Density-Functional Formalism

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A new Density-Functional (DF) formula is constructed for atoms. The kinetic energy of the electrons is divided into two parts: the kinetic self-energy and the orthogonalization energy where these concepts are borrowed from the pseudopotential theory. For the radial part of the orthogonalization energy which replaces the radial part of the Fermi-energy of the Thomas-Fermi model we derived the expression

$$E=\frac{1}{2\,m}\sum_{k=0}^{\infty} a_k\, p_\varepsilon^{k}\, p^{2-k}\,,$$

where p is the momentum, the a_k's are constants and p_ε is the momentum width associated with the self-energy for which an expression is derived. Calculations were made for the total energies of neutral atoms, positive ions and for the He isoelectronic series. For neutral atoms the results match the Hartree-Fock energies within 1% for atoms with $N<36$; for atoms with $N>36$ the results generally match the HF energes within 0.1%. For positive ions the results are fair; for the He series we achieved four or five-digit agreement between our energies and the HF results. For molecular applications a simplified model is developed in which the kinetic energy consist of the Weizsäcker term plus the Fermi energy reduced by a continuous function $\eta(N)$. It is shown that the $\eta(N)$ can be constructed in such a way that the energies computed closely approximate the HF energies for all neutral atoms.

1. Introduction

The present paper deals with a new formulation of the Density-Functional (DF) formalism. The formalism will be developed for atoms with spherically symmetric electron distributions described by the single density function $\varrho(r)$, which must satisfy the normalization condition.

$$\int \varrho\, \mathrm{d}v = N\,, \tag{1.1}$$

where N is the number of electrons in the atom. The Density-Functional, $\varepsilon(\varrho)$ will be defined as a functional of ϱ in terms of which the total energy can be written as

$$E=\int \varepsilon(\varrho)\,\mathrm{d}v\,. \tag{1.2}$$

Although it will not be shown in the notations (except in Sec. 4) the Density-Functional ε will be permitted to depend explicitly on r also. Throughout the paper we shall work exclusively with the functional ε and *we shall not use any wave functions.*

The paper is motivated by the problem which may be formulated by the following question: "Is it possible to construct a DF formalism which for the calculation of bulk properties of atoms (and later molecules) would be as accurate as the Hartree-Fock (HF) formalism?"

The bulk properties are defined as the total energy and total density of a system and quantities derived from these. In the present paper it will be shown that a DF formalism approximating closely the accuracy of the HF method for the calculation of the *total energies of neutral atoms* can be constructed; strong evidence will be presented that the same formalism will also be able to approximate closely the accuracy of HF densities. The paper is devoted to the detailed investigation of the total energy of neutral atoms; questions related to the calculation of the density will be touched upon only briefly and will be left for a forthcoming publication.

The paper is organized as follows:

In order to define the accuracy of a DF formalism we will investigate first the accuracy of the HF model in Section 2. The new formulation of the DF formalism will be given in Section 3. In Sec. 4 the role played by the Virial Theorem in the formulation of a DF formalism will be analyzed. Section 5 deals with the actual construction of the new DF formula while the calculations are presented in Section 6. Section 7 contains a brief discussion.

2. The Accuracy of the HF Method

Since our goal is to construct a DF formalism which will match the accuracy of the HF method let us first ask the question: how accurate is the HF method? The answer to this question depends very strongly on which quantity we are considering. Here we restrict the discussion to the total energies of atoms. By HF method we mean the approximation in which the wave function of the system is a single determinant; no configuration interaction is included. It will be assumed that the experimental total energy of an atom can be approximated by the formula

$$E_{\text{exp}} = E_{\text{F}} + E_{\text{R}} + E_{\text{C}} \tag{2.1}$$

where E_{F} is the HF energy, E_{R} is the relativistic correction and E_{C} is the correlation energy.

The experimental value of the total energy is known only up to the Ca atom. HF calculations with [2] and without [3] the relativistic correction has been completed recently for many atoms. In Table 1 we have listed in the first column the E_{F} computed by C. Froese-Fischer for a number of atoms through the periodic system; in the second column we listed the results of relativistic HF calculations which are equivalent to $E_{\text{F}} + E_{\text{R}} \equiv \hat{E}_{\text{R}}$. The third column contains, up to the Ca atom the experimental value of the energy, the fourth column, up to the Ca, contains the correlation energy computed from the formula

$$E_{\text{C}} = E_{\text{exp}} - E_{\text{F}} - E_{\text{R}} . \tag{2.2}$$

The fifth column shows the deviation of the non-relativistic HF from the relativistic HF in percents. The sixth shows the error of the relativistic HF relative to the experimental values (i. e. the correlation energy) in percents; finally the seventh column shows the error of the HF model relative to the experimental values, in percents. Since the experimental values are not known for atoms heavier than Ca for these atoms we estimated the correlation energy using the data for the light atoms. We plotted E_{C} versus N for the range $2 \leqq N \leqq 20$ and observed that the data can be accurately approximated by the formula

$$E_{\text{C}} = -0.03906\, N \text{ (a. u.)} . \tag{2.3}$$

This formula will be sufficiently accurate in the context of the present discussion since E_{C} decreases rapidly with increasing N and while it is 1.48% of the total energy for He it is only 0.1% of the total

Table 1. The data discussed in Section 2. The Table shows the absolute values of the negative energies in atomic units. The non-relativistic HF values are from Ref. 3; the relativistic HF values from Ref. 2; the experimental values for $N \leqq 20$ from Ref. 1.

Atom	N	E_{F}	$\hat{E}_{\text{R}} = E_{\text{F}} + E_{\text{R}}$	$E_x \equiv E_{\text{exp}}$	E_{C}	$\frac{\hat{E}_{\text{R}} - E_{\text{F}}}{\hat{E}_{\text{R}}}$ %	$\frac{E_{\text{x}} + \hat{E}_{\text{R}}}{E_{\text{x}}}$ %	$\frac{E_{\text{x}} - E_{\text{F}}}{E_{\text{x}}}$ %
He	2	2.8616	2.8618	2.9049	0.0431	0.006	1.483	1.490
Li	3	7.4327	7.4335	7.4824	0.0488	0.010	0.653	0.664
Be	4	14.5730	14.5759	14.6764	0.1005	0.019	0.684	0.704
Ne	10	128.5474	128.6920	129.1200	0.4279	0.112	0.331	0.443
Si	14	288.8357	289.4503	290.0247	0.5743	0.212	0.198	0.409
Ar	18	526.8185	528.6854	529.3982	0.7128	0.353	0.134	0.487
Ca	20	676.7600	679.7128	680.4720	0.7592	0.434	0.111	0.545
Cr	24	1043.1770	1049.6820	1050.6194	0.9374	0.825	0.089	0.708
Ni	28	1506.8200	1519.3588	1520.4524	1.0936	0.619	0.071	0.896
Ge	32	2075.3430	2097.4862	2098.7361	1.2499	1.055	0.059	1.114
Kr	36	2752.0570	2788.8961	2790.3022	1.4061	1.320	0.050	1.370
Zr	40	3538.9720	3597.1652	3598.7276	1.5623	1.617	0.043	1.660
Ru	44	4441.3720	4529.3646	4531.0832	1.7186	1.942	0.037	1.979
Cd	48	5465.1430	5593.4802	5595.3550	1.8748	2.294	0.033	2.327
Xe	54	7232.1500	7447.2186	7449.3278	2.1092	2.887	0.028	2.915
Ce	58	8566.8820	8861.5422	8863.8076	2.2654	3.325	0.025	3.349
Gd	64	10820.2800	11275.3370	11277.8368	2.4998	4.035	0.022	4.057
Er	68	12498.0800	13093.7211	13096.3771	2.6560	4.549	0.020	4.568
W	74	15287.4500	16158.8640	16161.7544	2.8904	5.392	0.017	5.409
Pt	78	17330.9200	18438.9480	18441.9946	3.0466	6.009	0.016	6.024
Hg	80	18408.9700	19653.8700	19656.9948	3.1247	6.334	0.015	6.349
Rn	86	21866.7900	23611.5170	23614.8761	3.3591	7.389	0.014	7.402

for Ca. [We note that the N-dependence of E_C in formula (2.3) agrees with the N-dependence of E_C obtained from Thomas-Fermi theory. According to the TF model [4] $E_C \approx -0.056\,N$.]

For atoms heavier than Ca the fourth colum contains E_C computed from (2.3) and the third column contains the estimate for the experimental energy computed from the formula

$$E_{exp} = E_F + E_R - 0.03906\,N\,. \qquad (2.4)$$

Inspecting the table we see that the relativistic energy is very small for light atoms ranging from 0.01% for Li to 0.4% for Ca. Then E_R increases rapidly with increasing N and it is 2.88% for Xe and 7.4% for Rn. On the other hand the correlation energy is most significant for He where it is 1.48%; then E_C decreases rapidly and it is only 0.01% for Rn.

From these data we are able to form an opinion about the accuracy of the non-relativistic HF model with respect to the total energy (seventh column of Table 1). It is clear that the model is fairly accurate for light atoms, say up to $N=30$; for these atoms the combined error caused by disregarding the relativistic and correlation effects in less than 1% of the total energy. [The He is a notable exception to this statement.] For heavier atoms the results of nonrelativistic HF calculations become increasingly less accurate.

If we want to develop a DF formalism which should yield results for the total energy of an atom comparable in accuracy to the nonrelativistic HF results the deviation from E_F must be much smaller than the inaccuracy of the HF model since otherwise it would be impossible to disentangle the inaccuracy of the DF formalism relative to the HF model from the inaccuracy of the HF model relative to experimental data. What we mean by this is that if the error in any atomic calculation – carried out with a DF formalism – would be, say, 4%, then we would like to identify this error as not something the source of which is the inaccuracy of the DF formalism but as an error inherent in the HF formalism. Therefore we shall define arbitrarily as the desirable goal of a DF formalism to reproduce E_F within 0.1%. For all atoms (except perhaps for atoms in the range $N<30$) this error is much smaller than the error of E_F relative to experiment.

In Fig. 1 we plotted E_F and E_F+E_R versus N. It is interesting that the total energies of atoms form

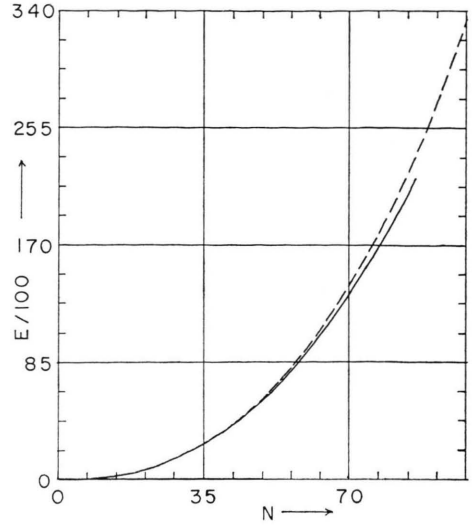

Fig. 1. The non-relativistic and the relativistic Hartree-Fock energies versus N. Full line (———) is E_F; broken line (– – –) is $\hat{E}_R = E_F + F_R$.

a smooth curve resembling a parabola; fluctuations caused by the different structure of the outer shells are not evident on such a diagram. This fact itself forms a powerful incentive for the development of a model describing accurately bulk properties i. e. for the development of a DF formalism.

