Independent-particle-model potentials for atoms and ions with $36 < Z \leq 54$ and a modified Thomas-Fermi atomic energy formula*

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Using the *ab initio* energy-minimization procedure of Bass, Green, and Wood, we determine two potential parameters, ξ and η, characterizing the independent-particle-model potential of Green, Sellin, and Zachor (GSZ) for atoms and positve ions with $36 < Z \leq 54$. This extends earlier modified-Hartree-Fock (MHF) calculations of Szydlik and Green and of Green, Garvey, and Jackman. We find that both of the parameters in question display, to a good approximation, a linear dependence on the degree of ionization $Z-N$ for fixed numbers of electrons N. The slopes and y intercepts associated with the linear dependence of ξ display marked shell-like behavior, while those associated with η vary rather smoothly with N. Our determinations of total energies are usually within 50 ppm of earlier Hartree-Fock calculations for those cases in which such calculations exist. Using the entire collection of energies and GSZ minimization parameters now available, we reexamine a modified version of the Thomas-Fermi statistical model (MTF) due to Green, Sellin, and Darewych. We show that this model is capable of yielding the linear $Z-N$ dependence of the GSZ parameters which we found empirically in the MHF work. By numerical adjustment of the coefficients of our MTF model, we obtain energies of stable atoms and ions, as well as GSZ potential parameters which are in good agreement with the MHF calculations.

I. INTRODUCTION

To formulate a meaningful and accurate treatment of a number of relevant physical problems involving highly charged atomic ions, it is necessary first to have a realistic quantum-mechanical description of these ions. For example, it is well known in astrophysics that highly ionized species are important radiators in stellar interiors. In experiments employing heavy-ion accelerators, many collisional and ionization phenomena arise involving highly charged ions not previously encountered in the laboratory.[1] In the fusion process, highly ionized trace impurities can act as strong radiators and thereby constitute important loss mechanisms. In addition, it is now recognized that inner-shell vacancies produced by x-ray or electron bombardment are often filled by Auger cascade processes which can lead to highly charged atomic states.

This work was undertaken in recognition of this need for knowledge of the quantum-mechanical properties of atoms of all states of ionization. At the outset, we find the two parameters for the independent-particle-model (IPM) potential in Green, Sellin, and Zachor[2] (GSZ) for atoms and positive ions with atomic number Z between 36 and 54 and for a few ions with $54 < Z \leq 57$. In this regard, this work is an extension of a modified form of Hartree-Fock theory (MHF) developed by Bass, Green, and Wood[3] (BGW) for neutral atoms, by Szydlik and Green[4] for atoms and ions with $Z \leq 18$, and by Green, Garvey, and Jackman[5] (GGJ) for atoms and ions with $18 < Z \leq 36$. In each of these earlier papers and in the present work, the two parameters of the GSZ potential for a given atom or ion are determined by the variational procedure of BGW. To the best of our knowledge, for most of the ions considered here, our results represent the first nonperturbative, nonstatistical calculations of the total energies and associated single-electron potentials. The single-particle wave functions which are easily obtained from these IPM potentials have numerous possible applications (cf. Refs. 6–16).

II. THE ANALYTIC IPM

In the IPM, the GSZ potential acting upon any one of the electrons in a given atom or ion is assumed to have the form

$$V(r) = 2[(N-1)\Upsilon - Z]/r, \tag{1}$$

where

$$\Upsilon = 1 - \Omega(r), \tag{2}$$

with

$$\Omega(r) = [(\eta/\xi)(e^{\xi r} - 1) + 1]^{-1}, \tag{3}$$

where N is the total number of electrons in the atom or ion and Z is the nuclear charge. Here the parameter ξ corresponds to $1/d$ used in GSZ and η/ξ corresponds to H. In the original GSZ work, it was found that this potential was most accurate in predicting single-electron energies if the parameters ξ and η in the screening function $\Omega(r)$ were readjusted for each atom or ion under consideration, and we have adopted such a

methodology here. The energy was obtained by a modified Hartree-Fock (MHF) calculation employing as eigenfunctions a Slater determinant composed of one-electron wave functions of the atom or ion, which are obtained from the GSZ potential. The detailed theory of these energy calculations has been presented in BGW and will not be repeated here.

