Study of Some Simple Approximations to the Non-Interacting Kinetic Energy Functional

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Within the framework of density functional theory, a study of approximations to the enhancement factor of the non-interacting kinetic energy functional $T_s[\rho]$ has been presented. For this purpose, the model of Liu and Parr (Liu and Parr, Phys Rev A 1997, 55, 1792) based on a series expansion of $T_s[\rho]$ involving powers of the density was employed. Application to 34 atoms, at the Hartree–Fock level has shown that the enhancement factors present peaks that are in excellent agreement with those of the exact ones and give an accurate description of the shell structure of these atoms. The application of Z-dependent expansions to represent some of the terms of these approximations for neutral atoms and for positive and negative ions, which allows $T_s[\rho]$ to be cast in a very simple form, is also explored. Indications are given as to how these functionals may be applied to molecules and clusters. © 2016 Wiley Periodicals, Inc.

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Introduction

One of the challenging problems in density functional theory (DFT) is how to express the non-interacting kinetic energy of a quantum mechanical multibody system as a functional of the density.[1–10] Having such a functional is, of course, crucial for the implementation of the orbital-free version of DFT.[11] In the Kohn–Sham formalism[12] the non-interacting kinetic energy is written as a functional of the N orbitals yielding N equations of which the solution becomes more and more difficult as N increases. For this reason, the use of a kinetic energy functional which depends only on the density is an alternative to reduce this problem. The use of orbital-free functional for the kinetic energy certainly lowers the computational cost and permits DFT to be applied to large many-particle systems and to solve a single equation for the density, regardless of the value of N.

To find adequate density functionals for the kinetic energy is difficult, due to the virial theorem, the kinetic energy is in the same magnitude as the total energy. Hence, this functional must have the same level of accuracy as the total energy (in contrast with the exchange and correlation functionals which comprise a small fraction of the total energy only). Since the work of Thomas[13] and Fermi[14] along with many decades of effort, (for reviews see Refs. 6,7,11,15) there has still been no satisfactory approximation of this functional.[16–24] A suitable form for the non-interactive kinetic energy functional can be derived from general principles; see for example, the derivation given in the context of the local-scaling transformation.[25–27]

This exact form corresponds to

$$T_s[\rho]=\frac{1}{8}\int d\vec{r}\frac{|\nabla\rho(\vec{r})|^2}{\rho(\vec{r})}+\frac{1}{2}\int d\vec{r}\rho^{5/3}(\vec{r})A_N[\rho(\vec{r});\vec{r}], \qquad (1)$$

where the first term is the Weizsäcker term[28] and the second contains the Thomas–Fermi function $\rho^{5/3}(\vec{r})$ times the enhancement factor $A_N[\rho(\vec{r});\vec{r}]$ where $\rho(\vec{r})$ is the one-electron density of the system. In this way, the challenge in modeling $T_s[\rho]$ is shifted to that of finding adequate approximations for the enhancement factor $A_N[\rho(\vec{r});\vec{r}]$, which is considered as a functional of ρ.

Among the alternatives for the non-interactive kinetic energy functionals[6,7] produced over years, this article focuses on the one introduced by Liu and Parr,[1] which expands it as a power series of the density $\rho(\vec{r})$. It generates an explicit expression for the enhancement factor as a functional of the one-electron density. A variational calculation based on this expansion has recently been given by Kristyan.[29,30]

In this article we analyze the representation of the enhancement factor via the Liu–Parr series expansion and compare it with the orbital formalism. This will be tested on atoms of the first, second and third row of the periodic table. In addition, we explore the possibility of simplifying the Liu–Parr functional by introducing Z-dependent expressions for some integrals containing $\rho(\vec{r})$. Finally, bearing in mind that the mathematical

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framework is presented rather concisely in the original Liu and Parr's article,[1] we include a more extended demonstration of their second theorem in the Appendix. We expect that this may contribute to a better understanding of the Liu and Parr approach and foster its applications.

The Enhancement Factor

Some properties of the enhancement factor

The Weizsacker term in eq. (1) is local[31] so the non-local part of the kinetic energy functional must be embodied in the non-Weizsacker term, that is, in the enhancement factor. As was pointed out by Ludeña,[32] the non-Weizsacker term contains the derivative of the correlation factor for the Fermi hole (see eq. [38] of Ref. 32). Hence, the enhancement factor contains terms responsible for localizing electrons with the same spin in different regions of space giving rise to shell structure. This phenomenon stems from the non-locality of the Fermi hole which may be described in terms of charge depletions followed by charge accumulations producing polarizations at different distances.[33]

This non-locality of the kinetic energy functional is well represented by orbital expansions

$$T_s\left[\{\phi_i\}_{i=1}^N\right]=\frac{1}{2}\sum_{i=1}^{N}\int d\vec{r}\,\nabla\phi_i^*(\vec{r})\nabla\phi_i(\vec{r}) \tag{2}$$

$$=-\frac{1}{2}\sum_{i=1}^{N}\int d\vec{r}\,\phi_i^*(\vec{r})\nabla^2\phi_i(\vec{r})+\frac{1}{4}\int d\vec{r}\,\nabla^2\rho(\vec{r}) \tag{3}$$

given in terms of gradients in eq. (2) or of Laplacians in eq. (3). Equations (2) and (3) are connected by integration by parts where the surface term goes to zero. Combining eqs. (1) and the gradient representation of eq. (2) yields the following exact orbital representation for the enhancement factor:

$$A_N[\rho(\vec{r}),\{\phi_i\};\vec{r}]=\frac{2}{\rho^{5/3}(\vec{r})}\left(\frac{1}{2}\sum_{i=1}^{N}\nabla\phi_i^*(\vec{r})\nabla\phi_i(\vec{r})-\frac{1}{8}\frac{|\nabla\rho(\vec{r})|^2}{\rho(\vec{r})}\right). \tag{4}$$

Obviously, when modeling the enhancement factor in terms of a series of the one-electron density one would like to reproduce the same characteristics as in orbital representation. Thus, in addition to yielding a desired accuracy for the non-interacting kinetic energy, the approximate enhancement factor should satisfy the condition[34]:

$$A_N[\rho(\vec{r});\vec{r}]\geq 0 \quad \text{for all} \quad \vec{r} \tag{5}$$

and should also be capable of generating shell structure. In this respect, the $A_N[\rho(\vec{r}),\{\phi_i\};\vec{r}]$ as given by eq. (4) differs by a constant only from the function $\chi(\vec{r})=D(\vec{r})/D_h(\vec{r})$ introduced in the definition of the electron localization function (ELF, Ref. 35). Moreover, bearing in mind that ELF and similar functions have been successfully related to shell structure of atoms and molecules,[36–44] it is clear that any proposed model for the enhancement factor must also agree with this requirement.