3. Theoretical and Semi-Theoretical Density-Functional Formalism

There are a variety of ways to derive a DF formalism. The presently available models are the Thomas-Fermi (TF) model [5] as formulated by Dirac [6]; the DF formula derived by Weizsäcker [7]; the gradient-expansion formulas of Kirsznits [8] and Hohenberg and Kohn [9]; the Fermi-energy-modified formula of Gombas [10]. All these models have been very useful in treating atomic and molecular problems and have yielded quite accurate results for many properties. Nevertheless they are not considered to be as accurate and reliable tools as e. g. the HF method. What is the reason for this?

It is obvious that neither the theoretical consistency nor the numerical accuracy of these models are considered to be of the same quality as those of the HF method. We will discuss the numerical accuracy of some of these models below and show that in the calculation of the total energy of atoms quite large deviations from E_F occur. Looking at the theoretical background of these models we observe that the derivation of the DF formula is

generally carried out starting from a quantum mechanical energy-expression which is a functional of wave functions (e. g. the HF energy expression) and which is then transformed into a density functional. This transformation is more or less plausible in the different models; its general feature however is that it does not provide a DF formula from which the physical quantities could be computed with arbitrary accuracy by successive approximations. In other words the DF formula is, in general, not in the form of an expansion which would converge toward the exact (quantum mechanical) result e. g. the HF energy E_F.

It is clear that the theoretical derivation of such an expansion would elevate the DF formalism to the level of the quantum mechanical methods. As a useful but less satisfactory substitute for such a theoretical derivation we wish to suggest here a method which we will call *semi-theoretical*, which may be described as follows: we shall select one of the DF models and attempt to change it in such a way as to match the accuracy of HF calculations. The change in the DF formula will be carried out guided by two considerations: 1) A set of general principles will have to be satisfied by the DF formula; 2) Only those terms will be permitted to be changed in the DF formula for which the theoretical derivation can be demonstrated to be inaccurate or ill-defined.

A semi-theoretical density-functional formalism may be formulated in terms of four principles which must be satisfied by it:

1) A well established quantum mechanical model e. g. the HF model or a semi-classical theory like the Fermi-gas model forms the starting point. The density-functional formula derived from this model is examined and possible reasons for its inaccuracy pinpointed. The functional form and/or the constants of the DF formula are changed in such a way as to match the accuracy of the quantum mechanical calculations.

2) We expect that the semi-theoretical model will yield accurate results for the *bulk properties* i. e. for the total energy and total density. For the total energy we shall arbitrarily choose the condition that it should match E_F within 0.1%.

3) For the total density ϱ we do not demand that it should match exactly the HF density; (a formalism in which we work with a single density can never produce that); we shall demand however that in the outer regions of atoms it should approximate the HF density as closely as possible. The outer regions of density are decisive for many quantities, e. g. scattering cross sections, interactions of atoms including the formation of certain molecules, etc. In order to satisfy this condition the assymptotic behavior of ϱ for $r \to \infty$ will have to be the same as in the HF model.

4) The DF formula must satisfy the Virial Theorem. This condition puts a restriction on the form of the density functional $\varepsilon(\varrho)$ and insures that if the total energy is equal to E_F then the kinetic and potential energies will be separately equal to the corresponding HF values. This condition is important especially for the construction of realistic formulas for the kinetic energy.

In the next section we demonstrate how the Virial Theorem can be used to determine the functional form of $\varepsilon(\varrho)$. In the subsequent sections the principles outlined above will be used to construct a semi-theoretical model.

4. The Virial Theorem

We will show in this section that if a DF model is subjected to the requirement that it must satisfy the Virial Theorem (VT) then the VT can be used to identify the functional forms permitted in the density-functional. Our method is based on the "scaling" theory of Fock [11]. Let ϱ be the density which makes the energy to a minimum for a particular, given $\varepsilon(\varrho)$ and let us indicate now that $\varepsilon(\varrho)$ may depend explicitly on r, i. e. we write $\varepsilon = \varepsilon(\varrho, r)$. Let us subject ε to the scaling i. e. let us vary the energy with respect to a scale factor λ which is considered a variational parameter. We define the "varied" density as

$$\varrho_\lambda = \lambda^3 \varrho(\lambda r) , \tag{4.1}$$

where the λ^3 factor insures that ϱ_λ will be normalized. Denoting the density-functionals of the kinetic and potential energy by ε_k and ε_p we get for the "varied" energy:

$$E^\lambda = E_k^\lambda + E_p^\lambda = \int \varepsilon_k(\varrho_\lambda, r)\,\mathrm{d}v + \int \varepsilon_p(\varrho_\lambda, r)\,\mathrm{d}v , \tag{4.2}$$

where E_k^λ and E_p^λ are the "scaled" expressions. We assume that ε_k and ε_p are of such structure that

$$E_k^\lambda = \lambda^2 E_k \tag{4.3}$$

and

$$E_p^\lambda = \lambda E_p . \tag{4.4}$$

If this is true then the virial theorem is satisfied. Since ϱ defines the minimum we must have that

$$\lim_{\lambda=1}(\partial E^{\lambda}/\partial\lambda)=0\,, \tag{4.5}$$

from which we get

$$\lim_{\lambda=1}\{2\,\lambda\,E_k+E_p\}=2\,E_k+E_p=0\,. \tag{4.6}$$

Now from Eq. (4.3) we get

$$E_k^{\lambda}=\int\varepsilon_k(\varrho_\lambda\,,\,r)\,\mathrm{d}v=(1/\lambda^3)\int\varepsilon_k(\varrho_\lambda\,,\,r)\mathrm{d}(\lambda\,\boldsymbol{r})=\lambda^2\,E_k\,. \tag{4.7}$$

Although it restricts somewhat the generality of the discussion we shall assume that the $\varepsilon_k(\varrho,r)$ is a simple function satisfying the relationship:

$$\varepsilon_k(\varrho_\lambda\,,\,r)=\lambda^M\varepsilon_k\left(\varrho(\lambda\,r),\lambda\,r\right). \tag{4.8}$$

Putting this into (4.7) we get

$$\begin{aligned}&(1/\lambda^3)\int\varepsilon_k(\varrho_\lambda\,,\,r)\,\mathrm{d}(\lambda\,\boldsymbol{r}) \qquad (4.9)\\ &\quad=\lambda^{M-3}\int\varepsilon_k\left(\varrho(\lambda\,r),\lambda\,r\right)\mathrm{d}(\lambda\,\boldsymbol{r})=\lambda^2\int\varepsilon_k(\varrho,r)\,\mathrm{d}v\,,\end{aligned}$$

from which we get that, for all λ we must have

$$\lambda^{M-3}=\lambda^2\,, \tag{4.10}$$

or

$$M=5\,. \tag{4.11}$$

Equation (4.7) is our general condition; for all cases which we shall discuss, Eq. (4.8) is valid so (4.11) can be used.

Examples

Let us suppose that we do not know what $\varepsilon_k(\varrho,r)$ looks like and want to test which functional forms satisfy the VT. First we put

$$\varepsilon_k(\varrho,r)=\varrho^K\,. \tag{4.12}$$

Now using (4.1) we get

$$\varepsilon_k(\varrho_\lambda\,,\,r)=[\lambda^3\,\varrho(\lambda\,r)\,]^K=\lambda^{3K}\,\varrho^K(\lambda\,r)\,. \tag{4.13}$$

Comparing this with (4.8) we see that $M=3\,K$ and using (4.11) we get

$$M=3\,K=5\,,\quad K=5/3\,, \tag{4.14}$$

which yields the Fermi density functional[5] for ε_k [apart from the constant, of course].

Next let us consider

$$\varepsilon_k(\varrho,r)=\varrho^K\,r^L\,. \tag{4.15}$$

We get

$$\begin{aligned}\varepsilon_k(\varrho_\lambda\,,\,r)&=[\lambda^3\,\varrho(\lambda\,r)\,]^K(\lambda\,r)^L\,\frac{1}{\lambda^L}\\ &=\lambda^{3K-L}[\varrho(\lambda\,r)\,]^K(\lambda\,r)^L \qquad (4.16)\end{aligned}$$

Using (4.8) and (4.11) we get

$$M=3\,K-L=5\,. \tag{4.17}$$

For $L=-1,\ -2,\ -3\ldots$ etc. we get the formula

$$\varepsilon_k(\varrho,r)=\varrho^{(5-l)/3}/r^l\,, \tag{4.18}$$

$(l=1,2,3\ldots)$.

This is the formula which we will introduce below as part of the kinetic energy density [Equation (5.37)].

Next let us consider

$$\varepsilon_k(\varrho,r)=(\bigtriangledown\,\varrho)^2\,\varrho^K\,. \tag{4.19}$$

We obtain

$$(\bigtriangledown_\lambda\,\varrho_\lambda)^2=\lambda^8\left\{\left(\frac{\partial\varrho(\lambda\,r)}{\partial(\lambda\,x)}\right)^2+\ldots\right\}, \tag{4.20}$$

and

$$\varrho_\lambda^K=\lambda^{3K}\,\varrho^K(\lambda\,r)\,. \tag{4.21}$$

Combining (4.20) and (4.21) with (4.8) we get

$$\varepsilon_k(\varepsilon_\lambda\,,\,r)=\lambda^{3K+8}\left\{\left(\frac{\partial\varrho(\lambda\,r)}{\partial(\lambda\,x)}\right)^2+\ldots\right\}\varrho^K(\lambda\,r)\,. \tag{4.22}$$

Using (4.11) we get

$$3\,K+8=5\,,\quad K=-1\,, \tag{4.23}$$

and for (4.19) we get

$$\varepsilon_k(\varrho)=(\bigtriangledown\,\varrho)^2/\varrho\,, \tag{4.24}$$

which is the so-called Weizsäcker inhomogenity correction[7] [see Eq. (5.3) and (5.4) below].

Investigating the properties of the inhomogeneous electron gas Hohenberg and Kohn stated[9] that the density-functional of the kinetic energy must have the form of the so-called gradient expansion consisting of Fermi energy, the Weizsäcker correction (4.24), and the higher order gradient terms for which the following formula was given:

$$\varepsilon_k(\varrho)=g_4^{(2)}(\varrho)\,(\bigtriangleup\,\varrho)^2+g_4^{(3)}(\varrho)\,(\bigtriangleup\,\varrho)\,(\bigtriangledown\,\varrho)^2+g_4^{(4)}(\varrho)\,(\bigtriangledown\,\varrho)^4+O(\bigtriangledown_i{}^6)\,. \tag{4.25}$$

In a recent paper[12] Hodges derived the formula

$$\varepsilon_k(\varrho)=\frac{1}{(3\,\pi^2)^{2/3}\,540}\left\{\varrho^{1/3}\left[\left(\frac{\bigtriangleup\,\varrho}{\varrho}\right)^2-\frac{9}{8}\left(\frac{\bigtriangleup\,\varrho}{\varrho}\right)\left(\frac{\bigtriangledown\,\varrho}{\varrho}\right)^2+\frac{1}{3}\left(\frac{\bigtriangledown\,\varrho}{\varrho}\right)^4\right]\right\}, \tag{4.26}$$

which identifies the g_4's of (4.25).

