

A relationship between the weighted density approximation and the local-scaling transformation version of density functional theory

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Abstract

A relationship between the auxiliary density, $\tilde{\rho}(\mathbf{r})$, defined within the framework of the weighted density approximation and the kinetic energy modulating factor, $A_N([\rho(\mathbf{r})]; \mathbf{r})$, which appears in the local-scaling transformation version of density functional theory is presented. This relationship imposes the condition of positiveness on the kinetic energy modulating factor and this, in turn, leads to an important mathematical condition on any approximate kinetic energy density functional. It is shown that two well-known approximate kinetic energy density functionals do not satisfy the above relationship at distances very close to the nucleus. By forcing a given approximate kinetic energy density functional to obey the above condition, both the kinetic and exchange energies can be obtained within a framework similar to that of the weighted density approximation. Results on some closed-shell atomic systems provide support for those ideas.

1. Introduction

Almost four decades ago, Hohenberg and Kohn [1] provided an existence theorem stating that there exists a relationship between the ground state electron density of a given system, $\rho(\mathbf{r})$, and the external potential, $v(\mathbf{r})$, in which the electrons move. This fact has the important consequence that the energy of the above ground state can be expressed as a functional of $\rho(\mathbf{r})$ instead of taking the usual approach of using the many-body wavefunction, $\Psi(\mathbf{r})$. Moreover, Hohenberg and Kohn defined a universal functional of the ground state density containing

the kinetic energy and the electron–electron interaction energy terms (for simplicity, $[\rho(\mathbf{r})]$ is replaced by $[\rho]$ throughout this work when explicit dependence must be indicated):

$$\begin{aligned} E[\rho] &= F[\rho] + \int v(\mathbf{r})\rho(\mathbf{r}) \, d\mathbf{r}, \\ F[\rho] &= T[\rho] + V_{ee}[\rho]. \end{aligned} \quad (1)$$

Unfortunately, no explicit form is supplied for such functionals by Hohenberg and Kohn.

Later, Kohn and Sham [2] featured an auxiliary set of functions, $\{\psi_i(\mathbf{r})\}$, which allow one to replace the unknown kinetic energy functional, $T[\rho]$, by the kinetic energy of a non-interacting system, $T_s[\rho]$. The error introduced in such an approach is included in the so-called exchange–correlation term, $E_{xc}[\rho]$, that also accounts for the non-classical part of the electron–electron interaction energy:

$$\begin{aligned} E[\rho] &= T[\rho] + V_{ee}[\rho] + \int v(\mathbf{r})\rho(\mathbf{r}) \, d\mathbf{r} \\ &= T_s[\rho] + \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} \, d\mathbf{r}' + \int v(\mathbf{r})\rho(\mathbf{r}) \, d\mathbf{r} + E_{xc}[\rho]. \end{aligned} \quad (2)$$

Thus, the only unknown quantity within the Kohn–Sham methodology is the exchange–correlation density functional, $E_{xc}[\rho]$. Equation (2) constitutes the basis of the modern implementations of the density functional theory (DFT). This theory is usually implemented within the local-density approximation (LDA) for $E_{xc}[\rho]$, which is valid for slowly varying densities. Many accurate improvements to the original LDA to the exchange–correlation density functional developed by Kohn and Sham [2] have been proposed. All of these improvements go beyond the LDA by resorting to the gradient of the density. They are collectively known as generalized gradient approximations (GGA) [3–5] and are widely used to calculate properties of atoms, molecules, and solids nowadays [6, 7].

Unfortunately, similar improvements to the non-interacting kinetic energy functional are lacking. Approximate kinetic energy functionals are usually developed by taking the Thomas–Fermi expression as the starting point and adding to it the corrections necessary to satisfy the limiting forms of the exact kinetic energy of the non-interacting electron gas. The Padé approximant proposed by DePristo and Kress [8] and a GGA version for the kinetic energy density functional suggested by Perdew [9] are examples of such developments. These functionals are considered in detail below.