III. PARAMETER VARIATION

To obtain the ξ and η which minimize E for a given atom or ion, we varied ξ and η five times in increments of (1–5)% of some initially chosen ξ and η, and the resulting energy surface was fitted to a quadratic surface from which the final values of ξ and η producing the energy minimum were calculated. Such a minimization technique is effective, provided the initial guesses for ξ and η are not too far from the actual parameters ξ_m and η_m which minimize E. We used the GGJ results as a basis for determining the initial parameter guesses for a given ion or atom. In examining the results of their MHF calculations, GGJ discovered a simple linear dependence of both ξ_m and η_m on $Z-N$ for a given N. We can write this dependence as

$$\xi_m = \xi_0 + \xi_1(Z-N) \tag{4}$$

and

$$\eta_m = \eta_0 + \eta_1(Z-N)\,. \tag{5}$$

Assuming these linear relationships to be valid

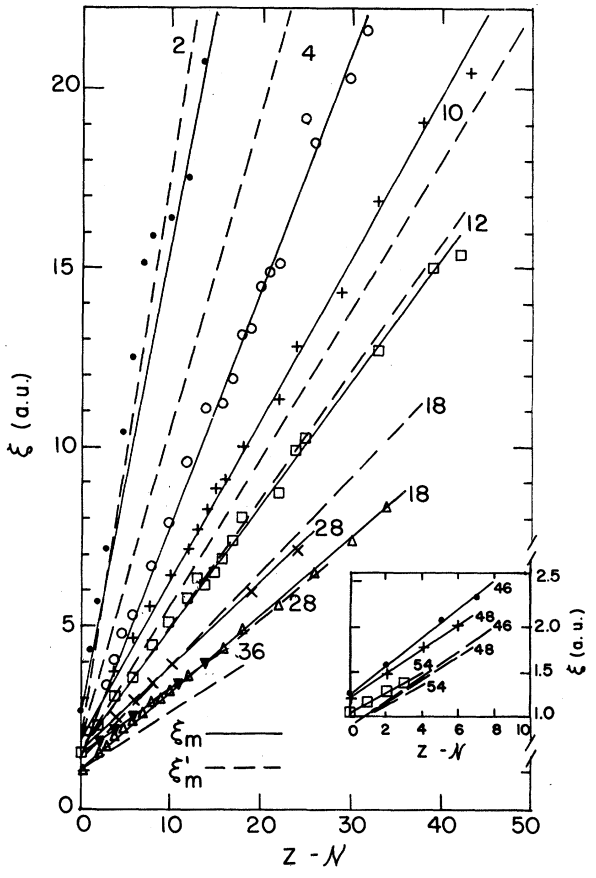

FIG. 1. The symbols represent the ξ parameters of the GSZ potential that yield minimum total energies for various degrees of ionization $Z-N$ of the ion or atom under consideration for various fixed values of N indicated on the graph. The solid lines are the corresponding values (ξ'_m) obtained by linear least-squares fits to the symbols. The dashed lines are the values of ξ_m obtained from the modified Thomas-Fermi (MTF) model described in Sec. V, using the coefficients in row B of Table III.

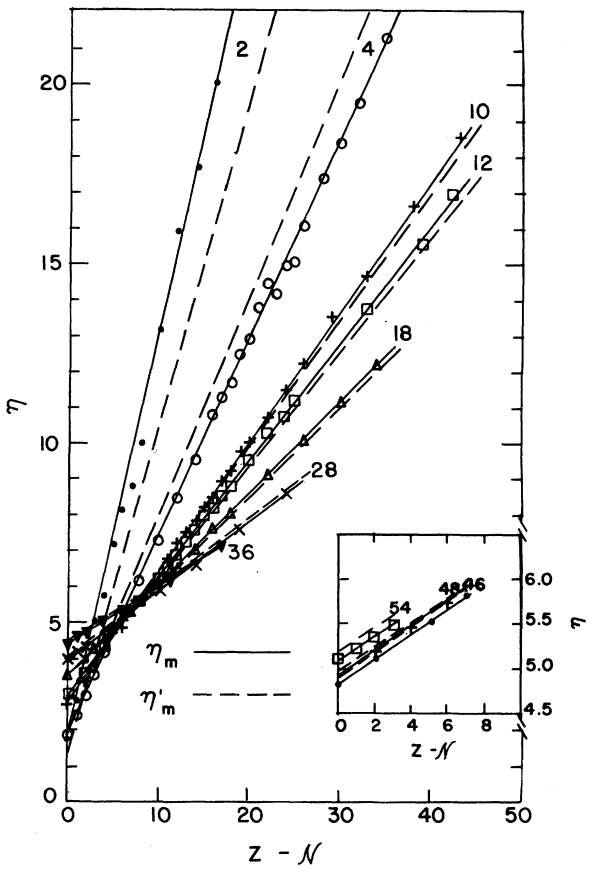

FIG. 2. The symbols represent the η parameters of the GSZ potential that yield minimum total energies against the degree of ionization $Z-N$ of the ion or atom under consideration for various fixed values of N indicated on the graph. The solid lines are the corresponding values of η_m obtained by linear least-squares fits to the symbols. The dashed lines are the values (η'_m) obtained from the MTF model described in Sec. V, using the coefficients in row B of Table III.

for values of Z and/or N larger than those considered by GGJ, we obtained our initial guesses for the potential parameters for ions with $N \leq 36$ and $36 < Z \leq 54$ by simply taking the relevant GGJ values for ξ_0, ξ_1, η_0, and η_1 and calculating ξ_m and η_m from Eqs. (4) and (5) for the Z and N in question. For atoms and ions with $N > 36$, we extrapolated the plots of these four parameters versus N to higher N and then used Eqs. (4) and (5) to obtain initial guesses for ξ and η. Usually, no more than three runs were necessary to obtain a true minimum of E for a given N and Z.

