

New Method for the Direct Calculation of Electron Density in Many-Electron Systems. I. Application to Closed-Shell Atoms

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Abstract

A new density-functional equation is suggested for the direct calculation of electron density $\rho(\mathbf{r})$ in many-electron systems. This employs a kinetic energy functional $T_2 + f(\mathbf{r})T_0$, where T_2 is the original Weizsäcker correction, T_0 is the Thomas-Fermi term, and $f(\mathbf{r})$ is a correction factor that depends on both \mathbf{r} and the number of electrons N . Using the Hartree-Fock relation between the kinetic and the exchange energy density, and a nonlocal approximation to the latter, the kinetic energy-density functional is written (in a.u.)

$$t[\rho] = -\frac{1}{4}\nabla^2\rho + \frac{1}{8}(\nabla\rho \cdot \nabla\rho)/\rho + C_k f(\mathbf{r})\rho^{5/3},$$

where $C_k = \frac{3}{10}(3\pi^2)^{2/3}$. Incorporating the above expression in the total energy density functional and minimizing the latter subject to N representability conditions for $\rho(\mathbf{r})$ result in an Euler-Lagrange nonlinear second-order differential equation

$$[-\frac{1}{2}\nabla^2 + v_{\text{nuc}}(\mathbf{r}) + v_{\text{cou}}(\mathbf{r}) + v_{\text{XC}}(\mathbf{r}) + \frac{5}{3}C_k g(\mathbf{r})\rho^{2/3}]\phi(\mathbf{r}) = \mu\phi(\mathbf{r}),$$

where μ is the chemical potential, we have $\rho(\mathbf{r}) = |\phi(\mathbf{r})|^2$, and $g(\mathbf{r})$ is related to $f(\mathbf{r})$. Numerical solutions of the above equation for Ne, Ar, Kr, and Xe, by modeling $f(\mathbf{r})$ and $g(\mathbf{r})$ as simple sums over Gaussians, show excellent agreement with the corresponding Hartree-Fock ground-state densities and energies, indicating that this is likely to be a promising method for calculating fairly accurate electron densities in atoms and molecules.

1. Introduction

In recent years, a large number of research papers and review articles have highlighted the fundamental importance of electron density $\rho(\mathbf{r})$ in predictive and interpretive theories of chemistry (see, e.g., Ref. 1). Apart from bringing about great conceptual and computational simplifications, the density approach also suggests that a macroscopic description of a microscopic quantum system may be possible. Therefore, it has been tempting to think of an alternative formulation [1a,2] of quantum mechanics of many-electron systems in terms of the electron density rather than the wave function.

In order to realize this long-cherished dream, the most important task is to develop an *exact* method for the *direct* evaluation of electron density, bypassing the wave function. The earliest attempt in this direction was that of Thomas and Fermi leading to the well-known Thomas–Fermi (TF) method [3]; this was the first among density-functional theories. The past few years have seen several exciting developments in density calculation schemes (for a review, see Ref. 4) although, so far, neither of these has been able to provide a completely satisfactory solution to the problem.

What we are looking for is a differential (or an integro-differential) equation in terms of the electron density. Yuan and Light [5] have proposed a Milne equation for atomic systems. The solution of this second-order differential equation has yielded good results for the density and energy of the krypton atom. In a more recent work, Lawes and March [6] have suggested approximate differential equations (third-order) for atomic and molecular systems whose solutions would yield the corresponding densities. However, since no numerical results based on these equations seem to be reported so far, their practical utility remains to be assessed.

Modern density-functional theory rests on the Hohenberg–Kohn theorem [7] according to which the ground-state energy is a unique functional of the density and assumes a minimum value for the exact density function. Minimization of this energy functional with respect to density yields an Euler equation which can serve as a deterministic equation for $\rho(\mathbf{r})$. However, since the actual form of the energy functional is unknown, approximations have to be invoked. Thus, the local density approximation (LDA) has been employed for the exchange-correlation (XC) energy and Thomas–Fermi (T_0), Weizsäcker (T_2), and higher-order (e.g., T_4) gradient correction terms have been suggested for the kinetic energy functional.*

Although these kinetic energy functionals have yielded quite accurate values for “global” quantities like energy, they do not show proper “local” behavior [8] of the kinetic energy density. As a result, the solution of the resulting Euler equation yields [9] only a poor quality smeared out electron density and the shell structure in the radial density of atomic systems never appears. However, if one uses trial densities incorporating certain parameters which are adjusted to make the energy functional a minimum, even the Thomas–Fermi–Weizsäcker kinetic energy expression might be suitable to yield the shell structure in atomic systems, provided shell structure is already incorporated in the trial radial density by assuming the density to be piecewise exponentially decaying [10] function or by a superposition of hydrogenic orbitals [11]. The major drawback of such variational procedures is that modeling of the density or imposition of constraints on its variation severely restricts the generality and applicability of the method.

It is the purpose of the present work to demonstrate that the solution of the Euler equation can yield a very good quality (atomic) density including the shell structure if a kinetic energy-density functional exhibiting proper “local” behavior is employed. At this point, it may be worthwhile giving a brief account of the earlier attempts to define a kinetic energy functional.

* In the conventional density-functional theory (DFT) of Hohenberg, Kohn, and Sham [7], the kinetic energy is treated exactly by drawing an analogy between the actual system and a fictitious system of non-interacting particles with the same density $\rho(\mathbf{r})$. Thus, one solves several one-particle Hartree-like equations to evaluate the density.

The most popular form of the kinetic energy functional is $T[\rho] = T_0 + \lambda T_2$, where the parameter λ is popularly assumed to have a value $1/9$ or $1/5$, although the controversy regarding the choice of the parameter λ is still unresolved (see, e.g., Ref. 12). However, there has recently been a growing interest in using a correction factor in the TF term T_0 . In fact, long ago it had been pointed out by Gombas [13], using semiclassical arguments, that the TF term should be modified* and the Weizsäcker term should be employed in the *original* form. The same conclusion has been reached by Goodman [15] who suggested that the correction factor in the TF term should depend not only on the number of electrons but also on \mathbf{r} . Thus, the kinetic energy functional should be $T_2 + f(\mathbf{r})T_0$, where $f(\mathbf{r})$ should satisfy the boundary conditions $f(\mathbf{r}) \rightarrow 0$ as $\mathbf{r} \rightarrow 0$ and $f(\mathbf{r}) = 1$ as $r \rightarrow \infty$. Baltin [16] has also proposed a similar correction and evaluated the correction factor within certain approximations. Wong [17] has presented a comparative survey of these approaches as applied to nuclear systems.

The fact that the full Weizsäcker term is a part of the exact kinetic energy functional and a correction term is needed in the TF term has also been recently established in a more rigorous and systematic way by a number of workers [18–20].

In Section 2 we derive an expression for the TF correction factor $f(\mathbf{r})$ using the relation between kinetic and exchange energy densities with a nonlocal treatment of the latter. A Euler–Lagrange equation is then derived which serves as a deterministic equation for the density. Section 3 deals with the method of calculation, while Section 4 presents a discussion of the results. Finally, Section 5 offers a few concluding remarks.

2. Theoretical Formulation

A. Kinetic Energy Density

The Hohenberg–Kohn energy functional $E[\rho]$ for a many-electron system, characterized by electron density $\rho(\mathbf{r})$ and external potential $v(\mathbf{r})$, is given by [7]

$$E[\rho] = T[\rho] + E_{\text{XC}}[\rho] + \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \int v(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r}, \quad (1)$$

where $T[\rho]$ and $E_{\text{XC}}[\rho]$ are the kinetic and XC functionals, respectively. Minimization of this functional with respect to $\rho(\mathbf{r})$ subject to the normalization constraint

$$\int \rho(\mathbf{r}) d\mathbf{r} = N \quad (2a)$$

leads to the Euler equation

$$\delta E / \delta \rho - \mu = 0, \quad (3)$$

where μ is the Lagrange multiplier and has been interpreted as chemical potential [21]. Equation (3) may serve as a deterministic equation for the density, provided one knows the forms of the unknown functionals $T[\rho]$ and $E_{\text{XC}}[\rho]$.

* Some authors [14] have suggested the use of correction factors in both TF and Weizsäcker terms leading to the expression $T = \alpha T_0 + \beta T_2$, where the correction factors α and β depend on the number of particles N .