A popular generalized gradient approximation (GGA) for the kinetic energy takes the form[45]

$$T_s[\rho]=T_W[\rho]+\int d\vec{r}\,\rho^{5/3}(\vec{r})F[s(\vec{r})], \tag{6}$$

where $T_W[\rho]$ is the Weiszäcker term[28], and $F[s(\vec{r})]$ is the Pauli GGA enhancement factor[15] containing

$$s(\vec{r})=\frac{|\nabla\rho(\vec{r})|}{2(3\pi^2)^{1/3}\rho^{4/3}(\vec{r})}. \tag{7}$$

The variable $s(\vec{r})$ is the reduced density gradient describing the rate of variation of the one-electron density. Large values of $s(\vec{r})$ correspond to fast variations on the one-electron density and vice versa.[46] The above approximation of the Pauli term containing GGA factor $F[s(\vec{r})]$ is the basis of the conjoint gradient expansion of the kinetic energy introduced by Lee, Lee, and Parr.[47]

A full review of the functionals of the kinetic energy expressed in terms of the one-electron density and its derivatives is given by Wesolowski.[6] For some more recent representations of the enhancement factor of the non-interacting kinetic energy as a functional of ρ and its derivatives $\nabla\rho$, $\nabla^2\rho$, etc., see Refs. 18,20–22,48–50. However, in the present work we examine a different approximation to the enhancement factor in eq. (1), namely, a representation of $A_N[\rho(\vec{r});\vec{r}]$ as a local functional of the one-electron density.[1]

An approximate representation of the enhancement factor

We adopt the Liu and Parr[1] expansion of the non-interacting kinetic energy functional given in terms of homogeneous functionals of the one-electron density:

$$T_{LP97}[\rho]=\sum_{j=1}^{n}C_j\left[\int d\vec{r}\,\rho^{[1+(2/3j)]}(\vec{r})\right]^j, \tag{8}$$

where in $T_{LP97}[\rho]$ the index LP97 stands for Liu and Parr and the year of publication. Following the original work, we truncate eq. (8) after $j=3$ as

$$T_{LP97}[\rho]=C_{T_1}\int d\vec{r}\,\rho^{5/3}(\vec{r})+C_{T_2}\left[\int d\vec{r}\,\rho^{4/3}(\vec{r})\right]^2+C_{T_3}\left[\int d\vec{r}\,\rho^{11/9}(\vec{r})\right]^3. \tag{9}$$

Liu and Parr[1] have determined the coefficients C_{T_j}'s by least-square fitting and setting $\rho=\rho_{HF}$, the Hartree–Fock density: $C_{T_1}=3.26422$, $C_{T_2}=-0.02631$, and $C_{T_3}=0.000498$ (a typographical error in the values of the coefficients in the original article, has

