

Semiempirical Atomic-Energy Formula*

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We study the Thomas-Fermi-Dirac statistical model of the atom in the energy-functional formulation. We obtain minima of the total energy for five analytic-screening-function-density combinations. Total energies, average radii, and rms radii vary from model to model quite markedly, and depart quite substantially from "data" based upon Hartree-Fock or Hartree-Fock-Slater calculations. For the model based upon the analytic screening function due to Green, Sellin, and Zachor and for a closely related "regularized" model, the dependence of the component energies upon the electron number N , the model parameters, and certain integral constants is represented analytically. Minimization of the total energy with respect to the potential parameters leads to simple algebraic equations. The results again are poor. However, by making reasonable semiempirical modifications in the component terms, we find we can achieve stability with binding energies and potential parameters which are close to the data obtained from Hartree-Fock (HF) or Hartree-Fock-Slater (HFS) studies.

I. ANALYTIC INDEPENDENT-PARTICLE MODEL (IPM) AND THE THOMAS-FERMI (TF) MODEL

In a previous work, Green, Sellin, and Zachor¹ (to be referred to as GSZ) have proposed an IPM potential for atoms which uses a potential of the form (in Rydberg units)

$$V(r) = 2r^{-1}[N\Upsilon(r) - Z]. \quad (1)$$

Here Z is the number of nuclear protons and N the number of core electrons, and $2r^{-1}\Upsilon(r)$ is the electrostatic potential associated with an average electron cloud. The screening function $\Omega(r) = 1 - \Upsilon(r)$, which they utilize, has a simple analytic form, which we shall discuss in Sec. III. Poisson's equation permits us to derive from an analytic screening function the radially symmetric charge distribution

$$n(r) = (4\pi r)^{-1} \frac{d^2\Omega}{dr^2}. \quad (2)$$

The availability of approximate analytic potentials and density functions permits us to carry out certain approximate calculations on atoms and ions which are extremely complicated from an exact many-electron point of view.

The starting point of the GSZ study was an analytic characterization of the universal TF^{2,3} potential, which had some degree of analytic convenience and accuracy with respect to earlier representations. In the present study we turn to the TF model of the atom in a variational form. This has been the subject of a number of recent investigations,⁴ most of which have been concerned primarily with the exchange energy arising from statistical theory.⁵ This exchange energy has been used in attempts to find independent-particle-model simplifications of Hartree-Fock (HF), e. g., the Hartree-Fock-Slater (HFS) or Hartree-Fock Kohn-Sham (HFKS) equations. Here, we will attempt to deal with many of the terms of the statistical theory of the atom and endeavor to

relate this total energy to the total energy as obtained from HF and HFS calculations.

II. THOMAS-FERMI-DIRAC (TFD) ENERGY FUNCTIONAL

In the statistical theory,⁵ we may express the total energy of a many-electron system containing N electrons and Z protons in the form

$$E_T = \sum_i E_i, \quad (3)$$

where E_i represents the various identifiable components of the total energy expressed in terms of the electron density and the electrostatic potential. These components include the energy of the electron cloud in the field of the nucleus

$$E_1 = E_n = -2ZN \int r^{-1}n(r) d\tau, \quad (4)$$

the electrostatic interaction energy between the various electrons

$$E_2 = E_e = N^2 \int |\vec{r} - \vec{r}'|^{-1} n(r)n(r') d\tau d\tau' \\ = N^2 \int r^{-1}\Upsilon(r)n(r) d\tau, \quad (5)$$

and the main kinetic energy of the electrons

$$E_3 = E_k = C_k N^{5/3} \int n^{5/3} d\tau, \quad C_k = \frac{3}{5} (3\pi^2)^{2/3}. \quad (6)$$

Equations (4)–(6) constitute the major energy components and the ones that are well established in the literature. In addition, however, there is the Weizsäcker⁶ correction to the kinetic energy given by

$$E_4 = E_{kw} = C_{kw} N \int [(\nabla n)^2/n] d\tau, \quad C_{kw} = \frac{1}{36}. \quad (7)$$

This value for C_{kw} is that of Kompaneets and Pavlovskii,⁷ which has been verified by other authors.^{8,9} It is $\frac{1}{9}$ of that originally proposed by Weizsäcker.