There exist, nevertheless, some other approaches for dealing with the non-interacting kinetic energy functional. One of them is the weighted density approximation (WDA) [10, 11] which exploits the fact that the kinetic and exchange–correlation energies are related through the one-particle density matrix. Another approach is the local-scaling transformation version of the DFT (LST) [12, 13]. In the LST, an initial (or ‘generating’) many-body wavefunction is transformed to a final, density-dependent many-body wavefunction. Then, by solving the Schrödinger equation for the transformed wavefunction, a density-dependent kinetic energy functional is obtained.

The goal of the present work is to show that key quantities of the WDA and the LST are closely related through their kinetic energy expressions. Interestingly, the above relationship introduces an important mathematical condition that must be obeyed by any approximate kinetic energy functional.

The rest of the present work is organized as follows. Section 2 is devoted to providing a brief overview of the WDA and the LST. Then, the relationship mentioned in the last paragraph is presented in section 3. Finally, in section 4 some numerical results are provided to make clear the above connections.

2. An overview to the weighted density approximation and the local-scaling transformation version of density functional theory

2.1. The WDA

The WDA starts by writing the exchange energy in terms of the one-particle density matrix as [11]

$$E_x[\rho] = -\frac{1}{2} \int \frac{\rho(\mathbf{r}_1, \mathbf{r}_2)\rho(\mathbf{r}_2, \mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2. \quad (3)$$

The one-particle density matrix can in turn be written in terms of the correlation function, $h(\mathbf{r}_1, \mathbf{r}_2)$, as

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \sqrt{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)(-2h(\mathbf{r}_1, \mathbf{r}_2))}. \quad (4)$$

Within the WDA, the correlation function for a system with density $\rho(\mathbf{r}_1)$ is

$$h(\mathbf{r}_1, \mathbf{r}_2) = -\frac{9}{2} \left(\frac{\sin x - x \cos x}{x^3} \right)^2, \quad (5)$$

where $x = |\mathbf{r}_1 - \mathbf{r}_2|(3\pi^2\tilde{\rho}^{1/3}(\mathbf{r}_1))$. The auxiliary density, $\tilde{\rho}(\mathbf{r}_1)$, is numerically evaluated at every point \mathbf{r}_1 to satisfy the Fermi hole sum rule

$$\int \rho(\mathbf{r}_2)h(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = -1. \quad (6)$$

In the WDA, the kinetic energy is written in terms of the one-particle density matrix, too:

$$T_s[\rho] = -\frac{1}{2} \int \nabla_1^2 \rho(\mathbf{r}_1, \mathbf{r}_2)|_{\mathbf{r}_2=\mathbf{r}_1} d\mathbf{r}_1. \quad (7)$$

Now, using equations (4) and (5) and assuming that

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_2, \mathbf{r}_1), \quad (8)$$

equation (7) becomes

$$T_s[\rho] = C_k \int \rho(\mathbf{r})\tilde{\rho}^{2/3}(\mathbf{r}) d\mathbf{r} + \frac{1}{8} \int \frac{(\nabla\rho(\mathbf{r}))^2}{\rho(\mathbf{r})} d\mathbf{r} - \frac{1}{4} \int \nabla^2\rho(\mathbf{r}) d\mathbf{r}, \quad (9)$$

where $C_k = 3(3\pi^2)^{2/3}/10$. Equation (9) is the WDA practical expression for calculating the kinetic energy of a given system with density $\rho(\mathbf{r})$.

2.2. The LST

In the LST the kinetic energy is written in terms of the locally scaled orbital set $\{\psi_{\rho,i}(\mathbf{r})\}$ as [12]

$$T_s[\rho] = -\frac{1}{2} \sum_i^{occ} \int \psi_{\rho,i}^*(\mathbf{r}_2)\nabla_1^2\psi_{\rho,i}(\mathbf{r}_1)|_{\mathbf{r}_2=\mathbf{r}_1} d\mathbf{r}_1, \quad (10)$$

where each locally scaled orbital is related to a generating orbital by means of

$$\psi_{\rho,i}(\mathbf{r}) = \sqrt{\frac{\rho(\mathbf{r})}{\rho_g(\mathbf{f}(\mathbf{r}))}} \psi_{g,i}(\mathbf{f}(\mathbf{r})). \quad (11)$$

