

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

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Within the framework of density functional theory, we present a study of approximations to the enhancement factor of the non-interacting kinetic energy functional $T_s[\rho]$. For this purpose, we employ the model of Liu and Parr [S. Liu and R.G. Parr, Phys. Rev. A **55**, 1792 (1997)] based on a series expansion of $T_s[\rho]$ involving powers of the density. Applications to 34 atoms, at the Hartree-Fock level showed 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 approximation 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.

Keywords: Density Functional Theory, Enhancement Factor, Kohn-Sham, Hartree-Fock, Kinetic Energy Functional.

INTRODUCTION.

One of the challenging problems in density functional theory, DFT, is how to express the non-interacting kinetic energy of a quantum mechanical many-body system as a functional of the density [1–9].

Having such a functional is, of course, crucial for the implementation of the orbital-free version of DFT.[10] Let us recall that in the Kohn-Sham [11] version of DFT, as a result of writing the non-interacting kinetic energy as a functional of the orbitals there arise N Kohn-Sham

equations whose solution becomes progressively more difficult as N gets larger. For this reason, a treatment that dispenses with orbitals and is based on the use of a kinetic energy functional which only depends on the density has been proposed as an alternate way for handling this problem. To focus on an orbital-free functional for the energy would certainly lower the computational cost and would permit to extend the domain of application of DFT to large many-particle systems as all one has to solve is a single equation for the density, regardless of the value of N .

To find an adequate density functional for the kinetic energy is a difficult task because, due to the virial theorem, the kinetic energy is equal in magnitude to the total energy. Hence this functional must have the same

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level of accuracy as that of the total energy (in contrast with the exchange and correlation functionals in DFT which only comprise small portions of the total energy). This fact probably explains why since the first works of Thomas [12] and Fermi [13] in 1927 and in spite of the continued efforts carried out throughout many decades, (for reviews see Refs.[6, 10, 14]) still no definite and satisfactory approximation to this functional has been found. The search for suitable approximations is, however, an ongoing activity.[15–23] Although an exact analytical expression for the non-interactive kinetic energy functional is still lacking, the exact form of this functional, however, is known and can be derived from general principles (see, for example, the derivation given in the context of the local-scaling transformation version of DFT [24–26]) This exact form corresponds to:

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

where the first term is the Weizsäcker term [27] and where 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. Clearly, as is seen in the above expression, the challenge in modelling $T_s[\rho]$ is shifted to that of attaining adequate approximations for the enhancement factor $A_N[\rho(\vec{r}); \vec{r}]$, which is considered to be expressible as a functional of ρ .

Among the alternatives produced over the years to represent the non-interactive kinetic energy functional [6], we focus in this paper on the one introduced by Liu and Parr [1], which is given as a power series of the density $\rho(\vec{r})$. This series generates an explicit expression for the enhancement factor as a functional of the one-particle density. A variational calculation based on this expansion has recently been given by Kristyan.[28]

In this paper we analyze the representation of the enhancement factor given by the Liu-Parr series expansion and compare it with the exact values extracted from an orbital expression. This is done for the 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 of the integrals containing $\rho(\vec{r})$. Finally, bearing in mind that the mathematical framework is presented rather concisely in the original Liu and Parr's paper, [1] we include in Appendix A of the present work a more extended demonstration of their second theorem. 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

From an information theory perspective,[29] the Weizsäcker term in Eq. (1) is local. Clearly then, since the non-local part of the kinetic energy functional must be

embodied in the non-Weizsäcker term, this non-locality must be ascribed to the enhancement factor. In fact, as was pointed out by Ludeña,[30] the non-Weizsäcker term contains the derivative of the correlation factor for the Fermi hole (see Eq.[38] of Ref.[30]). 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.[31] This non-locality of the kinetic energy functional is well represented by orbital expansions

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

$$= -\frac{1}{2} \sum_{i=1}^N \int d\vec{r} \phi_i^*(\vec{r}) \nabla^2 \phi_i(\vec{r}) \quad (3)$$

$$+ \frac{1}{4} \int d\vec{r} \nabla^2 \rho(\vec{r})$$

given in terms of gradients in Eq. (2) or of Laplacians in Eq. (3). Combining Eqs. (1) and the gradient representation of Eq.(2), we obtain the following exact orbital representation for the enhancement factor:

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

Obviously, when modelling the enhancement factor in terms of a series of the one-particle density one would like to reproduce the same characteristics it manifests in an orbital representation. Thus, in addition to yielding a desired accuracy for the calculated values of the non-interacting kinetic energy, the approximate enhancement factor should satisfy the positivity condition[32]:

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

and should also be capable of generating shell structure. In this respect, let us note that $A_N [\rho(\vec{r}), \{\phi_i\}; \vec{r}]$ as given by Eq. (4) differs by just a constant from the function $\chi(\vec{r}) = D(\vec{r})/D_h(\vec{r})$ introduced in the definition of the electron localization function, ELF (see Ref. [33]). Moreover, bearing in mind that ELF and similar functions have been successfully related to the appearance of shell structure in atoms and molecules[34–42] it is clear that any proposed model of the enhancement factor must also comply with this requirement.

A popular generalized gradient approximation (GGA) for the kinetic energy takes the following form [43]

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

where $T_W[\rho]$ is the Weiszäcker term [27], and the second term is the Pauli term [14] containing the GGA enhancement factor $F[s(\vec{r})]$ which depends on $s(\vec{r})$

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

The variable $s(\vec{r})$, the reduced density gradient, describes the rate of variation of the electronic density, i.e, large values of $s(\vec{r})$ correspond to fast variations on the electron density and vice versa [44]. The above approximation to the Pauli term containing GGA $F[s(\vec{r})]$ factors are at the basis of the conjoint gradient expansion to the kinetic energy introduced by Lee, Lee and Parr [45].

A full review of the functionals of the kinetic energy expressed in terms of the 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. [17, 19–21, 46–48]

In the present work we examine, however, a different approximation to the enhancement factor, more in line with Eq. (1), namely, a representation of $A_N[\rho(\vec{r}); \vec{r}]$ as a local functional of the 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-particle density:

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

where in $T_{LP97}[\rho]$ the subindex *LP97* stands for Liu and Parr and the year of publication, 1997. Following the original work, we truncate Eq. (8) after $j = 3$ and obtain:

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

Liu and Parr[6] determine the coefficients C_{T_j} 's by least-square fitting setting $\rho = \rho_{HF}$, the Hartree-Fock density and obtain: $C_{T_1} = 3.26422$, $C_{T_2} = -0.02631$ and $C_{T_3} = 0.000498$ (a typographical error in the values of the coefficients in the original paper, has been corrected). Clearly, 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-particle density can

be found from Eqs. (9) and (1):

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

Local corrections to the enhancement factor.