In this work we have chosen to stress isoelectronic sequences; consequently, the total energies of a few atoms and ions have been calculated with the ion or atom in an electronic configuration which is not necessarily the one producing the lowest total energy. Such anomalies occur for atoms with N between 37 and 46, where Hartree-Fock calculations indicate the neutrals have their lowest energy in the configuration in which the $5s$ shell is filled, or partially filled, before the $4d$ shell, while the ions with such N have their lowest energy in the configuration in which the $4d$ shell is filled before the $5s$ shell.

IV. RESULTS OF MHF CALCULATIONS

For $N \leq 36$ we examined those ions whose electronic configurations correspond to closed shells or subshells, i.e., $N = 2, 4, 10, 12, 18, 28, 30, 36$, and we also considered ions with $N = 23$, which corresponds to a half-filled $3d$ shell. For each electronic configuration considered, we chose four ions with $36 < Z \leq 54$. We found that the linear behavior observed by GGJ for N and $Z \leq 36$ continued for larger Z. We obtained linear least-squares fits to the cumulative data for a given $N \leq 36$ with the ξ_0 and η_0 of Eqs. (4) and (5) fixed to the values obtained by GGJ. The new slopes obtained here are within 3% of the corresponding parameters obtained by GGJ, except for a few cases in which the GGJ parameters had been obtained from just a few "data" points, so that our results effectively doubled the number of points determining the straight-line fits, and, in these few cases, the change in slope is always less than 8%.

For species with $N > 36$, we considered atoms and ions with $N = 37$, 39, 41, 42, 44, 46, 48, 50, 52, and 54 as representative samples of species with outermost electrons in the $4d$, $5s$, and $5p$ shells. For a given N, we chose four values of Z between 36 and 54. Again, the values of ξ_m and η_m displayed a linear dependence on $Z - N$. Employing linear least-squares fits of the type described above, we obtained the slopes of the straight lines describing the behavior of ξ_m and η_m for $36 < N \leq 54$.

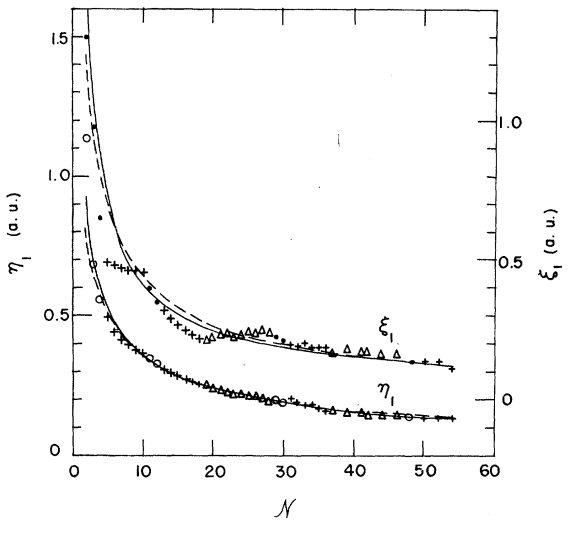

FIG. 3. The symbols are ξ_1 and η_1 values for various numbers of electrons N. The solid lines are plots of ξ_1 and η_1 vs N obtained from the MTF model using the coefficients in row B of Table III, while the dashed lines are similar plots obtained using the coefficients in row A of Table III.

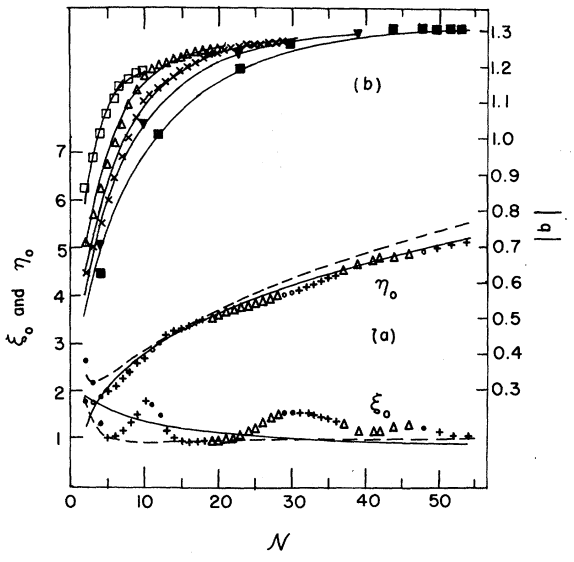

FIG. 4. (a) The symbols are ξ_0 and η_0 for various numbers of electrons N. The solid lines are plots of ξ_0 and η_0 vs N obtained from the MTF model using the coefficients in row B of Table III, while the dashed lines are similar plots obtained using the coefficients in row A of Table III. (b) The symbols are the magnitude of the reduced MHF energies $|E|/Z^{7/3}$ plotted vs N for various fixed values of Z, while the solid lines are the corresponding reduced MTF energies obtained using the coefficients in row B of Table III.

