

# Correction to kinetic energy density using exactly solvable model

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**Abstract.** Herein we present an accurate correction to the Thomas–Fermi approximation for the non-interacting kinetic energy. The correction is derived from an entirely solvable model and not through the application of the truncated gradient expansion. The used approach exploits the comparable nature of the difference between the Thomas–Fermi approximation and the non-interacting kinetic energy and its analogue within a model of non-interacting electrons that resembles the actually studied problem. For atom, the used model is a system of  $N$  non-interacting electrons moving independently in the Coulomb field of the nuclear charge. It is shown numerically that this correction enhances the accuracy of the Thomas–Fermi approximation for atoms by an order of magnitude.

## 1. Introduction

The original density functional theory (DFT) is based on the prominent work of Hohenberg and Kohn [1], where it was proved that the ground state of a many-electron system is completely characterized by its electronic density and that the energy functional attains its minimum at the density of the system in its ground state. However, expressing the kinetic energy as a density functional has proven to be a challenging task. The difficulty is apparent as the accuracy is undesirably insufficient and the proposed kinetic energy density functionals (KEDF) have had limited applications [2, 3, 4, 5]. Alternatively, Kohn and Sham (KS-DFT) [6] suggested an approach where the “orbitals” are reintroduced while the sum of these orbitals’ individual densities is equal to the total density of the real system, yet only while the kinetic energy is defined as that of the imposed “fictitious” system. Within the framework of KS-DFT, this means converting the problem back from 3-dimensional (3D) to  $3N$ -dimensional- where  $N$  is the number of the particles.  $N$  orbitals are determined by solving the governing  $N$  equations self-consistently [6, 7, 8]. Despite this computational drawback, KS-DFT

presently dominates the field of atomistic calculations [7]. Surviving in parallel to KS-DFT, efforts to find an accurate KEDF are still modestly active. In recent years, this effort has started gaining more attention [9, 10, 11, 5]. To distinguish this DFT doctrine from KS-DFT (which depends on application of orbitals), the method is referred to as “orbital-free” DFT (OF-DFT) [12, 13].

Since the first independently proposed KEDF by Thomas [14] and Fermi [15] (TF), a huge number of KEDFs has been suggested. However, Thomas–Fermi model with various corrections dominates the field [3, 11, 13]. The usual corrections are either based on gradient expansion [16, 17, 18] or they are obtained by adding other forms of KEDF [11, 19, 20, 21]. Furthermore, Thomas–Fermi-based KEDF are used in some applications satisfying the assumption that the density is nearly uniform. For example, they are used for metals [22] and warm dense matter [23, 24]. As for the correction, it would be abstractly assumed that the gradient expansion should pave a reasonable route. However, it is known that the high order gradient-based corrections diverge for finite systems. Therefore, seeking a non-gradient-expansion based correction is desirable. One of the recent corrections suggested by Burke and coworkers [5] is based on uniform WKB analysis in 1-dimensional case. The correction has neither sums nor derivatives.

In this paper, we present a new non-gradient based method to enhance the Thomas–Fermi approximation by adding a correction factor derived using an exactly solvable model. The used model is for  $N$  non-interacting particles moving in the Coulomb field of the nuclear charge. It allows to calculate part of the energy using the simple Rydberg formula and to express the particle density in an analytic form through Laguerre polynomials and exponential functions. The correction exploits the fact that the difference between the Thomas–Fermi approximation and the non-interacting kinetic energy is comparable to the difference between the same values within the proposed solvable model. The concept can be presented best using the following equation

$$T_s = T_{\text{TF}}[\rho] + (T_s - T_{\text{TF}}[\rho]) \approx T_{\text{TF}}[\rho] + (\tilde{T}^{(Z)} - \tilde{T}_{\text{TF}}^{(Z)}). \quad (1)$$

where  $T_s$  is the non-interacting kinetic energy and  $T_{\text{TF}}$  is Thomas–Fermi approximation. In the same equation, we use the notation  $\tilde{T}^{(Z)}$  and  $\tilde{T}_{\text{TF}}^{(Z)}$  for the kinetic energy and the Thomas–Fermi energy of the proposed model. These values are labeled by a superscript ( $Z$ ) to show that the central field for the model is the same as for the atom. Our work follows a similar approach that was developed to estimate the correlation energy for two-electron atoms [25]. In our numerical experiments, we show that the correction factor can increase the precision of Thomas–Fermi approximation by around an order of magnitude for atoms. To apply it for molecules, or other potential systems, the method needs further extensions in the sense of using a solvable model which resembles the particular problem of interest. As it is shown in (1), the kinetic energy is expressed as Thomas–Fermi energy plus the correction obtained from the exactly solvable model. We calculated the results numerically for noble and alkali-earth atoms up to radon ( $Z = 88$ ). Our results appear to be more accurate in comparison with Thomas–Fermi approximation by a factor between 11 (for helium) and 101 (for barium). We also discuss

the large- $Z$  limit of the energy and the density and compare the gradient expansion for atoms with that for the model.