We show now that the V.T. can be used to identify the functional form of the g_4's. Proceeding term by term and observing that the g_4's depend only on ϱ we consider first

$$\varepsilon_k(\varrho) = \varrho^K(\triangle\,\varrho)^2\,, \tag{4.27}$$

where we have assumed that $g_4^{(2)}$ has the form of ϱ^K. Simple calculation yields

$$(\triangle_\lambda\,\varrho_\lambda)^2 = \lambda^{10}\left\{\frac{\partial^2\varrho(\lambda\,r)}{\partial(\lambda\,x)^2} + \ldots\right\}^2, \tag{4.28}$$

and combining (4.28) with (4.21) we get

$$\varepsilon_k(\varrho_\lambda\,, r) = \lambda^{3K+10}\left\{\frac{\partial^2\varrho(\lambda\,r)}{\partial(\lambda\,x)^2} + \ldots\right\}^2 \varrho^K(\lambda\,r)\,, \tag{4.29}$$

which gives

$$K = -5/3\,. \tag{4.30}$$

This is indeed the functional form of $g_4^{(2)}$ as seen from (4.26). Next we put

$$\varepsilon_k(\varrho, r) = \varrho^K(\triangle\,\varrho)\,(\bigtriangledown\,\varrho)^2\,. \tag{4.31}$$

We have

$$(\triangle_\lambda\,\varrho_\lambda) = \lambda^5\left\{\frac{\partial^2\varrho(\lambda\,r)}{\partial(\lambda\,x)^2} + \ldots\right\}, \tag{4.32}$$

and using for $(\bigtriangledown\varrho)^2$ and ϱ^K Eqs. (4.20) and (4.21) we obtain

$$\varepsilon_k(\varrho_\lambda\,, r) = \lambda^{3K+5+8}\left\{\frac{\partial^2\varrho(\lambda\,r)}{\partial(\lambda\,x)^2} + \ldots\right\}\left\{\left(\frac{\partial\varrho(\lambda\,r)}{\partial(\lambda\,x)}\right)^2 + \ldots\right\}\varrho^K(\lambda\,r)\,. \tag{4.33}$$

Using (4.11) again we get

$$K = -8/3\,, \tag{4.34}$$

which gives the correct form of $g_4^{(3)}$ as is clear from comparing the result with (4.26). A similar simple calculation gives the correct form of $g_4^{(4)}$. It is clear that it would be simple to derive the functional form of the terms containing $(\bigtriangledown_i^6)$.

As a final example let us relax now the requirement that $g_4^{(2)}$ can depend only on ϱ and let us assume that we permit a term of the following type in our DF formula:

$$\varepsilon_k(\varrho, r) = \varrho^K r^L(\triangle\,\varrho)^2\,. \tag{4.35}$$

Using (4.21) and (4.28) we get

$$\varepsilon_k(\varrho_\lambda\,, r) = \lambda^{3K+10-L}\left\{\frac{\partial^2\varrho(\lambda\,r)}{\partial(\lambda\,x)^2} + \ldots\right\}^2 \times\varrho^K(\lambda\,r)\,(\lambda\,r)^L\,. \tag{4.36}$$

Using (4.11) we get

$$K = (L-5)/3\,. \tag{4.37}$$

For each value of L we get one possible K value e. g. $L=0$ gives again (4.30); $L=1$ gives $K=-4/3$ which leads to the following DF formula

$$\varepsilon_k(\varrho, r) = r(\triangle\,\varrho)^2/\varrho^{4/3}\,, \tag{4.38}$$

while $L=-1$ gives $K=-2$ so we get

$$\varepsilon_k = (1/r\,\varrho^2)\,(\triangle\,\varrho)^2\,, \tag{4.39}$$

and so on.

It is interesting to note that the V.T. selects, from the multitude of possible formulas, a relatively small number of possibilities. For the kinetic energy the only power of ϱ which is permitted is $\varrho^{5/3}$ i. e. the Fermi term; from all functions of the form $\varrho^K r^L$ the V.T. selects the terms which have the combination given by (4.17), which means that if L is a negative integer, the only form permitted is given by (4.18). Similarly, a single equation defining the possibilities can be derived for any combination of powers of ϱ, of r and of gradient terms.

5. Construction of a new Density-Functional Formula

An inspection of the available DF formulas shows that the weak point of all theories is always the formula for the kinetic energy. The problem is this: let us start with the HF expression for the kinetic energy constructed with the one-electron functions $\varphi_1, \varphi_2, \ldots, \varphi_N$:

$$E_k = \sum_{i=1}^{N}\int\varphi_i^*\left(-\frac{\hbar^2}{2\,m}\triangle\right)\varphi_i\,\mathrm{d}v\,. \tag{5.1}$$

Using plane waves for the φ_i's one gets the TF expression [5]:

$$E_k = \frac{3}{10}\,(3\,\pi^2)^{2/3}\int\varrho^{5/3}\,\mathrm{d}v\,,\ \text{(a. u.)}\,. \tag{5.2}$$

The source of the difficulties is that the gradient operator $(\bigtriangledown^2)$ is lost in this transformation. We must realize that both (5.1) and (5.2) are used in such a way (in the HF and TF models) that the energy is *minimized* in terms of the wave functions or in terms of ϱ. The presence of $\bigtriangledown^2$ in (5.1) will minimize fluctuations in the wave functions; since there is no gradient in (5.2) the application of the

energy minimum principle will not minimize fluctuations in ϱ. It is remarkable that the TF model, using (5.2) gives meaningful results at all.

This problem – how to restore the ∇-dependence into the DF formula – has been investigated by a number of scientists and two basic methods emerged: the so-called gradient expansion [8, 9, 12] and the Fermi-energy reduction formulas [10]. The gradient expansion formula is as follows:

$$E_k = \alpha_1 \int \varrho^{5/3}\,dv + \alpha_2 \int \frac{(\nabla \varrho)^2}{\varrho}\,dv + \alpha_3 \int \varrho^{1/3}\left(\frac{\triangle \varrho}{\varrho}\right)dv + \alpha_4 \int \varrho^{1/3}\left(\frac{\triangle \varrho}{\varrho}\right)\left(\frac{\nabla \varrho}{\varrho}\right)^2 dv + \alpha_5 \int \varrho^{1/3}\left(\frac{\nabla \varrho}{\varrho}\right)^4 dv + \ldots \qquad (5.3)$$

where the first term is the Fermi energy the second term is the so-called Weizsäcker term [7] and the rest are the higher order gradient terms. The Fermi-energy-reduced formula is as follows:

$$E_k = \beta_1 \int \frac{(\nabla \varrho)^2}{\varrho}\,dv + E_F{}^a + E_F{}^r\,, \qquad (5.4)$$

where the $E_F{}^a$ and $E_F{}^r$ are the azimuthal and radial parts of the Fermi energy for which the following formulas were given [10]:

$$E_F{}^a = \beta_2 \int \varrho^{5/3}\,dv\,, \qquad (5.5)$$

$$E_F{}^r = \int \left(\beta_3\,\varrho^{5/3} + \beta_4(\varrho^{4/3}/r) + \beta_5(\varrho/r) + \beta_6(1/r^5)\right) dv\,. \qquad (5.6)$$

In the formulas above the limits of integration are from 0 to ∞ except in (5.6) where the limits are r_i and r_0 defined by a special equation for ϱ.

For the set of constants α_i $(i = 1, 2, \ldots)$ and β_i $(i = 1, 2, \ldots)$ different values were derived using different quantum mechanical models for background.

In the present paper we have derived a generalized form of the Fermi-energy reduced formula and we base a semi-theoretical DF formalism on this formula. Our reasons for choosing this approach rather than that leading to the gradient expansion are as follows:

1) We have tested (5.3) – without the higher order gradient terms but with several different sets of constants – and have not obtaind satisfactory results (see below, Section 6 A).

2) We are reluctant to include the higher order gradient terms in a DF formalism as long as there are other possibilities to obtain accurate results. The inclusion of these terms would mean a differential equation of higher than second order for ϱ and also would result in an assymptotic behavior of ϱ different from the HF theory.

3) It must be kept in mind that the formula (5.3) rests on a different quantum mechanical background from formula (5.4). The gradient expansion formula (5.3) rests on the HF model; the Fermi-energy-reduced formula (5.4) rests on the *pseudopotential formalism*. It is our intention to show in a forthcoming publication that the transition from the pseudopotential formalism to a DF formalism is much smoother (involves more plausible approximations) than the corresponding transition from the HF model.

5 A) A New Formula for the Density-Functional of the Kinetic Energy

We start the discussion by referring to a paper in the process of publication [13] in which it is shown that the wave equation of any (core or valence) electron in an atom can be written in the form

$$(-\tfrac{1}{2}\triangle + V_F + V_i)\,\psi_i = E_i\,\psi_i\,, \quad (i = 1, 2, \ldots, N)\,, \qquad (5.7)$$

where ψ_i is a (nodeless) pseudowavefunction, V_F is the usual type of HF potential and V_i is a pseudopotential. Qualitatively this means that the kinetic energy of an electron consist of two parts: first the expectation value of the Laplacian with respect to ψ_i and second, the expectation value of V_i with respect to ψ_i (the latter is not exclusively kinetic in nature but it can be shown to be *almost* entirely kinetic). For the first Gombas introduced [10] the term "self-energy"; we call the second the "orthogonalization" energy.

Now let us consider the first two terms of both (5.3) and (5.4) i. e. the sum of the Fermi and Weizsäcker energies:

$$E_k = E_W + E_F = \beta_1 \int \frac{(\nabla \varrho)^2}{\varrho}\,dv + \beta_2 \int \varrho^{5/3}\,dv\,, \qquad (5.8)$$

where

$$\beta_1 = \tfrac{1}{8}\,(\text{a. u.})\,, \quad \beta_2 = \tfrac{3}{10}\,(3\pi^2)^{2/3} \quad (\text{a. u.})\,. \qquad (5.9)$$

In order to interpret (5.8) let us consider first the usual derivation of the Fermi energy. Let us consider a Fermi-gas at $T = 0$ when the electron fill

a sphere of radius p_F in the momentum space. The electrons with momentum p will be in a shell of width dp and their kinetic energy is given as $(p^2/2m)$. The Fermi energy is obtained by integrating from $p=0$ to $p=p_F$. It is clear that the Fermi energy E_F will contain both the self-energy and the orthogonalization energy (the latter being equivalent to the requirement that each electron fills a different volume in the momentum space).

It is plausible to assume that the Weizsäcker term represents the self-energy. This assumption is based on the following interpretation of E_W: if N electrons would occupy the *same state* ψ then (assuming that $\psi^* = \psi$) the *exact* quantum mechanical expression for the kinetic energy would be E_W [14]. In other words if there would be no orthogonalization energy then E_k would be exactly equal to E_W. We note that in a DF formalism which necessarily implies some form of averaging over the one-electron wave functions we can assume that E_W will represent the *average* of the self-energy of electrons distributed over different states.

