

Improved Local Density Functional Approach for Atomic Systems

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Abstract

Through a new local density approximation to the kinetic energy density functional introduced by us recently, a simple Thomas–Fermi-like scheme for the direct calculation of electron density in atoms is proposed. The calculated density is nonsingular at the nucleus and the energy values are in very good agreement with the corresponding Hartree–Fock results for atoms. © 1994 John Wiley & Sons, Inc.

I. Introduction

Density functional theory [1–3] (DFT), which employs the single-particle electron density $\rho(\mathbf{r})$ as the basic variable, is a highly versatile tool for the investigation of the electronic structure of many-electron systems. In this theory, the energy density functional for an N -electron system characterized by an external potential $v(\mathbf{r})$, is expressed as

$$E[\rho] = \int d\mathbf{r} v(\mathbf{r})\rho(\mathbf{r}) + (1/2) \iint d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r})\rho(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'| + G[\rho], \quad (1)$$

where $G[\rho]$ is a universal functional of density consisting of kinetic and exchange-correlation contributions. For a fixed $v(\mathbf{r})$, the energy functional $E[\rho]$ is minimum when evaluated at the true density, and, consequently, its minimization with respect to $\rho(\mathbf{r})$ subject to the normalization constraint $\int d\mathbf{r} \rho(\mathbf{r}) = N$ yields the Euler–Lagrange equation

$$\mu = (\delta E/\delta \rho) = v(\mathbf{r}) + \phi(\mathbf{r}) + (\delta G/\delta \rho), \quad (2)$$

where the Lagrange multiplier μ is the chemical potential [2,4] and $\phi(\mathbf{r})$ is the classical electrostatic potential due to the electron cloud given by

$$\phi(\mathbf{r}) = \int d\mathbf{r}' \rho(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'|. \quad (3)$$

The crux of the problem lies in the fact that the exact functional form of $G[\rho]$ explicitly in terms of density is not known. Some methods have been proposed for evaluating $G[\rho]$ for

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a given density (yielding quite accurate numerical results [3] for the He atom, e.g.), through constrained search, local scaling transformations, etc. (for an excellent review, see [3]). These approaches, however, involve sophisticated and time-consuming calculations and also do not provide a direct route to the functional derivative ($\delta G/\delta \rho$) appearing in Eq. (2). It is thus highly important to have suitable simple approximations expressing $G[\rho]$ explicitly in terms of the density.

The practical scheme of DFT is based on the self-consistent solution of Eqs. (1)–(3) for the density and, hence, the energy and different approximations to the functional $G[\rho]$ lead to different prescriptions for density calculation. The earliest version of DFT is the Thomas–Fermi (TF) theory [5], where $G[\rho]$ is represented by only the kinetic energy (KE) functional in the simplest local density approximation given by (atomic units are used throughout)

$$T_0[\rho] = C_k \int d\mathbf{r} \rho(\mathbf{r})^{5/3}; \quad C_k = (3/10)(3\pi^2)^{2/3}, \quad (4)$$

and neglecting the exchange-correlation energy contribution.

Although the extreme simplicity of the TF theory has been responsible for its popularity and wide applicability in many directions, this theory also suffers from serious limitations. It is not surprising that this theory, which is derived from homogeneous electron gas results and provides reasonable predictions of many aspects for solids, fails for highly inhomogeneous systems like atoms. The electron density obtained from atomic TF theory diverges at the nucleus and decays only slowly in the asymptotic region and the resulting energy is far too low compared to the true values. A nonsingular density at the nucleus and also better estimates of the energies can, however, be obtained [6, 7] through an improved TF theory by imposing the finiteness of the integral $\int d\mathbf{r} \nabla^2 \rho$, which should actually vanish but is infinite in conventional TF theory.

Modifications of the TF theory are, however, mostly centered around a nonlocal correction to the KE functional through a gradient expansion. A correction term of second order in density gradient for the KE [8, 9] functional is given through the Weizsacker term as

$$T_2[\rho] = (1/72) \int d\mathbf{r} |\nabla \rho(\mathbf{r})|^2 / \rho(\mathbf{r}). \quad (5)$$

The density obtained using the KE functional ($T_0 + T_2$) does not suffer from any divergence problem and the resulting energy values are also good. The Euler equation to be solved is, however, an integrodifferential equation [10]. A correction involving the first power of the density gradient, suggested by Haq et al. [11], leads to a nondifferential (quadratic) equation for density and good estimates of the energy [12, 13] of atoms and ions, but still does not eliminate the drawback of density divergence at the nucleus.