## 2. The correction

As aforementioned, the general idea of the proposed correction is that the difference between the Thomas–Fermi approximation and the non-interacting kinetic energy is comparable to the difference between the same values within a solvable model providing that the used model resembles the actual studied problem as shown in (1). This approach follows a successful and analogous method used to estimate the correlation energy for two-electron atoms [25]. Although the model of an  $N$  non-interacting particles is restricted to the Coulomb field of the nuclear charge, the method can be applied for a wide range of potential models. The focus of the paper is to present the approach and to illustrate its applicability for simple systems like atoms. So, we suggest a model that in many respects resembles the atoms and that has an analytical quantum-mechanical solution. Another important reason for selecting such a model is that it is possible to write the correction  $\tilde{T}^{(Z)} - \tilde{T}_{\text{TF}}^{(Z)}$  as a function of the electric charge  $Z$  only. Furthermore, this form for  $\tilde{T}^{(Z)}$  and  $\tilde{T}_{\text{TF}}^{(Z)}$  provides more in-depth understanding of the model as it will be shown.

Since we are interested in an equivalent system of non-interacting particles, the energy  $\tilde{T}^{(Z)}$  does not include correlation effects. The inter-electron interaction affects the effective potential and therefore the difference between our model and an atom is disregarding the screening of nuclear charge by inner electrons. The presented model retains Coulomb singularity at the origin, as well as Coulomb attraction for large distance, however the attraction force at large distance is much larger in the presented model. The region of applicability of the Thomas–Fermi model,  $dp_{\mu}^{-1}/dr \ll 1$ , where  $p_{\mu} = \sqrt{2(\mu - V)}$  and  $\mu$  is the chemical potential, is violated in a small region of radius  $r_0 = Z^{-1}$  adjoining the nucleus, where quantum effects become significant. In the neighborhood of the nucleus, the field is practically identical to the Coulomb field  $-Z/r$ . Unlike the approach of Kirzhnits and Shpatakovskaya [26] where the quantum corrections to the Thomas–Fermi model were calculated in a neighborhood of nuclei, we treat the Coulomb problem exactly, without considering the quantum corrections separately.

The assumed model has the same nuclear charge  $Z = N$  as the atom under consideration. Thus, the screened Coulomb potential for the atom has the same behavior  $-Z/r$  at the origin, but differs far from it. Without inter-particle interaction, each electron can be considered as occupying an orbital characterized by the principal quantum number  $n = 1, 2, \dots$ . For example, two electrons with  $n = 1$  in a configuration  $1s^2$  form the closest inner K-shell (in X-ray notations), eight electrons with  $n = 2$  form L-shell in a configuration  $2s^2 2p^6$ . Generally, a completely filled  $n$ -th shell has  $2n^2$  electrons with possible quantum numbers  $l = 0, 1, \dots, n - 1$ ,  $m = -l, -l + 1, \dots, l$ , and spins  $\sigma = \pm \frac{1}{2}$ .

Let us denote  $n_{\max}$  as the quantum number of the last shell with a non-zero occupation number. In the ground state, all lowest shells with  $n < n_{\max}$  are completely filled, while the last shell with  $n = n_{\max}$  can be filled either partially or completely. For simplicity, we consider initially only the states in closed-shell configurations, i.e. when all shells up to  $n = n_{\max}$  are completely filled. The same model can be extended for other configurations either by considering angular dependence or simply by interpolation between closed shells as it will be shown later. The total number of electrons on shells with  $n = 1, 2, \dots, n_{\max}$  can be obtained by summation of the occupation numbers for each individual shell,

$$N = \sum_{n=1}^{n_{\max}} 2n^2 = \frac{1}{3}n_{\max}(n_{\max} + 1)(2n_{\max} + 1). \quad (2)$$

The kinetic energy of the proposed model can be calculated by exploiting the kinetic energies for individual orbitals. This energy for each orbital is given by Rydberg formula, that is  $Z^2/(2n^2)$  in atomic units, where  $n$  is the principal quantum number. Atomic units are used throughout this paper. Now, the total kinetic energy can be calculated by summation of contributions from each shell,

$$\tilde{T}^{(Z)} = \sum_{n=1}^{n_{\max}} 2n^2 \left( \frac{Z^2}{2n^2} \right) = n_{\max}Z^2. \quad (3)$$

where the kinetic energy of the model  $\tilde{T}^{(Z)}$  corresponds to the same value in (1).