In order to develop an approximate functional form of $T[\rho]$, we first express [22] it in terms of the one-particle (spinless) density matrix $\rho(\mathbf{r};\mathbf{r}')$, viz.,*

$$T[\rho] = -\frac{1}{2} \int_{\mathbf{r}=\mathbf{r}'} \nabla^2 \rho(\mathbf{r};\mathbf{r}') d\mathbf{r}. \quad (4)$$

Since the exact formulation of $\rho(\mathbf{r};\mathbf{r}')$ in terms of $\rho(\mathbf{r})$ is not known, we restrict ourselves initially to the Hartree-Fock (HF) theory. Within the HF approximation, $\rho(\mathbf{r};\mathbf{r}')$ and $\rho(\mathbf{r})$ are related through the two-particle (spinless) density function $\Gamma_2(\mathbf{r},\mathbf{r}')$ and hence a correlation factor $C(\mathbf{r},\mathbf{r}')$. The (spinless) density matrix, $\rho(\mathbf{r};\mathbf{r}')$ is expressed† as

$$\Gamma_2(\mathbf{r},\mathbf{r}') = \rho(\mathbf{r})\rho(\mathbf{r}') - \frac{1}{2} \rho(\mathbf{r};\mathbf{r}')\rho(\mathbf{r}';\mathbf{r}). \quad (5)$$

Using the relation

$$\Gamma_2(\mathbf{r},\mathbf{r}') = \rho(\mathbf{r})\rho(\mathbf{r}')[1 + C(\mathbf{r},\mathbf{r}')], \quad (6)$$

and assuming‡ that

$$\rho(\mathbf{r};\mathbf{r}') = \rho(\mathbf{r}';\mathbf{r}), \quad (7)$$

one obtains

$$\rho(\mathbf{r};\mathbf{r}') = A(\mathbf{r},\mathbf{r}')[\rho(\mathbf{r})\rho(\mathbf{r}')]^{1/2}, \quad (8)$$

where

$$A(\mathbf{r},\mathbf{r}') = [-2C(\mathbf{r},\mathbf{r}')]^{1/2}.$$

Using Eq. (8), the kinetic energy density $t(\mathbf{r};\rho)$, defined by the relation

$$T[\rho] = \int t(\mathbf{r};\rho) d\mathbf{r}, \quad (9a)$$

i.e.,

$$t(\mathbf{r};\rho) = -\frac{1}{2} \nabla^2 \rho(\mathbf{r};\mathbf{r}')|_{\mathbf{r}=\mathbf{r}'} \quad (9b)$$

becomes [23]

$$t(\mathbf{r};\rho) = -\frac{1}{4} \nabla^2 \rho(\mathbf{r}) + \frac{1}{8} \frac{\nabla \rho(\mathbf{r}) \cdot \nabla \rho(\mathbf{r})}{\rho(\mathbf{r})} - \frac{1}{2} \nabla \rho(\mathbf{r}) \cdot \nabla A(\mathbf{r},\mathbf{r}')|_{\mathbf{r}=\mathbf{r}'} - \frac{1}{2} \rho(\mathbf{r}) \nabla^2 A(\mathbf{r},\mathbf{r}')|_{\mathbf{r}=\mathbf{r}'} \quad (10)$$

This is a formally exact expression for the kinetic energy density within the HF approximation and restrictions of validity of Eq. (7). However, in order to proceed further, one has to assume some form for the correlation factor $C(\mathbf{r},\mathbf{r}')$.

In the local density approximation, it is assumed that $C(\mathbf{r},\mathbf{r}') = C_{\rho(\mathbf{r})}(\mathbf{r},\mathbf{r}')$, i.e., the

*Atomic units are used throughout this paper.

† For simplicity we are considering a system with equal number of up- and down-spin electrons, e.g., a closed-shell system. The normalization convention of McWeeny and Sutcliffe [22] has been used.

‡ This assumption may not be valid [23] in general but is true for atoms with filled shells, homogeneous electron gas and cases where ψ is real, e.g., a nondegenerate ground state.

correlation factor, is described locally by only the density at the reference point. Further, one uses the expression for a correlation factor for a homogeneous electron gas which is exactly known* and is given by

$$C(\mathbf{r}, \mathbf{r}') = -\frac{9}{2} \left(\frac{\sin y - y \cos y}{y^3} \right)^2 = -\frac{9}{2} \frac{j_1^2(y)}{y^2}, \quad (11)$$

where $j_1(y)$ is the first-order spherical Bessel function given by

$$j_1(y) = (\sin y - y \cos y)/y^2, \quad (12)$$

with $y = k_F |\mathbf{r} - \mathbf{r}'|$ and $k_F = [3\pi^2 \rho(\mathbf{r})]^{1/3}$. Using this expression for $C(\mathbf{r}, \mathbf{r}')$, Eq. (10) simplifies [23] to

$$t(\mathbf{r}; \rho) = -1/4 \nabla^2 \rho + 1/8 (\nabla \rho \cdot \nabla \rho) / \rho + 3/10 (3\pi^2)^{2/3} \rho^{5/3}. \quad (13)$$

Equation (13) is the expression of kinetic energy density within a local density approximation and can be compared with the usual TF and Weizsäcker terms, viz.,

$$T_0 = 3/10 (3\pi^2)^{2/3} \int \rho^{5/3} d\mathbf{r} \quad (14a)$$

and

$$T_2 = \frac{1}{8} \int \frac{\nabla \rho \cdot \nabla \rho}{\rho} d\mathbf{r}. \quad (14b)$$

Since the first term in Eq. (13) vanishes on integration, the total kinetic energy functional $T[\rho]$ consists of the full Weizsäcker term and the TF term.

A nonlocal approximation to the kinetic energy density can be obtained by using the same functional form for the correlation factor but replacing its argument $\rho(\mathbf{r})$ by a density parameter $\tilde{\rho}(\mathbf{r})$, determined by requiring satisfaction of the sum rule

$$\int \rho(\mathbf{r}') C_{\tilde{\rho}(\mathbf{r})}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = -1. \quad (15)$$

Thus, the correlation factor is chosen to be

$$C_{\tilde{\rho}(\mathbf{r})}(\mathbf{r}, \mathbf{r}') = -9/2 j_1^2(\tilde{y})/\tilde{y}^2, \quad (16)$$

where $\tilde{y} = |\mathbf{r} - \mathbf{r}'| [3\pi^2 \tilde{\rho}(\mathbf{r})]^{1/3}$. The final expression for the kinetic energy density thus becomes [23]

$$t(\mathbf{r}; \rho) = -1/4 \nabla^2 \rho + 1/8 (\nabla \rho \cdot \nabla \rho) / \rho + 3/10 (3\pi^2)^{2/3} \tilde{\rho}^{2/3} \rho, \quad (17)$$

which can be rewritten

$$t(\mathbf{r}; \rho) = -1/4 \nabla^2 \rho + 1/8 (\nabla \rho \cdot \nabla \rho) / \rho + 3/10 (3\pi^2)^{2/3} f(\mathbf{r}) \rho^{5/3}, \quad (18)$$

where the function $f(\mathbf{r})$ is given by

$$f(\mathbf{r}) = [\tilde{\rho}(\mathbf{r}) / \rho(\mathbf{r})]^{2/3}. \quad (19)$$

Thus the kinetic energy-density functional consists of the full Weizsäcker term and

* Note that the correlation factor $C(\mathbf{r}, \mathbf{r}')$ includes only the Fermi correlation, i.e., exchange contribution to the pair correlation function, and does not include the Coulomb correlation. It is $C_{ex}(\mathbf{r}, \mathbf{r}')$ which is exactly known for a homogeneous electron gas; $C_{XC}(\mathbf{r}, \mathbf{r}')$ is not known [24] even for this case.

a modified TF term with an \mathbf{r} -dependent correction factor. This fact is in conformity with the conclusion of other authors [13,15–20] using different approaches.