In addition, we must include the exchange energy¹⁰

$$E_5 = E_x = -C_x N^{4/3} \int n^{4/3} d\tau, \quad C_x = \frac{3}{2} (3/\pi)^{1/3}, \quad (8)$$

and the inhomogeneity correction for the exchange energy

$$E_6 = E_{xw} = -C_{xw} N^{2/3} \int [(\nabla n)^2 / n^{4/3}] d\tau, \\ C_{xw} = 2\pi / (3\pi^2)^{4/3}. \quad (9)$$

Finally, we shall give some consideration to a correlation energy,¹¹ which in the approximate form interpolated by Lewis¹² may be given by

$$E_7 = E_c = -c_c N \int n \ln[1 + b(Nn)^{1/3}] d\tau, \quad (10)$$

where $c_c = (2/\pi^2)(1 - \ln 2) = 0.06225$ and

$$b = (3\pi^2)^{4/3} [0.89 (4/9\pi)^{1/3} \pi - 1] / 2\pi^3 c_c = 10.86.$$

In principle, we may choose any analytic form of potential and the corresponding density function obtained from Poisson's equations to evaluate the various integrals given in Eqs. (3)–(10). Thus, we may obtain each component energy in terms of the N , Z , and the parameters which characterize the density and potential. The stable atom should correspond to the parameters which give the least total energy. Let us see how such a conceptual procedure works out for the GSZ potential.

III. GENERALIZED DISTRIBUTION FUNCTION (GDF)

The screening function of GSZ has the analytic form

$$\Omega(r) = [H(e^{r/d} - 1) + 1]^{-1}. \quad (11)$$

A good fit to the universal Thomas-Fermi screening function is obtained if we choose $d = \mu_0 \delta / Z^{1/3}$, where $\mu_0 = 0.8853$, $\delta = 4.478$, and $H = \delta + 1 = 5.478$. These relations imply that the reduced parameter $h = H/dZ^{1/3} = 1.382$. In the course of the GSZ study, it was found that a closer approximation to HF and HFS results could be obtained by permitting the parameters H and d to take on values which varied throughout the periodic table. The values of d , H , and h obtained by fitting the HFS screening functions of Herman and Skillman,¹³ as modified in the asymptotic region to yield an r^{-1} asymptotic potential, are given in Table I for seven sample substances. Also given are the total energies and the reduced binding energies $b = -E_T/N^{7/3}$ which have been obtained from HF calculations.¹⁴ In attempting to

TABLE I. HF data (all lengths are in Bohr radii and energies are in Rydbergs).

Z	d	H	h	$-E$	b
10	0.443	1.06	1.134	257	1.193
20	1.08	3.05	1.041	1354	1.247
30	0.559	2.15	1.238	3556	1.272
40	1.01	4.73	1.369	7078	1.294
50	0.789	3.74	1.286	12046	1.308
70	0.752	4.46	1.439	26783	1.326
90	1.09	7.10	1.453	48719	1.342

adapt the statistical model we shall use the values for d , h , and b as empirical "data" which realistically characterize atoms.

The normalized electron density corresponding to Eq. (11) is given by

$$n(r) = \frac{H}{4\pi d^3} \frac{e^{r/d}}{r} \frac{He^{r/d} + H - 1}{(He^{r/d} - H + 1)^3}. \quad (12)$$

This density function is singular at the origin as r^{-1} . While this is weaker than the $r^{-3/2}$ singularity of the strict TF model, it occasions, as we shall see, a difficulty with E_{kw} , the inhomogeneity correction to the kinetic energy.