To fully specify the proposed functional, we also need to calculate the Thomas-Fermi approximation of energy for the model. As previously stated, the  $\tilde{T}_{\text{TF}}^{(Z)}$  can be presented as a function of the electric charge  $Z$  when the proposed model is used. For closed-shell configurations which are spherically symmetric, Thomas-Fermi kinetic energy is

$$T_{\text{TF}}[\rho] = 4\pi \int_{r=0}^{\infty} r^2 \tau_0(r) dr, \quad (4)$$

where the KEDF  $\tau_0$  is

$$\tau_0(\vec{r}) = \frac{3}{10} (3\pi^2)^{2/3} \rho^{5/3}(\vec{r}). \quad (5)$$

To calculate the Thomas-Fermi approximation using (4) for the used model, it is necessary to have the corresponding electron density  $\tilde{\rho}$ . The density  $\tilde{\rho}$  can be obtained by combining the wave functions for individual electrons as follows. A wavefunction of an electron on the orbital  $(n, l, m)$  is

$$\psi_{n,l,m}(\vec{r}) = R_{n,l}(r)Y_{l,m}(\theta, \phi), \quad (6)$$

where  $(n, l, m)$  are the principal, orbital, and azimuthal quantum numbers respectively,  $Y_{l,m}(\theta, \phi)$  is the spherical harmonic, and  $(\theta, \phi)$  are polar and azimuthal angles respectively. In (6),  $R_{n,l}$  is the radial component of the wavefunction expressed through Laguerre polynomials as follows,

$$R_{n,l}(r) = \sqrt{\left(\frac{2Z}{n}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}} \exp\left(-\frac{Zr}{n}\right) \left(\frac{2Zr}{n}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2Zr}{n}\right). \quad (7)$$

Using (6), the electronic density  $\tilde{\rho}$  is given as the sum

$$\tilde{\rho}(\vec{r}) = \sum_{n=1}^{n_{\max}} \sum_{l=0}^{n-1} \sum_{m=-l}^l R_{n,l}^2(r) |Y_{l,m}|^2(\theta, \phi). \quad (8)$$

By exploiting the properties of the spherical harmonics and by summing over  $m$ , the above equation is reduced to

$$\tilde{\rho}(r) = \frac{1}{4\pi} \sum_{n=1}^{n_{\max}} \sum_{l=0}^{n-1} (2l+1) R_{n,l}^2(r). \quad (9)$$

which is angular independent. Finally, the value of  $\tilde{T}_{\text{TF}}^{(Z)}$  can be calculated by substitution of  $\tilde{\rho}$  given by equations (9) and (7) into equation (4).

After determining the values of  $\tilde{T}^{(Z)}$  and  $\tilde{T}_{\text{TF}}^{(Z)}$ , we can explicitly write the functional for calculating the kinetic energy of an atom using the correction based on the proposed model. The new functional is given by the following equation

$$T_s[\rho, Z] = T_{\text{TF}}[\rho] + \delta\tilde{T}^{(Z)}, \quad (10)$$

where  $\delta\tilde{T}^{(Z)}$  is found by considering the exactly solvable model with the same nuclear charge  $Z$ ,

$$\delta\tilde{T}^{(Z)} = \tilde{T}^{(Z)} - \tilde{T}_{\text{TF}}^{(Z)}. \quad (11)$$

When using the proposed functional for the kinetic energy of an atom, we would calculate the  $T_{\text{TF}}$  based on some electron density approximation and the correction using the value of  $Z$ . In practical application, it is necessary to consider the case when the last shell is partially filled. In such cases, it is not possible to apply (2) directly with an integer  $n_{\max}$ . Since the closed shells occur only for a few values of the nuclear charge given by the sequence of ‘‘magic numbers’’ 2, 10, 28, 60, 110,  $\dots$ , we need to define the interpolation of the function  $Z \mapsto \delta\tilde{T}^{(Z)}$  to other integer values of  $Z$ . Here, we use an interpolation by a cubic polynomial through four data points at  $Z = 2, 10, 28$ , and 60:

$$\delta\tilde{T}^{(Z)} = 0.21210 - 0.19860Z + 0.12815Z^2 + 0.00010Z^3. \quad (12)$$

### 3. The $Z$ expansion of the model

For many applications, it is more convenient to express the energy of the system through the total nuclear charge  $Z$ . The energy as a function of the nuclear charge can be obtained by solving (2) in respect to  $n_{\max}$  and by substituting the result into (3),

$$\tilde{T}^{(Z)} = \frac{1}{2} \left( 3^{-1/3} D^{-1} + 3^{-2/3} D - 1 \right) Z^2, \quad D = \left( 54Z + \sqrt{2916Z^2 - 3} \right)^{1/3}. \quad (13)$$

A more suitable format for (13) is in the form of an expansion in powers of  $Z^{-1/3}$ . The transformed equation has the following form

$$\begin{aligned} \tilde{T}^{(Z)} \sim & (3/2)^{1/3} Z^{7/3} - \frac{1}{2} Z^2 + \frac{1}{6 \times 12^{1/3}} Z^{5/3} - \frac{1}{3888 \times 18^{1/3}} Z^{1/3} \\ & + \frac{1}{69984 \times 12^{1/3}} Z^{-1/3} + O(Z^{-5/3}), \end{aligned} \quad (14)$$

where the terms proportional to  $Z^{\pm 4/3}$ ,  $Z^{\pm 1}$ ,  $Z^{\pm 2/3}$ , and  $Z^0$  are identically zero. Numerically, it is simply

$$\begin{aligned} \tilde{T}^{(Z)} &\sim 1.144714Z^{7/3} - 0.5Z^2 + 0.072798Z^{5/3} \\ &- 0.000098Z^{1/3} + 0.000006Z^{-1/3} + O(Z^{-5/3}). \end{aligned} \quad (15)$$