Examples of the linear behavior of ξ_m and η_m are presented in Figs. 1 and 2, where we have included the GGJ results for completeness. In Fig. 1 we have plotted the values of ξ_m against $Z-N$ for the various values of N we considered, along with the accompanying straight-line fits shown by the solid lines. In Fig. 2, the corresponding information for η_m is presented. These plots are typical for $N \geq 4$. As can be seen, the scatter is reasonably small and apparently nonsystematic. For $N=2$, the energy surface appears to be very flat, since there is very little screening, and it is difficult to obtain a definite minimum; consequently, there is appreciably more scatter in the results in this case. Still, even here, a linear trend is readily discernible in the data, as can be seen in the plots for $N=2$ in Figs. 1 and 2.

The occurrence of this linear behavior of the two potential parameters allows a particularly compact presentation of the GSZ potentials of all atoms and ions with $N \leq 54$, consistent with this energy-minimization procedure. All we need do is present ξ_0, η_0, ξ_1, and η_1 of the straight lines associated with ξ_m and η_m for $N=2$–54 [see Figs. 3 and 4(a) and Table I]. Data corresponding to particular shells have been characteristically labeled in Figs. 3 and 4, with circles used to denote the s shell, crosses the p shell, and triangles the d shell. We have included the GGJ results for completeness. There is a marked shell-like behavior superposed on a gradual decline with increasing N in both ξ_0 and ξ_1. A strong shell-like dependence associated with the ξ parameter of the GSZ potential has been noticed in earlier IPM work[2,3] in which ξ and η were obtained by fitting IPM single-electron energy levels of atoms to experimental values. The shell-like dependence of the η parameter is much less noticeable, although the graph of η_0 vs N goes through a definite change of slope near $N=14$ and a somewhat smaller change of slope near $N=42$. This weak shell dependence in η is also consistent with the results of earlier IPM work.

The shell-like behavior of all the graphs in Figs. 3 and 4(a) diminishes rapidly beyond $N=30$; so it is a simple matter to interpolate from these graphs the values of ξ_0, ξ_1, η_0, and η_1 corresponding to various N between 36 and 54 not given explicitly in Table I.

The total MHF energies we obtained are usually less than 50 ppm above the corresponding Hartree-Fock-Roothaan values of Clementi and Roetti, [17] who, in the range of Z and N we considered, have examined only the neutrals and singly ionized species. This close agreement between the MHF and Clementi results has been the case in all the earlier MHF calculations for species with N and

TABLE I. Slopes and y intercepts for the straight lines $\xi=\xi_0+\xi_1(Z-N)$ and $\eta=\eta_0+\eta_1(Z-N)$. C represents the configuration of the outermost electron in the electronic configuration corresponding to a given value of N.

N	C	ξ_0	$10\times\xi_1$	η_0	$10\times\eta_1$
2	$1s^2$	2.625	12.996	1.770	11.402
3	$2s^1$	2.164	9.764	1.750	6.821
4	$2s^2$	1.300	6.465	1.880	5.547
5	$2p^1$	1.031	4.924	2.000	4.939
6	$2p^2$	1.065	4.800	2.130	4.434
7	$2p^3$	1.179	4.677	2.270	4.143
8	$2p^4$	1.360	4.613	2.410	3.925
9	$2p^5$	1.508	4.602	2.590	3.755
10	$2p^6$	1.792	4.515	2.710	3.671
11	$3s^1$	1.712	3.923	2.850	3.469
12	$3s^2$	1.492	3.452	3.010	3.269
13	$3p^1$	1.170	3.191	3.170	3.087
14	$3p^2$	1.012	2.933	3.260	2.958
15	$3p^3$	0.954	2.659	3.330	2.857
16	$3p^4$	0.926	2.478	3.392	2.739
17	$3p^5$	0.933	2.368	3.447	2.633
18	$3p^6$	0.957	2.165	3.500	2.560
19	$3d^1$	0.964	2.151	3.516	2.509
20	$3d^2$	0.941	2.248	3.570	2.404
21	$3d^3$	0.950	2.324	3.627	2.328
22	$3d^4$	0.998	2.345	3.667	2.238
23	$3d^5$	1.061	2.243	3.709	2.171
24	$3d^6$	1.138	2.291	3.745	2.187
25	$3d^7$	1.207	2.408	3.803	2.090
26	$3d^8$	1.308	2.391	3.840	2.088
27	$3d^9$	1.397	2.462	3.891	2.048
28	$3d^{10}$	1.455	2.397	3.973	1.925
29	$4s^1$	1.520	2.246	4.000	1.985
30	$4s^2$	1.538	2.106	4.050	1.878
31	$4p^1$	1.541	1.988	4.110	2.001
32	$4p^2$	1.512	1.914	4.182	1.897
33	$4p^3$	1.492	1.990	4.230	1.782
34	$4p^4$	1.460	1.857	4.290	1.772
35	$4p^5$	1.407	1.897	4.369	1.686
36	$4p^6$	1.351	1.872	4.418	1.611
37	$4d^1$	1.286	1.686	4.494	1.619
39	$4d^3$	1.129	1.784	4.618	1.509
41	$4d^5$	1.139	1.702	4.680	1.485
42	$4d^6$	1.136	1.694	4.749	1.412
44	$4d^8$	1.197	1.601	4.769	1.435
46	$4d^{10}$	1.246	1.587	4.829	1.397
48	$5s^2$	1.205	1.358	4.904	1.414
50	$5p^2$	1.130	1.395	4.990	1.324
52	$5p^4$	1.050	1.354	5.050	1.314
54	$5p^6$	1.044	1.107	5.101	1.316