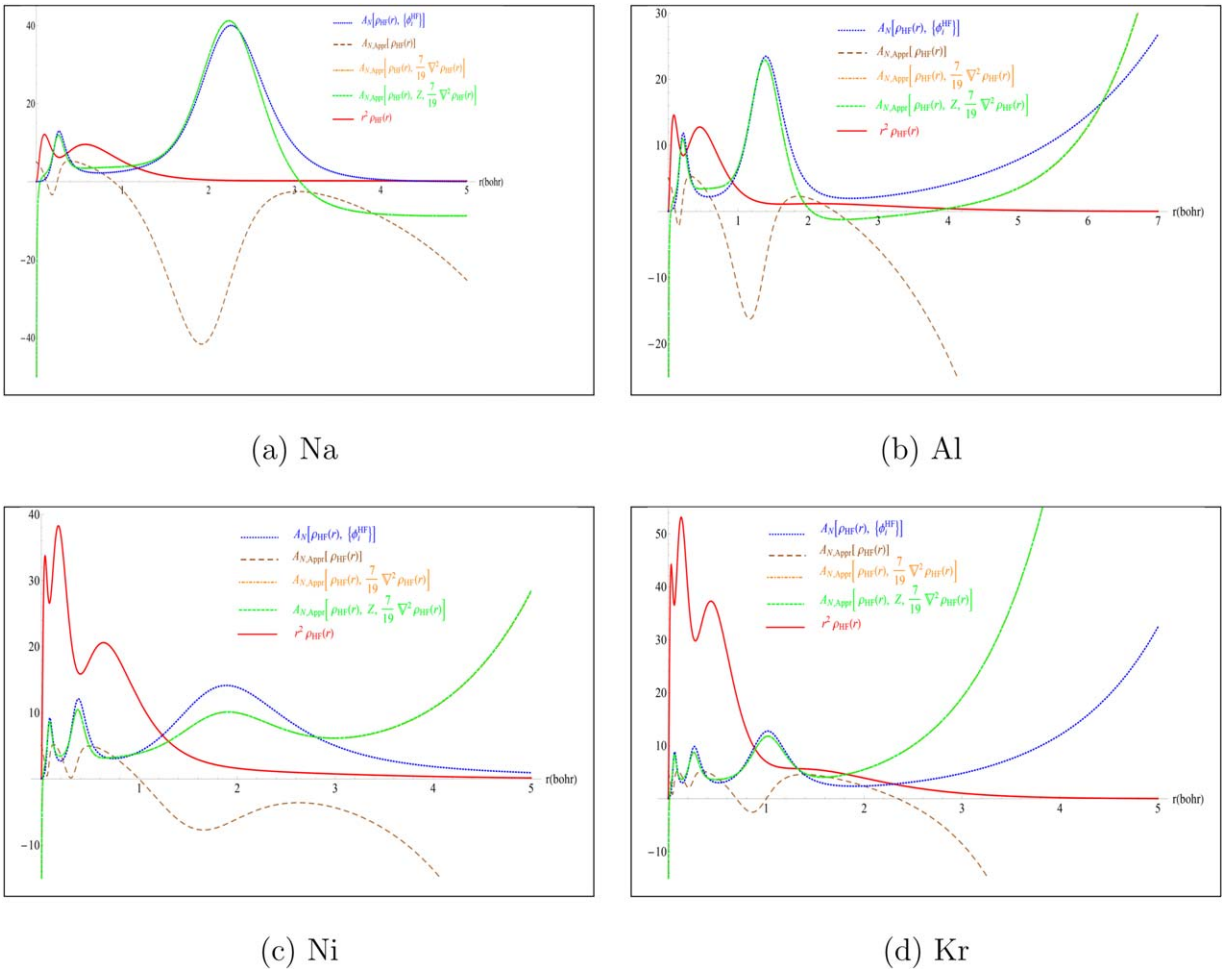


Figure 1. Kohn–Sham based enhancement factor (dotted blue), approximate enhancement factor in eq. (12) (dashed brown) with $\lambda = 0$, with $\lambda = \frac{7}{19}$ (dotted green), approximate enhancement factor with 9th-degree Z polynomial and $\lambda = \frac{7}{19}$ (dotted orange) in eq. (17), and radial distribution function of the density (full red) for the atoms: 1 (a) Na, 1 (b) Al, 1 (c) Ni, 1 (d) Kr.

been corrected). This expansion provides a very simple way to express the kinetic energy as a local functional of the density.

In this context, an approximate expression for $A_N[\rho(\vec{r});\vec{r}]$ as a functional of the one-electron density can be found from eqs. (9) and (1):

$$A_{N,appr}[\rho] = 2(C_{T_1} + C_{T_2}\rho^{-1/3}(\vec{r})\int d\vec{r}\rho^{4/3}(\vec{r}) + C_{T_3}\rho^{-4/9}(\vec{r})\left[\int d\vec{r}\rho^{11/9}(\vec{r})\right]^2 - \frac{1}{8}\frac{|\nabla\rho(\vec{r})|^2}{\rho^{8/3}(\vec{r})}). \quad (10)$$

Local corrections to the enhancement factor

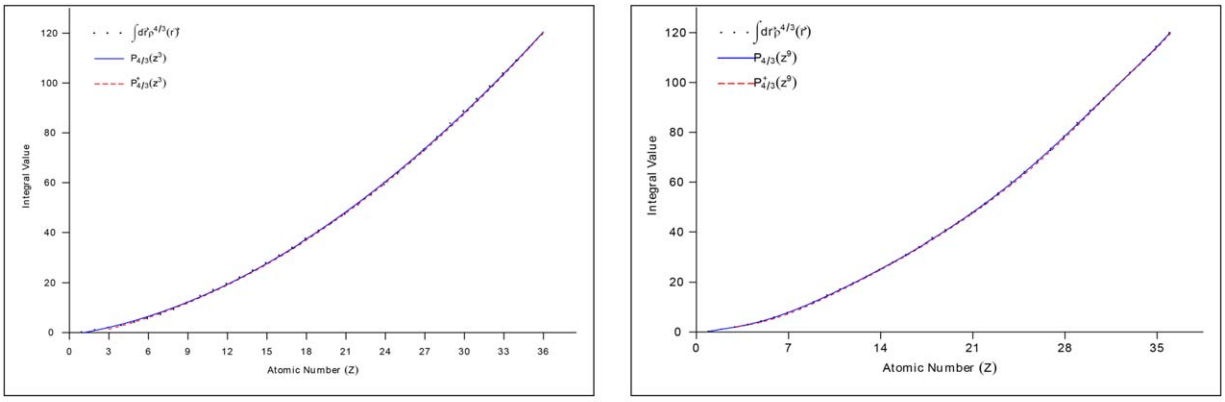
Using eqs. (4) and (10), the graphs for Kohn–Sham based versus current approximate enhancement factors are plotted in Figures 1a–1d for the Na, Al, Ni, and Kr atoms. Calculations for these atoms do not include relativistic corrections. One can see that the Kohn–Sham based enhancement factor is a positive function, in contrast to the approximate one which shows negative regions violating eq. (5).[51]

Due to the fact that the kinetic energy is not uniquely approximated in DFT and, as illustrated by eqs. (2) and (3), there are expressions that yield different kinetic energy locally in spite of the fact that they integrate to the same value. It is possible to modify the non-positive approximate enhancement factor by adding terms that do not alter the integral value of the non-interacting kinetic energy, but make contributions locally to the enhancement factor to become positive. This is an acceptable procedure in view of the non-unique nature of the definition of the local kinetic energy expressions.[52–54]

In this way, we have added a term to the non-interacting kinetic energy expression using the Laplacian of the density times an arbitrary real valued constant λ as

$$T_s[\rho] = C_{T_1}\int d\vec{r}\rho^{5/3}(\vec{r}) + C_{T_2}\left[\int d\vec{r}\rho^{4/3}(\vec{r})\right]^2 + C_{T_3}\left[\int d\vec{r}\rho^{11/9}(\vec{r})\right]^3 + \lambda\int d\vec{r}\nabla^2\rho(\vec{r}). \quad (11)$$

This extends eq. (10) for a new approximate enhancement factor:



(a) (b)

Figure 2. Interpolation curves for the values of the $\int d\vec{r}\,\rho^{4/3}(\vec{r})$: a) a 3rd degree polynomial $P_{4/3}(Z^3)$ (full blue) for 36 atoms and a 3rd degree polynomial $P^{+}_{4/3}(Z^3)$ (dashed red) for 34 positive ions, and b) a 9th degree polynomial $P_{4/3}(Z^9)$ (full blue) for 36 atoms and a 9th degree polynomial $P^{+}_{4/3}(Z^9)$ (dashed red) for 34 positive ions.