With the goal of being able to assess the model, we compare (15) with the corresponding expansion of the non-interacting kinetic energy of an atom with large nuclear charge  $Z$ . This expansion can be derived using the virial theorem from the corresponding expansion of the total energy and can be written as an asymptotic series in powers of a small parameter  $Z^{-1/3}$  [27, 28],

$$T_s \sim 0.768745Z^{7/3} - 0.5Z^2 + 0.269900Z^{5/3}. \quad (16)$$

The most significant difference between equations (15) and (16) is the leading term. This is mainly due to the inclusion of Coulomb repulsion between electrons which decreases the leading term  $\sim Z^{7/3}$  by a factor of 1.489 because of the increase of the size of the atom. The second subdominant term  $\sim Z^2$  remains the same. This term comprises the correction of strongly bound electrons [29, 30] which is not affected by the inter-electron repulsion.

To assess the accuracy of the Thomas–Fermi approximation, we analyze the asymptotic behavior of the Thomas–Fermi energy in the limit of large number of electrons  $N = Z$ . To estimate the large- $N$  behavior, we have calculated  $\tilde{T}_{\text{TF}}^{(Z)}$  for increasing values of  $n_{\text{max}}$  and found, using Richardson’s extrapolation [31], that for large  $n_{\text{max}}$

$$\tilde{T}_{\text{TF}}^{(Z)} \sim 1.144714Z^{7/3} - 0.625856Z^2 + 0.146878Z^{5/3}. \quad (17)$$

We characterize the accuracy of the approximation by comparing the terms of the expansion (17) with the corresponding terms in (15) [32]. We find that the Thomas–Fermi approximation correctly reproduces the leading term  $1.144714Z^{7/3}$ , but makes a 25% error in the subdominant term  $-0.5Z^2$ . Thus we can say following the definition from [33] that the Thomas–Fermi approximation is large- $N$  asymptotically exact to the zero degree (AE0).

Comparing equations (15) and (17), we obtain

$$\delta\tilde{T}^{(Z)} = \tilde{T}^{(Z)} - \tilde{T}_{\text{TF}}^{(Z)} \sim 0.126Z^2 - 0.074Z^{5/3}, \quad (18)$$

which is close to the same quantity for atoms,  $T_s - T_{\text{TF}}[\rho] \sim 0.16Z^2$  [28]. Thus, our approximation given by (1) is exact in the leading term  $0.768745Z^{7/3}$  and it makes only a small 7% error ( $0.16Z^2 - 0.126Z^2$ ) in the subdominant term  $-0.5Z^2$ , i.e. it is large- $N$  asymptotically exact almost to the first degree (AE1).

#### 4. Numerical results and discussion

In this section, the developed functional and the presented approach are implemented for verification. First we compare the electron density of the proposed model with

its large- $Z$  limit. Then, we compare the kinetic energy of the model with the known Thomas–Fermi gradient expansion. Finally, we perform computational experiments to show that the proposed functional gives a significant improvement to the standard Thomas-Fermi approximation when applied to atoms. An improvement by about an order of magnitude is achieved.

#### 4.1. Electron density in the limit of large $Z$

In this subsection, we analyze the behavior of electron density of the proposed model for different values of the nuclear charge  $Z$  and compare it to the one acquired using the Thomas-Fermi formalism. We start with some remarks regarding the density of the model. In Section 2, the electron density is derived from the wavefunction as a sum of  $n_{\max}(n_{\max} + 1)/2$  terms given by (9). For large  $Z$ , the number of terms grows to infinity. Here, we use an alternative approach based on Thomas–Fermi formalism to derive the limit of the density for large values of  $Z$  in a more explicit way. Without an inter-particle interaction, the Thomas–Fermi equation relating the electron density and the potential takes especially simple form[34],

$$\rho = \frac{1}{3\pi^2} [2(\mu - V)]^{3/2}, \quad (19)$$

where  $\mu$  can be determined from the equation (assuming spherical symmetry)

$$\int_0^{r_m} 4\pi r^2 \rho(r) dr = N. \quad (20)$$

In (20),  $N$  is the number of electrons and  $r_m$  is the Thomas–Fermi radius of the atom, or a turning point in the potential  $V$ , that is determined from the equation

$$V(r_m) = \mu. \quad (21)$$

For the Coulomb potential  $V = -Z/r$ , we obtain

$$r_m = -\frac{Z}{\mu} \quad (22)$$

From equations (20) and (22), it can be shown that

$$r_m = Z^{-1} (3\sqrt{2}N)^{2/3}. \quad (23)$$

As we consider the case of a neutral atom ( $N = Z$ ), then, the dependence on  $Z$  can be eliminated by introducing scaled radius and scaled electron density

$$\hat{r} = Z^{1/3}r, \quad (24)$$

$$\hat{\rho} = \rho/Z^2, \quad (25)$$

so that now (19) can be rewritten as

$$\hat{\rho} = \frac{2\sqrt{2}}{3\pi^2} \left( \frac{1}{\hat{r}} - 18^{-1/3} \right)^{3/2} \quad (26)$$