We interpret (5.8) therefore as consisting of the Fermi energy which contains both the self-energy and the orthogonalization energy and of the Weizsäcker term which is (some kind of average) of the self-energy. The result of introducing E_W is therefore that the ∇-dependence is restored but the self-energy is (roughly) doubled. An accurate expression will be obtained if we substract the self-energy from E_F without touching E_W, i. e. without reducing the "amount of gradient" in E_k. [We note here that this argument would be essentially the same if the self-energy would be represented by an expression different from E_W e. g. by several terms of the gradient expansion.]

In order to extract the self-energy from E_F let us consider a Fermi gas and let us assume that the volume Ω contains N electrons which fill the sphere of radius p_F in the momentum space. The relationship between p_F and the density $\varrho = N/\Omega$ is given as [5]

$$p_F = (3\pi^2)^{1/3}\varrho^{1/3}, \quad \text{(a. u.)} . \tag{5.10}$$

In the Fermi gas the kinetic energy of one electron with momentum $0 \leqq p \leqq p_F$ is given by $p^2/2m$. Restricting the discussion to spherically symmetric densities we observe that the energy density of the Weizsäcker term is also spherically symmetric meaning that the self-energy represented by E_W is purely radial; therefore we resolve the kinetic energy $(p^2/2m)$ into azimuthal and radial parts [10] in the ratio 2 to 1 i. e. we put

$$K^a = \tfrac{2}{3}\, p^2/2m , \tag{5.11}$$

and

$$K^r = \tfrac{1}{3}\, p^2/2m , \tag{5.12}$$

where the radial part K^r must be reduced by the self energy.

Let us consider now a spherical shell in the momentum sphere with inner radius p_n and outer radius $p_n + p_\varepsilon$. The momentum of the electrons in this shell will be such that

$$p_n \leqq p \leqq p_n + p_\varepsilon . \tag{5.13}$$

We shall identify $p_n^2/2m$ with the orthogonalization energy i. e. we assume that the orthogonalization energy is identical with the energy needed to raise the electron to the inner surface of the shell p_ε. For p^2 we put the volume average of the kinetic energy in the shell p_ε i. e. we put

$$p^2 = \frac{1}{V_\varepsilon}\int_{p_n}^{p_n+p_\varepsilon} p^2 (4\pi p^2\, dp) , \tag{5.14}$$

where V_ε is the volume of the shell

$$V_\varepsilon = \frac{4\pi}{3}\left[(p_n + p_\varepsilon)^3 - p_n^3\right] . \tag{5.15}$$

For electrons with momentum p satisfying (5.13) the total radial kinetic energy is (5.12); this expression contains the orthogonalization energy as well as the radial self-energy. According to our assumption about p_n the radial self-energy is eliminated if (5.12) is replaced by

$$\hat{K}^r = \tfrac{1}{3}\, p_n^2/2m . \tag{5.16}$$

From (5.14) we get by simple calculation

$$p_n^2 = p^2 - \tfrac{1}{6}p_\varepsilon^2 - p\,p_\varepsilon\left[1 - \frac{5}{12}\left(\frac{p_\varepsilon}{p}\right)^2\right]^{1/2} = p^2 - \tfrac{1}{6}p_\varepsilon^2 - p\,p_\varepsilon \sum_{\nu=0}^{\infty}\binom{1/2}{\nu}\left(-\frac{5}{12}\frac{p_\varepsilon^2}{p^2}\right)^\nu$$

$$= p^2 - p_\varepsilon\, p - \frac{1}{6}p_\varepsilon^2 + \left(\frac{5}{24}\right)p_\varepsilon^3\, p^{-1} - \left(\frac{5}{96}\right)p_\varepsilon^5\, p^{-3} + \left(\frac{5}{192}\right)p_\varepsilon^7\, p^{-5} + \ldots , \tag{5.17}$$

which can be written in the form

$$p_n^2 = \sum_{k=0}^{\infty} a_k p_\varepsilon^k p^{2-k}, \tag{5.18}$$

where the a_k are numbers. The formulas (5.17) and (5.18) are subject to the condition that

$$p_n^2 \geqq 0. \tag{5.19}$$

This condition puts a restriction on the range of p since the formulas for p_n^2 can be integrated only for those values of p for which (5.19) is satisfied. If many terms are taken into account in (5.18) the condition (5.19) may lead to a complicated formula for the range of p; in the present paper we have gone only to $k=4$ and for $k=2, 3, 4$ we can always assume that the range of p extends from a minimum value p_m (depending on the "expansion length") to p_F. Keeping this in mind we get by integration for the azimuthal and radial kinetic energy density with the radial part reduced by the self energy:

$$\varepsilon_k{}^a = \int_0^{p_F} \frac{2}{3} \frac{p^2}{2m} \frac{8\pi p^2 \,\mathrm{d}p}{h^3} = \frac{8\pi}{15 m h^3} p_F{}^5, \tag{5.20}$$

and

$$\varepsilon_k{}^r = \int_{p_m}^{p_F} \frac{1}{3} \frac{p_n^2}{2m} \frac{8\pi p^2 \,\mathrm{d}p}{h^3} = \frac{1}{6\pi^2 m \hbar^3} \sum_{k=0}^{\infty} a_k p_\varepsilon{}^k \left\{ \frac{p_F^{(5-k)}}{(5-k)} - \frac{p_m^{(5-k)}}{(5-k)} \right\}, \tag{5.21}$$

where we have, by definition of the p_m, the condition

$$p_F \geqq p_m. \tag{5.21 a}$$

For the above mentioned cases, $k=2, 3, 4$ the p_m can always be written in the form

$$p_m = K_0 p_\varepsilon, \tag{5.22}$$

where the number K_0 depends on the expansion length. Using (5.10) and (5.22) and introducing atomic units [15] we get

$$\varepsilon_k{}^a = \tfrac{1}{5} (3\pi^2)^{2/3} \varrho^{5/3}, \tag{5.23}$$

$$\varepsilon_k{}^r = \sum_{k=0}^{\infty} \frac{1}{6\pi^2} \frac{a_k}{(5-k)} \cdot \{ (3\pi^2)^{(5-k)/3} \varrho^{(5-k)/3} p_\varepsilon{}^k - K_0^{5-k} p_\varepsilon{}^5 \}, \tag{5.24}$$

and the condition $p_F \geqq p_m$ becomes, using (5.22),

$$\varrho \geqq (K_0{}^3/3\pi^2) p_\varepsilon{}^3. \tag{5.25}$$

In the Eq. (5.23), (5.24) and (5.25) only the p_ε remains unspecified. We recall that p_ε determines the thickness of the shell giving rise to the self-energy. One of the possible choices for p_ε may be obtained as follows. In the Quantum Theory the azimuthal component of the angular momentum is quantized according to the formula

$$M_l = \sqrt{l(l+1)}\hbar. \tag{5.26}$$

For use in the Thomas-Fermi model Fermi suggested [5] instead of (5.26) the formula

$$M_l = (l + \tfrac{1}{2})\hbar. \tag{5.27}$$

Let us resolve the momentum of a particle into azimuthal and radial components p_a and p_r. The formulas (5.26) and (5.27) then provide a quantization rule for p_l; we get from (5.26)

$$p_l = \sqrt{l(l+1)}\hbar/r, \tag{5.28}$$

and from (5.27)

$$p_l = (l + \tfrac{1}{2})\hbar/r. \tag{5.29}$$

A possible choice for p_ε is the azimuthal momentum interval corresponding to $\mathrm{d}l = 1$. Choosing Fermi's formula, (5.29) we get

$$p_\varepsilon = p_{l+\mathrm{d}l} - p_l = \hbar/r, \quad (\mathrm{d}l = 1). \tag{5.30}$$

In order to keep our formulas as general as possible, we put, in atomic units

$$p_\varepsilon = K(1/r), \tag{5.31}$$

where K is an arbitrary constant. Using this equation we get for (5.24):

$$\varepsilon_k{}^r = \sum_{k=0}^{\infty} \frac{1}{6\pi^2} \frac{a_k}{(5-k)} \left\{ (3\pi^2)^{(5-k)/3} \varrho^{(5-k)/3} K^k \left(\frac{1}{r}\right)^k - K_0^{5-k} K^5 \left(\frac{1}{r}\right)^5 \right\}, \tag{5.32}$$

and the condition (5.25) becomes

$$\varrho \geqq \left(\frac{K_0{}^3 K^3}{3\pi^2}\right)\left(\frac{1}{r}\right)^3. \tag{5.33}$$

In order to simplify the formulas let

$$b_k \equiv \frac{1}{6\pi^2} \frac{a_k}{(5-k)} (3\pi^2)^{(5-k)/3} K^k, \tag{5.34}$$

$$c_k \equiv \frac{1}{6\pi^2}\frac{a_k}{(5-k)} K_0^{5-k} K^5, \qquad (5.35)$$

and

$$d \equiv K_0^3 K^3/3\pi^2. \qquad (5.36)$$

Using these notations we get the final formulas for the energy density (5.32) and for the condition (5.33):

$$\varepsilon_k{}^{\mathrm{r}} = \sum_{k=0}^{\infty}\left\{b_k \varrho^{(5-k)/3}\frac{1}{r^k} - c_k\frac{1}{r^5}\right\}, \qquad (5.37)$$

and

$$\varrho \geqq d/r^3. \qquad (5.38)$$

We note that $\varepsilon_k{}^{\mathrm{r}}$ has one of the forms permitted by the Virial Theorem [Equation (4.18)].

We shall now demonstrate that Gombas' formula, quoted above, Eq. (5.6) is a special case of (5.37). The formula used by Gombas is obtained by terminating the series (5.18) after the third term, i. e. by putting $a_0 = 1$, $a_1 = -1$, $a_2 = -\frac{1}{6}$, with the rest of the a_i's equal to zero. The Eq. (5.19) becomes

$$p_{\mathrm{n}}{}^2 = p^2 - p_\varepsilon p - \tfrac{1}{6}p_\varepsilon{}^2 \geqq 0, \qquad (5.39)$$

from which we get two values of p for which $p_n{}^2 = 0$:

$$p_{1,2} = \left(\frac{1}{2} \pm \sqrt{\frac{5}{12}}\right)p_\varepsilon. \qquad (5.40)$$

In this equation we must choose the positive sign in order to get positive p. For p values greater than p_1 the $p_{\mathrm{n}}{}^2$ given by (5.39) will be positive. Comparing (5.40) to (5.22) we see that the minimum of p i. e. p_{m} is obtained with

$$K_0 = \frac{1}{2} + \sqrt{\frac{5}{12}}. \qquad (5.41)$$

For K Gombas used $K = 1$. The DF formula becomes [10]

$$\varepsilon_k{}^{\mathrm{r}} = b_0\varrho^{5/3} + b_1\frac{\varrho^{4/3}}{r} + b_2\frac{\varrho}{r^2} - (c_0 + c_1 + c_2)\frac{1}{r^5}, \qquad (5.42)$$

which is the formula quoted above, Equation (5.6). The constants $b_0 - b_2$ and $c_0 - c_2$ can be computed from (5.34) and (5.35). For the condition (5.38) we get

$$\varrho \geqq \frac{1}{3\pi^2}\left(\frac{1}{2} + \sqrt{\frac{5}{12}}\right)^3\frac{1}{r^3}. \qquad (5.43)$$

[this is the special equation referred to in the text after Equation (5.6)]. Integration of the radial energy density must be restricted to that range of r for which ϱ satisfies (5.43).