The transformation function, $\mathbf{f}(\mathbf{r})$, can be obtained through a first-order differential equation:

$$\frac{1}{r^3} \mathbf{r} \cdot \nabla f^3(\mathbf{r}) = \frac{\rho(\mathbf{r})}{\rho_g(\mathbf{f}(\mathbf{r}))}, \quad (12)$$

which, for spherically averaged systems, reduces to

$$\left(\frac{f(r)}{r}\right)^2 \frac{\partial f(r)}{\partial r} = \frac{\rho(r)}{\rho_g(f(r))}. \quad (13)$$

Using equations (11) and (13), equation (10) becomes

$$T_s[\rho] = \frac{1}{2} \int \rho^{5/3}(\mathbf{r}) A_N([\rho]; \mathbf{r}) d\mathbf{r} + \frac{1}{8} \int \frac{(\nabla \rho(\mathbf{r}))^2}{\rho(\mathbf{r})} d\mathbf{r} - \frac{1}{4} \int \nabla^2 \rho(\mathbf{r}) d\mathbf{r}, \quad (14)$$

where the kinetic energy modulating factor $A_N([\rho]; \mathbf{r})$ depends on the transformation function, the generating orbitals and the generating density (see [12] and [13] for details).

Within the LST, the exchange energy can be evaluated using an expression similar to equation (3), with the locally scaled one-particle density matrix written in terms of the locally scaled orbitals:

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \sum_i^{occ} \psi_{\rho,i}(\mathbf{r}_1) \psi_{\rho,i}^*(\mathbf{r}_2). \quad (15)$$

Then, the LST exchange energy is [12]

$$E_x[\rho] = -\frac{1}{2} \int \rho^{4/3}(\mathbf{r}) B_N([\rho]; \mathbf{r}) d\mathbf{r}, \quad (16)$$

where the exchange energy modulating factor $B_N([\rho]; \mathbf{r})$ depends on the same factors as the kinetic energy one.

It is worth mentioning that another exchange energy functional can be written within the LST if the Levy–Perdew relationship [14] is used as starting point (see [15] for details).

Finally, it should be noted that if the kinetic energy operator $\frac{1}{2} \nabla_1 \nabla_2$ is used instead of the operator appearing in both equations (7) and (10), the relationship

$$-\frac{1}{2} \nabla_1^2 \rho(\mathbf{r}_1, \mathbf{r}_2)|_{\mathbf{r}_2=\mathbf{r}_1} = \frac{1}{2} \nabla_1 \nabla_2 \rho(\mathbf{r}_1, \mathbf{r}_2)|_{\mathbf{r}_2=\mathbf{r}_1} - \frac{1}{4} \nabla_1^2 \rho(\mathbf{r}_1, \mathbf{r}_1) \quad (17)$$

or, in terms of orbitals,

$$-\frac{1}{2} \sum_i^{occ} \psi_i^*(\mathbf{r}_2) \nabla_1^2 \psi_i(\mathbf{r}_1)|_{\mathbf{r}_2=\mathbf{r}_1} = \frac{1}{2} \sum_i^{occ} \nabla_2 \psi_i^*(\mathbf{r}_2) \cdot \nabla_1 \psi_i(\mathbf{r}_1)|_{\mathbf{r}_2=\mathbf{r}_1} - \frac{1}{4} \nabla_1^2 \rho(\mathbf{r}_1) \quad (18)$$

must be taken into account to ensure the correct local behaviour of the kinetic energy density, t . In this case, two equations completely similar to equations (9) and (14) are obtained.