$Z \leq 36$.

For most of the ions we considered here, no other previous nonperturbative or nonstatistical calculations of the total energy or single-electron potentials exist.[18] Table II contains the energies we obtained for such ions. The parameters characterizing the GSZ potentials describing these ions can be calculated readily from the data in Table I and with the use of Eqs. (4) and (5).

V. THE MODIFIED THOMAS-FERMI MODEL

We have attempted to gain some understanding of the origins of the linear behavior of ξ_m and η_m by examining a modified Thomas-Fermi (MTF) model. Although such a model cannot predict any shell-like behavior without the *ad hoc* addition of quantum effects, the model can possibly predict the general behavior of the two potential parameters. The model we used is based on an adaptation of the Thomas-Fermi statistical theory[19] due to Green, Sellin, and Darewych[20] (GSD). In this MTF model, the total energy of a many-electron system containing N electrons and Z protons is given by the sum of E_1, the electrostatic energy of the electron cloud in the field of the nucleus, E_2, the electrostatic interaction energy between the various electrons, E_3, the main kinetic energy of the electrons, E_4, the Weizsäcker correction to the kinetic energy,[21,22] E_5, the exchange energy,[23] and E_6, the inhomogeneity correction[24] for the exchange energy [see Eqs. (4)–(9) of GSD]. Each of these terms may be written as an integral involving the radially symmetric charge distribution $n(r)$, which, from Poisson's equation applied to the IPM potentials obtained in the MHF calculations, we determine to be

$$n(r) = \frac{\eta\xi}{4\pi}\frac{e^{\xi r}}{r}\frac{(\eta/\xi)(e^{\xi r}+1)-1}{[(\eta/\xi)(e^{\xi r}-1)+1]^3}\,. \tag{6}$$

We have ignored the correlation energy,[25,26] which should be a relatively small term and can be absorbed, in part, into the other energy terms, particularly E_5.

Following GSD, we reexpress each of these energy integrals with the major dependence on the parameter $\eta = H/d$, which completely determines the GSZ potential in the important inner region of the species, written explicitly, and obtain [cf. Eq. (20) of GSD]

$$E_T = \alpha ZN\eta + \beta N^2\eta + \gamma N^{5/3}\eta^2 + \delta N\eta^2 - \mu N^{4/3}\eta - \tau N^{2/3}\eta, \tag{7}$$

where the six successive terms in Eq. (7) correspond to the density integrals in the six components of the total energy of the system. It was shown analytically by GSD that $\alpha = \alpha_0$ with $\alpha_0 = 2$, $\beta = \beta_0 + \beta_1\xi/\eta$ with $\beta_0 = \frac{1}{3}$ and $\beta_1 = \frac{1}{6}$. By numerical integration of γ, the coefficient of the main kinetic-energy term, we find we can represent γ accurately by

$$\gamma = \gamma_0 + \gamma_1\xi/\eta + \gamma_2(\xi/\eta)^2\,, \tag{8}$$

with $\gamma_0 = 0.5045$, $\gamma_1 = -0.1019$, and $\gamma_2 = 0.0853$. This result, which is a much better approximation than the $\gamma = 0.487$ used by GSD, is crucial to the improvements which we have made in the MTF model. In addition, we use an improved representation of the exchange-energy coefficient μ, so that

$$\mu = \mu_0 + \mu_1\xi/\eta\,, \tag{9}$$

with $\mu_0 = 0.2810$ and $\mu_1 = 0.0757$.