Summarizing our results we obtain the density of the kinetic energy by adding to the Weizsäcker inhomogenity term the Fermi energy where the latter is reduced by the "self-energy". We get from (5.8), (5.23) and (5.37):

$$\varepsilon_k(\varrho) = \varepsilon_k{}^{\mathrm{i}} + \varepsilon_k{}^{\mathrm{a}} + \varepsilon_k{}^{\mathrm{r}}, \qquad (5.44)$$

where

$$\varepsilon_k{}^{\mathrm{i}} = \frac{1}{8}\frac{(\nabla\varrho)^2}{\varrho}, \qquad (5.45)$$

$$\varepsilon_k{}^{\mathrm{a}} = \tfrac{1}{5}(3\pi^2)^{2/3}\varrho^{5/3}, \qquad (5.46)$$

$$\varepsilon_k{}^{\mathrm{r}} = \sum_{i=0}^{\infty}\left\{b_i\varrho^{(5-i)/3}\frac{1}{r^i} - c_i\frac{1}{r^5}\right\}, \qquad (5.47)$$

and the constants b_i and c_i are given by (5.34), (5.35), (5.18), (5.17), (5.22) and (5.31). The formula (5.47) is valid only if

$$\varrho \geqq d/r^3, \qquad (5.48)$$

where d is given by (5.36), (5.31) and (5.22). For those values of r for which (5.48) is not satisfied, $\hat{\varepsilon}_k{}^{\mathrm{r}} = 0$.

5 B) The Density of Potential Energy

For the potential energy we adopt the formula of the conventional TF model [5, 6]. According to that model the potential energy consist of the Coulomb interaction between the nucleus and the electrons, the electrostatic interaction energy of the electrons and the exchange interaction energy of the electrons. The formula is

$$\varepsilon_p(\varrho) = -\frac{Z}{r}\varrho - \frac{1}{2}V_{\mathrm{e}}(\varrho)\varrho - \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\varrho^{4/3}, \qquad (5.49)$$

where V_{e} is the electrostatic potential of the electrons at the point $\boldsymbol{r}$:

$$V_{\mathrm{e}}(\varrho, \boldsymbol{r}) = -\int\frac{\varrho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}\,\mathrm{d}v'. \qquad (5.50)$$

The last term is the exchange energy as given by Dirac [6].

5 C) The Total Energy. Corrections for Small N

We are now able to write down the formula for the total energy. Using the results of the previous two sections we get the following formula for the

density-functional:

$$\varepsilon(\varrho) = \varepsilon_k(\varrho) + \varepsilon_p(\varrho)\,, \tag{5.51}$$

where

$$\varepsilon_k(\varrho) = \varepsilon_k{}^{\mathrm{i}}(\varrho) + \varepsilon_k{}^{\mathrm{a}}(\varrho) + \varepsilon_k{}^{\mathrm{r}}(\varrho)\,, \tag{5.52}$$

and

$$\varepsilon_p(\varrho) = \varepsilon_p{}^{\mathrm{n}}(\varrho) + \varepsilon_p{}^{\mathrm{c}}(\varrho) + \varepsilon_p{}^{\mathrm{e}}(\varrho)\,. \tag{5.53}$$

The terms in the kinetic energy are defined by (5.45) – (5.47) while the terms of the potential energy are the terms of Equation (5.49). In a general notation we get

$$\varepsilon_k{}^{\mathrm{i}}(\varrho) = A_1(\nabla\varrho)^2/\varrho\,, \tag{5.54}$$

$$\varepsilon_k{}^{\mathrm{a}}(\varrho) = A_2\,\varrho^{5/3}\,, \tag{5.55}$$

$$\varepsilon_k{}^{\mathrm{r}} = b_0\,\varrho^{5/3} + b_1\frac{\varrho^{4/3}}{r} + b_2\frac{\varrho}{r^2} + b_3\frac{\varrho^{2/3}}{r^3} + b_4\frac{\varrho^{1/3}}{r^4} + b_5\frac{1}{r^5} + \ldots + (c_0 + c_1 + c_2 + \ldots)\frac{1}{r^5}\,, \tag{5.56}$$

$$\varepsilon_p{}^{\mathrm{n}}(\varrho) = -(Z/r)\,\varrho\,, \tag{5.57}$$

$$\varepsilon_p{}^{\mathrm{c}}(\varrho) = -\tfrac{1}{2}\,V_{\mathrm{e}}(\varrho)\,\varrho\,, \tag{5.58}$$

$$\varepsilon_p{}^{\mathrm{e}}(\varrho) = B_1\,\varrho^{4/3}\,, \tag{5.59}$$

$$V_{\mathrm{e}}(\varrho) = -\int\frac{\varrho(\boldsymbol{r}')\,\mathrm{d}v'}{|\boldsymbol{r}-\boldsymbol{r}'|}\,. \tag{5.60}$$

We wish to collect now the values of the constants; computing the b_i's and c_i's up to $i=4$ we get from (5.34). (5.35) and (5.17):

$$\begin{aligned}
A_1 &= \frac{1}{8}\,, & A_2 &= \frac{1}{5}\,(3\pi^2)^{2/3}\,,\\
B_1 &= -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\,, & b_0 &= \frac{1}{10}\,(3\pi^2)^{2/3}\,,\\
b_1 &= -\frac{1}{8}\,(3\pi^2)^{1/3}K\,, & b_2 &= -\frac{1}{36}K^2\,,\\
b_3 &= \frac{5}{288\,\pi^2}\,(3\pi^2)^{2/3}K^3\,, & b_4 &= 0\,,\\
c_0 &= \frac{1}{30\,\pi^2}K_0{}^5K^5\,, & c_1 &= -\frac{1}{24\,\pi^2}K_0{}^4K^5\,,\\
c_2 &= -\frac{1}{108\,\pi^2}K_0{}^3K^5\,, & c_3 &= \frac{5}{288\,\pi^2}K_0{}^2K^5\,,\\
& & c_4 &= 0\,.
\end{aligned} \tag{5.61}$$

The b_i's depend on K and the c_i's depend on K_0 as well as on K. The constant K_0 was introduced by the equation (5.22) and defines the lower limit of integration in the expression for the radial kinetic energy, Equation (5.21). K_0 and p_m must be determined in such a way that Eq. (5.19) is satisfied i. e. the integration over p in Eq. (5.21) must be restricted to such values of p for which $p_{\mathrm{n}}{}^2 \geqq 0$. K_0 therefore depends on how many terms are taken into account in $\varepsilon_k{}^{\mathrm{r}}$. We will show below how K_0 is determined for various "lengths" of $\varepsilon_k{}^{\mathrm{r}}$. The constant K determines the "momentum width" p_ε, by equation (5.31).

We wish to introduce now two corrections into the density-functional which are important only for small N. First we observe that while in the HF approximation the Coulomb self-energy of the electrons is exactly cancelled by the exchange self-energy, this is not the case in the TF expressions $\varepsilon_p{}^{\mathrm{c}}$ and $\varepsilon_p{}^{\mathrm{e}}$. Both of these expressions include the self-energy, therefore a certain amount of cancellation will take place; how accurate it will be is not known. A slightly more satisfactory procedure is to introduce that kind of correction factor which was first suggested by Fermi and Amaldi [16]. In the TF model the density of one electron is (ϱ/N); the electrostatic potential of $(N-1)$ electrons is therefore

$$\hat{V}_{\mathrm{e}}(\boldsymbol{r}) = -(N-1)\int\frac{[\varrho(\boldsymbol{r}')/N]}{|\boldsymbol{r}-\boldsymbol{r}'|}\,\mathrm{d}v'\,. \tag{5.62}$$

The total electrostatic interaction energy therefore will be the following:

$$\begin{aligned}
\hat{E}_p{}^{\mathrm{c}} &= -\frac{1}{2}N\int\hat{V}_{\mathrm{e}}\frac{\varrho}{N}\,\mathrm{d}v \qquad (5.63)\\
&= -\frac{1}{2}\left(1-\frac{1}{N}\right)\int V_{\mathrm{e}}\,\varrho\,\mathrm{d}v = \left(1-\frac{1}{N}\right)\int\varepsilon_p{}^{\mathrm{c}}(\varrho)\,\mathrm{d}v\,.
\end{aligned}$$

The result is that the Coulomb self-energy of the electrons can be eliminated by multiplying the density functional with the factor $(1-1/N)$.

We can apply a similar argument to the exchange energy. Since each electron has exchange interaction only with electrons having parallel spin the number of which is $N/2$ for atoms with closed shells, the correction factor which eliminates the self-exchange energy is given by

$$(1-\sigma(N)/N)\,, \tag{5.64}$$

where

$$\sigma(N) = \begin{cases} 1 \text{ for } N=1\,, \\ 2 \text{ for all other } N\,. \end{cases} \tag{5.65}$$

The corrected expression for the density functional therefore will be the following

$$\hat{\varepsilon}_p(\varrho) = \varepsilon_p{}^{\mathrm{n}}(\varrho) + \hat{\varepsilon}_p{}^{\mathrm{c}}(\varrho) + \hat{\varepsilon}_p{}^{\mathrm{e}}(\varrho)\,, \tag{5.66}$$

with

$$\hat{\varepsilon}_p{}^{c}(\varrho) = (1 - 1/N)\,\varepsilon_p{}^{c}(\varrho)\,, \qquad (5.67)$$

and

$$\hat{\varepsilon}_p{}^{e}(\varrho) = \big(1 - \sigma(N)/N\big)\,\varepsilon_p{}^{c}(\varrho)\,, \qquad (5.68)$$

where $\varepsilon_p{}^{c}$ and $\varepsilon_p{}^{e}$ are given by (5.58) and (5.59). We note that these corrections made the potential energy exact for $N=1$ and $N=2$ (for $N=2$ exact in the HF approximation, ground state].

In connection with the density functional of the kinetic energy we observe that the Weizsäcker term is the exact expression for $N=1$ and $N=2$ [for $N=2$ again we mean the HF approximation and ground state]. The Fermi energy must be zero for these cases. We can construct a density functional fulfilling this requirement by multiplying the Fermi energy with the factor (5.64), i. e. by putting

$$\hat{\varepsilon}_k(\varrho) = \varepsilon_k{}^{i}(\varrho) + \varepsilon_k{}^{a}(\varrho) + \varepsilon_k{}^{r}(\varrho)\,, \qquad (5.69)$$

where

$$\hat{\varepsilon}_k{}^{a}(\varrho) = \big(1 - \sigma(N)/N\big)\,\varepsilon_k{}^{a}(\varrho)\,, \qquad (5.70)$$

and

$$\varepsilon_k{}^{r}(\varrho) = \big(1 - \sigma(N)/N\big)\,\varepsilon_k{}^{r}(\varrho)\,, \qquad (5.71)$$

where $\varepsilon_k{}^{i}$, $\varepsilon_k{}^{a}$ and $\varepsilon_k{}^{r}$ are given by (5.54), (5.55) and (5.56). The expression (5.69) is the exact kinetic energy for $N=1$ and $N=2$. For larger N this correction cannot be justified satisfactorily but we note that the correction factor is significant only up to about $N=30$ and up to this N the Weizsäcker term is more important than the Fermi term; for larger N, where the Fermi term is dominant the effect of the correction factor is small.