$$A_{\mathrm{N,appr}}[\rho] = 2\Big(C_{\mathrm{T}_1} + C_{\mathrm{T}_2}\rho^{-1/3}(\vec{r})\int d\vec{r}\,\rho^{4/3}(\vec{r}) + C_{\mathrm{T}_3}\rho^{-4/9}(\vec{r})\Big[\int d\vec{r}\,\rho^{11/9}(\vec{r})\Big]^2 + \lambda\frac{\nabla^2\rho(\vec{r})}{\rho(\vec{r})^{5/3}} - \frac{1}{8}\frac{|\nabla\rho(\vec{r})|^2}{\rho^{8/3}(\vec{r})}\Big). \tag{12}$$

This additional term does not alter the integral value of the kinetic energy because the integral of the Laplacian of the one-electron density is zero.[55,56] The improvement from this additional term in eq. (12) for the Na, Al, Ni, and Kr atoms are shown in Figure 1.

We note that the new λ-dependent enhancement factor in eq. (12) closely reproduces the behavior of the Kohn–Sham based ones in the regions where the highest peaks are located. In all cases the agreement is quite good both for the first, and second shells. For Ni, the approximate enhancement factor is slightly below the Kohn–Sham based one in the region corresponding to the third shell. For Kr, however, the agreement is good for all shells although the tail is steeper for large $\vec{r}$.

As seen, the asymptotic behavior of the λ-dependent enhancement factor in the region where $r \to 0$ shows negative values in all cases studied. However, this behavior in A_{N} does not necessarily produce a problem for interatomic forces, as these forces are calculated by using the orbital-free analogue of the Hellmann–Feynman theorem (see eqs. (21–A2) in Ref. 57), for example, in molecular dynamics. According to these equations, the forces are defined by the one-electron density and the external potential, and thus, they do not depend on the local behavior of the kinetic energy density. On the other hand, in the region where r becomes large, that is, outside the atomic shells, the behavior of the approximate enhancement factor follows the trend of the exact ones, for example, in the cases of Na, Al, and Kr, although in the latter, the approximate enhancement factor grows more pronounced than the Kohn–Sham based one. In the case of Ni, however, one can observe a divergence in the behavior of the tail of the approximate enhancement factor. We mention that divergences in the tail region are not relevant and do not contribute to the kinetic energy value due to the fact that these divergences are suppressed by the exponentially decaying one-electron density tail.

Further Approximation of the Enhancement Factor with *Z*-Dependent Polynomials

The enhancement factor $A_{\mathrm{N,appr}}$ in eq. (10), depends on two integrals, $\int d\vec{r}\,\rho^{4/3}(\vec{r})$ and $\int d\vec{r}\,\rho^{11/9}(\vec{r})$. The values of these integrals, evaluated with $\rho = \rho_{\mathrm{HF}}$, are functions of the atomic number Z. We have selected to display this Z-dependent behavior in Figures 2 and 3. In these figures, the dots on the blue lines represent the values of the 4/3 and 11/9 integrals for the neutral atoms, respectively. These values are interpolated using the polynomial expansions: $\int d\vec{r}\,\rho^{4/3}(\vec{r}) \approx P_{4/3}(Z^n)$ and $\int d\vec{r}\,\rho^{11/9}(\vec{r}) \approx P_{11/9}(Z^n)$ where n is the degree of the Z polynomial. The blue lines in Figures 2a and 3a represent the approximations given by the third-degree polynomial Z^3. Similarly, the blue lines in Figures 2b and 3b correspond to the Z^9 polynomial approximation. The least square fit of these interpolation polynomials has yielded

$$P_{4/3}(Z^3) = -0.9691803682 + 0.7854208699Z + 0.0776145852Z^2 - 0.0001581219Z^3, \tag{13}$$

$$P_{4/3}(Z^9) = -1.0960551055 + 1.8518814624Z - 0.5991519550Z^2 + 0.1549675741Z^3 - 0.0180687925Z^4 + 0.0012312619Z^5 - 0.0000517284Z^6 + 0.0000013252Z^7 - 0.0000000190Z^8 + 0.0000000001Z^9 \tag{14}$$

$$P_{11/9}(Z^3) = -0.7540383360 + 0.8813316184Z + 0.0373453207Z^2 - 0.0001408691Z^3, \tag{15}$$

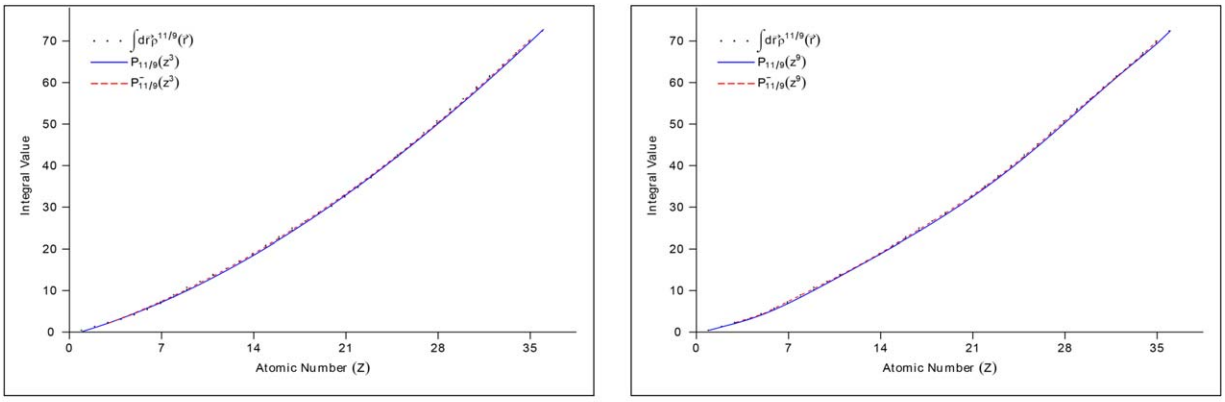


Figure 3. Interpolation curves for the values of the $\int d\vec{r}\,\rho^{11/9}(\vec{r})$: a) a 3rd degree polynomial $P_{11/9}(Z^3)$ (full blue) for 36 atoms and a 3rd degree polynomial $P^{-}_{11/9}(Z^3)$ (dashed red) for 27 negative ions, and b) a 9th degree polynomial $P_{11/9}(Z^9)$ (full blue) for 36 atoms and a 9th degree polynomial $P^{-}_{11/9}(Z^9)$ (dashed red) for 27 negative ions.