3. The relationship between the WDA and the LST

Karasiev *et al* [16] suggest that the kinetic energy modulating factor can be calculated using one-electron Hartree–Fock or exchange-only Kohn–Sham orbitals:

$$\begin{aligned} \frac{1}{2} A_N([\rho]; \mathbf{r}) &= \frac{\frac{1}{2} \sum_i^N \nabla \psi_i^*(\mathbf{r}) \cdot \nabla \psi_i(\mathbf{r}) - \frac{1}{8} \frac{(\nabla \rho(\mathbf{r}))^2}{\rho(\mathbf{r})}}{\rho^{5/3}(\mathbf{r})} \\ &= \frac{-\frac{1}{2} \sum_i^N \psi_i^*(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r}) - \frac{1}{8} \frac{(\nabla \rho(\mathbf{r}))^2}{\rho(\mathbf{r})} + \frac{1}{4} \nabla^2 \rho(\mathbf{r})}{\rho^{5/3}(\mathbf{r})}. \end{aligned} \quad (19)$$

An approximate kinetic energy density, $t^{approx}[\rho]$, can be used in equation (19) instead of the exact one, $t^{exact} = -\frac{1}{2} \sum_i^N \psi_i^*(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r})$, to calculate the corresponding modulating factor. Note that the explicit dependence on the density is dropped from t^{exact} .

Then, equation (19) can be immediately generalized for any kinetic energy density $t[\rho] = t^{exact}, t^{approx}[\rho]$:

$$\frac{1}{2}A_N([\rho]; \mathbf{r}) = \frac{t[\rho] - \frac{1}{8} \frac{(\nabla\rho(\mathbf{r}))^2}{\rho(\mathbf{r})} + \frac{1}{4}\nabla^2\rho(\mathbf{r})}{\rho^{5/3}(\mathbf{r})}. \quad (20)$$

From equations (9) and (14), on the other hand, it is clear that

$$C_k \tilde{\rho}^{2/3}(\mathbf{r}) = \frac{1}{2}\rho^{2/3}(\mathbf{r})A_N([\rho]; \mathbf{r}). \quad (21)$$

The above equation shows that a close relationship between the WDA and the LST exists through $\tilde{\rho}(\mathbf{r})$ and $A_N([\rho]; \mathbf{r})$, even though they are calculated in very different ways.

If the above relationship is rewritten as

$$\tilde{\rho}^{1/3}(\mathbf{r}) = \rho^{1/3}(\mathbf{r})\sqrt{\frac{1}{2C_k}A_N([\rho]; \mathbf{r})} \quad (22)$$

and it is accepted that $\tilde{\rho}(\mathbf{r})$ is a *real* quantity related to the true density by means of non-local terms, it immediately follows that the kinetic energy modulating factor must obey

$$A_N([\rho]; \mathbf{r}) \geq 0, \quad \forall \mathbf{r}. \quad (23)$$

It is then evident from equations (20) and (23) that

$$t[\rho] - \frac{1}{8} \frac{(\nabla\rho(\mathbf{r}))^2}{\rho(\mathbf{r})} + \frac{1}{4}\nabla^2\rho(\mathbf{r}) \geq 0, \quad \forall \mathbf{r}, \quad (24)$$

with $t[\rho] = t^{exact}, t^{approx}[\rho]$. Equation (24) introduces an important mathematical condition to be satisfied by any kinetic energy density and it is expected to play a relevant role in the development of new kinetic energy density functionals.

Finally, it is very interesting to note that equations (20) and (22) lead to

$$\tilde{\rho}^{1/3}(\mathbf{r}) = \sqrt{\frac{t[\rho] - \frac{1}{8} \frac{(\nabla\rho(\mathbf{r}))^2}{\rho(\mathbf{r})} + \frac{1}{4}\nabla^2\rho(\mathbf{r})}{C_k\rho(\mathbf{r})}}. \quad (25)$$

We suggest that equation (25) could be thought of as a new version of the WDA in which the auxiliary density, $\tilde{\rho}(\mathbf{r})$, is calculated analytically instead of using the sum rule for the exchange hole, equation (6). One of the advantages of using equation (25) to evaluate $\tilde{\rho}(\mathbf{r})$ is that the term $\delta\tilde{\rho}(\mathbf{r})/\delta\rho(\mathbf{r})$, which appears as a consequence of applying the variational principle to the total energy expression, can also be obtained analytically.

It should be also stated that the above expression can be used together with a kinetic energy term calculated through equation (9) or through $t = -\frac{1}{2}\sum_i^N \psi_i^*(\mathbf{r})\nabla^2\psi_i(\mathbf{r})$ as in [17].