Summarizing our results, we get for the density functional

$$\varepsilon(\varrho) = \hat{\varepsilon}_k(\varrho) + \hat{\varepsilon}_p(\varrho)\,, \qquad (5.72)$$

where $\hat{\varepsilon}_k$ and $\hat{\varepsilon}_p$ are given by (5.69) and (5.66). The formula for $\varepsilon(\varrho)$ is valid for any arbitrary N; in fact the formula is exact for $N=1$ and 2 [in the HF approximation for $N=2$].

6. The Calculations

Having obtained the DF formula we now proceed to calculate atomic energies. The total energy of the atom is given by

$$E = \int \varepsilon(\varrho)\,\mathrm{d}v\,. \qquad (6.1)$$

The correct procedure would be to vary E with respect to ϱ i. e. to form

$$\partial E/\partial\varrho = 0\,, \qquad (6.2)$$

which would result in an integrodifferential equation for ϱ. Since we want to test a large number of cases this would be too time consuming. Instead of exact variation we put the density in analytic form:

$$\varrho = (N/A)\,e^{-x} \qquad (6.3)$$

where

$$x = (\lambda r)^{1/n}\,. \qquad (6.4)$$

Here λ and n are variational parameters. N is the number of electrons and A is a normalization constant. As seen from the formula, λ is a scale factor which ensures that the Virial Theorem will be satisfied for all calculations. We put ϱ into ε and ε into the integral (6.1); the energy hereby becomes a functional of λ and n. Varying E with respect to these parameters we form the equations

$$\frac{\partial E(\lambda, n)}{\partial\lambda} = 0\,, \quad \frac{\partial E(\lambda, n)}{\partial n} = 0\,, \qquad (6.5)$$

from which we get the minimum-defining values $\lambda = \lambda_0$ and $n = n_0$. Putting these back into E we get the minimum $E_0 = E_{\blacksquare}\,(\lambda_0, n_0)$.

It will be shown below on concrete examples, that despite of the simplicity of this "Ansatz" for ϱ *the results are very accurate for the energy i. e. the computed energies are very close to the values obtained from the solutions of the exact diff. Equation (6.2).* For the density itself (6.3) is only a crude approximation.

6 A) Previously Suggested Kinetic Energy Formulas

First we shall re-compute total energies with the most important, previously suggested DF formulas (some of which are tested systematically here for the first time). First we put

$$\varepsilon(\varrho) = \varepsilon_k(\varrho) + \hat{\varepsilon}_p(\varrho)\,, \qquad (6.6)$$

where $\hat{\varepsilon}_p$ is given by (5.66) and ε_k is given by

$$\varepsilon_k(\varrho) = A_1(\nabla\varrho)^2/\varrho + A_2\big(1 - \sigma(N)/N\big)\,\varrho^{5/3}\,. \qquad (6.7)$$

The *original Weizsäcker correction* [7] consist of putting

$$A_1 = \frac{1}{8}\,, \quad A_2 = \frac{3}{10}\,(3\pi^2)^{2/3}\,. \qquad (6.8)$$

The formula suggested by Kirzhnits [8] is

$$A_1 = \frac{1}{9.8}\,, \quad A_2 = \frac{3}{10}\,(3\pi^2)^{2/3}\,; \qquad (6.9)$$

and the formula of Tomishima [17] is

$$A_1 = \frac{1}{5.8}\,, \quad A_2 = \frac{3}{10}\,(3\pi^2)^{2/3}\,. \qquad (6.10)$$

The computed energies for the atoms Ne, Ar, Kr, Xe, and Hg ($N = 10$, 18, 36, 54, 80) are listed in Table 2, along with the HF values. The deviation from E_F is given in percents in such a way that if the computed value is higher than E_F the deviation is positive.

Next we have re-done the calculations of Gombas [10]. We use now the DF formula (5.72) containing all the Fermi-Amaldi type corrections. For the constants in $\hat{\varepsilon}_k$ [Eqs. (5.54), (5.55) and (5.56)] Gombas used two different sets: we call these $G1$ and $G2$. In both cases A_1 and A_2 are as given in (5.61). For $G1$ we get Gombas' formula by using the following constants in (5.18):

$$a_0 = 1\,, \quad a_1 = -1\,, \quad a_2 = \tfrac{1}{4}\,, \quad a_i = 0\,, \quad i = 3, 4 \ldots \tag{6.11}$$

which is slightly different from the first three terms of (5.18) as defined by (5.17). For K_0 one obtains from (5.19) and (5.22) $K_0 = 1/2$ and for K we put $K = 1$. For $G2$ we put

$$\left.\begin{aligned} a_0 &= 1\,, \quad a_1 = -1\,, \quad a_2 = -\tfrac{1}{6}\,, \\ a_i &= 0\,, \quad i = 3, 4 \ldots \end{aligned}\right\} \tag{6.12}$$

These are exactly the first three terms of (5.18). For K_0 one obtains (5.41) and K is again put $K = 1$. The energy values computed for our set of atoms with $G1$ and $G2$ are listed in Table 2.

6 B) *The Accuracy of Calculations with Analytic Densities*

The accuracy of variational calculations with analytic densities can be estimated by comparing the results of such a calculation with the results obtained from solving exactly the differential equation for ϱ. There are only very few calculations of the exact solutions of the equation for ϱ which contain inhomogenity correction for the kinetic energy. Tomishima solved [17] the ϱ-equation with the original Weizsäcker correction as well as with 1/5 times the original Weizsäcker correction. We have made analytic calculations for these cases with are slightly different from the calculations of the previous section since in order to work with the same DF formula as Tomishima [17] we removed all Fermi-Amaldi type corrections. In these calculations therefore ε is given by

$$\varepsilon(\varrho) = \varepsilon_k(\varrho) + \varepsilon_p(\varrho)\,, \tag{6.13}$$

where ε_p is given by (5.53) and ε_k is given by (6.7) with the $(1 - \sigma/N)$ removed. The results of calculations for Ne, Ar, Kr, and Xe are in Table 3. The column indicated by % is the deviation of the analytic result from the exact. As we see the energies computed with analytic densities are remarkably close to the exact minima showing thereby that analytic calculations are fairly reliable as far as the energy is concerned. It is not expected that they yield accurate results for the densities.

6 C) *Semi-Theoretical DF Formulas*

An inspection of Table 2 shows that using the previously developed DF formulas of Weizsäcker, Kirzhnits, Tomishima and Gombas we do not get very good approximations to the HF energy. This was the observation which we referred to in Sec. 5,

Table 2. The computed data for Section 6 A.

Atom	N	Weizsäker Eq. (6.8)	%	Kirzhnits Eq. (6.9)	%	Tomishima Eq. (6.10)	%	$G1$ Eq. (6.11)	%	$G2$ Eq. (6.12)	%	HF
Ne	10	102.10	20.6	173.70	−35.1	158.79	−23.5	117.13	8.9	121.81	5.2	128.55
Ar	18	412.67	21.7	630.65	−19.7	587.37	−11.5	475.88	9.7	495.08	6.0	526.82
Kr	36	2194.0	20.3	3056.7	−11.1	2893.7	−5.1	2524.5	8.3	2619.6	4.8	2752.1
Xe	54	5857.4	19.0	7809.0	−8.9	7451.0	−3.0	6714.6	7.2	6951.9	3.9	7232.2
Hg	80	15179.	17.5	19492.	−5.9	18723.	−1.7	17319.	5.9	17888.	2.8	18409.

Table 3. The computed data for Section 6 B.

Atom	N	Eq. (6.8) Exact ϱ	Eq. (6.8) Analytic ϱ	%	Eq. (6.10) Exact ϱ	Eq. (6.10) Analytic ϱ	%
Ne	10	86.43	85.15	1.48	128.83	127.79	0.81
Ar	18	378.51	370.88	2.02	524.91	520.62	0.82
Kr	36	2132.19	2074.6	2.70	2745.60	2723.1	0.82
Xe	54	5828.96	5638.4	3.27	7213.92	7153.7	0.83

when we discussed the general characteristics of the previously developed DF formulas. The next question is: Could these results be improved the way we described it in Sec. 5, i. e. adding more terms to the DF of the kinetic energy?

Apart from the higher order terms of the gradient expansion which we do not consider in this paper neither of the four formulas tested above is in the form of an expansion from which better results could be computed by adding more terms to the DF of the kinetic energy. Next we could try to include more terms of the formula which we derived in Sec. 5 for the orthogonalization energy, Equation (5.18). This is a plausible idea, since, as we see from Table 2, the second formula of Gombas referred to as $G2$ which consisted of the first three terms of (5.18) has come the closest to the HF energy. Unfortunately a look at (5.18) and (5.17) shows that this is an alternating series the convergence of which is probably quite slow even if it does converge toward E_F. Instead of including more terms in the form as they are in (5.18) we shall proceed now as we have outlined it in Section 3. We shall include more terms of (5.18) but at the same time we disengage (5.18) from (5.17) i. e. *we shall consider the parameters as adjustable and shall attempt to determine these parameter in such a way as to approximate the HF energies as closely as possible for all N.*

About the variation of the parameters we want to state the following. We have seen that (5.18) was introduced in such a way that we divided the kinetic energy into two parts, the self-energy and the orthogonalization energy; having observed that the Fermi energy contains both parts we obtained (5.18) by substracting the self-energy from the Fermi energy. In our opinion the division of the kinetic energy into these two parts is basically sound but the formula derived for the reduced energy, Eq. (5.18), is obviously only one of the possible approximations and does not necessarily describe this quantity with the highest accuracy. Therefore we shall consider the constants of (5.18), the a_i's and K which determines p_ε as adjustible parameters, but keep the other constants of the DF formula at their theoretical values. What we are emphasizing here is that we change only those parameters for which there is a plausible reason to do so. Actually we have kept even the first of the a_i's fixed at its theoretical value, i. e. we have put $a_0 = 1$ thereby keeping the Fermi energy intact and changing only the parameters representing the self-energy [$\varepsilon_k{}^a$ and the first term of (5.18) add up to the Fermi energy].

The calculations are done in such a way that first an "expansion length" is selected which determines the formula for K_0. Then the a_i's are computed by an ad hoc trial and error method with the aim of getting as good approximations to E_F as possible, for the atoms Ne, Ar, Kr, Xe and Hg. As we shall see, if the approximation is good for these atoms it is good for all N.