The purpose of the present work was to propose a new nondifferential equation for the calculation of electron density in atoms. This is achieved through our recently proposed local density functional [14] for the KE whose functional derivative is free from gradients or integrals. The resulting Euler–Lagrange equation (nondifferential) for density therefore requires less effort in solving [12, 13] and is shown to yield divergence-free density and good estimates of energy.

II. An Improved Density Equation Through a New Kinetic Energy Density Functional

The new local density functional for the KE proposed [14] by us recently is based on a modification of the first-gradient expression of Haq et al. [11] and is given by

$$T[\rho] = T_0[\rho] + \beta \int d\mathbf{r} \{ \rho^{4/3}/r \} / \{ 1 + r\rho^{1/3}/\alpha_k \}. \quad (6)$$

Using this functional for $G[\rho]$ in the energy expression of Eq. (1), with $v(r) = -Z/r$ for an atom of atomic number Z , the Euler–Lagrange Eq. (2) reads

$$\begin{aligned} \mu = & (5/3)C_k\rho^{2/3} - Z/r + \phi(r) + (4/3)\beta\{\rho^{1/3}/r\}/\{1 + r\rho^{1/3}/\alpha_k\} \\ & - (1/3)(\beta/\alpha_k)\rho^{2/3}/[1 + r\rho^{1/3}/\alpha_k]^2, \end{aligned} \quad (7)$$

where $\mu = 0$ as in the TF theory. However, the singularity that appears in the density of conventional TF theory can now be made to disappear by a suitable choice of the parameter β in Eq. (7), viz.,

$$\beta = (3Z/4)\rho(0)^{-1/3}. \quad (8)$$

For any value of the parameter α_k , Eqs. (7) and (8) can thus be solved self-consistently to obtain the density and, hence, the energy from Eqs. (1) and (6). For the limiting value $\alpha_k = 0$, one recovers the conventional TF theory, whereas in the limit $\alpha_k \rightarrow \infty$, one obtains a theory [15] corresponding to the KE correction $\beta \int d\mathbf{r} (\rho^{4/3}/r)$. One can choose any intermediate single suitable value of α_k for all the atoms so as to obtain good predictions for the energy. We call this scheme method A.

Alternatively, one can also choose different values of α_k for different atoms such that the resulting density satisfies a suitable cusp condition. From Eq. (7), it is clear that the quantity

$$-(2Z\rho)^{-1}(d\rho/dr)|_{r \rightarrow 0} = (27/8\alpha_k)/[5C_k\alpha_k - 4\beta]. \quad (9)$$

For the exact electron density of an atom, the cusp condition corresponds to the value unity for the left-hand side of Eq. (9). For the density obtained from gradient-corrected TF theory corresponding to the KE functional correction of Eq. (5), this quantity [16] is, however, equal to 9. Since the gradient-corrected TF theory provides a reasonable prediction for energy, we propose to impose this cusp condition to determine α_k in the present theory and we call it method B.

So far, we have considered only the KE contribution to $G[\rho]$. Another important contribution comes from the exchange energy. Incorporating the exchange into the energy functional, e.g., through the local density form of Dirac [17] given by

$$E_x^{\text{LDA}}[\rho] = -C_x \int d\mathbf{r} \rho(r)^{4/3}; \quad C_x = (3/4)(3/\pi)^{1/3}, \quad (10)$$

along with the TF functional $T_0[\rho]$ or its present modification of Eq. (6) for the KE, the Euler equation leads to an asymptotically nondecaying density, thus requiring an arbitrary cutoff radius for density normalization. This difficulty is often eliminated in the Thomas–Fermi–Dirac theory by using the pure TF density to evaluate the Dirac exchange term and adding it to the total energy instead of incorporating the exchange contribution through the Euler equation as well. Although this procedure involves some approximation, a justification can be provided

TABLE I. Calculated total energies (au) of atomic systems.