$$\begin{aligned} P_{11/9}(Z^9) = &-0.8077949490 + 1.6355990588Z \\ &-0.4837629283Z^2 + 0.1255298989Z^3 \\ &-0.0150967704Z^4 + 0.0010441963Z^5 \\ &-0.0000439707Z^6 + 0.0000011196Z^7 \\ &-0.0000000159Z^8 + 0.0000000001Z^9. \end{aligned} \tag{16}$$

Thus, the enhancement factor takes the following form (where n is the degree of the Z polynomial) for atoms

$$\begin{aligned} \frac{1}{2}A_{Z^n,\mathrm{appr}}[\rho,Z] = &C_{T_1} + C_{T_2}\rho^{-1/3}(\vec{r})P_{4/3}(Z^n) \\ &+ C_{T_3}\rho^{-4/9}(\vec{r})P_{11/9}(Z^n)^2 \\ &+ \lambda\frac{\nabla^2\rho(\vec{r})}{\rho(\vec{r})^{5/3}} \\ &- \frac{1}{8}\frac{|\nabla\rho(\vec{r})|^2}{\rho^{8/3}(\vec{r})} \end{aligned} \tag{17}$$

Also, this leads to the following approximation for the non-interacting atomic kinetic energy functional

$$\begin{aligned} T_{\mathrm{LP97}+Z^n}[\rho,Z] = &C_{T_1}\int d\vec{r}\rho^{5/3}(\vec{r}) \\ &+ C_{T_2}\int d\vec{r}\rho^{4/3}(\vec{r})P_{4/3}(Z^n) \\ &+ C_{T_3}\int d\vec{r}\rho^{11/9}(\vec{r})P_{11/9}(Z^n)^2 \end{aligned} \tag{18}$$

Application to neutral atoms

The absolute relative percentage errors of the kinetic energy values for neutral atoms are presented in Figure 4. These errors were calculated with respect to the T_{HF} values reported by Clementi and Roetti,[58] and are defined by $\Delta\epsilon(T_i) \equiv |(T_i - T_{HF})/T_{HF}| \times 100$. The lines in Figure 4 correspond to the Liu–Parr functional T_{LP97} and to the Z–λ-dependent functionals T_{LP97+Z^3} and T_{LP97+Z^9}. The Z–λ-dependent functionals were evaluated both with the Liu–Parr original coefficients as well as with optimized ones.

The graphs of these new Z–λ-dependent enhancement factors in eq. (17) are also plotted in Figure 1 (dotted orange), coinciding with those of the locally adjusted λ-dependent factors (dotted green) from which they are visibly almost undistinguishable.

Application to positive and negative ions

We have also examined if the approximate functionals discussed above are applicable to positive and negative ions. For this purpose, we present in Figures 5 and 6 the absolute relative percentage errors for positive and negative atomic ions, respectively. Figure 5, $\Delta\epsilon(T^a_{LP97})$ corresponds to the Liu–Parr functional T_{LP97}, eq. (9), evaluated using the same optimized

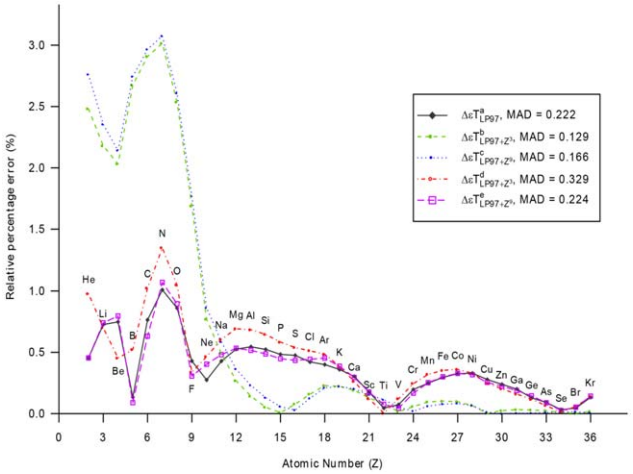


Figure 4. Relative percentage error $\Delta\epsilon$(Ti) for neutral atoms, for T^a_{LP97}, eq. (9), with Liu–Parr coefficients; $T^b_{LP97+Z^3}$, eq. (18), with reoptimized coefficients ($C_{T_1} = 3.1336517827$, $C_{T_2} = -0.0043445677$, and $C_{T_3} = -0.0000345496$); $T^c_{LP97+Z^9}$, eq. (18), with reoptimized coefficients ($C_{T_1} = 3.1257333712$, $C_{T_2} = -0.0030202454$, and $C_{T_3} = -0.0000669074$); $T^d_{LP97+Z^3}$, eq. (18), with Liu–Parr coefficients; $T^e_{LP97+Z^9}$, eq. (18), with Liu–Parr coefficients.