In the first calculation we kept 2 terms of (5.18) i. e. we put

$$p_n{}^2 = p^2 + a_1 p_\varepsilon p\,, \tag{6.14}$$

where $a_0 = 1$. The condition (5.19) leads to the equation

$$p \geqq -a_1 p_\varepsilon\,, \tag{6.15}$$

which means that a_1 must be negative. Using (5.22) we get

$$K_0 = |a_1|\,. \tag{6.16}$$

For K we have put $K = 1$. The trial and error method gave for a_1 the value

$$\mathbf{a_1 = -1.12}\,. \tag{6.17}$$

The results for the "test atoms" are in Table 4, where we have indicated the deviation from E_F in the usual manner. The results are very satisfactory since the deviations are less than 1% which is better than any of the cases presented in Section 6 A.

Table 4. The computed data for Section 6 C.

Atom	N	Best 2-Term	%	Best 3-Term	%	Best 4-Term	%	HF
Ne	10	128.86	−0.24	128.20	+0.27	128.10	+0.35	128.55
Ar	18	521.88	+0.94	526.16	+0.13	525.12	+0.32	526.82
Kr	36	2743.6	+0.31	2759.3	−0.26	2754.6	−0.09	2752.1
Xe	54	7251.8	−0.27	7242.7	−0.15	7235.9	−0.05	7232.2
Hg	80	18589.	−0.98	18398.	+0.06	18406.	+0.002	18409.

Next we have kept 3 terms of (5.18), i. e. we put

$$p_n^2 = p^2 + a_1 p_\varepsilon p + a_2 p_\varepsilon^2 . \qquad (6.18)$$

The condition (5.19) leads to the equation

$$p^2 + a_1 p_\varepsilon p + a_2 p_\varepsilon^2 \geqq 0 . \qquad (6.19)$$

The zeroes of this equation are

$$p_{1,2} = \tfrac{1}{2}(-a_1 \pm \sqrt{a_1^2 - 4a_2})\, p_\varepsilon . \qquad (6.20)$$

For p_m we must choose that value for which p_n^2 will be positive between $p_m \leqq p \leqq p_F$. The K_0 becomes the function of the a_i's since comparing (6.20) to (5.22) we get

$$K_0 = \tfrac{1}{2}(-a_1 \pm \sqrt{a_1^2 - 4a_2}) . \qquad (6.21)$$

The constants must also satisfy the equation

$$a_1^2 - 4a_2 \geqq 0 . \qquad (6.22)$$

We obtained by trial and error

$$a_1 = 2.7 , \quad a_2 = -10.10 , \qquad (6.23)$$

which yields $K_0 = 2.1029$ and K was again chosen as $K = 1$. Finally repeating the procedure with the 4-term expression

$$p_n^2 = p^2 + a_1 p_\varepsilon p + a_2 p_\varepsilon^2 + a_3 p_\varepsilon^3 p^{-1} , \qquad (6.24)$$

we obtained

$$a_1 = 2.0 , \quad a_2 = -7.455 , \quad a_3 = -2.0 , \qquad (6.25)$$

where K was again chosen as $K = 1$. The results with the 3 and 4 term expressions are in Table 4.

As we see from Table 4 the results generally improve by the addition of more terms of (5.18) although we do not have "convergence" for all N; in the range $N < 36$ the results are less good with 4 terms than with 3 terms. Nevertheless we feel that these results – which we consider the main results of the paper – prove our point which is that using the expression (5.18), energy values closely approximating the HF energies can be computed. Using the set (6.25) we computed the energies of some atoms from $N = 2$ to $N = 92$. The results for the energies along with the minimum-defining values of λ_0 and n_0 are in Table 5. As we see from the table for atoms larger than Kr we have achieved accuracies which are either better than 0.1% or only slightly worse; in other words for most of the atoms in this range we have achieved the accuracy of 0.1% which we have chosen in Section 3 as the goal for a DF formula. For $N < 36$ the results are less good but still the deviation is always less than 1%. Comparing these results with Table 2 we conclude also that *the semi-theoretical DF formula based on (5.18) yields better results than any of the previously developed DF formulas.*

Table 5. The computed data for Section 6 C. Best 4-Term results from $N = 15$ to $N = 92$. Results with $\varepsilon_k^r = 0$ for $2 \leqq N \leqq 10$. The HF energies are for the average configuration as in Table 1 (Ref. 3).

Atom	N	E_{calc}	E_F	%	λ_0	n_0
He	2	2.8610	2.8616	+0.02	4.236	1.115
Li	3	7.3806	7.4327	+0.70	6.449	1.244
Be	4	14.462	14.573	−0.76	9.211	1.356
B	5	24.460	24.529	+0.28	12.55	1.453
C	6	37.692	37.660	−0.08	16.46	1.537
N	7	54.446	54.296	−0.28	20.87	1.610
O	8	74.988	74.769	−0.29	26.10	1.679
F	9	99.566	99.409	−0.16	31.91	1.740
Ne	10	128.41	128.55	+0.11	38.26	1.793
P	15	339.13	340.65	+0.45	103.9	2.119
Ar	18	525.12	526.82	+0.32	159.0	2.250
Fe	26	1266.4	1262.3	−0.32	415.0	2.544
Se	34	2403.5	2399.8	−0.15	862.8	2.763
Kr	36	2754.6	2752.1	−0.09	1021.2	2.813
Tc	43	4207.1	4204.6	−0.06	1731.0	2.969
Xe	54	7235.9	7232.2	−0.05	3583.9	3.182
Gd	64	10837.5	10820.3	−0.02	4989.0	3.269
W	74	15299.5	15287.5	−0.08	7894.0	3.400
Hg	80	18406.6	18409.0	+0.01	9149.8	3.438
Rn	86	21846.6	21866.8	+0.09	12336.0	3.525
U	92	25633.3	25664.2	+0.12	15713.0	3.594

About the results in Table 5 we wish to note the following. During the calculations we observed that the radial part of the kinetic energy rapidly diminishes as we decrease N below 10 and almost zero for $N < 8$. Therefore for the range $2 \leqq N \leqq 10$ we have completely omitted the radial kinetic energy from the calculations i. e. for these atoms we put

$$\varepsilon_k^r = 0 , \qquad (6.26)$$

and the kinetic energy is given by

$$\varepsilon_k(\varrho) = \varepsilon_k^i(\varrho) + \varepsilon_k^a = A_1(\nabla \varrho)^2/\varrho + (1 - \sigma(N)/N)\, A_2 \varrho^{5/3} , \qquad (6.27)$$

where A_1 and A_2 are the theoretical values (5.61). Since A_2 is 2/3 of the original Fermi constant this approximation amounts to reducing the Fermi energy by 1/3 (plus correcting it by the Fermi-Amaldi factor). The results in Table 5 for $2 \leqq N \leqq 10$ are obtained with this approximation.

Is it realistic that the orthogonalization energy vanishes for $N \leqq 10$? This result is not surprising for the reader familiar with the *pseudopotential*

method. For $N=10$ the electron configuration is $(1s)^2(2s)^2(2p)^6$. The (2p) electrons are orthogonal to the 1s and 2s because of the angular part – *this is the Azimuthal kinetic energy in our calculation.* In a calculation for this configuration we would need a pseudopotential only for the 2s electrons. Our model treats the electrons in a statistical fashion i. e. we use an average for the orthogonalization energy. Since for 8 out of 10 electrons the orthogonalization energy is zero, it is not surprising that it is a good approximation to put the average equal to zero. This is the meaning of Equation (6.26).

6 D) *Positive Ions*

We have used the best 2-parameter DF formula to see how good is our formalism for positive ions. We have computed the energies of ions with $N=10$ and $Z=10$, 14, 18 and 22; with $N=18$ and $Z=$ 18, 22, 26 and 30; and similarly for the isoelectronic series with $N=36$, and 54. The results are collected in Table 6 along with the HF results.

Table 6. The computed data for Section 6 D. The calculated energies are with the best 2-Term expression.

N	Z	E_{calc}	E_{F}	%
10	10	128.86	128.55	−0.24
10	14	289.31	285.18	−1.45
10	18	514.87	505.97	−1.76
10	22	805.55	790.81	−1.86
18	18	521.88	526.82	+0.94
18	22	851.70	845.19	−0.77
18	26	1263.8	1242.2	−1.74
18	30	1758.2	1717.5	−2.37
36	36	2743.6	2752.1	+0.31
36	40	3552.2	—	—
36	44	4467.0	—	—
36	48	5491.1	—	—
54	54	7251.8	7232.2	−0.27
54	58	8637.1	—	—
54	62	10146.9	—	—
54	66	11781.6	—	—

In these calculations the DF formula which was seen to reproduce the atomic energies of neutral atoms fairly well for all N is applied without change to the isoelectronic sequence in which $N=\text{const}$ but the nuclear potential (Z/r) is increasing. The results are quite good measured against the accuracy of previous models but not as good as our results for neutral atoms and become worse as Z increases. The reason for this is obvious. Our formula for the density of kinetic energy describes the kinetic energy well for neutral atoms where the density changes slowly as N increases. The result of the increasing Z however is a sharp contraction of the electron density with a corresponding increase in the kinetic energy represented by the gradient of ϱ. In our DF for the kinetic energy only the Weizsäcker term depends on the gradient of ϱ; obviously this term alone is not capable to describe very accurately the change of the kinetic energy with increasing $(\nabla\varrho)$. We note that the calculated values are too low which means that the kinetic energy is too small.

6 E) *Helium Isoelectronic Series*

As we have pointed out above, our DF formula is exact for the He and its isoelectronic series. Let us consider the HF wave function for this series:

$$\overline{\Psi}=\begin{vmatrix}\varphi_1(1) & \varphi_1(2)\\ \varphi_2(1) & \varphi_2(2)\end{vmatrix}, \tag{6.27}$$

where φ_1 and φ_2 are the $1s\alpha$ and $1s\beta$ spin-orbitals. Deriving from (6.27) the HF energy expression and transforming it into a density-functional we get *exactly:*

$$E=\int\varepsilon(\varrho)\,\mathrm{d}v\,, \tag{6.28}$$

with

$$\varepsilon(\varrho)=\frac{1}{8}\frac{(\nabla\varrho)^2}{\varrho}-\frac{Z}{r}\varrho+\int\frac{\varrho(r')\,\mathrm{d}v'}{|\boldsymbol{r}-\boldsymbol{r}'|}\varrho(r)\,, \tag{6.29}$$

which is the same that we get from (5.72). The integro-differential equation obtained from (6.28) by varying E with respect to ϱ would be, according to Hohenberg and Kohn [9], exactly equivalent to the HF equation for the 1s orbital.

We have computed analytic densities with our variational procedure for the He isoelectronic series from $Z=2$ to $Z=10$. The results which are listed in Table 7 are exceptionally good since, as we see we achieved 4 and in some cases 5 digit agreement with the HF calculations. Moreover, in these cases, the densities are also very good approximations to the HF densities: on a normal size diagram our densities and the HF densities are practically indistinguishable. This an interesting result since in order to compute the HF results Clementi used [18] a linear combination of 4 Slater functions i. e. the HF orbital is an 8 parameter expression, while our density function (6.3) contains only 2 parameters.