B. Derivation of the Euler-Lagrange Equation

The Euler–Lagrange equation obtained by minimization of the energy functional $E[\rho]$ with respect to variations of $\rho(\mathbf{r})$ subject to the normalization condition as a constraint is of the form

$$\delta E / \delta \rho - \mu = 0. \quad (3)$$

This equation, on solution, is expected to yield the density function directly. However, the calculated density should satisfy the N -representability conditions [25]—one of which, the normalization condition [Eq. (2a)], has already been incorporated in the derivation of Eq. (3). The other condition, viz., positive semidefinite nature of the density [$\rho(\mathbf{r}) \geq 0, \forall \mathbf{r}$] can easily be imposed by writing the density as the square of a function ϕ , i.e.,

$$\rho(\mathbf{r}) = |\phi(\mathbf{r})|^2. \quad (20)$$

Using Eq. (1), the Euler–Lagrange equation (3) can be rewritten

$$\frac{\delta T}{\delta \rho} + \frac{\delta E_{XC}}{\delta \rho} + v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' - \mu = 0. \quad (21)$$

The XC potential term $v_{XC} = \delta E_{XC} / \delta \rho$ can be derived with the help of either a local density approximation or nonlocal treatment [26]. The simplicity and the practical success [7] of the LDA and the complexity of the nonlocal expressions prompt us to use the former in the present work although a nonlocal treatment can also be followed in principle. Thus, within the framework of LDA, the following expressions for the XC terms are well known [7b]:

$$\begin{aligned} E_{XC}[\rho] &= \int \rho(\mathbf{r}) \epsilon_{XC}[\rho(\mathbf{r})] d\mathbf{r}, \\ \epsilon_{XC} &= \epsilon_x + \epsilon_c, \\ \epsilon_x &= -(3/4\pi)(3\pi^2\rho)^{1/3} = -C_x\rho^{1/3}, \\ \epsilon_c &= -C[(1 + x_c^3) \ln(1 + 1/x_c) + x_c/2 - x_c^2 - 1/3], \\ v_{XC} &= \delta E_{XC} / \delta \rho = v_x + v_c, \\ v_x &= 4/3\epsilon_x, \\ v_c &= -C \ln(1 + 1/x_c), \end{aligned} \quad (22)$$

where

$$\begin{aligned} x_c &= r_s/A, \quad 4/3\pi r_s^3 = 1/\rho, \\ A &= 21, \quad \text{and} \quad C = 0.0225. \end{aligned}$$

We now evaluate $\delta T / \delta \rho$ using the expression for kinetic energy density given by

Eq. (17). Writing the total kinetic energy functional as

$$T = T_w + T_{\text{MTF}}, \quad (23)$$

where T_w and T_{MTF} denote the Weizsäcker and the modified TF terms, respectively, we obtain

$$\delta T / \delta \rho = \delta T_w / \delta \rho + \delta T_{\text{MTF}} / \delta \rho. \quad (24)$$

Using Eq. (20), the contribution of the Weizsäcker term becomes

$$\delta T_w / \delta \rho = -1/2 \nabla^2 \phi / \phi. \quad (25)$$

Now, since

$$T_{\text{MTF}} = C_k \int \tilde{\rho}^{2/3} \cdot \rho \, d\mathbf{r} = C_k \int f(\mathbf{r}) \rho^{5/3} \, d\mathbf{r}, \quad (26)$$

where

$$C_k = 3/10 (3\pi^2)^{2/3},$$

we have

$$\delta T_{\text{MTF}} = C_k \int \tilde{\rho}(\mathbf{r})^{2/3} \delta \rho(\mathbf{r}) \, d\mathbf{r} + 2/3 C_k \int \rho(\mathbf{r}) \tilde{\rho}(\mathbf{r})^{-1/3} \delta \tilde{\rho}(\mathbf{r}) \, d\mathbf{r}. \quad (27)$$

Substituting

$$\delta \tilde{\rho}(\mathbf{r}) = \int \frac{\delta \tilde{\rho}(\mathbf{r}')}{\delta \rho(\mathbf{r}')} \delta \rho(\mathbf{r}') \, d\mathbf{r}', \quad (28)$$

one obtains the functional derivative

$$\frac{\delta T_{\text{MTF}}}{\delta \rho(\mathbf{r})} = C_k \tilde{\rho}(\mathbf{r})^{2/3} + 2/3 C_k \int d\mathbf{r}' \rho(\mathbf{r}') \tilde{\rho}(\mathbf{r}')^{-1/3} \frac{\delta \tilde{\rho}(\mathbf{r}')}{\delta \rho(\mathbf{r})}, \quad (29)$$

where

$$\frac{\delta \tilde{\rho}(\mathbf{r}')}{\delta \rho(\mathbf{r})} = -C_{\tilde{\rho}(\mathbf{r}')(\mathbf{r}, \mathbf{r}')} \left(\int \rho(\mathbf{r}'') \frac{\delta C_{\tilde{\rho}(\mathbf{r}')(\mathbf{r}', \mathbf{r}'')}}{\delta \tilde{\rho}(\mathbf{r}')} \, d\mathbf{r}'' \right)^{-1}. \quad (30)$$

Equation (29) can also be written

$$\delta T_{\text{MTF}} / \delta \rho(\mathbf{r}) = 5/3 C_k \rho(\mathbf{r})^{2/3} g(\mathbf{r}), \quad (31)$$

where

$$g(\mathbf{r}) = 3/5 f(\mathbf{r}) + 2/5 \rho(\mathbf{r})^{-2/3} \int d\mathbf{r}' \rho(\mathbf{r}') \tilde{\rho}(\mathbf{r}')^{-1/3} \frac{\delta \tilde{\rho}(\mathbf{r}')}{\delta \rho(\mathbf{r})}. \quad (32)$$

Finally, using Eqs. (24), (25), and (31), Eq. (21) becomes

$$\left(-\frac{1}{2} \nabla^2 + v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}' + v_{\text{XC}}(\mathbf{r}) + 5/3 C_k g(\mathbf{r}) \rho(\mathbf{r})^{2/3} \right) \phi = \mu \phi. \quad (33)$$

The solution of this equation yields the eigenfunction ϕ and the eigenvalue μ . The density can be calculated by using Eq. (20), i.e., $\rho(\mathbf{r}) = |\phi(\mathbf{r})|^2$. The energy can thus

be calculated by using the relation

$$E[\rho] = \frac{1}{8} \int \frac{\nabla \rho \cdot \nabla \rho}{\rho} d\mathbf{r} + C_k \int f(\mathbf{r}) \rho(\mathbf{r})^{5/3} d\mathbf{r} \\ + \int v(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \iint \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{XC}[\rho], \quad (34)$$

where E_{XC} is given by Eq. (22). The energy can also be expressed in terms of the eigenvalue μ (chemical potential) by the following relation:

$$E[\rho] = N\mu - \frac{1}{2} \iint \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \int \rho(\mathbf{r}) [\epsilon_{XC} - v_{XC}] d\mathbf{r} \\ + C_k \int [f(\mathbf{r}) - {}^{5/3}g(\mathbf{r})] \rho(\mathbf{r})^{5/3} d\mathbf{r}. \quad (35)$$

Either Eq. (34) or (35) can be used for the calculation of energy.

3. Method of Calculation

Equation (33) is the density equation for which we are looking. Its solution is expected to yield the eigenfunction ϕ and the eigenvalue μ from which one can calculate the density and the energy of the system. However, the two functions $f(\mathbf{r})$ and $g(\mathbf{r})$ have to be evaluated for this purpose.

A. Evaluation of the $f(\mathbf{r})$ and $g(\mathbf{r})$ Functions

The function $f(\mathbf{r})$ determines the modified TF term through Eq. (26) and $g(\mathbf{r})$ appears in the density equation (39). Both these functions depend on the density $\rho(\mathbf{r})$ in a very complicated manner [see Eqs. (15) and (19) for $f(\mathbf{r})$ and Eqs. (30) and (32) for $g(\mathbf{r})$]. These expressions can, however, be used if one attempts to solve the density equation variationally.* However, if the functions $f(\mathbf{r})$ and $g(\mathbf{r})$ are to be evaluated through these expressions during iterative solution of Eq. (33) in a self-consistent procedure, not only the simplicity of the equation will be lost but it is also doubtful whether a meaningful convergent self-consistent solution can be attained at all. This has prompted us to resort to an alternative approach. In order to know the nature of function $f(\mathbf{r})$, we have calculated it with the help of Eq. (18) by evaluating the right-hand side with Hartree–Fock density and the left-hand side from Hartree–Fock density matrix. The calculations have been done for four noble gas atoms† using the Hartree–Fock wave functions reported by Clementi and Roetti [28]. The plots of the calculated $f(r)$ functions for the atoms Ne, Ar, Kr, and Xe are shown in Figures 1 to 4, respectively. They contain peaks and valleys and reflect quite clearly the shell

* Equation (33) can be solved variationally using the variational principle [27] for the nonlinear Schrödinger-type equation. However, in that case again, $\rho(\mathbf{r})$ will depend on the initial form of the trial density chosen, which is not desirable.

† Since for He atom, the Weizsäcker term describes Hartree–Fock kinetic energy completely, $f(\mathbf{r}) = g(\mathbf{r}) = 0$. In the present work, we have, therefore, studied the atoms Ne, Ar, Kr, and Xe. For such systems, the three-dimensional equation (33) reduces to a one-dimensional one.

