−523.3(0.66)

[a]Models and energy components defined in text. These are three-shell models.
[b]$T=-E$. Energies are in hartrees.
[c]Errors are relative to $E_{\rm HF}$, which are given in Table IX.

TABLE XII. Fixed-shell and modified Thomas-Fermi-Dirac-$\frac{1}{9}$Singular-Weizsacker models for second-row atoms: electron densities.[a]

Model	Atom	λ_1	λ_2	λ_3	R_1	R_2	N_1	N_2	A_1	D_1[b]	D_2[b]
FTFD$\frac{1}{9}$SW	Na	9.668	1.847	0.3090	0.236	2.376	2	8	690	7.18	0.0026
	Mg	10.52	2.095	0.5035	0.212	1.717	2	8	902	10.57	0.0192
	Si	12.21	2.569	0.7790	0.175	1.146	2	8	1450	20.19	0.1374
	S	13.91	3.033	0.9819	0.149	0.871	2	8	2186	34.49	0.4334
	Ar	15.69	3.602	1.176	0.128	0.686	2	8	3229	59.08	1.059
MTFD$\frac{1}{9}$SW	Na	18.89	4.673	1.348	0.089	0.465	0.546	3.302	1791	61.6	1.835
	Mg	20.31	4.925	1.394	0.083	0.442	0.564	3.545	2294	78.2	2.272
	Si	23.07	5.399	1.479	0.074	0.405	0.599	4.018	3549	118.8	3.314
	S	25.73	5.841	1.558	0.066	0.376	0.632	4.480	5170	170.1	4.589
	Ar	28.29	6.256	1.631	0.061	0.352	0.664	4.931	7192	232.9	6.110

[a]See text for definitions of models and parameters. These are three-shell models.
[b]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 shells.

$T_2^1, T_2^2, T_2^3, \ldots$ are the corresponding inhomogeneity energies. These ratios are good measurements of the relative importance of T_2 in each shell. As shown in Table XV, the ratios α_1 and α_2 decrease monotonically from Li to Kr.[22] Similar trends exist for the ratios α_3, α_4, and the total ratio α. This indicates that the relative importance of T_2, as compared with T_0, decreases as Z increases.

For first-row atoms, the ratio α_2/α_1 decreases from about two for lithium to about one-half for neon. For second-row atoms, the ratio for the "intermediate" shell α_2 is smaller than either α_1 or α_3. For third-row atoms, we have two intermediate shells. The quantity α_2 is the lowest while α_3 is the second lowest among four shells. Looking at the trend for the alkali atoms Li, Na, and K, the ratios in the outmost shells increase from 0.2476 to 0.3623. A similar trend exists for alkali-earth atoms. For other columns, no significant trends are found.

A comparison of the ratio $|K_0/T_0|$, which also decreases monotonically, with the ratio α reveals that T_2 and K_0 may have different Z dependence, with T_2 higher than K_0. The calculations by Kim and Gordon[2] and by Shih[3(b)] support this argument. The discrepancies between the predictions of some authors[12(a),13(a)] and the actual calculations may be due to their failure to take the cusp condition into consideration. The exponential parameter in the innermost region of an atom is quite Z dependent. Failure to recognize this can lead to very poor predictions.

TABLE XIII. Fixed-shell Thomas-Fermi-Dirac-$\frac{1}{9}$Singular-Weizsacker model for third-row atoms: energies and energy components.[a,b]

Atoms(Z)	E_{HF}[c]	T_0	T_2	T_s	V_{ne}	J	K_0	E(% error)
K(19)	−599.2	533.8	36.89	9.78	−1394.2	263.1	−29.85	−580.5(3.12)
Ca(20)	−676.8	604.4	41.02	11.18	−1576.1	295.3	−32.46	−656.6(2.98)
Cr(24)	−1043.3	939.5	59.79	17.77	−2439.1	448.9	−43.92	−1017.1(2.51)
Ni(28)	−1506.9	1363.2	82.18	25.99	−3528.9	642.9	−56.86	−1471.4(2.36)
Ge(32)	−2075.4	1881.0	108.2	35.87	−4858.9	869.9	−71.20	−2025.1(2.42)
Se(34)	−2399.9	2176.6	122.7	41.43	−5617.7	1015.2	−78.88	−2340.7(2.47)
Kr(36)	−2752.1	2497.5	138.0	47.41	−6441.2	1162.3	−86.89	−2682.9(2.51)