We conclude that for the He isoelectronic series we have obtained results which are practically as

Table 7. The computed data for Section 6 E. The HF values are from the analytic calculations of Clementi (Ref. 18).

N	Z	E_{calc}	E_{F}	λ_0	n_0
2	2	2.861	2.862	4.19	1.11
2	3	7.236	7.236	6.16	1.07
2	4	13.610	13.611	8.29	1.06
2	5	21.986	21.986	10.13	1.04
2	6	32.360	32.361	12.29	1.04
2	7	44.736	44.736	14.17	1.03
2	8	59.110	59.111	15.98	1.03
2	9	75.483	75.486	18.41	1.03
2	10	93.860	93.861	20.14	1.02

accurate as the HF results in the energy as well as in the density and we obtained these results with a much simpler analytic expression than the HF orbitals.

6 F) *Numerical Densities*

As we have stated in Sec. 3 the ideal goal of a DF theory with a single density would be to match the HF energies and approximate the HF densities accurately in the outer regions of the atoms. Although in the present paper we concentrated on the energy and did not try to get good densities we made some calculations using the densities computed by Gombas [19]. These densities were obtained by solving exactly the integrodifferential equation for ϱ obtained by varying the energy expression. Unfortunately the energy expression used by Gombas was not the same from which the energies were computed: the energy expression was what we called $G1$ in Sec. 6 A but with all Fermi-Amaldi factors removed. These densities are therefore not in any clear-cut relationship to the DF formulas used by us but they were derived from an equation containing the original Weizsäcker term which means that the assymtotic behavior of Gombas' density will be the same as that of the density which we would obtain from the exact solution of a ϱ-equation derived from any of the DF formulas of Section 6 C.

In these calculations we considered ϱ_{G} as simply an "Ansatz" for ϱ. In connection with this procedure we recall that if ϱ_{ex} is the exact solution of the ϱ-equation obtained from the energy minimum principle and $\hat{\varrho}$ is any other normalized density then if

$$E_{\text{ex}} = \int \varepsilon(\varrho_{\text{ex}})\,\mathrm{d}v\,, \tag{6.30}$$

and

$$\hat{E} = \int \varepsilon(\hat{\varrho})\,\mathrm{d}v\,, \tag{6.31}$$

we obtain for *any* DF the relationship:

$$\hat{E} \geqq E_{\text{ex}}\,. \tag{6.32}$$

We substituted ϱ_{G} into the DF formulas denoted by $G1$ and $G2$ in Sec. 6 A and into the best 2- and 3-term expressions obtained in Section 6 C. All the constants in these expressions were the same as in the calculations above. We introduced a scale factor λ as a variational parameter and determined it in such a way as to satisfy the Virial Theorem. The results are in Table 8, for the noble gas atoms, for which Gombas computed ϱ_{G}. We note that if we would solve the ϱ-equation belonging to any of these four DF formulas we would get an energy deeper than the values in Table 8 because of the relationship (6.32). We computed the diamagnetic susceptibilities with ϱ_{G} and included them in the Table along with the HF values. The relationship of ϱ_{G} to the HF density is shown for the Ar atom in Figure 2.

We see from the Table that very good approximations to E_{F} were obtained both with the 2-term and with the 3-term formulas. That the 3-term formula is below E_{F} is not surprising but a result of matching E_{F} with a density other than ϱ_{ex}. If the parameters are determined by matching E_{F} with an approximate analytic density, as we have done, then using a better ϱ will result in an energy deeper than E_{F} because of the relationship (6.32). It is also seen that ϱ_{G} gives fair values for the diamagnetic susceptibility D. We conclude that the densities

Table 8. The computed data for Section 6 F. The diamagnetic susceptibilities (D) are in units of 10^{-6} cm^3/mole.

	$\varepsilon_k(\varrho)$					D		
Atom	$G1$	$G2$	Best 2-Term	Best 3-Term	E_{F}	With ϱ_{G}	HF	Exptl.
Ne	114.5	118.9	126.5	123.3	128.55	12.83	7.42	6.96
Ar	479.3	499.8	525.8	529.0	526.82	18.28	20.62	19.32
Kr	2549.	2654.	2762.	2814.	2752.1	28.28	31.31	29.0
Xe	6752.	7016.	7258.	7377.	7232.2	36.48	49.62	45.5

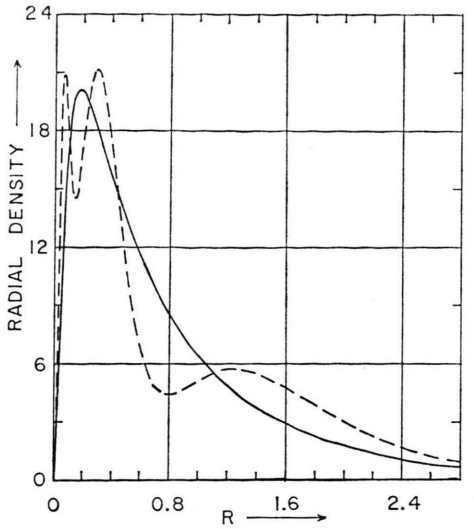

Fig. 2. The comparison between the radial density computed by Gombas (———) and the radial density obtained from HF calculations (— — —) for the Ar atom. See Section 6 F.

computed *by Gombas yield good approximations to* E_F *when used in our Semi-Theoretical DF formulas and at the same time approximate the HF densities fairly well in the outer regions of atoms.*

This result contains an obvious hint about how a DF formalism satisfying both principles No. 2 and No. 3 in Sec. 3 could be constructed. The constants in ε_k^r should be varied to get a good match for E_F but instead of using the analytic density, which we have used in this paper the exact solution of the ϱ-equation must be computed. This is a time-consuming procedure but our 2-term results (with ϱ_G) are so close to E_F that probably only small changes in the constants would be needed. We intend to pursue this idea in the future development of the theory; inspecting the numbers in Table 8 we may say that the success of this idea is highly probable.

6 G) Fermi Energy Reduced by Constant

The basic idea of our DF formalism is to reduce the Fermy-energy by a correction representing the self-energy. This can be accomplished in a crude approximation by the formula

$$\varepsilon_k(\varrho) = A_1(\nabla \varrho)^2/\varrho + \eta(N) A_2 \varrho^{5/3}, \quad (6.33)$$

where A_1 and A_2 are given by (6.8) and the N-dependent function η would yield a constant for each N reducing the Fermi energy by the amount of the self-energy. For $\eta(N) = 1$ this is the same as the original Weizsäcker formula. Obviously $\eta(N) < 1$ will be for all N. We note that the Virial Theorem is not violated by the introduction of η.

We have developed a simplified model based on (6.33) which, although not very sophisticated conceptually, might be useful in molecular calculations. We determined $\eta(N)$ by matching the HF energies for Ne, Ar, Kr, Xe and Hg. The matching is done by computing the energy minimum using our analytic densities and changing η until the minimum is equal to E_F. We obtained 5 points of $\eta(N)$ this way and a 6th point is added by the condition

$$\eta(2) = 0. \quad (6.34)$$

From these six points we constructed $\eta(N)$ by graphical interpolation. The curve is shown in Figure 3. The values of η for an arbitrary N can be determined graphically from a large scale diagram. We have determined $\eta(N)$ for a number of atoms and computed the energy minimum for these atoms.

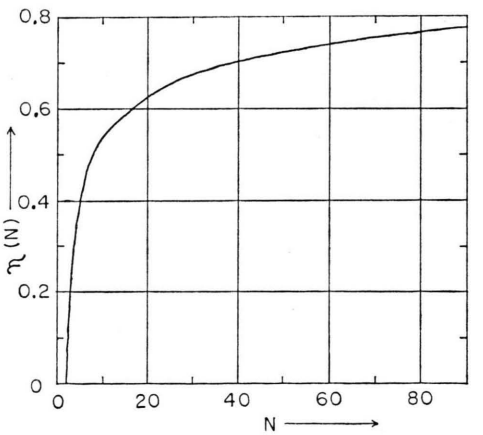

Fig. 3. The $\eta(N)$ curve versus N as defined in Section 6 G.

The results are in Table 9. As seen from the table we obtained remarkably good approximations of E_F in all cases except for small N where an accurate graphical interpolation is difficult since $\eta(N)$ changes rapidly in this region.

We conclude the calculations by noting that this simplified model which is meant primarily for molecular applications can be refined considerably by determining $\eta(N)$ from a procedure in which the exact solution of the ϱ-equation would be required to match E_F.

Table 9. The computed data for Section 6 G.

Atom	N	$\eta(N)$	E_{calc}	E_{F}	%
He	2	0	2.8610	2.8616	+0.02
C	6	0.4198	38.592	37.660	−2.47
Ne	10	0.5325	128.51	128.55	+0.03
Si	14	0.5787	288.55	288.84	+0.10
Ar	18	0.6112	526.76	526.82	+0.01
Ti	22	0.6344	857.25	848.37	−1.05
Fe	26	0.6536	1270.4	1262.3	−0.64
Zn	30	0.6697	1787.2	1777.8	−0.53
Kr	36	0.6914	2753.9	2752.1	−0.06
Zr	40	0.7019	3540.9	3539.0	−0.05
Ru	44	0.7109	4445.0	4441.4	−0.08
Cd	48	0.7191	5469.1	5465.1	−0.07
Xe	54	0.7310	7232.1	7232.2	−0.001
Ce	58	0.7376	8571.1	8566.9	−0.05
Sa	62	0.7443	10037.	10035.	−0.02
Ds	66	0.7493	11654.9	11641.	−0.12
Yb	70	0.7549	13391.	13391.	+0.000
W	74	0.7595	15282.	15287.	+0.03
Hg	80	0.7651	18406.	18409.	+0.02
Po	84	0.7690	20668.	20676.	+0.04
Rn	86	0.7705	21864.	21867.	+0.01
U	92	0.7757	25665.	25664.	−0.004

7. Discussion

The main results of the paper are the new formula for the radial part of the kinetic energy Eq. (5.18) and the DF formula derived from it, Equation (5.32). Among the calculations the main results are the best 2-, 3- and 4-parameter results presented in Section 6 C. We consider these results very satisfactory since as we see from Table 5, we approximated E_{F} within 0.5% for all atoms except for some very light ones for which the error is less than 1%; for the range $N>36$ the approximations generally better than 0.1%. In our opinion it is correct to say that the DF formula constructed in this paper is capable to reproduce the HF energies of neutral atoms with high accuracy. We conclude also from the results that the idea of dividing the kinetic energy into self-energy and orthogonalization energy is basically sound although the actual formulas used for these quantities are not necessarily the best possible approximations.

It is obvious that there is room for improvement in several directions. The results were not so good for positive ions as for neutral atoms showing the necessity of improving the gradient-dependence of the DF. Also, the Fermi-Amaldi type factors should be replaced by more sophisticated expressions, since, although these factors insure the correct behavior for $N=2$, they are crude approximations for medium values of N.

Besides the improvement of the model and its application to various atomic and molecular problems we intend to proceed with the derivation of the DF formula from a quantum mechanical model. As mentioned in Sec. 5, in contrast to other similar efforts we intend to derive the DF formalism not from the HF model but from the pseudopotential theory.

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