if  $\hat{r} < \hat{r}_m$  and zero otherwise, where the scaled turning point is

$$\hat{r}_m = 18^{1/3}. \quad (27)$$

Figure 1 shows the scaled densities  $\hat{\rho}(\hat{r}) = Z^{-2}\tilde{\rho}(Z^{-1/3}\hat{r})$ , where  $\tilde{\rho}$  is given by (8) for increasing numbers of electronic shells,  $n_{\max} = 1, 2, 3, 5$ , calculated using (8) together with the limiting case given by (26). It is clear that the deviation from the Thomas–Fermi limit,  $\hat{\rho} - \hat{\rho}_{\text{TF}}$  is an oscillating function having exactly  $n_{\max}$  local maxima, see the insert in Figure 1. The amplitude of the oscillations decreases as  $Z$  increases. These oscillation effects are related to the shell structure, with maxima corresponding to the filled shells. Clearly, the Thomas–Fermi model describes only the averaged physical quantities, and so it requires a special generalization [35] to treat such spatial irregularities. In the recent paper of Burke and coworkers [5], their approximation improves the accuracy everywhere including the turning points and reproduces the oscillations.

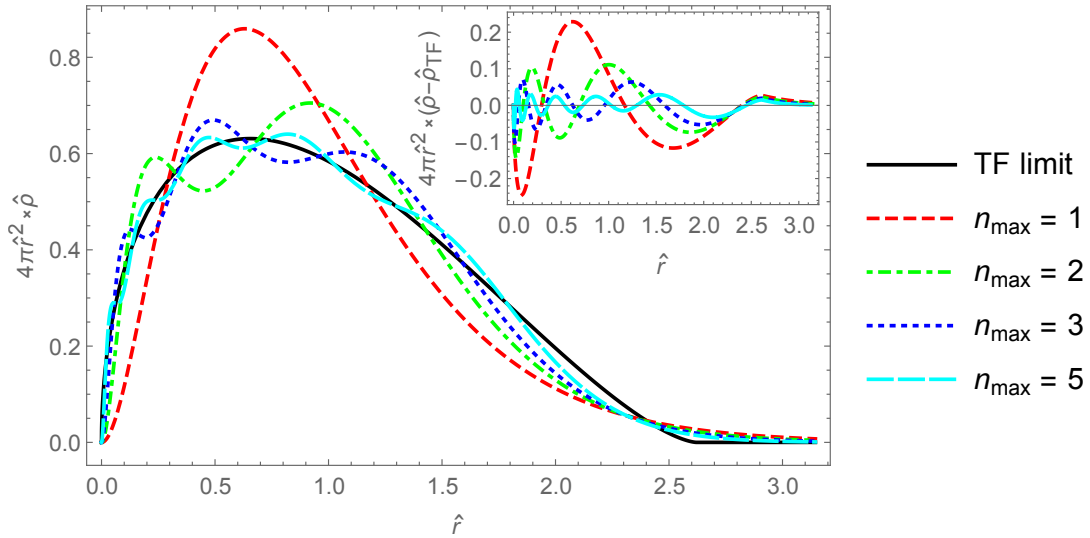


Figure 1. Scaled densities for increasing values of  $Z$  and the Thomas–Fermi limit at  $Z \rightarrow \infty$ .

#### 4.2. Thomas–Fermi vs. gradient expansion for the exactly solvable model

The leading term of the gradient expansion for the kinetic energy is just the Thomas–Fermi energy given by equations (4) and (5). We use the notation  $T_0 = T^{(0)} = T_{\text{TF}}[\rho]$ . The second order term is defined through Weizsäcker correction  $T_{\text{W}}$  as

$$T_2 = \frac{1}{9}T_{\text{W}}, \quad T_{\text{W}} = 4\pi \int_{r=0}^{\infty} r^2 \frac{(\rho')^2}{8\rho} dr, \quad (28)$$

and the second order approximation is  $T^{(2)} = T_0 + T_2$ , where spherical symmetry is assumed. In fourth order of the gradient expansion, we have

$$T_4 = 4\pi \int_{r=0}^{\infty} r^2 \tau_4(r) dr, \quad T^{(4)} = T_0 + T_2 + T_4, \quad (29)$$

where

$$\tau_4(\vec{r}) = \frac{(3\pi^2)^{-2/3}}{540} \rho^{1/3} \left[ \frac{(2\rho'_r + \rho'')^2}{\rho^2} - \frac{9(2\rho'_r + \rho'')(\rho')^2}{8\rho^3} + \frac{1}{3} \frac{(\rho')^4}{\rho^4} \right]. \quad (30)$$