From equations (4) and (10), we obtain the graphs for the exact and approximate enhancement factors, respectively. These graphs are displayed in Figures 1 through 6 for the Na, Al, Ar, Fe, Ni and Kr atoms. One can see that the exact enhancement factor is a positive function, in contrast to the approximate one which shows negative regions in violation of the positivity condition which must be met by $A_N[\rho(\vec{r}); \vec{r}]$. [49]

Due to the fact that the kinetic energy is not uniquely defined and, as illustrated by Eqs. (2) and (3), that there are expressions that yield locally different kinetic energy densities but which integrate to the same value, it is possible to modify the non-positive approximate enhancement factor by adding a term that does not alter the expected value of the non-interacting kinetic energy but which locally contributes to make the enhancement factor positive. This is an acceptable procedure in view of the non-uniqueness in the definition of the local kinetic energy expressions.[50–52]

In this vein, we add to non-interacting kinetic energy expression a term given by the Laplacian of the density times an arbitrary constant λ , where λ is a real number:

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

This leads to the following new expression for the approximate enhancement factor:

$$\begin{aligned} A_N[\rho] = & 2 \left(C_{T_1} + C_{T_2} \rho^{-1/3}(\vec{r}) \int d\vec{r} \rho^{4/3}(\vec{r}) \right. \\ & + C_{T_3} \rho^{-4/9}(\vec{r}) \left[\int d\vec{r} \rho^{11/9}(\vec{r}) \right]^2 \\ & \left. + \lambda \frac{\nabla^2 \rho(\vec{r})}{\rho(\vec{r})^{5/3}} - \frac{1}{8} \frac{|\nabla\rho(\vec{r})|^2}{\rho^{8/3}(\vec{r})} \right). \end{aligned} \quad (12)$$

With the addition of this term we see that the kinetic energy value does not alter, because the integral of the Laplacian of the density is zero.[53] The improvements that this added term brings about on the approximate enhancement factor for the Na, Al, Ar, Fe, Ni and Kr atoms are shown in Figs. [1] through [6].

brown), 9th-degree brown), 9th-degree brown), 9th-

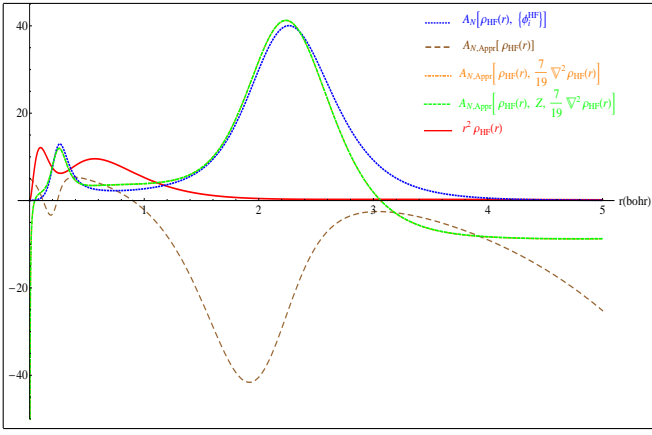


Figure 1. “Exact” enhancement factor (dotted blue), approximate enhancement factor (dashed brown), approximate enhancement factor with $\lambda = \frac{7}{19}$ (dotted green), approximate enhancement factor with 9th-degree Z polynomial and $\lambda = \frac{7}{19}$ (dotted orange), and radial distribution function of the density (full red) for the Na atom

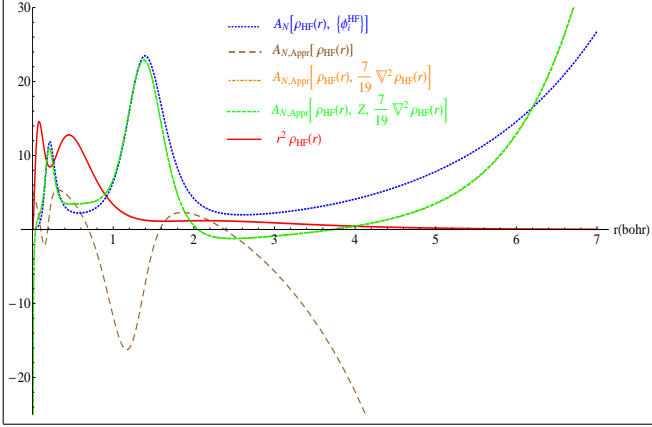


Figure 2. “Exact” enhancement factor (dotted blue), approximate enhancement factor (dashed brown), approximate enhancement factor with $\lambda = \frac{7}{19}$ (dotted green), approximate enhancement factor with 9th-degree Z polynomial and $\lambda = \frac{7}{19}$ (dotted orange), and radial distribution function of the density (full red) for the Al atom

degree brown), 9th-degree brown), 9th-degree

We note that the new λ -dependent enhancement factors closely reproduce the behavior of the exact ones in the regions where the highest peaks are located. In all cases the agreement is extremely good both for the first and second shells. For Ni and Fe, the approximate enhancement factors are slightly below the exact ones in the region corresponding to the third shell. For Kr, however, the agreement is quite good for all shells.

Concerning the asymptotic behavior of the enhancement factors, we observe that in the region where $r \rightarrow 0$ the approximate λ -dependent enhancement factors become rapidly negative in all cases studied. It is expected, however, that this divergence in A_N will not necessarily produce a problem for interatomic forces as these forces in molecular dynamics are calculated by using the

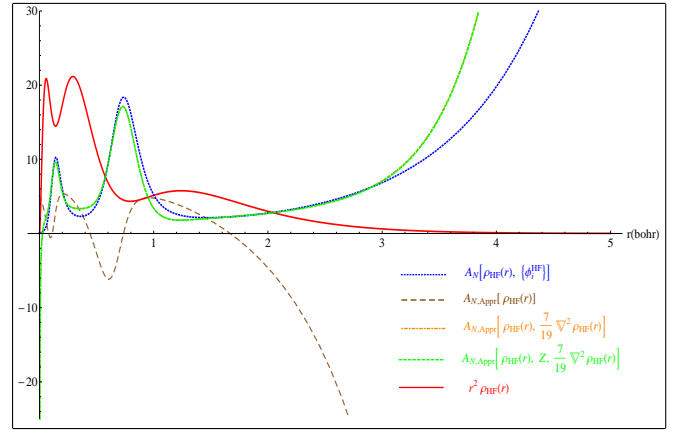


Figure 3. “Exact” enhancement factor (dotted blue), approximate enhancement factor (dashed brown), approximate enhancement factor with $\lambda = \frac{7}{19}$ (dotted green), approximate enhancement factor with 9th-degree Z polynomial and $\lambda = \frac{7}{19}$ (dotted orange), and radial distribution function of the density (full red) for the Ar atom