The exploitation of equation (25) to predict some atomic properties is currently in progress.

4. Some numerical tests

In this section, the behaviour of several well-known kinetic energy density functionals is tested against the condition imposed by equation (24).

Two kinetic energy density functionals were mentioned in the introduction, namely, the one due to DePristo and Kress (DPK) [8] and another proposed by Perdew (GGA) [9]. The DPK functional has the form

$$t^{DPK}[\rho] = t^{(0)}[\rho] \frac{1 + 0.95x + a_2x^2 + a_3x^3 + 9b_3x^4}{1 - 0.05x + b_2x^2 + b_3x^3} \quad (26)$$

where $x = t^{(2)}[\rho]/t^{(0)}[\rho]$ and

$$t^{(0)}[\rho] = C_k \rho^{5/3}(\mathbf{r}) \quad (27)$$

$$t^{(2)}[\rho] = \frac{1}{72} \frac{(\nabla \rho(\mathbf{r}))^2}{\rho(\mathbf{r})}. \quad (28)$$

It can be easily seen that

$$t^{DPK}[\rho] \rightarrow t^{(0)}[\rho] + t^{(2)}[\rho] \quad \text{as } x \rightarrow 0 \quad (29)$$

and

$$t^{DPK}[\rho] \rightarrow 9t^{(2)}[\rho] \quad \text{as } x \rightarrow \infty. \quad (30)$$

Equations (29) and (30) are the corresponding slowly and rapidly varying density limiting forms of the exact kinetic energy of the homogeneous electron gas, respectively.

On the other hand, the GGA functional is written as

$$t^{GGA}[\rho] = t^{(0)}[\rho] \frac{1 + 88.3960s^2 + 16.3683s^4}{1 + 88.2108s^2} \quad (31)$$

where $s = |\nabla \rho(\mathbf{r})|/2(3\pi^2)^{1/3} \rho^{4/3}(\mathbf{r})$. It can be seen in this case that

$$t^{GGA}[\rho] \rightarrow t^{(0)}[\rho] + t^{(2)}[\rho] \quad \text{as } s \rightarrow 0 \quad (32)$$

but

$$t^{GGA}[\rho] \rightarrow t^{(2)}[\rho] \quad \text{as } s \rightarrow \infty. \quad (33)$$

Equation (33) shows that the rapidly varying density limiting form of the exact kinetic energy for the homogeneous electron gas is underestimated by a factor of 9 in the GGA functional.

Figures 1–4 show the kinetic energy modulating factor, $A_N([\rho]; \mathbf{r})$, calculated for some closed-shell atoms using equation (20) with $t[\rho] = t^{exact}$, $t^{DPK}[\rho]$, and $t^{GGA}[\rho]$ giving rise to A_N^{HF} , A_N^{DPK} , and A_N^{GGA} , respectively. Moreover, the kinetic energy modulating factor A_N^{WDA} is calculated with the following expression:

$$A_N^{WDA}([\rho]; \mathbf{r}) = 2C_k \frac{\tilde{\rho}^{2/3}(\mathbf{r})}{\rho^{2/3}(\mathbf{r})}. \quad (34)$$

The Hartree–Fock orbitals and electronic densities needed for the different kinetic energy densities are taken from [18] and the WDA auxiliary densities required in (34) are evaluated numerically from equation (6). The calculations are not self-consistent.

It is observed in the figures that both A_N^{HF} and A_N^{WDA} obey equation (23) over the whole range for the systems under study. It can also be seen that the ‘peaks’ exhibited by A_N^{WDA} are much less pronounced than those of A_N^{HF} . On the other hand, the ‘valleys’ in the A_N^{WDA} -curves are shallower than the exact ones. The DPK and GGA functionals provide very similar modulating factors, being only slightly different at the beginning of the divergent region. Both A_N^{DPK} and A_N^{GGA} exhibit the wrong behaviour very close to the nucleus although they show the correct structure for larger distances. However, the ‘peaks’ shown by those functions are higher than those shown by A_N^{HF} . These results seem to suggest that the DPK and GGA kinetic energy functionals could be parametrized again but now taking equation (24) into account to ensure their correct local behaviour over the whole range.