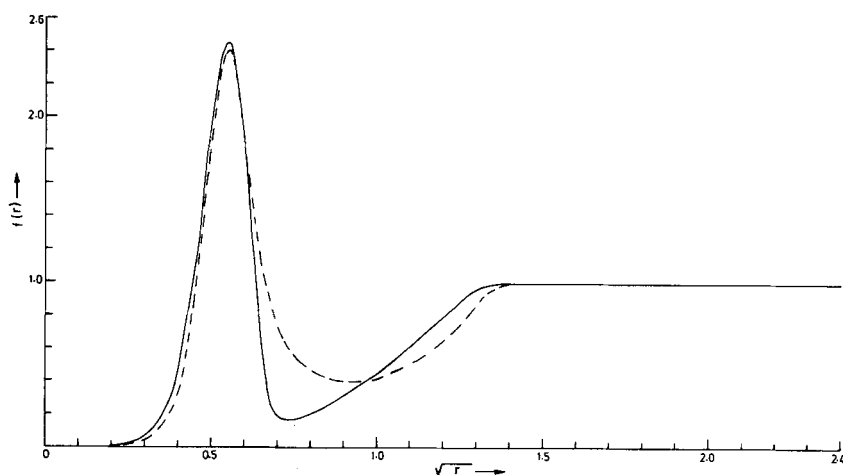


Figure 1. Plot of $f(r)$ for neon atom (r in a.u.). (—) Used in present calculation; (---) Hartree-Fock.

structure of the atom—the maxima in $f(r)$ corresponding to the minima in the radial density. The positions of the maxima (r_{\max}) and minima (r_{\min}) as well as the peak heights (h_m) are presented in Table I. These quantities have been fitted by expressions*

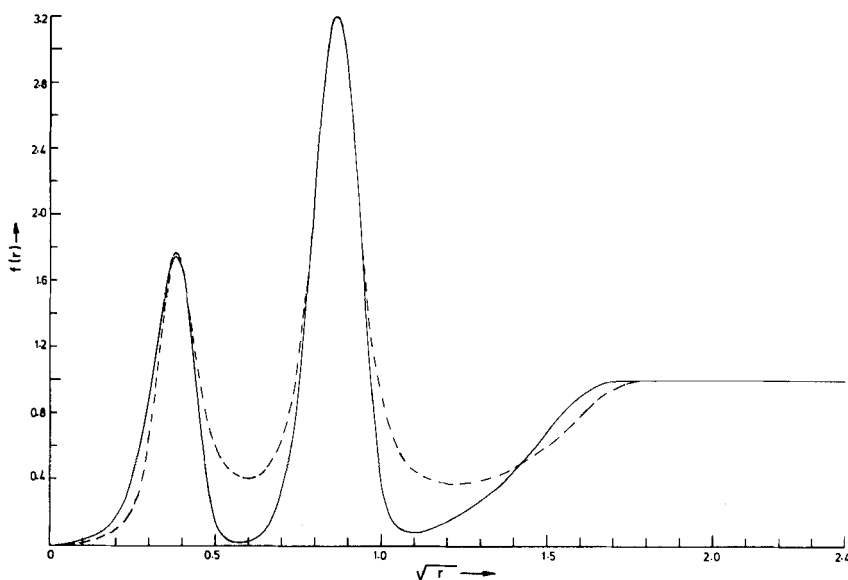


Figure 2. Plot of $f(r)$ for argon atom (r in a.u.). (—) Used in present calculation; (---) Hartree-Fock.

* Since the normalization integral of electron density gives the number of electrons which in turn fixes the number of shells, this scheme is consistent with the belief that all information about the system is contained in the density.

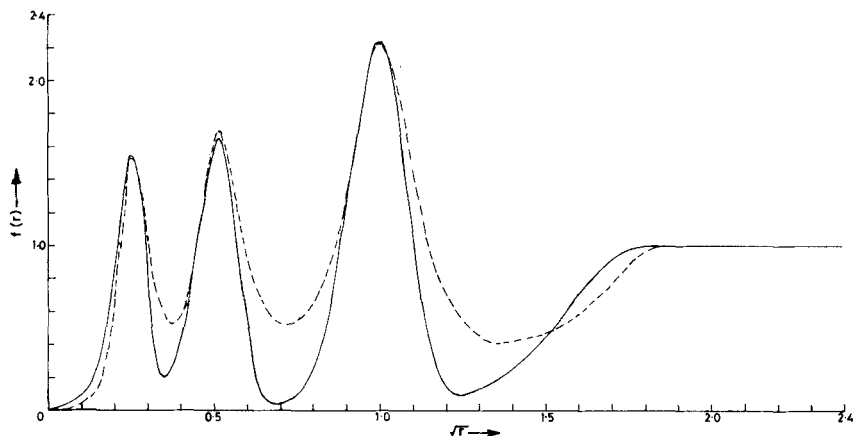


Figure 3. Plot of $f(r)$ for krypton atom (r in a.u.). (—) Used in present calculation; (---) Hartree-Fock.

in terms of the atomic number (Z) and the number of shells (n). These expressions are given in Table II and the corresponding calculated values of r_{\max} , r_{\min} , and h_m are included in Table I for comparison with the HF values.

We have attempted to reproduce $f(r)$ by expressing it as a sum of several Gaussians. At large r , $f(r)$ is assumed to have a value of unity. The Gaussian exponents were chosen so as to reproduce the best fit with HF $f(r)$. The $f(r)$ functions evaluated in this way are compared with the actual ones in Figures 1 to 4. The $g(r)$ functions which consist of 60% contribution from $f(r)$ and 40% from the integral in Eq. (32), have been assumed to have the same functional form as that of $f(r)$, i.e., a sum of similar

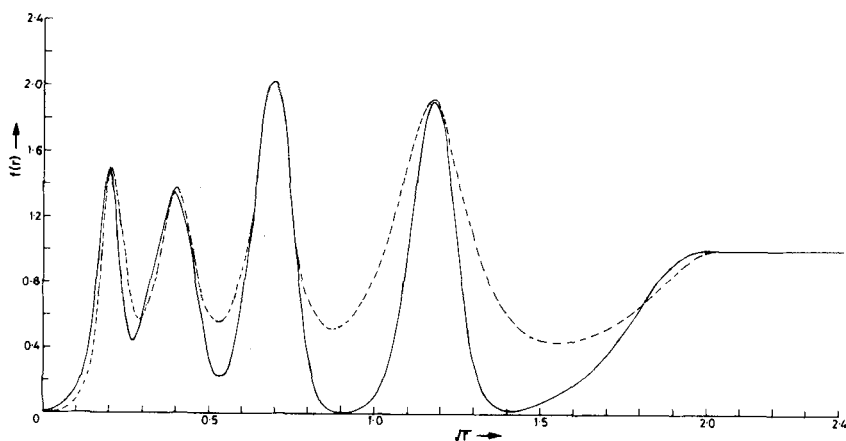


Figure 4. Plot of $f(r)$ for xenon atom (r in a.u.). (—) Used in present calculation; (---) Hartree-Fock.

TABLE I. Heights and positions (in a.u.) of the peaks^a in the function $f(r)$.

	Ne	Ar	Kr	Xe
Positions of maxima (r_{\max})	0.30 (0.30)	0.14 (0.144) 0.74 (0.75)	0.065 (0.0648) 0.27 (0.265)	0.04 (0.0397) 0.16 (0.158)
	-	-	1.02 (1.00)	0.47 (0.486)
	-	-	-	1.35 (1.39)
Positions of Minima (r_{\min})	0.80 (0.805)	0.35 (0.338) 1.45 (1.43)	0.14 (0.144) 0.52 (0.50)	0.09 (0.086) 0.29 (0.296)
	-	-	1.80 (1.78)	0.77 (0.772)
	-	-	-	2.35 (2.31)
Peak heights (h_m)	2.41 (2.457)	1.78 (1.739) 3.20 (3.20)	1.54 (1.613) 1.71 (1.752)	1.46 (1.424) 1.40 (1.356)
	-	-	2.22 (2.223)	2.13 (2.153)
	-	-	-	1.88 (1.902)
Atomic number (Z)	10	18	36	54
Number of shells (n)	2	3	4	5

^a Quantities in parentheses indicate values calculated with the help of the expressions given in Table II.