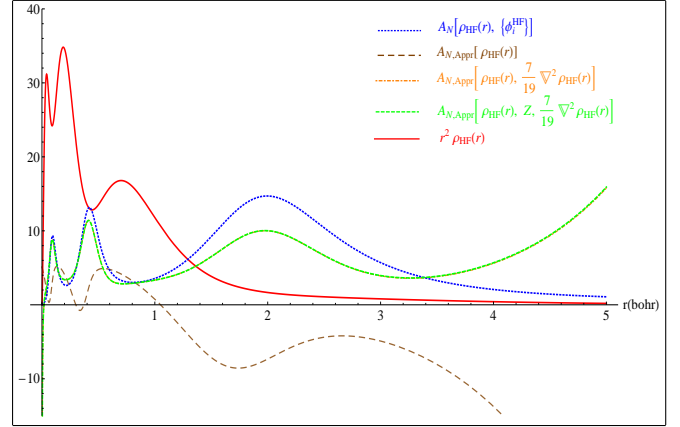


Figure 4. “Exact” enhancement factor (dotted blue), approximate enhancement factor (dashed brown), approximate enhancement factor with $\lambda = \frac{7}{19}$ (dotted green), approximate enhancement factor with 9th-degree Z polynomial and $\lambda = \frac{7}{19}$ (dotted orange), and radial distribution function of the density (full red) for the Fe atom

orbital-free analogue of the Hellmann-Feynman theorem (see Eqs. (21)-(23) in Ref. [54]) According to these equations the forces are defined by the density and the external potential and thus, they do not depend on the kinetic energy density local behavior. On the other hand, in the region where r becomes large, i.e., outside the atomic shells, the behavior of the approximate factor follows the trend of the exact ones for the cases of Na, Al, Ar and Kr, although in the latter case, the approximate factor grows more pronouncedly than the exact one. In the case of Ni and Fe, however, we observe a divergence in the behavior of the tails of the approximate enhancement factors. Let us mention, however, 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 density tail.

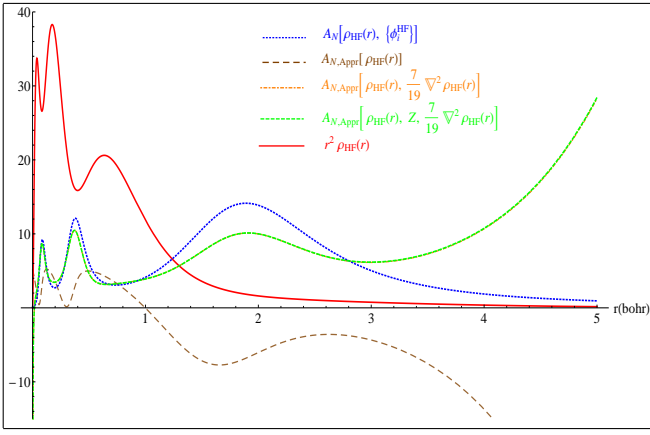


Figure 5. “Exact” enhancement factor (dotted blue), approximate enhancement factor (dashed brown), approximate enhancement factor with $\lambda = \frac{7}{19}$ (dotted green), approximate enhancement factor with 9th-degree Z polynomial and $\lambda = \frac{7}{19}$ (dotted orange), and radial distribution function of the density (full red) for the Ni atom

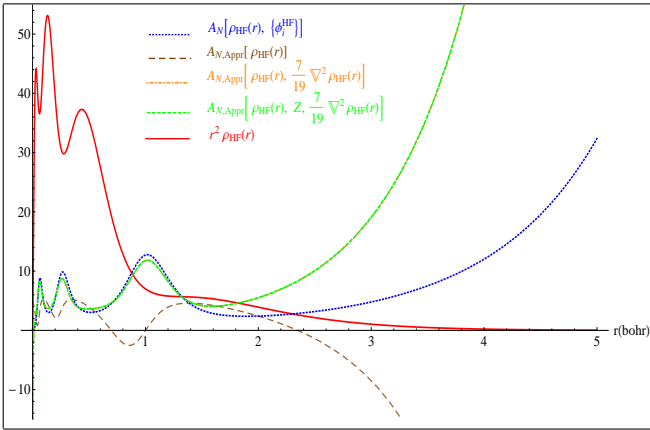


Figure 6. “Exact” enhancement factor (dotted blue), approximate enhancement factor (dashed brown), approximate enhancement factor with $\lambda = \frac{7}{19}$ (dotted green), approximate enhancement factor with 9th-degree Z polynomial and $\lambda = \frac{7}{19}$ (dotted orange), and radial distribution function of the density (full red) for the Kr atom

APPROXIMATION TO THE ENHANCEMENT FACTOR THROUGH Z -DEPENDENT POLYNOMIALS

We see that the enhancement factor $A_{N,Appr}$, 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 $\rho = \rho_{HF}$, are functions of the atomic number Z . We have selected to display this Z -dependent behavior in Figs. [7] and [8]. In these figures, the dots lying 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 frames (a) of Figs. [7] and [8] represents the approximations given by the third-

degree polynomial Z^3 . Similarly, the blue lines in frames (b) of these figures correspond to the Z^9 polynomial approximation.

These interpolation polynomials are explicitly defined by:

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

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

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

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

where the coefficients are determined by least-square fitting. Thus, the enhancement factor takes the following form (where n is the degree of the Z polynomial):

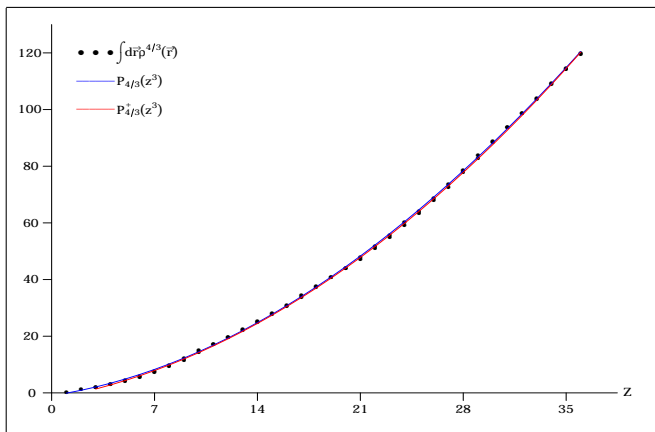
$$\begin{aligned} \frac{1}{2} A_{Z^n, Appr}[\rho, Z] = & C_{T_1} + C_{T_2} \rho^{-1/3}(\vec{r}) P_{4/3}(Z^n) \\ & + C_{T_3} \rho^{-4/9}(\vec{r}) P_{11/9}(Z^n)^2 \\ & + \lambda \frac{\nabla^2 \rho(\vec{r})}{\rho(\vec{r})^{5/3}} \\ & - \frac{1}{8} \frac{|\nabla \rho(\vec{r})|^2}{\rho^{8/3}(\vec{r})} \end{aligned}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