Except for the E_n and E_e terms, which can be evaluated analytically, the integrations were carried out using a 96-point-G quadrature routine several times to cover the region of integration. In addition, singular integrands were expanded in a power series about the origin to obtain the contribution from this region. These procedures yielded accuracy to about five decimal places. In the case of E_{kw} , we employed a cutoff procedure in which the denominator in Eq. (7) was replaced by $n^{4/3}/\bar{n}^{1/3}$, where \bar{n} is a reasonable nonsingular density which departs from n only at very short range.

It is simple to establish the dependence of the integrals upon the parameter d by using d as the unit of length. Apart from the small correlation term, all potential-energy components go as d^{-1} , whereas all kinetic-energy components go as d^{-2} . This makes it simple to minimize the total energy with respect to d so that the further minimization problem need only be carried out with respect to H .

Numerical calculations showed that the total energy is a very slowly varying function of H , having a minimum at large unrealistic values ($H \sim 100$). To look at component energies we imposed the *ad hoc* rule $H = 1.3Z^{1/3}$. Minimization with respect to d then led to the component energies presented in Table II for a sample of elements. The parameters H , d , h , the total energies, and reduced energies are given in Table III. Focusing on the reduced energies we note that at large Z the results (~ 1.35) are quite comparable to HF values (see Table I). However, for small atomic numbers the GDF model is too large (~ 1.4) compared to HF (~ 1.2). Furthermore, the parameter h (~ 1.6) is also too large compared to those obtained from fits to HFS screening functions (~ 1.3).

IV. OTHER MODELS AND COMPARISONS

Whether the source of difficulties in Sec. III was the GDF scattering function and its corresponding singular density or the energy functional can be examined by studying alternative models which do not have singular densities. In this section we examine four other screening functions—density combinations. These include a regularized screening

TABLE II. Individual contributions to total statistical energy for constrained case ($h = 1.3Z^{1/3}$).

Z	E_k	E_{kw}	E_n	E_e	E_x	E_{xw}	E_c
10	262.4	37.1	-686.4	134.8	-22.7	-24.8	-1.6
20	1344.2	123.1	-3474.1	661.1	-71.3	-50.2	-3.6
30	3515.6	248.7	-8997.8	1685.3	-140.0	-76.0	-5.8
40	6955.2	409.3	-17679	3277.8	-226.0	-102.1	-8.1
50	11803	601.8	-29848	5494.0	-327.8	-128.3	-10.6
70	26177	1074.3	-65724	11976	-574.2	-180.1	-15.7
90	47416	1653.5	-118473	21440	-872.8	-233.7	-21.0

function (RGDF) having the form

$$\Omega(r) = \frac{1}{H(e^{r/d} - 1) + 1} \left(1 + \frac{r}{2d} \frac{He^{r/d}}{H(e^{r/d} - 1) + 1} \right), \quad (13)$$

and the corresponding nonsingular density

$$n(r) = \frac{H}{8\pi d^3} \frac{H^2 e^{3r/d} + 4H(H-1)e^{2r/d} + (H-1)^2 e^{r/d}}{[H(e^{r/d} - 1) + 1]^4}. \quad (14)$$

The results for RGDF are illustrated in Table IV and essentially two difficulties are apparent. The energy minimum occurred at unreasonable values of d and H as compared with fits by Eq. (13) to HFS screening functions. In addition, the binding energies are too small.

We have also examined screening functions of the form

$$\Omega(r) = (1-A)e^{-r/a} [1 + (r/2a)] + Ae^{-r/d} [1 + (r/2d)]. \quad (15)$$

The corresponding density, obtained from Eq. (2), consists of a sum of two exponential terms and is finite at the origin, i. e.,

$$n(r) = (4\pi)^{-1} [(1-A)(2a^3)^{-1} e^{-r/a} + (A/2d^3) e^{-r/d}]. \quad (16)$$

When A is set equal to 0 this double exponential (DE) model becomes a one-parameter exponential (E) model. These models bear a close relationship to the regularized Yukawa potentials of Green¹⁵ and the regularization techniques of Pauli and Villars¹⁶ used in meson field theory.