Gaussians with same peak heights and peak positions but different exponents of the Gaussians. These exponents have been determined by adjusting to obtain a density close to the Hartree-Fock density. The $g(r)$ functions have also been set to unity at large values of r . Figures 5 to 8 show the plots of $g(r)$ functions used. Thus, we have

$$f(r) = \sum_{i=1}^n A_i \exp[-\alpha_i(r - R_i)^2] \quad (36a)$$

and

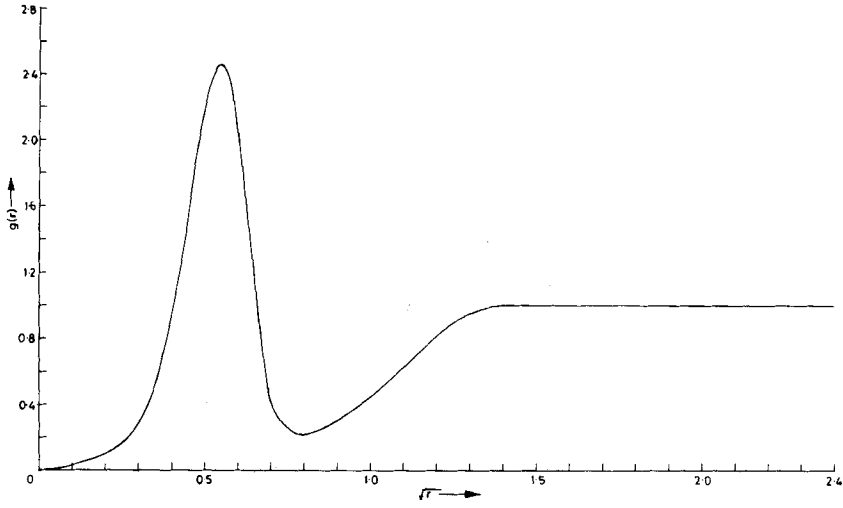
$$g(r) = \sum_{i=1}^n A_i \exp[-\beta_i(r - R_i)^2], \quad (36b)$$

Where $A_i [\equiv A_i(Z, n)]$ and $R_i [\equiv R_i(Z, n)]$ are the peak heights and the peak positions for the i th peak. Their values and the expressions are to be taken from Tables I and II, respectively. The exponent parameters α_i 's and β_i 's are presented in Table III. The values of r above which $f(r)$ and $g(r)$ functions have been set to unity are also given in Table III.

The use of this $g(r)$ function completely determines Eq. (33). The $f(r)$ function is to be used in the calculation of energy value.

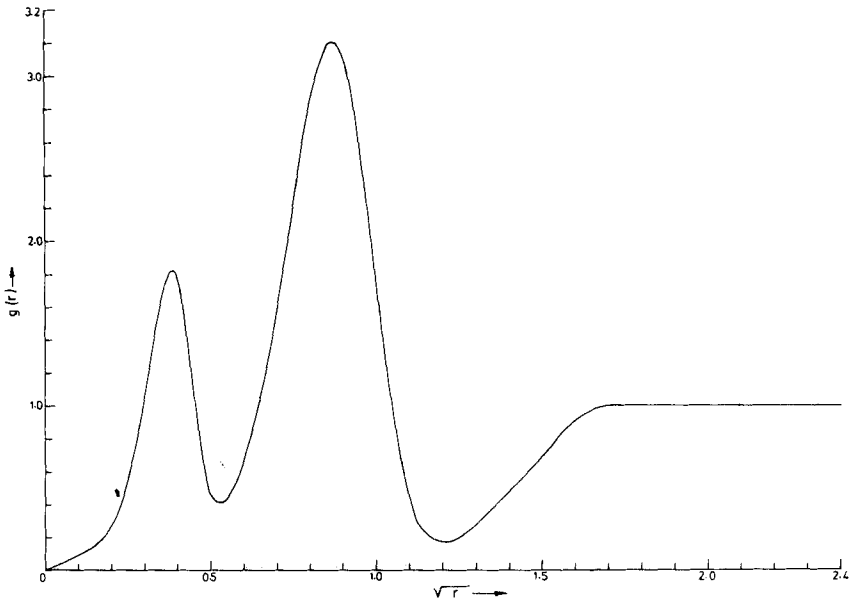
TABLE II. Expressions for peak heights and positions of extrema (in a.u.). ($Z \equiv$ atomic number; $n \equiv$ number of shells).

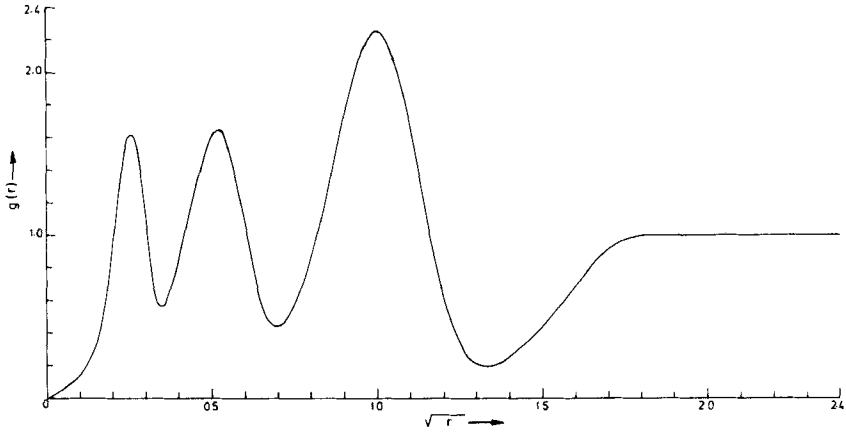
	First	Second	Third	Last
r_{\max}	$\frac{(n+10)}{(n+2)} \frac{1}{Z}$	$\frac{1}{3} \frac{(n+1)(n+7)}{(n-2)} \frac{1}{Z} + \frac{1}{100}$	$\frac{9}{20} \frac{n^2(n+1)(n+2)}{(n-2)(n-3)} \frac{1}{Z}$	$\frac{3}{4} \frac{n^2(n-1)}{Z}$
r_{\min}	$\frac{2(n+6)}{n} \frac{1}{Z} + \frac{1}{200}$	$\frac{6}{7} \frac{(n+2)(n+3)}{(n-2)} \frac{1}{Z}$	$\frac{2n^3}{(n-2)(n-3)} \frac{1}{Z}$	$\frac{n^3}{Z}$
h_{II}	$\exp[-2\{0.001 - \frac{2}{n(2n^2+3)}\}]$	$\exp[-2\{0.0002 - \frac{7}{2n^2(n-2)(n+3)}\}]$	$\exp[-2\{-\frac{355}{1000n^2}\}]$	$\exp[-2\{-\frac{156}{100(n+6)}\}]$

Figure 5. Plot of $g(r)$ for neon atom (r in a.u.).

B. Numerical Solution of the Density Equation

The density equation (33) is solved numerically. Since the present work concerns atoms, we discuss the numerical procedure for such systems only. Equation (33) can be considerably simplified by making use of the central-field approximation. Thus,

Figure 6. Plot of $g(r)$ for argon atom (r in a.u.).

Figure 7. Plot of $g(r)$ for krypton atom (r in a.u.).

introducing a new function

$$y(r) = r \phi(r), \quad (37)$$

Eq. (33) reduces to

$$\left(-\frac{1}{2} \frac{d^2}{dr^2} + v(r) + \int \frac{\rho(r')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(r) + \frac{5}{3} C_k g(r) \rho(r)^{2/3} \right) y = \mu y. \quad (38)$$

This is a two-point boundary value problem; the boundary conditions are

$$y \rightarrow 0 \text{ as } r \rightarrow 0, y \rightarrow 0 \text{ as } r \rightarrow \infty. \quad (39a)$$

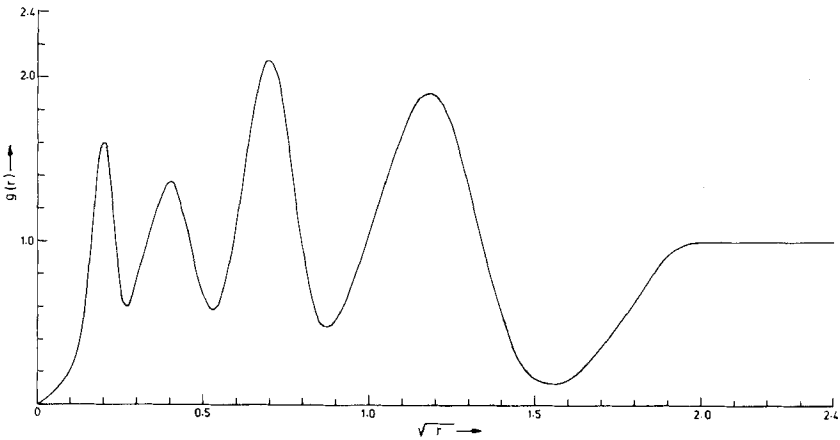
Figure 8. Plot of $g(r)$ for xenon atom (r in a.u.).

TABLE III. Gaussian exponents of $f(r)$ and $g(r)$ functions.

	Ne	Ar	Kr	Xe
α_i for	85.0	220.0	1000.0	3000.0
$f(r)$	1.0	35.0	118.0	170.0
	-	0.9	17.0	70.0
	-	-	0.9	20.0
	-	-	-	1.0
β_i for	49.0	185.0	936.0	2850.0
$g(r)$	1.0	10.2	58.0	123.0
	-	0.9	7.2	42.0
	-	-	0.9	4.0
	-	-	-	1.0
Value of	1.9	2.9	3.2	3.9
r (in a.u.) ^a				

^a Beyond this value of r , $f(r)$ and $g(r)$ have been taken as unity.