A clear benefit of forcing a given kinetic energy density functional to satisfy equation (24) is that the exchange energy term can then be calculated using an expression similar to that of the WDA—see equations (3) and (7)—and taking advantage of the relationship given by

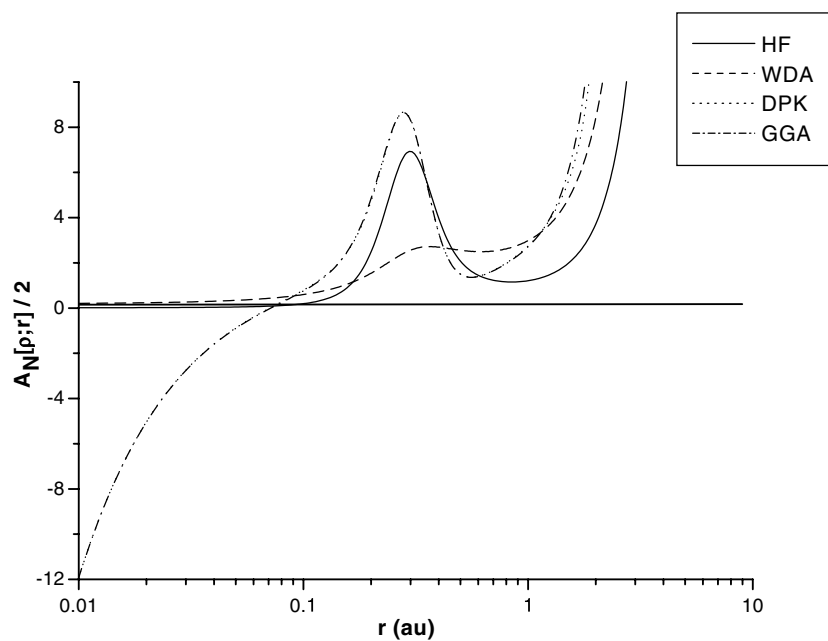


Figure 1. Comparison of modulating factors calculated with different kinetic energy functionals for the Ne atom.

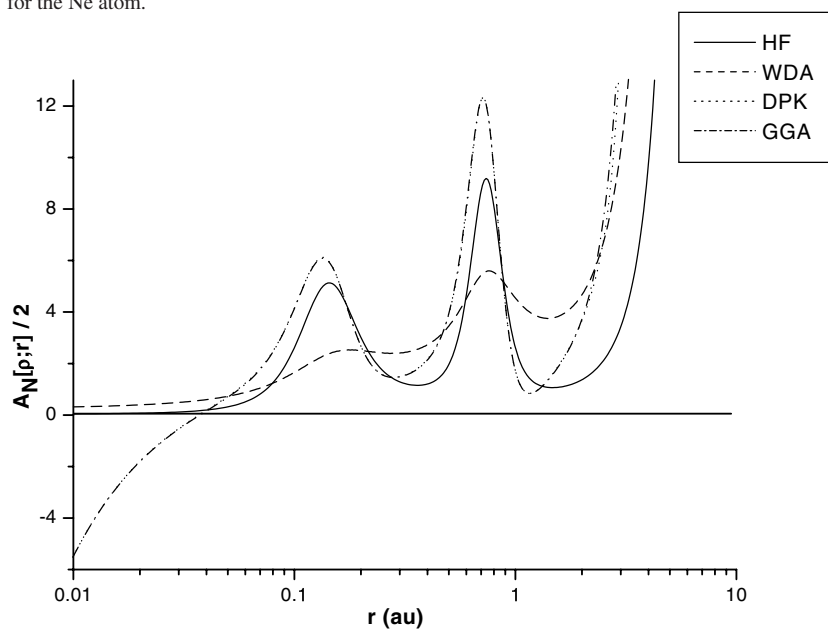


Figure 2. Comparison of modulating factors calculated with different kinetic energy functionals for the Ar atom.