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

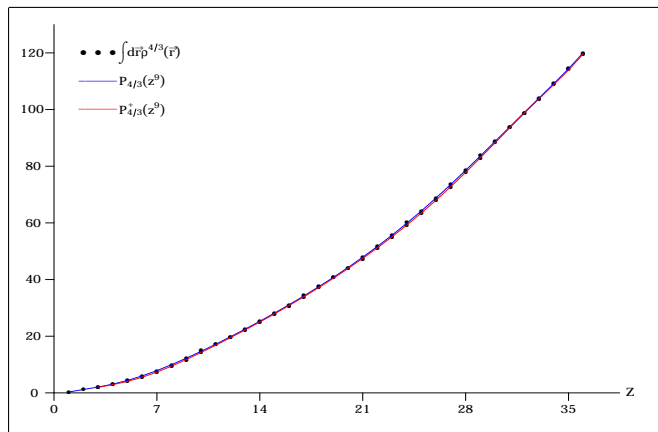
$$\begin{aligned} T_{LP97+Z^n}[\rho, Z] = & C_{T_1} \int d\vec{r} \rho^{5/3}(\vec{r}) \\ & + C_{T_2} \int d\vec{r} \rho^{4/3}(\vec{r}) P_{4/3}(Z^n) \\ & + C_{T_3} \int d\vec{r} \rho^{11/9}(\vec{r}) P_{11/9}(Z^n)^2 \end{aligned} \quad (18)$$

Application to neutral atoms

The kinetic energy values corresponding to these Z - λ -dependent functionals T_{LP97+Z^3} and T_{LP97+Z^9} evaluated both with the Liu and Parr and with newly optimized

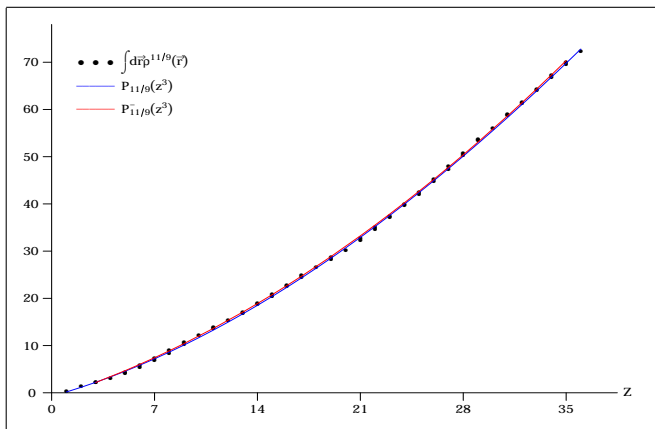


(a)

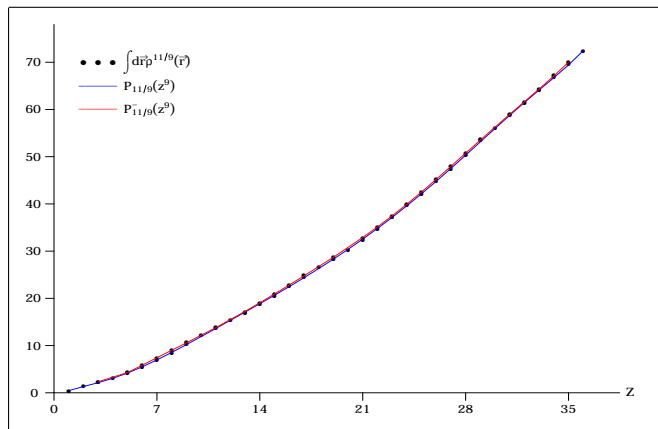


(b)

Figure 7. Interpolation curves for the values of the $\int d\vec{r} \rho^{4/3}(\vec{r})$ through: (a) a 3rd degree polynomial $P_{4/3}(Z^3)$ (full blue) for 36 atoms and a 3rd degree polynomial $P_{4/3}^+(Z^3)$ (full 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 $P_{4/3}^+(Z^9)$ (full red) for 34 positive ions.



(c)



(d)

Figure 8. Interpolation curves for the values of the $\int d\vec{r} \rho^{11/9}(\vec{r})$ through: (a) a 3rd degree polynomial $P_{11/9}(Z^3)$ (full blue) for 36 atoms and a 3rd degree polynomial $P_{11/9}^-(Z^3)$ (full 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 $P_{11/9}^-(Z^9)$ (full red) for 27 negative ions.

coefficients are presented in Table I. Also in this table the values of the Liu and Parr [1] functional T_{LP97} and the values of T_{HF} reported by Clementi and Roetti,[55] are presented for comparison purposes. The percentage relative errors are taken with respect to T_{HF} .

The graphs of these new Z - λ -dependent enhancement factors (17) are also plotted in Figs. [1] through [6]. Let us note that the graphs corresponding to these enhancement factors (dotted orange) coincide with those of the locally adjusted λ -dependent factors (dotted green) and hence they are undistinguishable in these figures.

Application to positive and negative ions

We have also examined whether the approximate functional forms discussed above are applicable to positive and negative ions. For this purpose, we list in column 2 of Table II the values of the non-interactive kinetic energy for positive ions calculated by means of the Liu-Parr expansion given by Eq. (9) using the same optimized coefficients as those of neutral atoms but the corresponding densities of positive ions taken from the Clementi-Roetti tables. Similar results are presented in column 2 of Table III for the case of negative ions. In column 3 of Tables II and III, we present the evaluation of Eq. (9) for positive and negative ions, respectively, but where in each case the coefficients of the homogeneous functional expansion have been reoptimized.

Table I. Non-interacting kinetic energy values for neutral atoms corresponding to the functionals T_{LP97} , T_{LP97+Z^3} , T_{LP97+Z^9} , and T_{HF} .