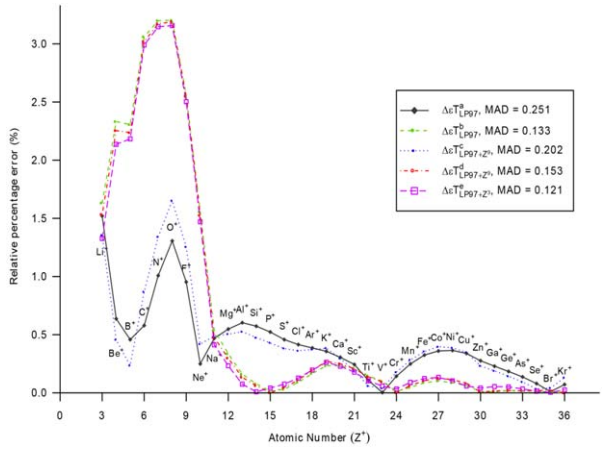


Figure 5. Relative percentage error $\Delta\epsilon$(Ti) for positive ions, for T^{a}_{LP97}, eq. (9), with Liu–Parr coefficients; T^{b}_{LP97}, eq. (9), with reoptimized coefficients ($C_{T_1} = 3.1288539558$, $C_{T_2} = -0.0034574267$, and $C_{T_3} = -0.0000591469$); $T^{c}_{LP97+Z^9}$, eq. (18), with both Z^9 and Liu–Parr coefficients for neutral atoms; $T^{d}_{LP97+Z^3}$, eq. (18), with Z^9 for neutral atoms and reoptimized coefficients ($C_{T_1} = 3.1267059586$, $C_{T_2} = -0.0039716465$, and $C_{T_3} = -0.0000518778$); $T^{c}_{LP97+Z^3}$, eq. (18), with Z^3 for positive ions and reoptimized coefficients ($C_{T_1} = 3.1370019499$, $C_{T_2} = -0.0048541396$, and $C_{T_3} = -0.0000240227$).

coefficients as those of neutral atoms but the densities of positive ions taken from the Clementi–Roetti tables. Similar results are presented by $\Delta\epsilon(T^{a}_{LP97})$ for negative ions in Figure 6. $\Delta\epsilon(T^{b}_{LP97})$ in Figure 5 corresponds to the functional T_{LP97} evaluated with the densities for positive ions and reoptimized coefficients. Similarly, $\Delta\epsilon(T^{b}_{LP97})$ in Figure 6 gives the corresponding values for negative ions.

In order to assess whether the Z^n approximations for neutral atoms can be transferred to positive and negative ions, we present in Figures 5 and 6 the values of $\Delta\epsilon(T^{c}_{LP97+Z^9})$ for positive and negative ions, respectively. The functional $T^{c}_{LP97+Z^9}$ was evaluated via eq. (18) with the Z^9 polynomial and the Liu–Parr coefficients fitted for neutral atoms and the Clementi–Roetti densities for positive and negative atomic ions, respectively. In the graph for $\Delta\epsilon(T^{d}_{LP97+Z^9})$ of Figures 5 and 6, the same results are presented for the case of the Z^9 polynomial approximation for neutral atoms, but the coefficients have been reoptimized. In the graph for $\Delta\epsilon(T^{e}_{LP97+Z^3})$ of Figures 5 and 6, we present values of the non-interacting kinetic energy calculated by eq. (18), but the Z^3 polynomial approximation was fitted for each particular case, and also, the coefficients of the homogeneous functional expansion were reoptimized.

The values of $\Delta\epsilon(T^{b}_{LP97})$ in Figures 5 and 6, indicate that the Liu–Parr homogeneous functional expansion works quite well for positive and negative atomic ions. Making use in this analysis of the mean absolute deviation of the $\Delta\epsilon(T_i)$s, namely, the MAD values, we see that in the case of positive ions, the MAD value is 0.133, while for negative ions, 0.107. In both of these cases, the accuracy increases with atomic number. The transferability of the Z^n polynomial approximation for neutral atoms as well as the use of the Liu–Parr coefficients (optimized for neutral atoms) may be assessed by examining the values of $\Delta\epsilon(T^{c}_{LP97+Z^9})$ in Figures 5 and 6. The results show a MAD value of 0.202 and 0.213 for positive and negative ions, respectively. Again, the approximation improves with the increasing atomic number. These results are, in fact, quite comparable to those of the original Liu–Parr expression [eq. (9)]. Obviously, the best fit is obtained when both the Z^n function and the coefficients have been optimized for the ions. The MAD values in this case are 0.121 and 0.080, respectively, for positive and negative ions.

Extensions to molecular systems and clusters

Based on our previous work,[2] a good approximation of the kinetic energy enhancement factor for two neighboring atoms in molecular environment is given by the sum of the atomic enhancement factors of the participating atoms. Let us consider an electronic system, a molecule or a cluster which contains M atoms. We divide the whole space into M subvolumes $\{\Omega_A\}_{A=1,\ldots,M}$, each containing a given atom A. For, example, for the system composed by the same atoms the space can be divided as

$$\vec{r} \in \Omega_A \quad \text{if} \quad \min|\vec{r}-\vec{R}_B| = |\vec{r}-\vec{R}_A|, \tag{19}$$

where the vectors $\vec{R}_A$ and $\vec{R}_B$ denote the nuclear positions, and thus, $\mathbf{R}^3 = \cup_{A=1}^{M}\Omega_A$. The one-electron density of a system formed by M atoms is $\rho(\vec{r}) \equiv \rho(\vec{r}, \{\vec{R}_A\}_{A=1,\ldots,M})$, indicating the nuclear coordinates in the argument. Let us define

$$\rho_A(\vec{r}) \equiv \rho(\vec{r} \in \Omega_A). \tag{20}$$

For any particular one-electron density $\rho(\vec{r})$ of the molecular system, $\rho_A(\vec{r})$ is the corresponding one-electron density associated with an atomic volume Ω_A. Bearing this in mind one may write the second term of eq. (1) as