The results of minimization for the exponential models are presented in Table V for a sample of elements. Note that the single-parameter form is not sufficiently flexible to effectively minimize the total energy, i. e., the resulting statistical binding energies are substantially smaller than the HF

TABLE III. Parameters and energies for the constrained case.

Z	H	d	h	$-E$	b
10	2.80	0.8161	1.594	301	1.396
20	3.52	0.8120	1.602	1471	1.355
30	4.04	0.8081	1.609	3770	1.348
40	4.44	0.8048	1.616	7373	1.347
50	4.78	0.8023	1.620	12415	1.348
70	5.36	0.7989	1.628	27267	1.350
90	5.82	0.7966	1.632	49091	1.352

values.

The results of minimization with respect to a , A , and d in the DE model are also shown in Table V. Here the values of the individual terms are quite similar to those in Table II. The total reduced energies compare more favorably with the HF data in Table I except at low values of Z .

We have also considered the normalized density function of Kirzhnits (K),⁹

$$n(r) = [\beta\alpha^3/4\pi\Gamma(3/\beta)] e^{-(\alpha r)^\beta}, \quad (17)$$

and the corresponding screening function

$$\Omega(r) = [\Gamma(3/\beta, u) - \alpha r \Gamma(2/\beta, u)] / \Gamma(3/\beta), \quad (18)$$

where $\Gamma(x)$ and $\Gamma(x, u)$ are the complete and incomplete Γ functions, respectively, and $u = (\alpha r)^\beta$. The reduced energies and the corresponding parameters are also given in Table V. It is noted that the total energies are good for high Z values but, like the GDF and DE models, give too strong a binding at low Z values. The component energies (not given) are quite similar to those in Table II.

Another way of viewing the various models is given in Fig. 1. Here we show the composite IPM densities

$$4\pi r^2 n(r) = Z^{-1} \sum w_{ni} P_{ni}^2(r), \quad (19)$$

for $Z = 50$ using a semilog representation. The solid line represents the IPM densities based upon GDF with $H = 3.991$ and $d = 0.841$, the values which fit the HF eigenvalues. The circles are densities obtained from HFS model using the code of Herman and Skillman. The K distribution is shown by the long dashes and, as one sees, it visually appears quite reasonable. The E and DE models are not shown because they are quite unreasonable. The former has much too high a peak (e.g., 2.4 at 0.23). The latter has a double peak (1.53 at 0.033 and

TABLE IV. Regularized GDF parameters and energies.

Z	d	H	$-E$	h	b	d^a	h^a
10	15.7	100	277	2.957	1.286	0.362	2.02
50	23.31	250	10941	2.912	1.188	0.623	2.14
90	19.15	250	42811	2.914	1.180	0.850	2.35

^aFrom fits to HFS screening functions.

TABLE V. E and K parameters and reduced energies.

Z	Single				Double			Kirzhnits	
	a	b	a	d	A	b	β	$\alpha(10^5)$	b
10	0.1827	0.982	0.03030	8.0	0.91	1.330	0.2504	0.262	1.3935
20	0.1500	0.899	0.2294	9.0	0.91	1.270	0.2280	1.23	1.3614
30	0.1324	0.874	0.02000	9.0	0.91	1.255	0.2169	3.04	1.3619
40	0.1209	0.862	0.01637	10.0	0.92	1.249	0.2098	5.76	1.3662
50	0.1126	0.854	0.01517	10.0	0.92	1.242	0.2048	9.38	1.3709
70	0.1010	0.846	0.01352	10.0	0.92	1.247	0.1978	19.30	1.3792
90	0.09308	0.839	0.01240	10.0	0.92	1.242	0.1931	32.58	1.3858

1.65 at 1.3) and a minimum of 0.84 at 0.1.

A more quantitative representation of the differences of the various models is given in Table VI. Here the values of $\langle r \rangle$ and $\langle r^2 \rangle^{1/2}$ are given. Using the Schrödinger model as "data" we see clearly that the E and DE models are collapsed, whereas the K model is inflated and the GDF and RGDF models at equilibrium are exploded.