Atoms	T_{LP97}^a (error%)	$T_{LP97+Z^3}^b$ (error%)	$T_{LP97+Z^9}^c$ (error%)	$T_{LP97+Z^3}^d$ (error%)	$T_{LP97+Z^9}^e$ (error%)	T_{HF}^f
H	0.327 (34.600)	0.316 (36.800)	0.314 (37.200)	0.328 (34.400)	0.326 (34.800)	0.500
He	2.875 (0.454)	2.791 (2.481)	2.783 (2.760)	2.890 (0.978)	2.875 (0.454)	2.862
Li	7.487 (0.726)	7.271 (2.179)	7.258 (2.354)	7.485 (0.700)	7.488 (0.740)	7.433
Be	14.682 (0.748)	14.277 (2.031)	14.261 (2.141)	14.639 (0.453)	14.689 (0.796)	14.573
B	24.496 (0.135)	23.873 (2.674)	23.856 (2.744)	24.401 (0.522)	24.507 (0.090)	24.529
C	37.400 (0.764)	36.592 (2.908)	36.570 (2.966)	37.302 (1.024)	37.450 (0.632)	37.688
N	53.852 (1.009)	52.761 (3.015)	52.728 (3.075)	53.666 (1.351)	53.819 (1.070)	54.401
O	74.165 (0.861)	72.912 (2.536)	72.859 (2.607)	74.025 (1.048)	74.139 (0.896)	74.809
F	98.982 (0.430)	97.731 (1.688)	97.649 (1.770)	99.073 (0.338)	99.105 (0.306)	99.409
Ne	128.900 (0.275)	127.557 (0.770)	127.438 (0.863)	129.144 (0.464)	129.065 (0.403)	128.547
Na	162.550 (0.428)	161.064 (0.490)	160.909 (0.586)	162.838 (0.606)	162.635 (0.481)	161.857
Mg	200.660 (0.526)	199.075 (0.268)	198.886 (0.363)	200.992 (0.692)	200.674 (0.533)	199.610
Al	243.190 (0.545)	241.528 (0.142)	241.315 (0.230)	243.527 (0.684)	243.120 (0.516)	241.872
Si	290.360 (0.523)	288.697 (0.052)	288.472 (0.130)	290.713 (0.646)	290.254 (0.487)	288.848
P	342.360 (0.483)	340.741 (0.008)	340.522 (0.056)	342.702 (0.583)	342.240 (0.448)	340.714
S	399.390 (0.475)	397.812 (0.078)	397.617 (0.029)	399.643 (0.539)	399.228 (0.434)	397.502
Cl	461.400 (0.421)	460.189 (0.158)	460.037 (0.125)	461.816 (0.512)	461.499 (0.443)	459.464
Ar	528.920 (0.400)	528.019 (0.229)	527.929 (0.212)	529.371 (0.485)	529.199 (0.453)	526.814
K	601.320 (0.360)	600.499 (0.223)	600.489 (0.221)	601.470 (0.385)	601.478 (0.386)	599.164
Ca	678.810 (0.304)	678.040 (0.190)	678.123 (0.202)	678.540 (0.264)	678.750 (0.295)	676.756
Sc	761.070 (0.176)	760.702 (0.128)	760.883 (0.151)	760.650 (0.121)	761.066 (0.175)	759.733
Ti	848.790 (0.045)	849.099 (0.081)	849.372 (0.114)	848.447 (0.005)	849.047 (0.075)	848.408
V	942.190 (0.073)	943.030 (0.016)	943.378 (0.052)	941.736 (0.122)	942.473 (0.043)	942.883
Cr	1041.300 (0.196)	1042.751 (0.057)	1043.144 (0.020)	1040.800 (0.244)	1041.604 (0.167)	1043.348
Mn	1147.000 (0.248)	1148.759 (0.095)	1149.148 (0.062)	1146.177 (0.320)	1146.958 (0.252)	1149.857
Fe	1258.600 (0.295)	1261.033 (0.103)	1261.360 (0.077)	1257.872 (0.353)	1258.532 (0.301)	1262.328
Co	1376.900 (0.326)	1380.061 (0.097)	1380.260 (0.083)	1376.425 (0.361)	1376.874 (0.328)	1381.405
Ni	1501.900 (0.329)	1505.871 (0.066)	1505.884 (0.065)	1501.900 (0.329)	1502.075 (0.318)	1506.862
Cu	1634.400 (0.278)	1638.995 (0.002)	1638.785 (0.011)	1634.893 (0.248)	1634.776 (0.255)	1638.960
Zn	1773.600 (0.239)	1778.280 (0.025)	1777.860 (0.001)	1774.250 (0.202)	1773.877 (0.223)	1777.842
Ga	1919.400 (0.200)	1923.884 (0.033)	1923.330 (0.004)	1920.187 (0.159)	1919.643 (0.188)	1923.254
Ge	2072.700 (0.128)	2075.981 (0.030)	2075.442 (0.004)	2072.940 (0.117)	2072.346 (0.145)	2075.360
As	2232.200 (0.091)	2234.766 (0.024)	2234.444 (0.009)	2232.779 (0.065)	2232.254 (0.089)	2234.237
Se	2399.100 (0.032)	2400.099 (0.010)	2400.173 (0.013)	2399.625 (0.010)	2399.257 (0.025)	2399.865
Br	2573.600 (0.045)	2572.359 (0.003)	2572.813 (0.015)	2573.947 (0.059)	2573.782 (0.052)	2572.432
Kr	2755.700 (0.133)	2751.565 (0.018)	2751.863 (0.007)	2755.845 (0.138)	2755.967 (0.142)	2752.048
MAD	0.222	0.129	0.166	0.329	0.224	

^a T_{LP97} , Eq. (9), with Liu-Parr coefficients^b T_{LP97+Z^3} , Eq. (18), with reoptimized coefficients ($C_{T_1} = 3.1336517827$, $C_{T_2} = -0.0043445677$ and $C_{T_3} = -0.0000345496$)^c T_{LP97+Z^9} , Eq. (18), with reoptimized coefficients ($C_{T_1} = 3.1257333712$, $C_{T_2} = -0.0030202454$ and $C_{T_3} = -0.0000669074$)^d T_{LP97+Z^3} , Eq. (18), with Liu-Parr coefficients^e T_{LP97+Z^9} , Eq. (18), with Liu-Parr coefficients^f T_{HF} , Eq. (2), reported by Clementi and Roetti[55]

Table II. Non-interacting kinetic energy values for positive ions corresponding to the functionals T_{LP97} , T_{LP97+Z^3} , T_{LP97+Z^9} , and T_{HF} .