The standard methods [29,30], viz., the initial-value method, finite-difference method, or integral equation method can be employed for solving this problem. Since this equation has a similar structure as that of the Schrödinger-type equation for an s orbital in atomic calculations, it is tempting to solve this equation iteratively by a procedure described by Hartree [31] for atomic calculations, where the boundary-value problem is solved by converting into an initial-value problem. We had modified the Herman-Skillman [32] program and tried to iterate by generating a new potential from the results of the previous iterations. Unfortunately, no convergence was observed at all. This suggests that it may not be possible to treat such a nonlinear equation as a linear* one of the form

$$-\frac{1}{2} \frac{d^2 y}{dr^2} + V(r)y = \mu y, \quad (40a)$$

where

$$V(r) = v(r) + \int \frac{\rho(r')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc} + \frac{5}{3} C_k g(r) \rho(r)^{2/3}. \quad (40b)$$

* Equation (40a) is actually nonlinear, but during numerical solution it is treated as linear in the sense that during a particular iteration $V(r)$ is fixed and has been calculated from the results of previous iterations.

However, if the equation is rewritten in the form

$$-\frac{1}{2} \frac{d^2 y}{dr^2} + V_c y + \frac{5}{3} C_k g(r) r^{-4/3} y^{7/3} - \frac{4}{3} C_x r^{-2/3} y^{5/3} - C y \ln(1 + 1/x_c) = \mu y, \quad (41a)$$

where

$$C_x = \frac{3}{4\pi} (3\pi^2)^{1/3}, \quad \frac{1}{x_c} = A \left(\frac{4}{3} \pi \right)^{1/3} r^{-2/3} y^{2/3}, \quad (41b)$$

and only the Coulomb potential

$$V_c = v(r) + \int \frac{\rho(r')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (41c)$$

is kept fixed during a particular iteration after being calculated from the results of earlier iterations, the integration of the differential equation (41a) has been found to yield [9, 33] a stable and convergent solution.

In the present work, we have solved Eq. (41a) using a finite-difference method with successive linearization following the work of Yonei and Tomishima [9, 34].

Since ϕ is larger in magnitude at small and medium values of r and exponentially damped at large r , it is necessary to use a variable mesh such that the interval between adjacent points increases with increasing r . Although a logarithmic mesh is common in atomic calculations [35], a convenient change of variable for the present problem is from r to x , where

$$r = x^2. \quad (42)$$

A uniform mesh size in x yields a desired variable mesh in r . Thus, Eq. (41a) becomes

$$\begin{aligned} \frac{d^2 y}{dx^2} - \frac{1}{x} \frac{dy}{dx} - \frac{40}{3} C_k g x^{-2/3} y^{7/3} + \frac{32}{3} C_x x^{2/3} y^{5/3} \\ + 8C x^2 y \ln \left[1 + A \left(\frac{4\pi}{3} \right)^{1/3} x^{-4/3} y^{2/3} \right] + 8(U - \mu x^2) y = 0, \end{aligned} \quad (43)$$

where

$$U(r) = -rV_c(r) = Z - r \int \frac{\rho(r')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (44)$$

for an atom of atomic number Z and the boundary conditions are

$$\begin{aligned} y = 0 \quad \text{at} \quad x = 0, \\ y = 0 \quad \text{at} \quad x \rightarrow \infty. \end{aligned} \quad (39b)$$

Differential equation (43) can be replaced by a set of difference equations by

choosing a uniform step size h for the variable x in the interval 0 to X , where

$$x_j = jh \quad \text{and} \quad X = (J + 1)h. \quad (45)$$

Here, J , which denotes the number of mesh points chosen, is a large number such that $y(x_{J+1})$ can be taken as zero. We have chosen $J = 240$ in our calculation. Thus, the boundary conditions are

$$\begin{aligned} y_0 &= y(0) = 0, \\ y_{J+1} &= y(x_{J+1}) = y(X) = 0, \end{aligned} \quad (39c)$$

and the difference equations are

$$\begin{aligned} y_{j-1} + \left(\frac{h}{x_j} - 2 - \frac{40}{3} C_k h^2 x_j^{-2/3} g y_j^{4/3} + \frac{32}{3} C_x h^2 x_j^{2/3} y_j^{2/3} \right. \\ \left. + 8Chh^2 x_j^2 \ln(1 + k_j y_j^{2/3}) + 8h^2(U_j - \mu x_j^2) \right) y_j \\ + \left(1 - \frac{h}{x_j} \right) y_{j+1} = 0, \quad j = 1, 2, \dots, J, \end{aligned} \quad (46)$$

where

$$k_j = A(4/3 \pi)^{1/3} x_j^{-4/3}.$$

Now, in order to introduce linearization, let us write

$$y_j = \tilde{y}_j + \delta y_j, \quad (47)$$

where \tilde{y}_j is an approximate solution and δy_j is a correction to it. Substituting Eq. (47) into (46) and retaining terms up to linear in δy_j , one obtains

$$\delta y_{j-1} + \theta_j \delta y_j + \Phi_j \delta y_{j+1} = \tilde{\psi}_j, \quad 1 \leq j \leq J, \quad (48)$$

where

$$\begin{aligned} \theta_j \equiv \theta_j(x_j, \tilde{y}_j, \mu) &= \frac{h}{x_j} - 2 - \frac{280}{9} C_k h^2 x_j^{-2/3} \tilde{y}_j^{4/3} g + \frac{160}{9} C_x h^2 x_j^{2/3} \tilde{y}_j^{2/3} \\ &+ 8Chh^2 x_j^2 \left(\ln(1 + k_j \tilde{y}_j^{2/3}) + \frac{2}{3} k_j \tilde{y}_j^{2/3} (1 + k_j \tilde{y}_j^{2/3})^{-1} \right) + 8h^2(U_j - \mu x_j^2), \end{aligned} \quad (49a)$$

$$\Phi_j \equiv \Phi_j(x_j) = (1 - h/x_j), \quad (49b)$$

and

$$\begin{aligned} \tilde{\psi}_j &\equiv \tilde{\psi}_j(x_j, \tilde{y}_{j-1}, \tilde{y}_j, \tilde{y}_{j+1}, \mu) \\ &= - \left[\tilde{y}_{j-1} + \left(\frac{h}{x_j} - 2 - \frac{40}{3} C_k h^2 x_j^{-2/3} g \tilde{y}_j^{4/3} + 8h^2(U_j - \mu x_j^2) \right. \right. \\ &\quad \left. \left. + \frac{32}{3} C_x h^2 x_j^{2/3} \tilde{y}_j^{2/3} + 8Chh^2 x_j^2 \ln(1 + k_j \tilde{y}_j^{2/3}) \right) \tilde{y}_j + (1 - h/x_j) \tilde{y}_{j+1} \right]. \end{aligned} \quad (49c)$$

Equation (48) represents a set of J simultaneous equations which are solved for J unknowns $\delta y_j (1 \leq j \leq J)$. The boundary conditions imply that

$$\delta y_0 = \delta y_{J+1} = 0. \quad (39d)$$

Equation (48) can also be written in matrix notation as

$$AY = \tilde{\psi}, \quad (50)$$

where Y and $\tilde{\psi}$ are J -dimensional column vectors given by

$$Y \equiv \begin{pmatrix} \delta y_1 \\ \delta y_2 \\ \vdots \\ \delta y_J \end{pmatrix}, \quad \tilde{\psi} \equiv \begin{pmatrix} \tilde{\psi}_1 \\ \tilde{\psi}_2 \\ \vdots \\ \tilde{\psi}_J \end{pmatrix}, \quad (51)$$

and A is the $J \times J$ matrix

$$A = \begin{pmatrix} \theta_1 & \Phi_1 & 0 & 0 & \cdots & 0 \\ 1 & \theta_2 & \Phi_2 & 0 & \cdots & 0 \\ 0 & 1 & \theta_3 & \Phi_3 & \cdots & 0 \\ \cdots & \cdots & \cdots & 1 & \cdots & 0 \\ 0 & \cdots & \cdots & 0 & \theta_{J-1} & \Phi_{J-1} \\ 0 & 0 & 0 & \cdots & 1 & \theta_J \end{pmatrix}. \quad (52)$$

The tridiagonal form of the matrix A permits a very efficient application of the Gaussian elimination procedure (see, e.g., p. 74 of Ref. 29).