equation (22). To exemplify those assertions, tables 1 and 2 show the kinetic and exchange energies of some closed-shell atoms calculated using

$$T_s^M[\rho] = \frac{1}{2} \int \rho^{5/3}(r) A_N^M([\rho]; r) dr + \frac{1}{8} \int \frac{(\nabla \rho(r))^2}{\rho(r)} dr - \frac{1}{4} \int \nabla^2 \rho(r) dr \quad (35)$$

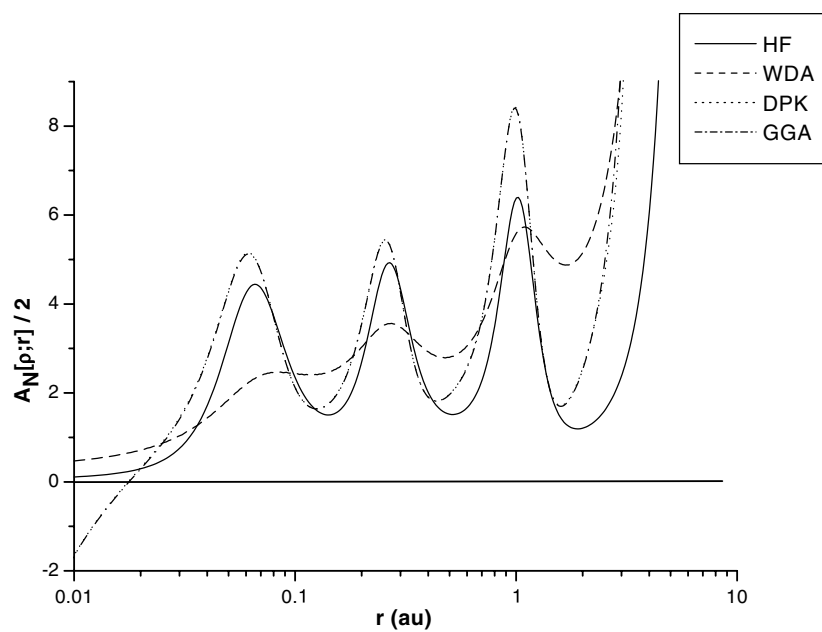


Figure 3. Comparison of modulating factors calculated with different kinetic energy functionals for the Kr atom.

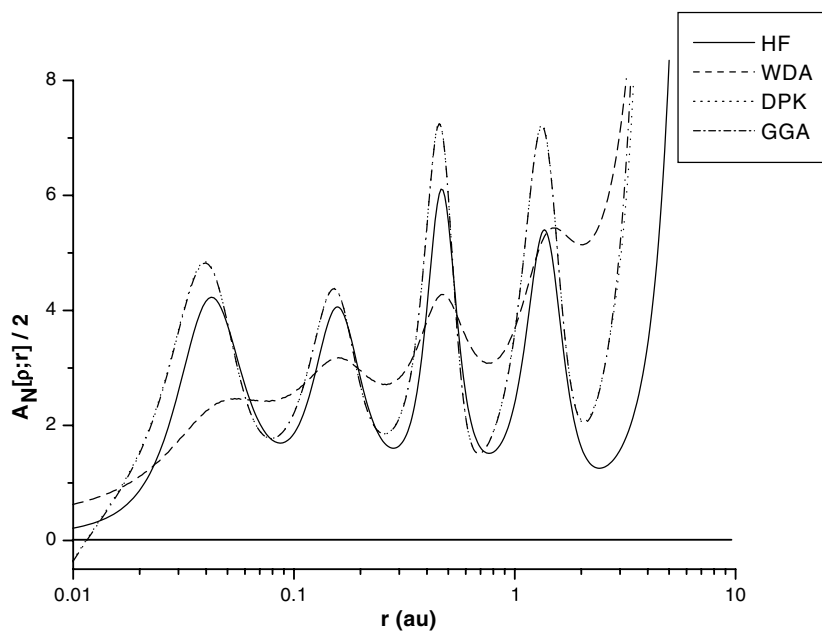


Figure 4. Comparison of modulating factors calculated with different kinetic energy functionals for the Xe atom.

and

$$E_x^M[\rho] = -\frac{9}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \left(\frac{\sin x^M - x^M \cos x^M}{x^{M^3}} \right)^2 d\mathbf{r} d\mathbf{r}' \quad (36)$$

Table 1. Kinetic energies (in au) of some closed-shell atoms calculated with equation (35) using different modulating factors. Hartree–Fock results are given for reference. See the text for the meaning of the labels.