[a]See text for definitions of model and energy components. This is a four-shell model.
[b]$T=-E$. Energies are in hartrees.
[c]Errors are relative to E_{HF}, which are from Ref. 17(b).

TABLE XIV. Fixed-shell Thomas-Fermi-Dirac-$\frac{1}{9}$Singular-Weizsacker model for third-row atoms: electron densities.[a]

Atom(Z)	λ_1	λ_2	λ_3	λ_4	R_1	R_2	R_3	A_1	D_1[b]	D_2[b]	D_3[b]
K(19)	16.46	3.671	1.327	0.4736	0.1226	0.6384	2.806	3701	65.37	1.482	0.0047
Ca(20)	17.31	3.884	1.477	0.6476	0.1156	0.5831	2.108	4334	79.23	2.097	0.0232
Cr(24)	20.71	4.724	2.054	0.9964	0.0939	0.4327	1.162	7586	154.8	6.307	0.3150
Ni(28)	24.11	5.548	2.640	1.232	0.0791	0.3428	0.8166	12165	268.9	14.41	1.181
Ge(32)	27.50	6.358	3.242	1.432	0.0682	0.2831	0.6299	18301	429.9	27.96	2.951
Se(34)	29.19	6.759	3.550	1.523	0.0638	0.2602	0.5651	22026	530.5	37.29	4.282
Kr(36)	30.89	7.158	3.862	1.611	0.0600	0.2407	0.5122	26225	646.0	48.61	5.970

[a]See text for definitions of model and parameters. This is a four-shell model.
[b]The quantities $D_1 = R_1^2 \rho_{R_1}$, etc., are the electron densities at the radii which separate the shells.

C. Stability of neutral atoms

For the modified statistical models developed in paper I, the revised results still show that all neutral atoms are unstable with respect to the corresponding positive ions with the same number of shells. For the present fixed-shell models, we find similar but improved results, as shown in Table XVI. This is undesirable; nevertheless, we note two favorable trends: (1) The better the energy functional used, the better the ionization potential obtained; and (2) for the same energy functional the better the density used, the better the ionization potential obtained. In the revised MTFD$\frac{1}{9}$SW model for the Ne atoms and ions, Ne^+ is still unstable with respect to the ionization process. In the FTFD$\frac{1}{9}$SW model, which gives a much better density, Ne^+ is stable.

D. Energy functional for particles in a spherical box energy

One may inquire whether the energy formula derived from free particles in a spherical box with radius R, which can be written in the following form for its lowest energy orbital

$$T = E = \frac{2\pi}{R^2} , \tag{15c}$$

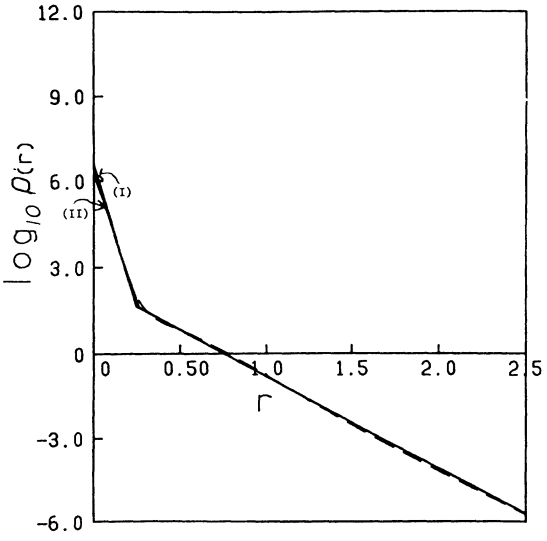

FIG. 1. Electron densities of neon atom: (a) Dashed line is the HF density; (b) solid line (I) is the FTFD density; solid line (II) is the FTFD$\frac{1}{9}$W density.