The $1/r$ singularity in $n(r)$ [see Eq. (6)] prohibits us from obtaining an analytic form for δ, the coefficient in the Weizsäcker correction to the kinetic energy. However, guided by the form obtained for γ, the coefficient of the principal kinetic-energy term, we treat the relatively minor term δ by assuming it to have a similar functional form and write

$$\delta = \delta_0 + \delta_1\xi/\eta + \delta_2(\xi/\eta)^2\,. \tag{10}$$

Since the inhomogeneity-exchange correction term is relatively smaller than any of the other energy terms, we assume, with GSD, that $\tau = \tau_0$, a constant. With these parametrizations, Eq. (7) reduces to a simple biquadratic in ξ and μ of the form

$$E_T = -A\xi - B(Z)\eta + C_0\eta^2 + C_1\xi\eta + C_2\xi^2\,, \tag{11}$$

where

$$A = -\beta N^2 + \mu_1 N^{4/3}\,, \tag{12}$$

$$B(Z) = \alpha_0 ZN - \beta_0 N^2 + \mu_0 N^{4/3} + \tau_0 N^{2/3}\,, \tag{13}$$

and

$$C_i = \gamma_i N^{5/3} + \delta_i N\,. \tag{14}$$

We can now obtain those potential parameters ξ_m and η_m which characterize the stable system by minimizing Eq. (11) with respect to ξ and η. Such a procedure leads to expressions for ξ_m and η_m having precisely the form of the empirical equations (4) and (5) found by Green, Garvey, and Jackman with the values of ξ_0, ξ_1, η_0, and η_1 now explicitly given by

$$\xi_0 = [2AC_0 - B(N)C_1]/\Delta\,, \tag{15}$$

$$\xi_1 = -\alpha_0 C_1 N/\Delta\,, \tag{16}$$

$$\eta_0 = [2B(N)C_2 - AC_1]/\Delta\,, \tag{17}$$

and

$$\eta_1 = 2\alpha_0 C_2 N/\Delta\,, \tag{18}$$

TABLE II. MHF values of the magnitude of the total energies (in rydbergs) of atoms and ions whose energies have not been calculated previously.

N	Z	$\lvert$Total energy$\rvert/10^3$	N	Z	$\lvert$Total energy$\rvert/10^3$
2	38	2.840 721 2	29	32	4.146 523 4
2	45	3.993 970 5	29	34	4.787 324 2
2	48	4.548 222 7	29	36	5.477 027 3
2	52	5.343 222 7	30	32	4.148 847 7
4	39	3.681 575 2	30	34	4.792 050 8
4	43	4.489 003 9	30	36	5.484 757 8
4	47	5.376 433 6	30	40	7.018 125 0
4	54	7.121 941 4	30	46	9.687 066 4
10	39	5.431 125 0	30	48	10.674 949
10	43	6.672 925 8	30	54	13.933 086
10	48	8.405 183 6	31	34	4.795 121 1
10	53	10.337 453	31	36	5.490 351 6
12	37	5.041 261 7	32	34	4.797 351 6
12	45	7.641 855 5	32	36	5.494 953 1
12	51	9.946 992 2	32	38	6.243 085 9
12	54	11.213 566	33	36	5.498 562 5
18	40	6.496 746 1	33	38	6.249 433 6
18	44	7.995 359 4	34	36	5.501 214 8
18	48	9.650 464 8	34	38	6.254 636 7
18	52	11.462 031	34	40	7.059 550 8
19	32	3.998 968 3	35	37	5.874 347 7
19	34	4.580 293 0	35	38	6.258 761 7
19	36	5.182 625 0	35	40	7.066 617 2
20	32	4.025 789 1	36	38	6.261 859 4
20	34	4.614 871 1	36	40	7.072 460 4
20	36	5.244 902 3	36	42	7.935 558 6
21	32	4.049 608 4	36	47	10.322 168
21	34	4.646 085 9	36	50	11.910 777
21	36	5.284 418 0	36	53	13.616 734
22	32	4.070 563 7	37	37	5.876 421 9
22	34	4.674 105 5	37	45	9.338 253 9
22	36	5.320 402 3	37	48	10.854 750
23	32	4.088 756 4	37	53	13.645 723
23	34	4.699 003 9	39	39	6.662 953 1
23	36	5.352 914 1	39	44	8.871 480 5
23	39	6.415 613 3	39	49	11.417 898
23	45	8.835 355 5	39	54	14.300 422
23	49	10.666 492	41	45	9.364 140 6
23	54	13.200 539	41	48	10.902 199
24	32	4.104 378 9	41	53	13.740 082
24	34	4.720 945 3	42	47	10.382 059
24	36	5.382 101 6	42	50	12.008 016
25	32	4.117 496 1	42	53	13.758 563
25	34	4.740 023 4	44	48	10.921 898
25	36	5.408 082 0	44	51	12.600 297
26	32	4.128 261 7	44	54	14.405 742
26	34	4.756 390 6	46	48	10.928 426
26	36	5.430 964 8	46	51	12.616 426
27	32	4.136 832 0	46	53	13.813 820
27	34	4.769 984 4	48	50	12.044 066
27	36	5.450 910 2	48	52	13.216 785
28	32	4.143 324 2	48	54	14.447 816
28	34	4.781 500 0	50	52	13.221 297
28	36	5.468 011 7	50	54	14.456 301
28	38	6.202 820 3	52	54	14.461 531
28	42	7.816 941 4	52	55	15.103 180
28	47	10.105 305	54	55	15.107 184
28	52	12.694 137	54	56	15.765 691
			54	57	16.439 301