	A_N^{HF}	A_N^{WDA}	A_N^{DPK} ^a	A_N^{GGA} ^b	HF ^c
Ne	128.55	133.66	136.01 (128.22)	135.87 (127.85)	128.55
Ar	526.82	546.48	556.50 (527.56)	550.85 (524.29)	526.82
Kr	2752.05	2813.53	2869.79 (2750.90)	2854.83 (2733.34)	2752.05
Xe	7232.14	7338.00	7499.52 (7224.97)	7464.59 (7184.41)	7232.14

^a Values obtained with equation (26) are given in parentheses.

^b Values obtained with equation (31) are given in parentheses.

^c From [19].

Table 2. Exchange energies (with the opposite sign and in au) of some closed-shell atoms calculated with equation (36) using different modulating factors. Hartree–Fock results are given for reference. See the text for the meaning of the labels.

	A_N^{HF}	A_N^{WDA}	A_N^{DPK}	A_N^{GGA}	HF ^a
Ne	16.69	12.83	9.78	9.82	12.11
Ar	44.51	32.22	31.03	30.77	30.19
Kr	133.97	100.56	99.97	100.49	93.89
Xe	248.87	191.67	198.57	199.55	179.19

^a From [20].

where $x^M = |\mathbf{r} - \mathbf{r}'|(3\pi^2\rho(\mathbf{r}))^{1/3} \sqrt{\frac{1}{2C_k} A_N^M([\rho]; \mathbf{r})}$, with $M = \text{HF, WDA, DPK, and GGA}$. Those points for which $A_N^M([\rho]; \mathbf{r})$ does not obey equation (23) are merely excluded from the integration domain.

It should not be a surprise that A_N^{HF} gives the exact kinetic energy values in table 1 since it is generated from Hartree–Fock orbitals. The rather large values provided by A_N^{WDA} indicate that the ‘valleys’ mentioned above tend to dominate the overall behaviour. On the other hand, the kinetic energy values obtained with the DPK and GGA functionals after applying the condition given by equation (23) are systematically larger than the values obtained using equations (26) and (31). This is not surprising at all since the relationship mentioned above eliminates negative contributions to the kinetic energy, thus favouring greater values.

It can be seen from table 2 that A_N^{HF} provides very small exchange energy values, whereas the other three kinetic energy modulating factors give very reasonable results (smaller than the exact ones, too), especially taking into account that they are not self-consistent. It is not easy to analyse the nature of the discrepancies in those cases due to the form of the variable x^M in equation (36).

In any case, it is clear from the tables that the results are quite encouraging considering their non-self-consistent nature. It is worth noting that both the kinetic and exchange energies obtained with the DPK and GGA kinetic energy density functionals are comparable to the WDA values. This is very promising considering that self-consistent WDA calculations give very acceptable results (see [21] for example).

It should be clear, of course, that even though any new kinetic energy density functional is designed considering the condition given by equation (24), the exchange energy can

be evaluated using any of the several well-known approximate exchange energy density functionals instead of using a WDA-like philosophy such as the one presented in this work.

5. Summary

A relationship between key quantities of the WDA and the local-scaling transformation version of the DFT was presented in this work. This relationship imposes an important mathematical condition on every approximate kinetic energy density functional.

It was shown that two well-known approximate kinetic energy density functionals do not satisfy the above relationship at distances very close to the nucleus. It is proposed that their empirical parameters could be recalculated taking into account the mathematical condition introduced in this work.

One of the advantages of forcing a given approximate kinetic energy density functional to obey the above condition is that both the kinetic and exchange energies can be calculated within a framework similar to that of the WDA. Some numerical tests performed on atomic systems seem to support those ideas.

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