Ions	T_{LP97}^a (error%)	T_{LP97}^b (error%)	$T_{LP97+Z^9}^c$ (error%)	$T_{LP97+Z^9}^d$ (error%)	$T_{LP97+Z^3}^e$ (error%)	T_{HF}^f
Li ⁺	7.346 (1.520)	7.118 (1.631)	7.334 (1.354)	7.125 (1.534)	7.140 (1.327)	7.236
Be ⁺	14.369 (0.637)	13.945 (2.332)	14.343 (0.455)	13.956 (2.255)	13.973 (2.136)	14.278
B ⁺	24.348 (0.458)	23.678 (2.306)	24.294 (0.235)	23.695 (2.236)	23.708 (2.183)	24.237
C ⁺	37.076 (0.579)	36.150 (3.062)	36.968 (0.869)	36.166 (3.019)	36.177 (2.990)	37.292
N ⁺	53.345 (1.008)	52.164 (3.199)	53.166 (1.340)	52.178 (3.173)	52.192 (3.147)	53.888
O ⁺	73.401 (1.306)	71.990 (3.203)	73.143 (1.653)	72.000 (3.189)	72.024 (3.157)	74.372
F ⁺	97.889 (0.953)	96.302 (2.559)	97.592 (1.254)	96.313 (2.548)	96.357 (2.503)	98.831
Ne ⁺	127.498 (0.249)	125.829 (1.555)	127.282 (0.418)	125.866 (1.526)	125.936 (1.471)	127.816
Na ⁺	162.437 (0.469)	160.810 (0.537)	162.470 (0.490)	160.910 (0.475)	161.010 (0.413)	161.678
Mg ⁺	200.463 (0.548)	198.700 (0.336)	200.374 (0.504)	198.778 (0.297)	198.905 (0.233)	199.370
Al ⁺	243.131 (0.603)	241.285 (0.161)	242.945 (0.526)	241.348 (0.134)	241.492 (0.075)	241.673
Si ⁺	290.220 (0.573)	288.343 (0.077)	289.938 (0.475)	288.389 (0.061)	288.540 (0.009)	288.566
P ⁺	342.124 (0.523)	340.297 (0.014)	341.803 (0.429)	340.342 (0.001)	340.485 (0.041)	340.344
S ⁺	398.990 (0.458)	397.291 (0.031)	398.678 (0.380)	397.349 (0.045)	397.465 (0.075)	397.169
Cl ⁺	460.947 (0.415)	459.465 (0.092)	460.707 (0.362)	459.554 (0.111)	459.627 (0.127)	459.044
Ar ⁺	528.301 (0.386)	527.142 (0.166)	528.228 (0.372)	527.291 (0.194)	527.305 (0.196)	526.271
K ⁺	601.150 (0.357)	600.404 (0.233)	601.311 (0.384)	600.637 (0.271)	600.579 (0.262)	599.011
Ca ⁺	678.633 (0.305)	678.139 (0.232)	678.559 (0.294)	678.256 (0.249)	678.118 (0.229)	676.569
Sc ⁺	761.309 (0.244)	761.077 (0.213)	760.885 (0.188)	761.032 (0.207)	760.813 (0.178)	759.459
Ti ⁺	848.965 (0.107)	849.283 (0.145)	848.552 (0.059)	849.221 (0.138)	848.929 (0.103)	848.054
V ⁺	942.467 (0.003)	943.441 (0.100)	942.141 (0.038)	943.380 (0.094)	943.039 (0.058)	942.496
Cr ⁺	1041.397 (0.143)	1043.016 (0.012)	1041.026 (0.178)	1042.902 (0.001)	1042.546 (0.033)	1042.887
Mn ⁺	1146.500 (0.249)	1148.804 (0.048)	1146.107 (0.283)	1148.631 (0.063)	1148.312 (0.091)	1149.359
Fe ⁺	1258.002 (0.325)	1261.002 (0.087)	1257.622 (0.355)	1260.772 (0.105)	1260.548 (0.123)	1262.102
Co ⁺	1376.016 (0.360)	1379.581 (0.102)	1375.505 (0.397)	1379.216 (0.128)	1379.151 (0.133)	1380.989
Ni ⁺	1500.922 (0.365)	1505.084 (0.088)	1500.588 (0.387)	1504.711 (0.113)	1504.858 (0.103)	1506.416
Cu ⁺	1632.914 (0.339)	1637.470 (0.061)	1632.779 (0.347)	1637.113 (0.083)	1637.498 (0.059)	1638.468
Zn ⁺	1772.639 (0.276)	1777.364 (0.011)	1773.437 (0.232)	1777.679 (0.007)	1778.277 (0.041)	1777.553
Ga ⁺	1918.639 (0.229)	1923.234 (0.010)	1919.421 (0.189)	1923.362 (0.016)	1924.076 (0.054)	1923.047
Ge ⁺	2071.275 (0.184)	2075.501 (0.020)	2072.113 (0.143)	2075.479 (0.019)	2076.137 (0.051)	2075.085
As ⁺	2230.704 (0.137)	2234.199 (0.019)	2231.664 (0.094)	2234.165 (0.018)	2234.536 (0.034)	2233.766
Se ⁺	2397.498 (0.080)	2399.722 (0.013)	2398.622 (0.033)	2399.891 (0.020)	2399.765 (0.014)	2399.418
Br ⁺	2571.623 (0.010)	2572.071 (0.007)	2572.959 (0.041)	2572.410 (0.020)	2571.761 (0.005)	2571.893
Kr ⁺	2753.535 (0.072)	2751.537 (0.001)	2755.166 (0.131)	2751.572 (0.000)	2750.878 (0.025)	2751.567
MAD	0.251	0.133	0.202	0.153	0.121	

^a T_{LP97} , Eq. (9), with Liu-Parr coefficients for neutral atoms^b T_{LP97} , Eq. (9), with reoptimized coefficients ($C_{T_1} = 3.1288539558$, $C_{T_2} = -0.0034574267$ and $C_{T_3} = -0.0000591469$)^c T_{LP97+Z^9} , Eq. (18), with both Z^9 and Liu-Parr coefficients for neutral atoms^d T_{LP97+Z^9} , Eq. (18), with Z^9 for neutral atoms and reoptimized coefficients ($C_{T_1} = 3.1267059586$, $C_{T_2} = -0.0039716465$ and $C_{T_3} = -0.0000518778$)^e T_{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 $C_{T_3} = -0.0000240227$)^f T_{HF} , Eq. (2), reported by Clementi and Roetti[55]

Table III. Non-interacting kinetic energy values for negative ions corresponding to the functionals T_{LP97} , T_{LP97+Z^3} , T_{LP97+Z^9} , and T_{HF} .