Atom	HF total energy ^a	HF exchange energy ^b	Method A ($\alpha_k = 0.215$)				Method B (cusp = 9.00)			
			Energy ^c	Cusp	β	$\rho(0)/Z^3$		Energy ^c	α_k	β
						Present value	HF value ^d			
He	2.862	1.026	3.028	9.44	0.4063	6.291	0.4495	2.999	0.2202	0.4166
			2.890					2.863		
			2.332					2.308		
Ne	128.55	12.11	130.36	9.21	0.4014	6.523	0.6199	129.96	0.2175	0.4060
			129.25					128.85		
			120.15					119.77		
Ar	526.81	30.19	525.37	9.03	0.4019	6.500	0.6584	525.13	0.2154	0.4027
			523.06					522.82		
			498.16					497.93		
Kr	2752.0	93.89	2724.8	8.68	0.4049	6.357	0.6909	2735.1	0.2108	0.3972
			2719.5					2729.7		
			2638.5					2648.6		
Xe	7232	179.2	7135	8.36	0.4083	6.199	0.7063	7185	0.2063	0.3925
			7126					7176		
			6965					7014		

^aEnergy values are from [19]. Negative signs of all energy quantities have been omitted.
^bExchange energy values are from [20].
^cValues from the bottom to the top are, respectively, E_{cal} , $E_{\text{cal}} + E_x^{\text{LDA}}$, and $E_{\text{cal}} + E_x^{\text{LDA}} + E_x^{\text{corr}}$.
^dHF values are from [6].

since the density change due to the exchange contribution through the Euler equation is small and affects the energy terms only through the higher-order correction.

We thus propose to include the exchange contribution by first solving the density Eq. (7) without exchange and then using this density to evaluate the exchange energy as a part of the total energy functional of Eq. (1). For this purpose, we use our recently proposed [14] exchange energy functional given by

$$E_x[\rho] = E_x^{\text{LDA}} - C_x \int d\mathbf{r} \{ \rho^{4/3} \} / \{ 1 + r^2 \rho^{2/3} / \alpha_x \}, \quad (11)$$

where the parameter α_x has been determined [14] empirically so as to obtain good predictions of the exchange energies of atoms. This new local density form has been proposed [14] in the spirit of the gradient-corrected nonlocal exchange energy functionals [18] and is as accurate as the latter. Also, the corresponding exchange potential does not show asymptotic divergence.

III. Results and Discussion

In method A, we numerically solved the density Eq. (7) self-consistently using β given by the expression of Eq. (8) and a constant $\alpha_k = 0.215$ for the noble gas atoms He to Xe. In method B, different values of α_k are chosen for each atom such that the cusp condition [lhs of Eq. (9) equal to 9] is satisfied. The calculation has been done self-consistently to the desired accuracy and the long-range behavior of TF density has been used. In both methods, the exchange energy is evaluated using the exchange-free density in Eq. (10) for the Dirac LDA estimate and Eq. (11) with the parameter $\alpha_x = 0.0244$ for the modified LDA result suggested [14] recently by us for atoms.

In Table I, we compare our results on calculated energies with the Hartree–Fock (HF) values [19]. Of the three calculated energy values reported for each atom, viz., the energy without exchange and energies with exchange contributions from Eqs. (10) and (11), respectively, the first one is to be compared with the Hartree energy (obtained, e.g., by subtracting the HF exchange from the HF total energy), whereas the other two are estimates of the HF energies directly. It is clear that although the agreement is quite good in all cases the overall best prediction corresponds to method B and the energy with LDA exchange. This method is parameter-free as well since α_k is determined here from the cusp condition.

We have also plotted in Figure 1 the electron density obtained from the present scheme (method A with $\alpha_k = 0.215$) along with the HF [19] and TF densities for the argon atom. Since the density at the nucleus is finite in the present calculation, we compared the results for this quantity with the corresponding Hartree–Fock values [6] also in Table I. Our calculated values are still too high, about 10 times the corresponding HF values. The finiteness of the calculated density at the nucleus has, however, led to vast improvement in energy although the difference with the TF density away from the nucleus cannot be distinguished in the logarithmic plot of Figure 1. The results on the value of the cusp [lhs of Eq. (9)] are also noted for method A, whereas for method B, the values of α_k required in each case are tabulated. For method A, the cusp value is close to 9.

An important aspect of this work is that since the form of the KE functional is local, one has obtained a nondifferential Euler–Lagrange equation for the calculation of density [12, 13], which is rather easy to solve. At the same time, since the derivative of the present KE density