with

$$\Delta = 4C_0C_2 - C_1^2. \tag{19}$$

The key steps in arriving at these simple results are the use of Eq. (8) as a more accurate representation of the numerically evaluated kinetic-energy functional γ, and the assumption of a corresponding representation of the unknown kinetic-energy-correction functional δ [Eq. (10)].

VI. THOMAS-FERMI COEFFICIENTS

We next endeavored to determine how closely the predictions of the MTF model presented in Sec. V correspond to the results of the MHF calculations, and to determine what numerical adjustments of the energy coefficients α_0, β_i, γ_i, δ_i, μ_i, and τ_0 might bring the MTF model into closest harmony with the MHF results. To determine these numerical adjustments we varied various combinations of the energy coefficients so as to minimize the composite

$$S^2 = \epsilon_b + \epsilon_\eta + \epsilon_\xi, \tag{20}$$

where

$$\epsilon_b = \sum_s (b_m - b'_m)_s^2 \omega_1, \quad \epsilon_\eta = \sum_s (\eta_m - \eta'_m)_s^2 \omega_2, \quad \epsilon_\xi = \sum_s (\xi_m - \xi'_m)_s^2 \omega_3. \tag{21}$$

The primes here denote the MHF parameters for various weights, ω_1, ω_2, and ω_3, which were normalized so that $\omega_1 + \omega_2 + \omega_3 = 1$. In Eq. (21) the summation is over all species s; b_m and b'_m are the reduced energies obtained from MHF and MTF calculations, respectively; and the reduced energy of a species is defined as its total energy divided by $Z^{7/3}$.[27] The most important results of this minimization procedure are given in Table III. The columns in that table labeled S.D.$_b$, S.D.$_\eta$, and S.D.$_\xi$ are the standard deviations for the fits of the b, η, and ξ parameters, respectively, obtained in calculating S^2. These standard deviations have been calculated so that they are independent of the weights used in calculating S^2.

The row labeled GSD in Table III gives the values of the coefficients obtained by GSD and the standard deviations we obtained with these coefficients. The row labeled MGSD contains the coefficients we obtained with the better representations of γ and μ given by Eqs. (8) and (9), respectively. As the standard deviations for those two rows indicate, neither set of coefficients yields good fits to ξ_m and η_m.

In row A of Table III, we present the coefficients that yield the best over-all fit to the three parameters that we obtained by fixing the coefficients α_0, β_i, and γ_i, which are related to the dominant terms in the MTF energy expression, and varying the correction coefficients δ_i, μ_i, and τ_0. Here, the MTF reduced energies are usually (5–10)% above the MHF reduced energies. As an indication of the quality of the fits to the potential parameters obtained with these coefficients, we have plotted with dashed lines in Figs. 3 and 4(a) the ξ_0, ξ_1, η_0, and η_1 calculated with these coefficients.

In row B, we present the coefficients and weight ratio that yielded the best of all the over-all fits we obtained. To determine these coefficients, we varied all the parameters, including α_0, β_i, and γ_i. The quality of the potential parameter fits is displayed by the solid-line plots in Figs. 3 and 4(a), which are the MTF ξ_0, ξ_1, η_0, and η_1 obtained with these coefficients. These graphs indicate that the fits to η_m are quite good, while the fits to ξ_m are somewhat poorer—partly owing to the more marked shell-like behavior in that parameter, although the general behavior of the MTF ξ_0 and ξ_1 reflects that of the MHF values. In Figs. 1 and 2 we have plotted with dashed lines the MTF ξ_m and η_m against $Z - N$ for several fixed values of N. The quality of the fits to the MHF reduced ener-

TABLE III. MTF energy coefficients for various weight ratios, ω. r. $\equiv \omega_1 : \omega_2 : \omega_3$. Only species with $N > 7$ were included in the fits.