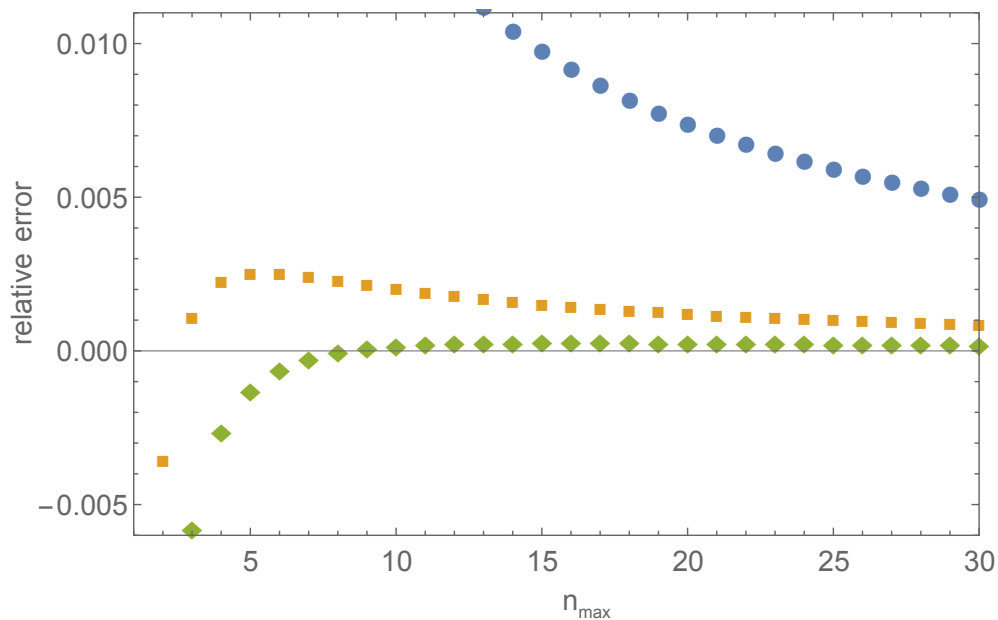


Figure 2. Relative error of  $T_s$  for Thomas–Fermi ( $T^{(0)} = T_{\text{TF}}[\rho]$ , marked by circles), second ( $T^{(2)} = T_0 + T_2$ , square markers), and fourth order approximation ( $T^{(4)} = T_0 + T_2 + T_4$ , diamond markers) in gradient expansion. The relative errors are defined as  $(T_s - T^{(n)})/T_s$  where  $n = 0, 2, 4$ .

There were several studies of the gradient expansion for atoms[36, 37, 38]. The Thomas–Fermi method always underestimates the energy, and the accuracy slowly improves with increase of number of electrons, remaining on the level of few percent even for heavy atoms. The first correction of the gradient expansion always improves the accuracy, but applying the fourth order correction typically makes the results worse. The analysis of trends of the gradient expansion for atoms remains somehow inconclusive, because of very slow asymptotical behavior (typically as  $\sim Z^{-1/3}$ ) and because of shell effects (oscillations of density).

For the exactly solvable model, relative error as a function of the number of shells is shown on Figure 2, where the non-interacting kinetic energy  $T_s = \tilde{T}^{(Z)}$  is defined by (3), the Thomas–Fermi energy is defined by (4), and the gradient expansion is defined by equations (28) and (29). For the exactly solvable model, the relative error to  $T_s$  is shown on Figure 2 as a function of the number of shells. The values for  $T^{(0)}, T^{(2)}, T^{(4)}$  are calculated by substituting  $\tilde{\rho}$  into the corresponding equations. For large  $Z$ , the second order correction clearly improves the accuracy by a factor of 6, and including the fourth order correction improves the accuracy by an additional factor of 3. However, this trend is visible only for large  $n_{\max}$ , starting from  $n_{\max} \approx 10$  corresponding to unrealistic  $Z > 1000$ . It explains the fact that the fourth order correction for atoms improves the accuracy only for very heavy atoms.

Asymptotic behavior of accuracy at large  $Z$  is shown on Figure 3. The asymptotical expansion for the Thomas–Fermi energy has been presented in the previous section and has the form given in (17). In a similar way the terms of gradient expansion were