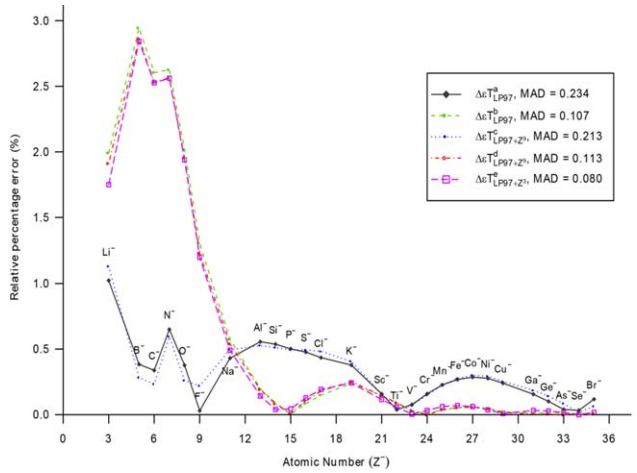


Figure 6. Relative percentage error $\Delta\epsilon(T_i)$ for negative ions, for T^{a}_{LP97}, eq. (9), with Liu–Parr coefficients; T^{b}_{LP97}, eq. (9), with reoptimized coefficients ($C_{T_1} = 3.1248445957$, $C_{T_2} = -0.0027038794$, and $C_{T_3} = -0.0000764926$); $T^{c}_{LP97+Z^9}$, eq. (18), with both Z^9 and Liu–Parr coefficients for neutral atoms; $T^{d}_{LP97+Z^9}$, eq. (18), with Z^9 for neutral atoms and reoptimized coefficients ($C_{T_1} = 3.1218035155$, $C_{T_2} = -0.0022915847$, and $C_{T_3} = -0.0000868695$); $T^{c}_{LP97+Z^3}$, eq. (18), with Z^3 for positive ions and reoptimized coefficients ($C_{T_1} = 3.1326163517$, $C_{T_2} = -0.0040144747$, and $C_{T_3} = -0.0000443462$).

$$\frac{1}{2}\int_{\mathbf{R}^3} d\vec{r}\,\rho^{5/3}(\vec{r})A_{\mathrm{N}}[\rho(\vec{r});\vec{r}] = \frac{1}{2}\sum_{A=1}^{M}\int_{\Omega_{\mathrm{A}}} d\vec{r}\,\rho_{\mathrm{A}}^{5/3}(\vec{r})A_{\mathrm{N}}[\rho_{\mathrm{A}}(\vec{r});\vec{r}] \tag{21}$$

The plausibility of this separation stems from the fact that the enhancement factor is defined for a given atom, or atomic region, which has yielded satisfactory results for the non-interacting kinetic energy also, when the charge of the neutral species is either increased to a negative ion, or decreased to a positive one.[59,60] However, there is some indirect evidence that the Liu–Parr expansion and approximation given by eqs. (1) and (12) should work for molecules without partitioning the whole space into atomic subvolumes.[1,61] Certainly, a division into subvolumes is required if one uses the polynomial representation eq. (17) for A_{N}. Application of these ideas to molecules and clusters will be dealt with elsewhere.

Conclusions

In the present work we have explored the possibility of expressing the enhancement factor $A_{\mathrm{N}}[\rho(\vec{r});\vec{r}]$ of the non interacting kinetic energy functional solely as a function of the one-electron density $\rho(\vec{r})$. This has been accomplished with the help of the Liu and Parr power series of the density.

We have analyzed the behavior of this approximate expression for $A_{\mathrm{N}}[\rho(\vec{r});\vec{r}]$ in the case of first, second and third row atoms (except H and He of which the kinetic energy functional is exactly given by the Weizsäcker term). The expression for $A_{\mathrm{N}}[\rho(\vec{r});\vec{r}]$ in eq. (10) violates the requirement of positivity in some regions; however, when a local correction term $\lambda\nabla^2\rho(\vec{r})/\rho(\vec{r})^{5/3}$ is added to this expression, the profiles become excellent as those of the enhancement factors derived from orbital representations. More specifically, for the second row atoms Na, Al, and Ar, the locations and heights of the maxima generated by the λ-dependent approximation $A_{\mathrm{N}}[\rho(\vec{r});\vec{r}]$ in eq. (12) fully coincide with those obtained from orbital representations in eq. (4). In the case of the third row atoms Fe and Ni, although the location is in perfect agreement, the maxima corresponding to the third shell fall below the exact ones. An exception is the Kr atom, where both location and height coincidence is quite good. The asymptotic behavior of these λ-dependent functions near the nucleus shows a negative divergence in all cases studied. At large distances from the nucleus of the Fe and Ni atoms we have observed a divergence, but in all other cases the asymptote follows the trend of the exact enhancement factor.

In addition, we have introduced a Z-dependent approximation in eqs. (13–15) to replace the integrals $\int d\vec{r}\,\rho^{4/3}(\vec{r})$ and $\int d\vec{r}\,\rho^{11/9}(\vec{r})$ of the enhancement factor, eq. (10). The non-interacting atomic kinetic energy density functionals generated from these new Z-dependent enhancement factors [eq. (17)] show a behavior very close to the Liu–Parr functional T_{LP97}. Inspecting the MAD values for functionals T_{LP97} (0.222), $T_{\mathrm{LP97}+Z^3}$ (0.329), and $T_{\mathrm{LP97}+Z^9}$ (0.224) evaluated with the Liu–Parr optimized coefficients, we conclude that the functional $T_{\mathrm{LP97}+Z^9}$ performs as well as the Liu–Parr functional T_{LP97}. However, with our re-optimized coefficients for the Z-dependent functionals, we have obtained the MAD values 0.129 and 0.166 for $T_{\mathrm{LP97}+Z^3}$ and $T_{\mathrm{LP97}+Z^9}$, respectively, thus showing a closer relationship to the exact Hartree Fock values. The behavior of the approximate enhancement factors in case of the Z-dependent functionals is almost the same as the λ-corrected Liu–Parr functionals.

With the Z–λ-representation of neutral atoms extended to positive and negative ions, see Figures 5 and 6, our non-interacting atomic kinetic energy density functionals perform quite well, even when we use the same Z^n functions as well as the Liu–Parr coefficients (the latter were adjusted for neutral atoms).

In summary, based on both the Liu–Parr power series density expansion and on the replacement of two integrals of this expansion by Z-dependent functions, a very simple form for the non-interacting kinetic energy enhancement factor has been found. These functionals bypass the usual gradient expansion representation, leading to non-interacting kinetic energy values which closely approximate (see the corresponding MAD values) the exact ones calculated from Hartree Fock wave functions. Moreover, the addition of the atomic enhancement factors opens a possible way to extend the present functionals to molecules and clusters.