Assuming the matrix A to be nonsingular, it can be factored into the product

$$A = LU, \quad (53)$$

where the matrices L and U , the lower and upper triangular matrices, respectively, are of the form

$$L = \begin{pmatrix} \beta_1 & 0 & 0 \cdots 0 & 0 \\ 1 & \beta_2 & 0 \cdots 0 & 0 \\ 0 & 1 & \beta_3 \cdots 0 & 0 \\ 0 & 0 & 0 \cdots 1 & \beta_J \end{pmatrix},$$

$$U = \begin{pmatrix} 1 & \gamma_1 & 0 & \cdots & 0 \\ 0 & 1 & \gamma_2 & \cdots & 0 \\ 0 & \cdots & \cdots & 1 & \gamma_{J-1} \\ 0 & \cdots & \cdots & 0 & 1 \end{pmatrix}. \quad (54)$$

β_j and γ_j must satisfy

$$\begin{aligned} \beta_1 &= \theta_1, \quad \gamma_1 = \Phi_1/\beta_1, \\ \beta_j &= \theta_j - \gamma_{j-1}, \quad 2 \leq j \leq J, \\ \gamma_j &= \Phi_j/\beta_j, \quad 2 \leq j \leq J-1. \end{aligned} \quad (55)$$

Thus, the solution of system (50) can be obtained by solving the following equivalent pair of systems, viz.:

$$LZ = \tilde{\psi}$$

and

$$UY = Z. \quad (56)$$

The solutions of these systems can be easily written

$$z_1 = \tilde{\psi}_1/\beta_1, \quad z_j = (\tilde{\psi}_j - z_{j-1})/\beta_j \quad \text{for } j = 2, 3, \dots, J$$

and (57)

$$\delta y_J = z_J, \quad \delta y_j = z_j - \gamma_j \delta y_{j+1} \quad \text{for } j = J-1, J-2, \dots, 1.$$

Thus, the δy_j values can be obtained by first calculating* β_j and γ_j 's and then evaluating an intermediate solution z_j .

Thus, starting with a trial function $\{\tilde{y}_j\}$ and a suitable value of μ , one can solve for the required correction $\{\delta y_j\}$, and modify $\{\tilde{y}_j\}$ to have a second trial function $\{\tilde{y}_j + \delta y_j\}$ that can be used as $\{\tilde{y}_j\}$ in the next iteration. However, although this new trial function will always satisfy the boundary conditions, it will not, in general, be normalized. This is because the value of μ employed has been a guess and not the actual one. Thus, one has to change the value of μ to a new one such that the solutions for $\{\delta y_j\}$ make the new trial function $\{\tilde{y}_j + \delta y_j\}$ normalized, i.e., satisfy the subsidiary condition

$$4\pi \int_0^\infty (\tilde{y} + \delta y)^2 dr = N. \quad (2b)$$

It would have been very convenient if it were possible to predict a correction $\Delta\mu$ in terms of the deviation of the normalization integral,[†] i.e., $(I - N)$ where I stands for the left-hand side of Eq. (2b). Although several schemes for eigenvalue correction estimates exist [36,37] and have been used in atomic calculations [31], none of them is appropriate in the present context and a proper formulation for evaluating $\Delta\mu$ in the present case still seems [38] to be lacking. However, fortunately the μ dependence of I is monotonic. As a result, we have evaluated I for several gradually decreasing μ values starting from $\mu = 0$ (since μ being an eigenvalue is expected to be negative) and searched for the sign change of the quantity $(I - N)$. μ has then been determined up to a desired accuracy (say, 0.0001) by the half-interval method so that $(I - N)$ deviates from zero within a prescribed tolerance (e.g., 1×10^{-4}). The corresponding values of $\{\delta y_j\}$ yield the new function $\{\tilde{y}_j + \delta y_j\}$ that can be used in the next iteration as trial function as well as for reevaluating $U(r)$.

However, if the calculated δy is large, the use of $(\tilde{y} + \delta y)$ as the corrected function often leads to instability and divergence. This is the case especially when the trial \tilde{y} is far from the true one, e.g., during the initial stages of iteration. This problem has been avoided by not adding the full correction at once, but calculating the new trial

* It has been assumed here that all β_j 's are nonzero. The difficulty arising because of zero value of some β_j 's can be, however, avoided by suitable modification of the above scheme (see, e.g., p. 75 of Ref. 29).

† In the present calculation, all numerical integrations have been performed using Simpson's rule.

function by using an attenuated mixing scheme for the density, i.e.,

$$\tilde{y}_{\text{new}} = [(1 - \alpha)\tilde{y}_{\text{old}}^2 + \alpha(\tilde{y}_{\text{old}} + \delta y)^2]^{1/2}, \quad (58)$$

which preserves the normalization condition

$$4\pi \int_0^\infty y^2 dr = N. \quad (2c)$$

Here, α is a parameter denoting the weighting factor.

The potential function $U(r)$ is reevaluated using this \tilde{y}_{new} . Employing \tilde{y}_{new} as the trial function, δy is again solved for in the next iteration and the process is repeated until self-consistency is achieved. We have defined the self-consistency criterion as $|\delta y_j / \tilde{y}_j| \leq 10^{-4}$. A value of $\alpha = 0.25$ to 0.5 has been found to lead to a stable and convergent numerical procedure. Although the number of iterations required depends on the trial function used, the choice of trial function is not critical in the present procedure. The use of a simple exponential function as the trial function has been found to lead to a good convergence and stability.

From the resultant $\{y_j\}$, the density and the energy values can be calculated using Eqs. (20), (37), (34), and (35) respectively.

4. Results and Discussion

With the help of the $g(r)$ function evaluated using the scheme described in Section 3.A, the density equation has been solved numerically. The exponents of the Gaussians used in the evaluation of $g(r)$ were adjusted to obtain a density showing good agreement with the HF density. The behavior of the resultant density due to variation of the exponents is so systematic that the proper exponent could be selected very easily.

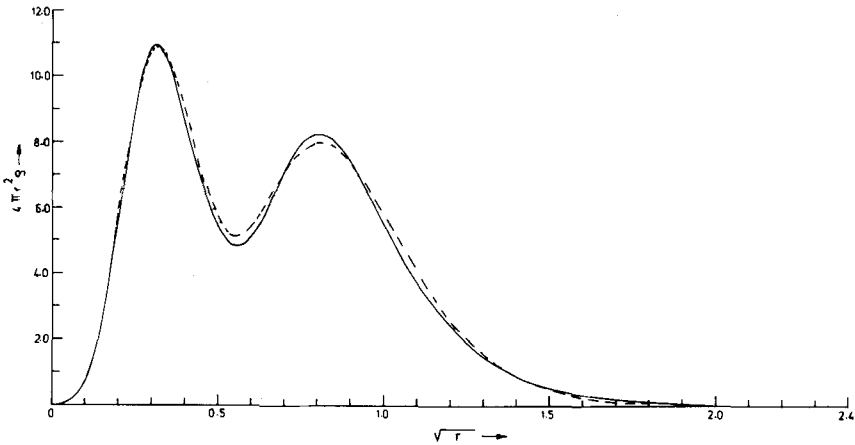


Figure 9. Radial density of neon atom (in a.u.). (—) Present calculation without correlation (merges with the curve with inclusion of correlation); (-----) Hartree-Fock.

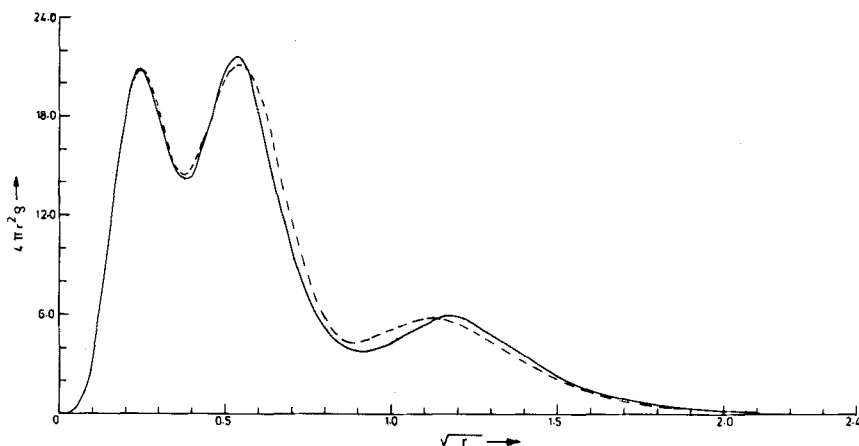


Figure 10. Radial density of argon atom (in a.u.). (—) Present calculation without correlation (merges with the curve with inclusion of correlation); (---) Hartree-Fock.