The next entry in Table VI represents the constrained GDF model discussed in Sec. III. These parameters when used with Eq. (12) yield $\langle r \rangle$ and $\langle r^2 \rangle^{1/2}$ closest to the data calculated with the individual electron densities. The corresponding density function is shown in Fig. 1 by the dashed lines. The next two entries are for GDF and RGDF parameters which have been obtained by GSZ by fitting HF energy values as discussed in Sec. V. The corresponding curves are also given on Fig. 1. The last entry, modified-Hartree-Fock generalized distribution function (MHF-GDF), will be discussed in Sec. VI.

V. ANALYTIC APPROACH

In this section we reexamine the energy integrals for the GDF and RGDF models using an approximate analytic approach. Thus, we characterize the dependence of the various integrals upon the parameter H analytically. This converts the energy functional into an explicit energy function of the parameters N, Z, d , and H and a set of coefficients arising from the numerical integrations. Then minimization with respect to d and H permits us to determine the total energy at stability as well as d_m and H_m as explicit functions of N and Z and, of course, the integration constants.

In the important inner region the screening function depends on H/d ; accordingly, we use the dependence upon d to factor out the corresponding H/d and thus reexpress each of the integrals in Eqs. (3)–(10). Thus, we write

$$E = -\alpha Z N \frac{H}{d} + \beta N^2 \frac{H}{d} + \gamma N^{5/3} \frac{H^2}{d^2} + \delta N \frac{H^2}{d^2} - \mu N^{4/3} \frac{H}{d} - \tau N^{2/3} \frac{H}{d}, \quad (20)$$

where the successive terms correspond to those

defined by Eqs. (4)–(9), and we have discarded the correlation energy. Analytically it is possible to show that $\alpha = 2$ and $\beta = \beta_1 + \beta_0/H$, where $\beta_1 = \frac{1}{3}$ and $\beta_0 = \frac{1}{8}$. By numerical evaluations we find to good approximation $\gamma = 0.487$; and $\delta = \delta_0 + \delta_1 H$, where $\delta_0 = 0.270$ and $\delta_1 = 0.01$; $\mu = 0.298$; and $\tau = 1.57$. If all the integrals were independent of H (i.e., we neglect β_0 and δ_1) then we readily minimize the total energy with respect to the reduced shape-scale parameter H/d . The terms β_0/H and $\delta_1 H$ in principle should permit us to solve for H and d simultaneously by minimizing the energy with respect to both parameters. To do this we write the total energy in the forms

$$E = -\frac{B}{d} + \frac{K}{d^2} = -\frac{B_1 H + B_0}{d} + \frac{K_2 H^2 + K_3 H^3}{d^2}, \quad (21)$$

where the meanings of B and K and of B_1, B_0, K_2 , and K_3 can readily be identified by comparison with

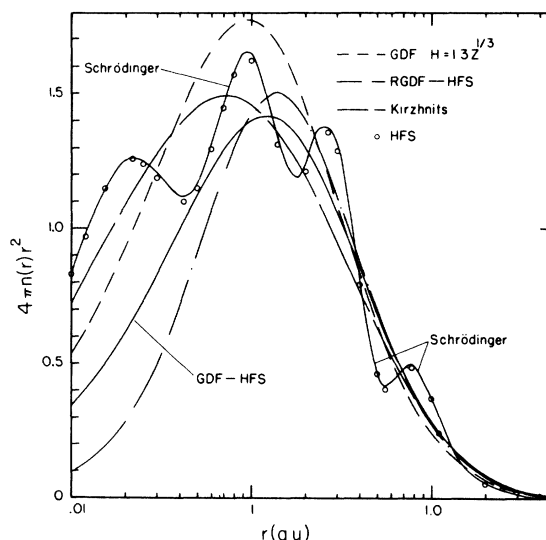


FIG. 1. Solid line labelled Schrödinger is the sum of the electron densities based upon the IPM using the GSZ potential with constants fitted to HF eigenvalues. The circles show the corresponding densities using the HFS program of Herman and Skillman's. The GDF-HFS and RGDF-HFS are based upon parameters which fit HFS screening functions. GDF* is the constrained model.