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APPENDIX

Liu and Parr Theorem 2 Revisited

For better understanding, we analyze some lines left out in the original proof of Theorem 2 of Liu and Parr.[1]

Theorem 2. Given the functional

$$Q_{\mathrm{j}}[\rho] = C_{\mathrm{j}}[H_{\mathrm{j}}]^{\mathrm{j}}, \tag{A1}$$

where H_{j} is a homogeneous and local functional, if it is homogeneous of degree m in coordinate scaling, it takes the form

$$Q_{\mathrm{j}}[\rho] = C_{\mathrm{j}}\left[\int d\vec{r}\,\rho^{[1+(m/3\mathrm{j})]}(\vec{r})\right]^{\mathrm{j}}. \tag{A2}$$

Furthermore, if $Q_{\mathrm{j}}[\rho]$ is homogeneous of degree k in density scaling, j is determined by the relation

$$j = k - \frac{m}{3}. \tag{A3}$$

Proof. It is known that any strictly local functional $L[\rho]$ satisfies the identity

$$L[\rho] = -\frac{1}{3}\int d\vec{r}\,\vec{r}\cdot\nabla\rho(\vec{r})\frac{\delta L[\rho]}{\delta\rho(\vec{r})} \tag{A4}$$

Taking the functional derivative of eq. (A1) with respect to ρ, that is:

$$\frac{\delta Q_j[\rho]}{\delta\rho} = C_j j H_j[\rho]^{j-1}\frac{\delta H_j[\rho]}{\delta\rho} \tag{A5}$$

and rewriting eq. (A1), we have

$$\begin{aligned} Q_j[\rho] &= C_j (H_j[\rho])^j \\ &= C_j H_j[\rho](H_j[\rho])^{j-1} \\ &= C_j\left(-\frac{1}{3}\int d\vec{r}\,\vec{r}\cdot\nabla\rho(\vec{r})\frac{\delta H_j[\rho]}{\delta\rho(\vec{r})}\right)(H_j[\rho])^{j-1} \\ &= -\frac{1}{3j}\int d\vec{r}\,\vec{r}\cdot\nabla\rho(\vec{r})C_j j(H_j[\rho])^{j-1}\frac{\delta H_j[\rho]}{\delta\rho(\vec{r})} \\ &= -\frac{1}{3j}\int d\vec{r}\,\vec{r}\cdot\nabla\rho(\vec{r})\frac{\delta Q_j[\rho]}{\delta\rho(\vec{r})}. \end{aligned} \tag{A6}$$

Because Q_j is homogeneous of degree m in coordinate scaling it follows that

$$-\int d\vec{r}\,\rho(\vec{r})\vec{r}\cdot\nabla\frac{\delta Q_j[\rho]}{\delta\rho(\vec{r})} = mQ_j[\rho]. \tag{A7}$$

Thus, if we integrate this equation by parts, we obtain

$$\begin{aligned} -\int d\vec{r}\,\rho(\vec{r})\vec{r}\cdot\nabla\frac{\delta Q_j[\rho]}{\delta\rho(\vec{r})} &= \int d\vec{r}\,[\vec{r}\cdot\nabla\rho(\vec{r}) \\ &\quad +3\rho(\vec{r})]\frac{\delta Q_j[\rho]}{\delta\rho(\vec{r})} \end{aligned} \tag{A8}$$

and by replacing eq. (A6) into (A8), it is found

$$\int d\vec{r}\,\rho(\vec{r})\frac{\delta Q_j[\rho]}{\delta\rho(\vec{r})} = \frac{m+3j}{3}Q_j[\rho]. \tag{A9}$$

This shows that $Q_j[\rho]$ is homogeneous of degree $(m+3j)/3$ in coordinate scaling. On the other hand, $H_j[\rho]$ is homogeneous, that is,

$$H_j[\rho] = \int d\vec{r}\,f_j[\rho(\vec{r})], \tag{A10}$$

so that if we replace eq. (A10) into eqs. (A1) and (A5) and these in turn into eq. (A9) we have

$$\begin{aligned} \int d\vec{r}\,\rho(\vec{r})jC_j(H_j[\rho])^{j-1}\frac{\delta H_j[\rho]}{\delta\rho(\vec{r})} &= \frac{m+3j}{3}C_j(H_j[\rho])^j \\ \int d\vec{r}\,\rho(\vec{r})\frac{\delta H_j[\rho]}{\delta\rho(\vec{r})} &= \left(1+\frac{m}{3j}\right)(H_j[\rho]) \\ \int d\vec{r}\,\rho(\vec{r})\frac{df_j(\rho)}{d\rho(\vec{r})} &= \left(1+\frac{m}{3j}\right)\int d\vec{r}\,f_j(\rho) \\ \int d\vec{r}\,\rho(\vec{r})\frac{df_j(\rho)}{d\rho(\vec{r})} &= \int d\vec{r}\left(1+\frac{m}{3j}\right)f_j(\rho). \end{aligned} \tag{A11}$$

If the two integrals are equal it follows:

$$\rho(\vec{r})\frac{df_j(\rho)}{d\rho(\vec{r})} = \left(1+\frac{m}{3j}\right)f_j(\rho). \tag{A12}$$

Therefore, we have to solve a simple differential equation

$$\begin{aligned} \int\frac{df_j(\rho)}{f_j(\rho)} &= \int\left(1+\frac{m}{3j}\right)\frac{d\rho(\vec{r})}{\rho(\vec{r})} \\ \ln f_j(\rho) &= \left(1+\frac{m}{3j}\right)\ln\rho(\vec{r})+C_j \\ f_j(\rho) &= C_j\rho^{[1+m/3j]}(\vec{r}), \end{aligned} \tag{A13}$$

where C_j is a constant of integration. This leads to:

$$H_j[\rho] = C_j\int d\vec{r}\,\rho^{[1+m/3j]}(\vec{r}) \tag{A14}$$

and

$$Q_j[\rho] = C_j\left[\int d\vec{r}\,\rho^{[1+m/3j]}(\vec{r})\right]^j. \tag{A15}$$

Finally, we see from eq. (A9) that k is $(m+3j)/3$, thus

$$j = k-\frac{m}{3}. \tag{A16}$$

Keywords: density functional theory · enhancement factor · Kohn–Sham formalism · kinetic energy functional

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