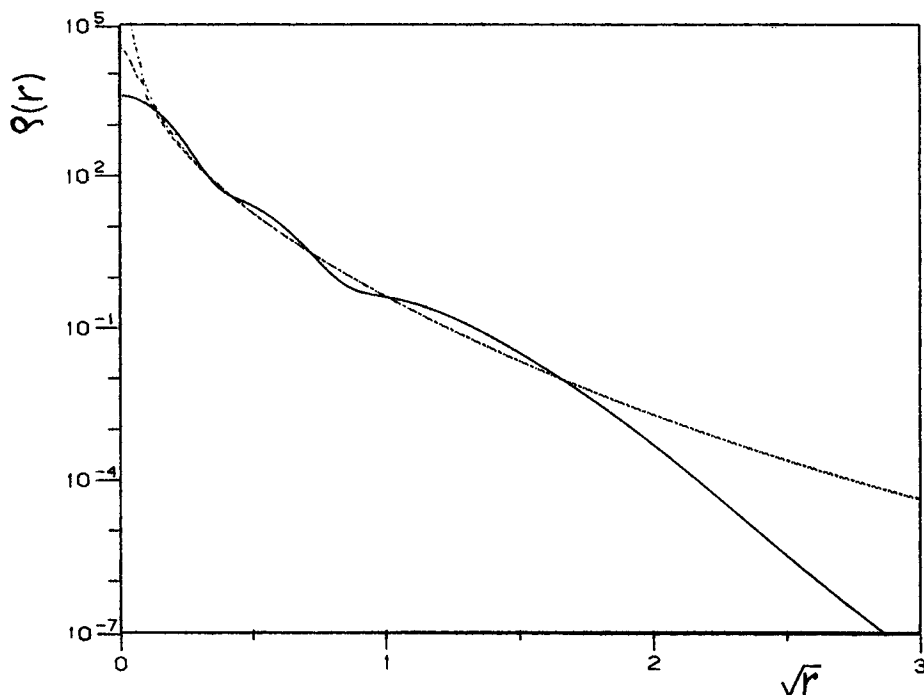


Figure 1. Plot of electron density $\rho(r)$ for the argon atom: (—) Hartree-Fock (HF) density; (- • - • -) Thomas-Fermi (TF) density; (---) density from present calculation.

functional has the correct singularity at the nucleus, it has been possible to eliminate a serious drawback of the conventional TF theory, viz., infinite density at the nucleus.

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Bibliography

- [1] N. H. March and B. M. Deb, Eds., *The Single Particle Density in Physics and Chemistry* (Academic Press, New York, 1987).
- [2] R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).
- [3] E. S. Kryachko and E. V. Ludena, *Energy Density Functional Theory of Many-Electron Systems* (Kluwer Academic, Dordrecht, 1990).
- [4] R. G. Parr, R. A. Donnelly, M. Levy, and W. E. Palke, *J. Chem. Phys.* **69**, 4431 (1978).
- [5] N. H. March, *Adv. Phys.* **6**, 1 (1957).
- [6] S. K. Ghosh and R. G. Parr, in *Density Matrices and Density Functionals*, R. Erdahl and V. H. Smith, Jr., Eds. (D. Reidel, Dordrecht, 1987), p. 663.
- [7] R. G. Parr and S. K. Ghosh, *Proc. Natl. Acad. Sci. U.S.A.* **83**, 3577 (1986).
- [8] P. K. Chattaraj and B. M. Deb, *J. Sci. Ind. Res.* **43**, 238 (1984).

- [9] S.K. Ghosh and L.C. Balbas, *J. Chem. Phys.* **83**, 5778 (1985).
- [10] B.M. Deb and S.K. Ghosh, *Int. J. Quantum Chem.* **23**, 1 (1983).
- [11] S. Haq, P.K. Chattaraj, and B.M. Deb, *Chem. Phys. Lett.* **111**, 79 (1984).
- [12] B.M. Deb and P.K. Chattaraj, *Phys. Rev. A* **37**, 4030 (1988).
- [13] B.M. Deb and P.K. Chattaraj, *Phys. Rev. A* **45**, 1412 (1992); see other references therein.
- [14] S.K. Ghosh and B.M. Deb, *J. Phys. B* (in press).
- [15] B.M. Deb, R. Singh, and R.P. Semwal, *J. Phys. B* **26**, 3447 (1993).
- [16] P.K. Chattaraj, *J. Math. Phys. Sci.* **25**, 19 (1991).
- [17] P.A.M. Dirac, *Proc. Camb. Philos. Soc.* **26**, 376 (1930).
- [18] See, e.g., H. Lee, C. Lee, and R.G. Parr, *Phys. Rev. A* **44**, 768 (1991).
- [19] E. Clementi and C. Roetti, *At. Data Nucl. Data Tables* **14**, 177 (1974).
- [20] S.K. Ghosh and R.G. Parr, *Phys. Rev. A* **34**, 785 (1986).

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