Ions	T_{LP97} ^a (error%)	T_{LP97} ^b (error%)	T_{LP97+Z^9} ^c (error%)	T_{LP97+Z^9} ^d (error%)	T_{LP97+Z^3} ^e (error%)	T_{HF} ^f
Li ⁻	7.504 (1.023)	7.280 (1.992)	7.512 (1.131)	7.286 (1.912)	7.298 (1.750)	7.428
B ⁻	24.386 (0.384)	23.759 (2.945)	24.411 (0.282)	23.779 (2.864)	23.784 (2.843)	24.480
C ⁻	37.474 (0.338)	36.622 (2.604)	37.513 (0.234)	36.650 (2.529)	36.651 (2.527)	37.601
N ⁻	53.835 (0.650)	52.764 (2.626)	53.865 (0.594)	52.797 (2.565)	52.799 (2.561)	54.187
O ⁻	74.512 (0.377)	73.283 (2.020)	74.599 (0.261)	73.333 (1.953)	73.344 (1.939)	74.794
F ⁻	99.489 (0.030)	98.161 (1.305)	99.677 (0.219)	98.237 (1.229)	98.265 (1.200)	99.459
Na ⁻	162.551 (0.431)	160.922 (0.575)	162.655 (0.496)	160.981 (0.539)	161.058 (0.491)	161.853
Al ⁻	243.169 (0.556)	241.344 (0.198)	243.099 (0.527)	241.361 (0.191)	241.478 (0.143)	241.824
Si ⁻	290.362 (0.537)	288.550 (0.090)	290.286 (0.511)	288.573 (0.082)	288.697 (0.039)	288.810
P ⁻	342.409 (0.502)	340.687 (0.003)	342.380 (0.494)	340.732 (0.010)	340.848 (0.044)	340.697
S ⁻	399.435 (0.477)	397.873 (0.084)	399.496 (0.493)	397.955 (0.105)	398.048 (0.128)	397.538
Cl ⁻	461.579 (0.435)	460.266 (0.149)	461.802 (0.483)	460.410 (0.181)	460.464 (0.192)	459.580
K ⁻	601.426 (0.378)	600.595 (0.239)	601.589 (0.405)	600.681 (0.253)	600.615 (0.242)	599.164
Sc ⁻	760.893 (0.158)	760.787 (0.145)	760.884 (0.157)	760.784 (0.144)	760.569 (0.116)	759.689
Ti ⁻	848.700 (0.038)	849.124 (0.088)	848.736 (0.042)	849.139 (0.090)	848.859 (0.057)	848.377
V ⁻	942.132 (0.077)	943.120 (0.028)	942.176 (0.072)	943.145 (0.030)	942.821 (0.004)	942.859
Cr ⁻	1041.659 (0.159)	1043.267 (0.005)	1041.757 (0.150)	1043.323 (0.000)	1042.990 (0.032)	1043.320
Mn ⁻	1147.102 (0.227)	1149.267 (0.039)	1147.103 (0.227)	1149.297 (0.036)	1149.002 (0.062)	1149.713
Fe ⁻	1258.973 (0.268)	1261.672 (0.054)	1258.887 (0.275)	1261.682 (0.053)	1261.484 (0.069)	1262.355
Co ⁻	1377.380 (0.286)	1380.531 (0.058)	1377.192 (0.300)	1380.514 (0.059)	1380.475 (0.062)	1381.335
Ni ⁻	1502.647 (0.277)	1506.098 (0.048)	1502.398 (0.293)	1506.104 (0.047)	1506.276 (0.036)	1506.819
Cu ⁻	1635.023 (0.240)	1638.596 (0.022)	1634.818 (0.253)	1638.696 (0.016)	1639.103 (0.009)	1638.959
Ga ⁻	1920.237 (0.156)	1923.472 (0.012)	1919.661 (0.186)	1923.128 (0.006)	1923.856 (0.032)	1923.236
Ge ⁻	2073.247 (0.101)	2075.651 (0.015)	2072.426 (0.141)	2075.253 (0.004)	2075.917 (0.028)	2075.343
As ⁻	2233.227 (0.040)	2234.458 (0.015)	2232.250 (0.084)	2234.129 (0.000)	2234.493 (0.016)	2234.130
Se ⁻	2400.688 (0.033)	2400.011 (0.005)	2399.491 (0.017)	2400.042 (0.006)	2399.888 (0.000)	2399.897
Br ⁻	2575.558 (0.118)	2572.456 (0.003)	2574.179 (0.064)	2572.791 (0.010)	2572.092 (0.017)	2572.531
MAD	0.234	0.107	0.213	0.113	0.080	

^a T_{LP97} , Eq. (9) with Liu-Parr coefficients for neutral atoms

^b T_{LP97} , Eq. (9) with reoptimized coefficients ($C_{T_1} = 3.1248445957$, $C_{T_2} = -0.0027038794$ and $C_{T_3} = -0.0000764926$)

^c T_{LP97+Z^9} , Eq. (18) with both Z^9 and Liu-Parr coefficients for neutral atoms

^d T_{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 $C_{T_3} = -0.0000868695$)

^e T_{LP97+Z^3} , Eq. (18) with Z^3 for negative ions and reoptimized coefficients ($C_{T_1} = 3.1326163517$, $C_{T_2} = -0.0040144747$ and $C_{T_3} = -0.0000443462$)

^f Values of T_{HF} reported by Clementi and Roetti[55]

In order to assess whether the Z^n approximations for neutral atoms can be transferred to positive and negative ions, we present in column 4 of Tables II and III, respectively, the values of the non-interactive energy computed by means of Eq. (18) where we have used the Z^9 polynomial approximation fitted for the case of neutral atoms as well as the Liu-Parr coefficients also optimized for neutral atoms. In column 5, of Tables II and III, the same results are presented for the case of the Z^9 polynomial approximation for neutral atoms but where the coeffi-

cients have been reoptimized. In column 6 of Tables II and III, we present values of the non-interacting kinetic energy calculated by means of Eq. (18), but where the Z^3 polynomial approximation is fitted for each particular case and where also the coefficients of the homogeneous functional expansion have been reoptimized. In the last column in Tables II and III, the Hartree-Fock values of Clementi and Roetti for the non-interacting kinetic energy of positive and negative ions are listed, respectively.

It is clearly seen from the values of columns 3 of Tables

II and III that the Liu-Parr homogeneous functional expansion works quite well for positive and negative atomic ions, respectively. In the case positive ions, the MAD value for the relative percent error is 0.133 ; for negative ions, 0.107. In both of these cases, the accuracy increases for ions with large 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) is examined in column 4 of Tables II and III. The results show a MAD value of 0.202 and 0.213 for positive and negative ions, respectively. Again, we see that the approximation improves with increasing atomic number. These results are, in fact, quite comparable to those of the original Liu-Parr expression (Eq. (9)). Naturally, the best fit is obtained when both the Z^n function and the coefficients have been optimized for the ions. The MAD results in this case are 0.121 and 0.080, respectively, for positive and negative ions.

Extensions to molecular systems and clusters

We base the present discussion on the fact, ascertained previously,[2] that to a good approximation the kinetic energy enhancement factor for two neighboring interacting atoms 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 consists of M atoms. We assume that the whole space can be divided into M subvolumes $\{\Omega_A\}_{A=1,\dots,M}$, each one of them corresponding to a given atom A . For, example, for the system composed by the same atoms the space can be divided in the following way:

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

where the vectors \vec{R}_A and \vec{R}_B denote the nuclear positions. Thus, $\mathbf{R}^3 = \bigcup_{A=1}^M \Omega_A$.

The one-particle density for a system formed by M atoms is $\rho(\vec{r}) \equiv \rho(\vec{r}, \{\vec{R}_A\}_{A=1,\dots,M})$, where we make explicit the presence of nuclear coordinates corresponding to the fixed atoms. Let us define

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

Clearly, the notion that $\rho_A(\vec{r})$ is an atomic density is not implicit in this definition as the one-particle density $\rho(\vec{r})$ corresponds to the whole system. The definition of $\rho_A(\vec{r})$ does imply, however, that the value of the molecular or cluster density is that associated to a particular volume Ω_A .