TABLE VI. Intercomparison of various models for $Z = 50 (\rho = \langle r^2 \rangle^{1/2} / \langle r \rangle)$.

Model	H	d	h	$\langle r \rangle$	$\langle r^2 \rangle^{1/2}$	ρ	b
IPM	3.991	0.841	1.289	0.6830	1.026	1.50	1.308
GDF	100.00	17.0	1.595	1.58	5.27	3.32	1.356
RGDF	250.00	23.31	2.91	1.543	6.367	4.11	1.188
E				0.3378	0.3901	1.16	0.854
D				0.4223	0.5043	1.19	1.242
K				0.9472	1.768	1.87	1.370
GDF ^a	4.780	0.8023	1.620	0.6641	1.039	1.56	1.348
GDF-HF	3.991	0.841	1.288	0.7783	1.178	1.513	1.307 ^b
RGDF	5.027	0.6312	2.145	0.7594	1.131	1.50	1.303 ^b
MHF-GDF	4.35	0.875	1.350	0.7680	1.180	1.54	1.308

^aFixed parameters.^bFrom atomic-energy formulas (see Sec. V).

Eq. (20). The minimization of E with respect to d now gives the condition

$$d_m = 2K/B = 2(K_2H^2 + K_3H^3)/(B_1H + B_0). \quad (22)$$

If we insert this in Eq. (21) we have for the energy at this minimum with respect to d

$$E_{dm} = -B^2/4K = -(B_1H + B_0)^2/4(K_2H^2 + K_3H^3). \quad (23)$$

We may now minimize this with respect to the parameter H which leads to a quadratic equation whose root may be expressed in the form

$$H_m = \left(\frac{2K_2B_0}{K_3B_1} \right)^{1/2} \left(1 + \frac{9K_3B_0}{8K_2B_1} \right)^{1/2} + \frac{3B_0}{2B_1}. \quad (24)$$

We may now insert this into Eqs. (22) and (23) to arrive at analytic expressions for the total energy of the atom and for the scale parameter d in terms of N and Z . In practice we again use the reduced parameters $h = H/dN^{1/3}$ and $b = -E_T/N^{1/3}$ as quantities to compare with data from the GSZ study.

When we use the parameters determined by the integrals we obtain reasonable values of b but $d \sim 1.95$ rather than ~ 0.8 and $h \sim 1.62$ rather than ~ 1.3 . Thus, we are very far from the empirical values of these screening function parameters.

We will now approach the atomic-energy-formula work from a nuclear-energy-formula^{17,18} standpoint by exploring various empirical adjustments of the integral parameters. We will attempt not only to fit the atomic-energy "data" but also the scale and

shape parameters determined by fitting HF screening functions. To mechanize our search for good parameters we have used a nonlinear least-squares program which minimizes the composite χ^2 :

$$\chi^2 = w_1(b - b_{\text{HF}})^2 + w_2(h - h_{\text{HFS}})^2 + w_3(d - d_{\text{HFS}})^2. \quad (25)$$

Since we wish to give the greatest emphasis to the well-defined energies, while h fluctuates and d fluctuates rather wildly, we have chosen for most of our work the weights $w_1 = 1$, $w_2 = \frac{1}{2}$, and $w_3 = \frac{1}{4}$. After many searches, we arrived at a number of simple solutions listed in Table VII. The second column shows the initial integral parameters. The χ^2 is very large, since the fits to the data are very poor. The remaining columns show the results of various restricted searches in which the parameters indicated by stars or zeros are held fixed. In the search represented by column H, the weights $w_1 = 1$, $w_2 = 0.12$, and $w_3 = 0.048$ were assigned on the basis of the standard deviation of b , d , and h from the G solution. Note that the parameters obtained are not significantly different in columns G and H indicating an insensitivity to weighting. Figure 2 shows the simultaneous fits to b , d , and h for the simple four-parameter-model case E. These fits are fairly representative of cases D, F, G, and H as well. One sees that we have found a variety of simple representations of the data.