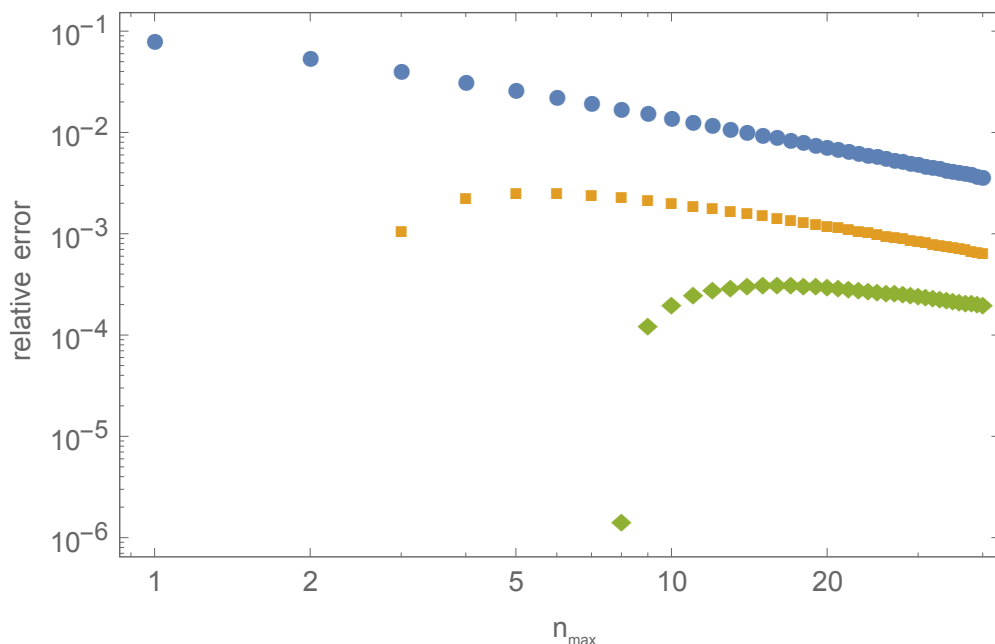


Figure 3. Relative error in logarithmic scale for very large number of electronic shells for Thomas–Fermi approximation and the approximations including second and fourth order terms of gradient expansion. The markers are the same as on Figure 2. Since the asymptotic dependence is linear with the tangent (-1) in all cases, it shows that the relative errors at large  $Z$  are proportional to  $Z^{-1/3}$  in all cases.

determined numerically and have the following form

$$T_2 \sim 0.10942Z^2 + 0.045Z^{5/3} + \dots \quad (31)$$

Notice that the expansion in (31) starts from the term  $Z^2$ , i.e. the coefficient of the leading term  $\sim Z^{7/3}$  is zero. This statement can be proven rigorously too, by calculating the integral (28) using the same semiclassical approximation. A similar expansion (starting from the term  $\sim Z^2$ ) was found for the fourth-order correction to the kinetic energy,

$$T_4 \sim 0.015052Z^2 + 0.0078Z^{5/3} + \dots \quad (32)$$

These calculation show that the leading term of the exact energy,  $1.447Z^{7/3}$ , is absorbed by the leading term of Thomas–Fermi energy, and the subdominant term of the exact energy,  $\sim -0.5Z^2$ , can be accurately resummed by selecting the corresponding terms in the series  $T^{(4)} = T_{\text{TF}}[\rho] + T_2 + T_4$ .

### 4.3. Calculations for atoms

In this subsection we discuss the effectiveness of the functional given by (10) for calculating the kinetic energy of atoms. This is done by comparing the results with the values of  $T_s$  taken from the paper [28]. To show explicitly the advantages of the proposed functional we compare the kinetic energies calculated using the new approach with the Thomas–Fermi approximation and the standard functionals based on gradient

Table 1. Comparison of Thomas–Fermi kinetic energy with the improved Thomas–Fermi, for noble and alkali-earth atoms. Results of the second and fourth order gradient expansion are included too. The relative error is calculated in comparison with the non-interacting kinetic energies  $T_s$  taken from the paper [28].

$Z$	Atom	Relative error, %			
		$T_{\text{TF}}[\rho]$	$T_{\text{TF}}[\rho] + T_2$	$T_{\text{TF}}[\rho] + T_2 + T_4$	$T_{\text{TF}}[\rho] + \delta\tilde{T}^{(Z)}$
2	He	-11	0.59	3.5	0.95
4	Be	-9.9	0.51	2.8	0.21
10	Ne	-8.4	-0.56	0.93	0.28
12	Mg	-7.8	-0.44	0.92	0.43
18	Ar	-7.0	-0.49	0.67	0.36
20	Ca	-6.9	-0.59	1.2	0.24
36	Kr	-5.8	0.81	0.17	0.11
38	Sr	-5.7	-0.67	0.17	0.12
54	Xe	-5.2	0.64	0.063	0.075
56	Ba	-5.1	-0.69	0.034	0.051
86	Rn	-4.6	0.47	-0.043	-0.063
88	Ra	-4.5	-0.64	-0.045	0.076

expansion. The Thomas–Fermi energies along with the second and fourth order gradient corrections are taken from the same source [28]. The correction  $\delta\tilde{T}^{(Z)}$  was calculated by (11) in case of closed shell atoms and by (12) in partially filled cases. The results are shown in Table 1.

We found that including the correction  $\delta\tilde{T}^{(Z)}$  increases the accuracy of Thomas–Fermi approximation by more than ten times. The results almost always give the upper bound for the kinetic energy.

Overall, the same table shows that the proposed method is competitive with functionals based on the second and fourth order gradient expansions in respect to the precision. It manages to give a lower error than the second/fourth order gradient expansion for all tested atoms with the nuclear charge less than 50 except helium. From the tabulated results, it is noticeable that the new functional is more robust than the other functionals in the sense that it performs well both for small and for large atoms.

## 5. Conclusion

In this paper we have presented a non-gradient-based correction to the Thomas–Fermi functional for atoms. The presented approach is general and should be extendable for molecules, if a suitable solvable model is used. The method uses an auxiliary system of noninteracting electrons that is in many respects similar to the atomic system with

the same number of electrons. It results in simplifying the calculation considerably comparing to the one based on the gradient expansion. The obtained accuracy is improved by at least an order of magnitude in comparison to the Thomas–Fermi model. Our numerical test also shows that the proposed method manages to achieve similar or slightly better precision than the standard gradient based functionals. As for the density, our presented approach allows the characteristic shell oscillations.