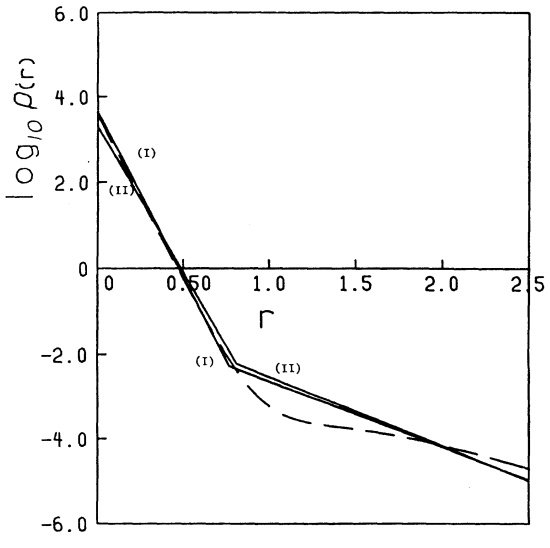

FIG. 2. The electron densities of beryllium atom: (a) Dashed line is the HF density; (b) Solid line (I) is the FTFD density; solid line (II) is the FTFD$\frac{1}{9}$W density.

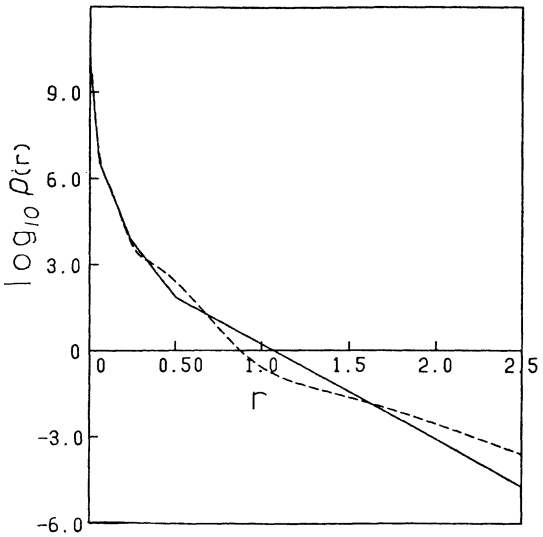

FIG. 3. Electron densities of krypton atom: (a) Dashed line is the HF density; (b) solid line is the FTFD$\frac{1}{9}$W density.

can give good kinetic energy values for the K-shell electrons of fixed-shell models. We use the FTFD$\frac{1}{9}$W model and its K-shell kinetic energy $(T_0^1+T_2^1)$ as the reference. The deviations increase monotonically from -44.3% for Li atom to $+13.7\%$ for Kr atom. The Si and P atoms exhibit the best agreement: -0.77% and $+0.85\%$, respectively.

E. Limitations on the gradient expansion in atomic systems

Most extant energy-functional theories assume that the electronic density is homogeneous or only slowly varying in space, i.e.,

$$\left|\frac{\vec{\nabla}\rho}{\rho}\right| \ll 1 \quad \text{and} \quad \left|\frac{\vec{\nabla}\rho\cdot\vec{\nabla}\rho}{\vec{\nabla}\rho}\right| \ll 1 . \tag{16}$$

Only the "intermediate regions," such as the L and M shells in fixed-shell models for third-row atoms, can satisfy the assumptions underlying the derivations of a gradient expansion. In the work of Kompaneets and Pavlovskii[13(a)] and of Kirzhnits,[12(a)] it was thought that the inhomogeneity corrections to the Fermi kinetic energy T_0 were not applicable in the region near the nucleus because the semiclassical approximations made were not valid there. On the other hand, Kohn and Sham[11(c)] have suggested that the inhomogeneous corrections to the kinetic energy are needed and should not be truncated because, without these corrections, the electron density and its gradient