Bearing in mind these considerations we see that we may write the second term of Eq. (1) as

$$\begin{aligned} & \frac{1}{2} \int_{\mathbf{R}^3} d\vec{r} \rho^{5/3}(\vec{r}) A_N[\rho(\vec{r}); \vec{r}] \\ &= \frac{1}{2} \sum_{A=1}^M \int_{\Omega_A} d\vec{r} \rho_A^{5/3}(\vec{r}) A_N[\rho_A(\vec{r}); \vec{r}] \quad (21) \end{aligned}$$

In the present context the plausibility of this separation stems from the fact that we have defined enhancement factors which are associated to a given atom, or atomic region, and which yield satisfactory results for the non-interacting kinetic energy when the charge of the neutral species is either increased yielding a negative ion, or decreased giving a positive one. There is some indirect evidence, however, that the Liu-Parr expansion and approximation given by Eqs. (1) and (12) should work for molecules without partition of the whole space into atomic subvolumes.[1, 56]

But, 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.

We have explored in the present work the possibility of expressing the enhancement factor $A_N[\rho(\vec{r}); \vec{r}]$ of the non interacting kinetic energy functional solely as a function of the one-particle density $\rho(\vec{r})$, dispensing thereby with the more usual representations of this term based on gradient expansions. This was done by adopting the representation given by Liu and Parr in terms of power series of the density.

We have analyzed the behavior of this approximate expression for $A_N[\rho(\vec{r}); \vec{r}]$ in the case of first, second and third row atoms (with the exception of H and He, whose non-interacting kinetic energy functional is exactly given by the Weizsacker term). It is seen that the expression for $A_N[\rho(\vec{r}); \vec{r}]$ given by Eq. (10) does not comply with the requirement of positivity. However, when a local correction term in the form of $\lambda \nabla^2 \rho(\vec{r}) / \rho(\vec{r})^{5/3}$ is added to this expression, we obtain profiles which are in excellent agreement with those of the enhancement factors derived from an orbital representation. More specifically, for the second row atoms Na, Al and Ar, the locations and heights of the maxima generated by the λ -dependent approximate $A_N[\rho(\vec{r}); \vec{r}]$ (Eq. (12)) fully coincide with those obtained from an orbital representation of the enhancement factor (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 those of exact ones. An exception is the Kr atom, where the coincidence both in location and height 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 for the Fe and Ni atoms we observe a divergence; in all other cases the asymptote follows the trend of the exact enhancement factor.

In addition, we have explored the possibility of introducing a Z -dependent approximation to represent 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), through the polynomials (13) - (15), respectively. The non-interacting atomic kinetic

energy density functionals generated from these new Z -dependent enhancement factors (Eq.(17)) show a behavior that very closely resembles that of the Liu-Parr functional T_{LP97} . From a comparison of the MAD values for T_{LP97} (0.222), T_{LP97+Z^3} (0.329), and T_{LP97+Z^9} (0.224), where all these functionals are evaluated with the Liu-Parr optimized coefficients, we see that the functional T_{LP97+Z^9} performs as well as the Liu-Parr functional T_{LP97} . However, when we re-optimize the coefficients of the Z -dependent functionals, we obtain the MAD values of 0.129 and 0.166 for T_{LP97+Z^3} and T_{LP97+Z^9} , respectively, thus showing a closer accord with the exact Hartree Fock values. The behavior of the approximate enhancement factors in the case of the Z -dependent functionals is undistinguishable from that of the λ -corrected Liu-Parr functionals.

Concerning the extension of the $Z - \lambda$ -representation of neutral atoms to positive and negative ions we see, from Tables II and III, that the non-interacting atomic kinetic energy density functionals generated from these new $Z - \lambda$ -dependent enhancement factors perform quite well, even in the case when we use the same Z^n functions as well as the Liu-Parr coefficients which were adjusted for neutral atoms.

Summing up, based both on the Liu-Parr power density expansion and on the replacement of some of the integrals of this expansion by Z -dependent functions, a very simple form for the non-interacting kinetic energy enhancement factor has been found. The corresponding functionals, which bypass the usual gradient expansion representation, lead to non-interacting kinetic energy values which closely approximate (as measured by the MAD values) the exact ones calculated from Hartree Fock wave functions. Moreover, the additivity of the atomic enhancement factors, opens a possible way for extending the present results to molecules and clusters.

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APPENDIX A. THEOREM 2 OF LIU AND PARR REVISITED

For ease of understanding of general readers we have included some taken-for-granted lines left out in the original proof of Theorem 2 of Liu and Parr.

Theorem 2. (*S. Liu and R. G. Parr [1]*). *Given the functional*

$$Q_j[\rho] = C_j[H_j]^j, \quad (\text{A1})$$

where H_j is a homogeneous and local functional, if it is homogeneous of degree m in coordinate scaling, it takes the form

$$Q_j[\rho] = C_j \left[\int d\vec{r} \rho^{[1+(m/3j)]}(\vec{r}) \right]^j. \quad (\text{A2})$$

Further, if $Q_j[\rho]$ is homogeneous of degree k in density scaling, j is determined by the relation

$$j = k - \frac{m}{3} \quad (\text{A3})$$

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

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

Taking the functional derivative of (A1) with respect to ρ , i.e:

$$\frac{\delta Q_j[\rho]}{\delta \rho} = C_j j H_j[\rho]^{j-1} \frac{\delta H_j[\rho]}{\delta \rho} \quad (\text{A5})$$

and rewriting Eq. (A1), we have

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

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

$$- \int d\vec{r} \rho(\vec{r}) \vec{r} \cdot \nabla \frac{\delta Q_j[\rho]}{\delta \rho(\vec{r})} = m Q_j[\rho]. \quad (\text{A7})$$

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

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

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

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

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, i.e.

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

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

$$\int d\vec{r} \rho(\vec{r}) j C_j (H_j[\rho])^{j-1} \frac{\delta H_j[\rho]}{\delta \rho(\vec{r})} = \frac{m+3j}{3} C_j (H_j[\rho])^j$$

$$\int d\vec{r} \rho(\vec{r}) \frac{\delta H_j[\rho]}{\delta \rho(\vec{r})} = \left(1 + \frac{m}{3j}\right) (H_j[\rho])$$

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

$$\int d\vec{r} \rho(\vec{r}) \frac{df_j(\rho)}{d\rho(\vec{r})} = \int d\vec{r} \left(1 + \frac{m}{3j}\right) f_j(\rho). \quad (\text{A11})$$

If the two integrals are equal it follows:

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

Therefore, we have to solve a simple differential equation

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

$$\ln f_j(\rho) = \left(1 + \frac{m}{3j}\right) \ln \rho(\vec{r}) + C_j$$

$$f_j(\rho) = C_j \rho^{[1+m/3j]}(\vec{r}), \quad (\text{A13})$$

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

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

and

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

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

$$j = k - \frac{m}{3}. \quad (\text{A16})$$

□

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