This type of approach can potentially be extended to systems other than atoms. One example is the modeling on  $N$ -electron quantum dots, where we could consider another solvable model, of  $N$  non-interacting particles bound in a harmonic potential. Our initial test on this problem has given promising results.

## 6. References

- [1] Hohenberg P and Kohn W 1964 *Phys. Rev. B* **136** B864
- [2] Burke K 2012 *J. Chem. Phys.* **136** 150901
- [3] Xia J, Huang C, Shin I and Carter E A 2012 *J. Chem. Phys.* **136** 084102
- [4] March N 2010 *Phys. Chem. Liq.* **48** 141–155
- [5] Ribeiro R F, Lee D, Cangi A, Elliott P and Burke K 2015 *Phys. Rev. Lett.* **114** 050401
- [6] Kohn W and Sham L J 1965 *Phys. Rev.* **140** 1133
- [7] Becke A D 2014 *J. Chem. Phys.* **140** 18A301
- [8] Mendoza M, Succi S and Herrmann H 2014 *Phys. Rev. Lett.* **113** 096402
- [9] Wang Y A and Carter E A 2000 Orbital-free kinetic-energy density functional theory *Theoretical Methods in Condensed Phase Chemistry* ed Schwartz S D (NY: Kluwer Academic) pp 117–184  
Progress in Theoretical Physics and Chemistry, Vol. 5
- [10] Karasiov V V, Chakraborty D and Trickey S B 2014 Progress on New Approaches to Old Ideas: Orbital-Free Density Functionals *Many-Electron Approaches in Physics, Chemistry, and Mathematics. A Multidisciplinary View* ed Bach V and Site L D (Heidelberg: Springer) pp 113–134  
Mathematical Physics Studies
- [11] Ke Y, Libisch F, Xia J, Wang L W and Carter E A 2013 *Phys. Rev. Lett.* **111** 066402
- [12] Wesolowski T A and Wang Y A (eds) 2013 *Recent Progress in Orbital-free Density Functional Theory (Recent Advances in Computational Chemistry: Volume 6)* (World Scientific Publishing Company)
- [13] Karasiev V V and Trickey S B 2012 *Comput. Phys. Commun.* **183** 2519–2527
- [14] Thomas L H 1927 *Math. Proc. Cambridge Philos. Soc.* **23** 542–548
- [15] Fermi E 1927 *Rend. Accad. Naz. Lincei* **6** 32
- [16] Alonso J A and Girifalco L A 1978 *Chem. Phys. Lett.* **53** 190–191
- [17] Ayers P and Liu S 2007 *Phys. Rev. A* **75** 022514
- [18] Borisov Y A and Surikov V V 1981 *J. Struct. Chem.* **22** 280–282
- [19] Wang Y A, Govind N and Carter E A 1999 *Phys. Rev. B* **60** 16350
- [20] Ho G S, Ligneres V L and Carter E A 2008 *Phys. Rev. B* **78** 8
- [21] Wang Y A, Govind N and Carter E A 1998 *Phys. Rev. B* **58** 13465–13471
- [22] Huang C and Carter E A 2012 *Phys. Rev. B* **85** 045126
- [23] White T, Richardson S, Crowley B, Pattison L, Harris J and Gregori G 2013 *Phys. Rev. Lett.* **111** 175002
- [24] Sjostrom T and Daligault J 2013 *Phys. Rev. B* **88** 195103
- [25] Kais S, Herschbach D R, Handy N C, Murray C W and Laming G J 1993 *J. Chem. Phys.* **99** 417–425
- [26] Kirzhnits A D and Shpatakovskaya G V 1995 *Sov. Phys. JETP* **81** 679
- [27] Englert B G and Schwinger J 1985 *Phys. Rev. A* **32** 47

- [28] Lee D, Constantin L A, Perdew J P and Burke K 2009 *J. Chem. Phys.* **130** 034107
- [29] Scott J M C 1952 *Philos. Mag.* **43** 859–867
- [30] Schwinger J 1980 *Phys. Rev. A* **22** 1827
- [31] Bender C M and Orszag S A 1980 *Advanced mathematical methods for scientists and engineers* (McGraw-Hill Book Company)
- [32] Elliott P, Lee D, Cangi A and Burke K 2008 *Phys. Rev. Lett.* **100** 256406
- [33] Cangi A, Lee D, Elliott P and Burke K 2010 *Phys. Rev. B* **81** 14
- [34] Murphy D R 1981 *Phys. Rev. A* **24** 1682–1688
- [35] Kirzhnits A D and Shpatakovskaya G V 1972 *Sov. Phys. JETP* **35** 1088
- [36] Murphy D R and Wang W P 1980 *J. Chem. Phys.* **72** 429–433
- [37] Wang W P 1980 *J. Chem. Phys.* **73** 416–418
- [38] Wang W P, Parr R G, Murphy D R and Henderson G A 1976 *Chem. Phys. Lett.* **43** 409–412