TABLE XV. Ratios of local energies for fixed-shell Thomas-Fermi-Dirac-$\frac{1}{9}$Weizsacker model of atoms.[a]

Atom	α_1	α_2	α_3	α_4	α	$\left\|\frac{K_0}{T_0}\right\|$
Li	0.1119	0.2476			0.1136	0.2428
Be	0.1045	0.1496			0.1063	0.1894
C	0.0971	0.0888			0.0963	0.1373
O	0.0938	0.0655			0.0896	0.1109
Ne	0.0923	0.0529			0.0846	0.0945
Na	0.0897	0.0523	0.2524		0.0819	0.0860
Mg	0.0876	0.0508	0.1685		0.0794	0.0796
Si	0.0844	0.0473	0.1067		0.0753	0.0700
S	0.0820	0.0445	0.0795		0.0720	0.0630
Ar	0.0800	0.0423	0.0640		0.0692	0.0576
K	0.0797	0.0407	0.0615	0.3623	0.0682	0.0552
Ca	0.0789	0.0395	0.0576	0.2234	0.0670	0.0530
Cr	0.0765	0.0357	0.0470	0.0944	0.0629	0.0460
Ni	0.0747	0.0329	0.0415	0.0618	0.0597	0.0410
Ge	0.0733	0.0308	0.0384	0.0466	0.0570	0.0372
Se	0.0727	0.0300	0.0373	0.0417	0.0558	0.0356
Kr	0.0722	0.0292	0.0364	0.0378	0.0548	0.0342

[a]See text for definitions of model and ratios.

TABLE XVI. Energies of modified and fixed-shell statistical models for Ne and its ions.[a]

Atom or ion	HF[b]	MTF	MTFD	MTFD$\frac{1}{9}$W	MTFD$\frac{1}{9}$SW	FTF	FTFD	FTFD$\frac{1}{9}$W	FTFD$\frac{1}{9}$SW
Ne	−128.5	−131.5	−143.3	−128.2	−125.9	−126.3	−137.5	−126.5	−124.8
Ne^+	−127.8	−133.9	−145.3	−129.4	−126.8	−127.03	−137.9	−126.9	−125.1
Ne^{2+}	−126.4	−135.7	−146.8	−130.0	−127.1	−127.05	−137.5	−126.6	−124.7
Ne^{4+}	−120.5	−137.0	−146.9	−128.3	−124.7	−124.2	−133.6	−122.6	−120.9

[a]See text for definitions of models, which are two-zone ones.
[b]Hartree-Fock energies are from Ref. 17(d).

are divergent at the nucleus in the original TF and TFD models. We know that the gradient expansion of the kinetic energy can be obtained without making the semiclassical approximation. However, the gradient expansion has to be truncated because of the cusp condition[5] at the nucleus. The form and the number of expansion terms may depend on the number of electrons of the system as well as on external potentials, such as that set up by the nuclear charge.

F. Other statistical models with shell structures

Statistical atomic models exhibiting shell structure have previously been obtained by several authors.[23–25] Gombas and co-workers[23] utilized a "shell" concept, which is similar to the HF model, to accommodate electrons and introduced a sophisticated pseudopotential to achieve the proper spatial exclusion between shells. The nuclear cusp condition was maintained since the full Weizsacker correction T_W was used. Their model exhibits shell structure because the resulting exponential parameters differ drastically from each other. Kirzhnits and Shpatakovskaya[24] started with the semiclassical approximations and obtained a density expression exhibiting shell structure. Light and Yuan[25] started from an accurate solution of the Milne equation[26] and made a semiclassical approximation to the density near the nucleus and derived a closed formula for the reduced density matrix. They obtained electron densities with shell structure through a SCF procedure.

Green and his co-workers[27] have developed an analytic semiempirical model which is similar in spirit to the present model. They also obtained a formula for the one-electron potential.

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