	α_0	β_0	β_1	γ_0	γ_1	γ_2	δ_0	δ_1
GSD[a]	2.000	0.333	0.167	0.487	•••	•••	0.270	0.010
MGSD[a]	2.000	0.333	0.167	0.504	−0.102	0.085	0.270	0.010
A	2.000	0.333	0.167	0.618	−0.150	0.097	0.673	−0.414
B	2.199	0.277	0.336	0.681	−0.241	0.140	0.785	−0.404

	δ_2	μ_0	μ_1	τ_0	S.D.$_b$	S.D.$_\eta$	S.D.$_\xi$	ω. r.
GSD[a]	•••	0.298	•••	1.570	0.103	1.017	3.730	•••
MGSD[a]	•••	0.281	0.076	1.570	0.092	0.932	4.335	•••
A	0.000	2.164	−0.277	−4.087	0.060	0.180	0.540	10:2:1
B	0.009	0.621	0.445	−1.789	0.008	0.132	0.577	100:3:1

[a]Here, $\delta = \delta_0 + \delta_1 \eta/\xi$.

gies is displayed in Fig. 4(b), where we have plotted against N the magnitude of b'_m which the coefficients in row B yielded for several fixed values of Z. The corresponding values of b_m obtained from the MHF calculations are represented by the symbols in Fig. 4(b), and the agreement between the two sets of reduced energies is very good—usually within 1% for species with low N and within 3% for species with high N.

With the coefficients given in row B, we have a hybrid statistical atomic model which predicts the linear dependence of ξ_m and η_m on $Z-N$ found in MHF calculations and yields total energies and values of ξ_0, ξ_1, η_0, and η_1 which are in reasonably good to excellent agreement with MHF results.

VII. SUMMARY, DISCUSSIONS, AND CONCLUSIONS

This work has three main components: (a) determinations of the GSZ-IPM potential parameters which minimize, in a MHF sense, the energies of atoms and positive ions with $36 < Z \leq 54$ and $N \leq 54$; (b) a study of the systematics of the energies and GSZ parameters based upon the accumulative determinations of MHF-GSZ parameters and energies for 550 atomic and ionic species with $Z \leq 54$; and (c) a refinement and readjustment of a modified Thomas-Fermi statistical model (MTF) developed by Green, Sellin, and Darewych (GSD) with the aid of the accumulated MHF-GSZ energy and parameter determinations. Let us begin by discussing and summarizing the third component of this study.

Our basic objective in this third component has been to find a better reconciliation of the generalized Thomas-Fermi statistical model with the Hartree-Fock model. We evaluate the GSZ paramters in the MTF model by energy-minimization procedures analogous to those in the MHF model. The most successful result of this effort is that we find in the MTF model an explanation in terms of the electron-nucleus interaction for the linear dependence of the MHF-GSZ parameters upon $Z-N$ which we had found empirically [see Eqs. (4), (5), and (15)–(19)]. Somewhat disappointing is the fact that when we evaluate the energies and GSZ parameters from the MTF model, they are not in good agreement with those of the MHF model. On the other hand, we can bring the two models into reasonably good correspondence by moderate adjustments of the coefficients of the energy terms in the MTF theory.

The fact that we could signficantly improve the predictions of the MTF model by adjusting these numerical coefficients may be a way of compensating either for the $1/r$ singularity in the number density derived from the GSZ potential or for other shortcomings in the shape of this potential form. Alternatively, the inhomogeneity-kinetic-energy and exchange components of the TF functionals themselves, which are of uncertain validity, may be in error. Or, perhaps we are attempting to reconcile two unreconcilable approaches. The importance of shell structure in the MHF model suggests this as a possibility.

Despite these reservations, it is satisfying that we have developed a version of the statistical model which provides an energy formula that can yield total energies within 1% of MHF results for species with $N > 25$ and within 3% for $N \leq 25$, while at the same time predicting with rather good accuracy the average behavior and linear $Z-N$ dependence of the GSZ potential parameters characterizing those species.

Returning to the first component of this study, it should be noted that our results represent the first accurate energy determinations for many of the species we have studied. In addition, our minimization method leads to IPM potential parameters which should provide an excellent representation of the average potential seen by an electron in these atomic or ionic species.

The second component of this study, which involves the systematics of the energies and MHF-GSZ parameters, is probably the most useful one. From this work it is possible to assign ξ and η values and hence the IPM potential seen by all electrons in any of the 1485 atomic and ionic species with $Z \leq 54$. Since our total energies are usually within 50 ppm of true Hartree-Fock, the analytic potentials and the other properties derived from these parameters should be far more realistic than the corresponding potential or properties derived from Thomas-Fermi theory. Therefore, the results should be useful for a variety of physical problems which involve atoms in various states of ionization. Now that we have established the trends in the systematics of the GSZ-IPM parameters with Z and N, it should not be very difficult, albeit tedious, to extend this work to encompass all known atoms (i.e., $Z \leq 105$) and their ionic states, which total 5565. It will, however, be necessary to base such work upon a relativistic Hartree-Fock model to allow for relativistic effects particularly of the K- and L-shell electrons.

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