Using Eqs. (13) and (14) it is possible to proceed analytically for the RGDF case just as for the GDF.

TABLE VII. Parameters for GDF.

	Initial	A	B	C	D	E	F	G	H
$\alpha - \beta_1$	1.666	1.956	1.98	1.99	2.00	2.04	2.04	2.04	2.04
β_0	0.1666	0.1666 ^a	0.0973	0.130	0.162	0.277	0.388	0.527	0.489
μ	0.298	0.298 ^a	0	0	0	0	0.298 ^a	0.679	0.573
τ	1.57	1.57 ^a	0	0	0	0	0	0	0
γ	0.487	0.683	0.719	0.712	0.705	0.637	0.664	0.635	0.642
δ_0	0.275	0.275 ^a	0	0	0	0	0	0	0
δ_1	0.010	0.109	0.06 ^a	0.08 ^a	0.100 ^a	0.177	0.248	0.339	0.314
$100\chi^2$	36.8	7.38	6.87	6.68	6.53	6.33	6.28	6.31	2.87

^aFixed parameters.

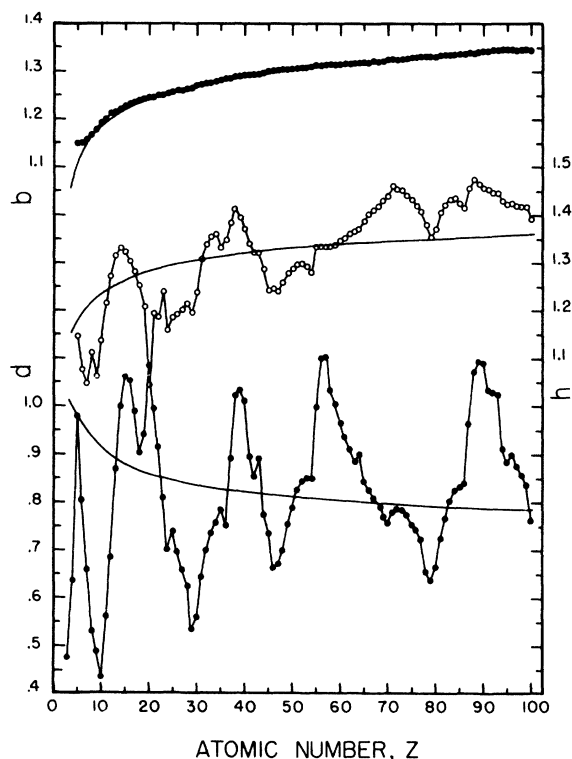


FIG. 2. Atomic-energy formula based upon GDF model. The points for d and h are from GSZ based upon fitting HFS screening functions. The points for the reduced energy $b = -E/Z^{1/3}$ are from the HF total energies of Mann. The curves represent the parameters of case E in Table VII, with reduced energies at minima using the semi-empirical atomic-energy formula.

The initial integral parameters so obtained are given in Table VIII ($\alpha = 1.00$ and $\beta_1 = 0.2$). For the minimal energies one finds $d \sim 1.4$, $h \sim 2.9$, and $b \sim 1.2$, which are quite far removed from the data. The remaining columns show various restricted searches. Again we have found a number of good representations of which case D illustrated in Fig. 3 is representative. Case F, a five-parameter search using realistic weights is quite close to case E based upon standard weights.