The density is observed to be sensitive on the form of the function $g(r)$. Since our $f(r)$ and $g(r)$ functions were based on the HF results, the density equation has been initially solved without inclusion of the correlation term and the $g(r)$ is fixed by adjustment of the exponents. Then using the same $g(r)$, the equation has again been solved—this time including the correlation term. Both the densities thus obtained are plotted* for

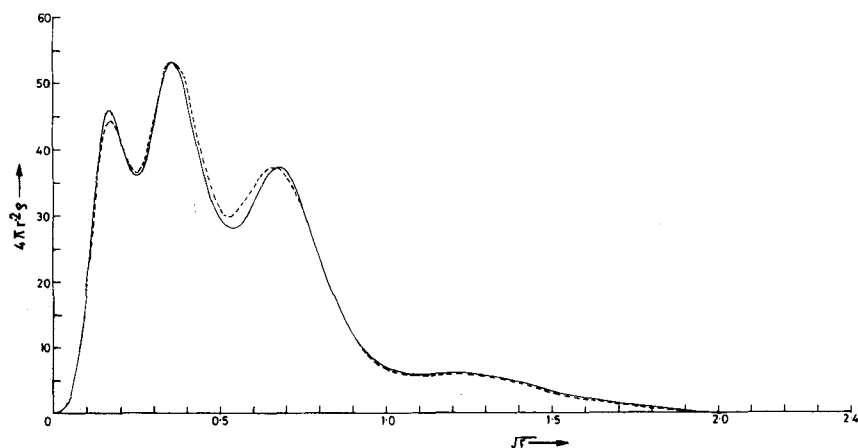


Figure 11. Radial density of krypton atom (in a.u.). (—) Present calculation without correlation (merges with the curve with inclusion of correlation); (---) Hartree-Fock.

* In order to have a better display of the shell structure and the behavior at small as well as large values of r , the radial density plots have been given against $x (\equiv \sqrt{r})$ instead of r . The same approach has been followed in the plots of $f(r)$ and $g(r)$.

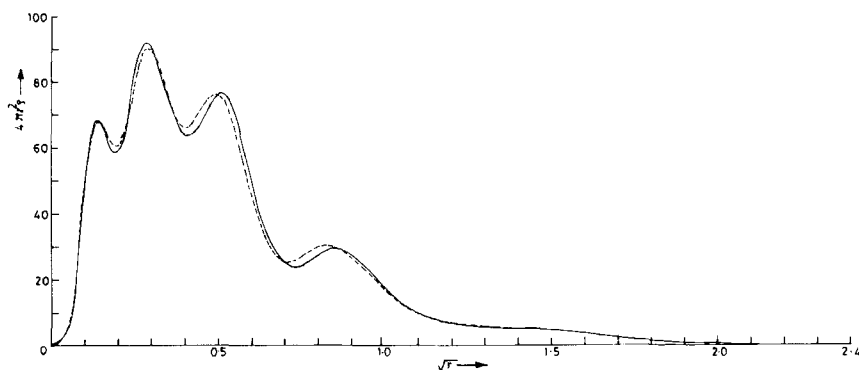


Figure 12. Radial density of xenon atom (in a.u.) (—) Present calculation without correlation (merges with the curve with inclusion of correlation); (- - -) Hartree-Fock.

the atoms Ne, Ar, Kr, and Xe along with the HF densities in Figures 9 to 12. The energy values are calculated using the function $f(r)$. In Table IV we have reported the values of the energies and the eigenvalues (chemical potentials) for all these atoms. The HF energies have also been shown for comparison.

The radial density plots reveal not only the appearance of the shell structure but also rather impressive agreement with the HF densities. The agreement of the energy values are also very good. One important observation from the plots of radial densities and $g(r)$ functions is that the maxima in $g(r)$ correspond to minima in radial density and vice versa. This fact is, however, understandable, but the most interesting aspect is the appearance of the first peak in radial density—which does not correspond to any extremum in $g(r)$ but occurs at a place (and the right place) where the behavior of $g(r)$ is smooth.

It may be of interest to note that the $f(r)$ and $g(r)$ functions have been represented by summation of simple Gaussians—one of the simplest type of functions. We hope to remove the existing discrepancies in the agreement of density by a better representation of these functions. One possible line of improvement may be to prevent the overlap of different Gaussians by imposition of suitable cutoffs without affecting the continuity of the functions. In Table V we have shown a comparison of our density values with the HF ones at some selected points where the deviations between the two are the highest for a particular atom. This would be useful in future refinements of the model.

In order to set the computational scheme, we had first applied the method to an atom consisting of noninteracting electrons. For such systems (with $Z = 10, 18, 36$, and 54) also we had observed very good agreement for both the density and energy with those calculated using hydrogenic orbitals. Although these results [39] are not being reported here, we would like to mention that the convergence was much faster as compared to the cases of actual atoms.

TABLE IV. Calculated^a and the Hartree-Fock Energy values in atomic units.

	Ne		Ar		Kr		Xe	
	Calc.	HF	Calc.	HF	Calc.	HF	Calc.	HF
Total energy	-128.211	-128.547	-513.903	-526.817	-2748.76	-2752.054	-7140.78	-7232.130
	(-129.000)		(-515.419)		(-2752.17)		(-7146.11)	
Eigen-value	-0.3962		-0.3028		-0.3149		-0.2839	
or chemical potential	(-0.4615)		(-0.3554)		(-0.3675)		(-0.3350)	

^a The values in parentheses represent the values calculated with inclusion of the correlation term.

TABLE V. Calculated and Hartree-Fock Densities $\rho(r)$ at selected points*
(in atomic units)

Atom	Values of \sqrt{r}	Calculated density with only exchange	Calculated density with exchange and correlation	Hartree-Fock density [†]
Ne	0.31	94.44	94.54	93.40
	0.40	27.18	27.21	28.34
	0.55	4.218	4.223	4.484
	0.80	1.609	1.616	1.549
	1.0	0.4403	0.4424	0.4613
	1.6	0.004154	0.004009	0.002651
Ar	0.23	590.9	591.0	588.4
	0.38	54.19	54.19	55.28
	0.53	21.88	21.92	21.28
	0.60	11.30	11.32	11.91
	0.90	0.4634	0.4642	0.5277
	1.20	0.2239	0.2250	0.2075
Kr	0.17	4358.7	4358.7	4202.5
	0.25	732.03	732.03	744.99
	0.40	148.23	148.38	154.75
	0.53	28.364	28.364	30.067
	0.60	19.458	19.482	21.145
	0.70	12.193	12.207	11.894
Xe	0.19	3560.2	3560.2	3681.2
	0.29	1033.0	1033.0	1007.1
	0.41	179.16	179.16	185.65
	0.45	130.58	130.69	139.25
	0.75	6.0451	6.054	6.7120
	0.80	5.2398	5.2469	5.7269

* These points have been selected to reveal the largest discrepancies between Hartree-Fock and our calculated densities.

[†] Taken from Ref. 28.

5. Concluding Remarks

The method for direct calculation of density presented in this paper seems to be a promising one. The present calculations have, however, been restricted to closed-shell atoms only. Extension to closed-shell ions, open-shell atoms and molecules would be of interest. The evaluation of $f(r)$ and $g(r)$ functions has been somewhat semiempirical in nature. Thus, a derivation of these functions starting from a completely ab initio theoretic approach would be desirable. The only such attempt for $f(r)$ seems to have been made almost a decade ago by Baltin [15] who evaluated $f(r)$ numerically within a locally linear approximation. However, considerable further development is needed in this direction and the derivation of an analytic expression is of immense importance. Work in this direction is in progress at present.

The proposed method is essentially a modification of the statistical model. And this seems to be probably the first time that the shell structure in atomic radial density is obtained within the statistical model with the help of numerical solution of a differential density equation. The same has, however, been obtained earlier by Wang and Parr [10] as well as Csavinszky [11] by using constraints on the form of the density in a variational approach.

Thus, the present work apart from describing a new density equation also establishes that it is possible to obtain shell structure in atomic radial density, without imposing any constraint on its form, by using a suitable kinetic energy density functional showing proper "local" behavior. The advantage of such a density equation is that with much less effort one can obtain the density and energy of nearly HF accuracy. Thus, if it can be properly developed for molecules, it may turn out to be a highly promising method for density calculations. Such calculations must provide high (local) accuracy for the density and high (global) accuracy for the energy. The function $\phi(\mathbf{r})$ seems to have the interesting interpretation of a *three-dimensional wave function* for a many-electron system.

Thus, if substantial effort is utilized towards the development of a proper kinetic energy functional, especially a variable correction factor for the TF term, density-functional theory may be advanced to a considerable extent. Let us hope [1a] that "there will be radically new and better schemes . . . Perhaps an accurate functional . . . will be found so that densities will be obtained directly, thus bypassing wave functions for most purposes. That really could be revolutionary" (see Ref. 40, p. 47).

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