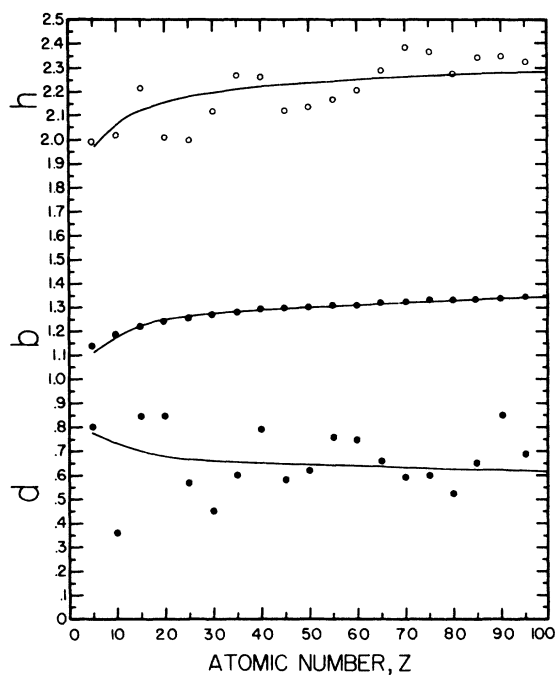


FIG. 3. Atomic-energy formula based upon RGDF model. The points for d and h are based upon fitting HFS screening functions. The curves represent case D in Table VIII. Note that the scale is reduced by factor of 2 from the scale in Fig. 2.

VI. DISCUSSION AND CONCLUSION

Two recent attempts^{19,20} have been made to improve the statistical model by incorporating some features of a pure quantum-mechanical model. In particular, it has been noted that the $1s$ shell is so tightly bound as to require special treatment. We might also call attention to a study by Wood and Green²¹ involving a MHF approach. Here the analytic GDF screening function is used to provide a complete set of one-electron wave functions and the HF energy is calculated and minimized numerically with respect to d and H to arrive at a first-principles determination of H and d values. The parameters arrived at in this way are quite reasonable in con-

TABLE VIII. Parameters for RGDF.

	Initial	A	B	C	D	E	F
$\alpha - \beta_1$	0.800	1.184	1.194	1.205	1.21	1.21	1.21
β_0	0.1029	0.0978	0.146	0.191	0.223	0.397	0.369
μ	0.1683	0	0	0	0	0.382	0.314
τ	0.683	0	0	0	0	0	0
γ	0.1333	0.2539	0.250	0.246	0.243	0.227	0.230
δ_0	0.030	0	0	0	0	0	0
δ_1	0.002	0.02 ^a	0.03 ^a	0.04 ^a	0.0478	0.0855	0.0795
$100\chi^2$	39.1	6.00	5.58	5.35	5.34	5.28	2.44

^aFixed parameters.

trast with the "explosions" using the TDF approach. Furthermore, the energies obtained are very close (~ 10 ppm) to the true HF energy. The $\langle r \rangle$ and $\langle r^2 \rangle^{1/2}$ obtained in this approach (see last row of Table VI) are very close to the IPM.

These results suggest that the difficulty with TDF is due, at least in part, to the assumption that Poisson's equation serves as a link connecting $n(r)$ to $\Omega(r)$, which is rather basic to the usual forms of the statistical model. Thus, on the statistical model the GDF Ω leads to a singular $n(r)$ whereas the MHF-GDF model or IPM-GDF model gives a regularized $n(r)$, albeit one with shell structure.

The greater realism of the MHF results suggest that one might treat the component energies in the HF scheme using analytical formulas suggested by our work in Sec. V. This approach might unite the HF and TFD methodologies into a convenient yet precise formalism. A complete set of MHF parameters would permit the realistic inclusion of shell effects which would carry one beyond the capabilities of any statistical model.

Granting the greater realism of the HF approach

does not preclude the possibility that within the framework described in Sec. II improvements can be made either by resorting to different potential or density functions or by introducing additional corrections to the energy functional.²² Our efforts in Sec. V, in which the various components in the energy functional are looked upon as to their parameter dependences, suggest that we must find a component which enhances the H^3N/d^2 term which arises out of the kinetic-energy inhomogeneity correction. With a sufficient enhancement we should be able to obtain good energy minima at H and d parameter values consistent with our analytic fits to HFS screening functions or HF energies.

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