

New Functional Orbital-free Within DFT for Metallic Systems

Vittoria Urso^{1, 2, *}

¹Department of Basic and Applied Sciences for Engineering, Sapienza University, Rome RM, Italy

²Department of Physics, University of Modena and Reggio Emilia, Modena MO, Italy

Email address:

vittoria.urso@uniroma1.it (Vittoria Urso)

To cite this article:

Vittoria Urso. (2024). New Functional Orbital-free Within DFT for Metallic Systems. *International Journal of Systems Science and Applied Mathematics*, 9(2), 30-36. <https://doi.org/10.11648/j.ijssam.20240902.12>

Received: 1 May 2024; **Accepted:** 9 July 2024; **Published:** 4 August, 2024

Abstract: I present the continuation of a study on Laplacian Level Kinetic Energy (KE) functionals applied to metallic nanosystems. The development of novel Kinetic Energy functionals is an important topic in density functional theory (DFT). The nanoparticles are patterned using gelatin spheres of different sizes, background density and number of electrons. To reproduce the correct kinetic and potential energy density of the various nanoparticles, the use of semilocal descriptors is necessary. Need an explicit density functional expression for the kinetic energy of electrons, including the first e second functional derivative, i.e. the kinetic potential and the kinetic kernel, respectively. The exact explicit form of the non interacting kinetic energy, as a functional of the electron density, is known only for the homogeneous electron gas (HEG), i.e., the Thomas-Fermi (TF) local functional and for 1 and 2 electron systems, i.e., the von Weizsacker (VW) functional. In between these two extreme cases, different semilocal or non local approximations were developed in recent years. Most semilocal KE functionals are based on modifications of the second-order gradient expansion (GE2) or fourth-order gradient expansion (GE4). I find that the Laplacian contribute is fundamental for the description of the energy and the potential of nanoparticles. I propose a new LAP2 semilocal functional which, better than the previous ones, allows us to obtain fewer errors both of energy and potential. More details of the previous calculations can be found in my 2 previous works which will be cited in the text.

Keywords: Density Functional Theory, Kinetic Energy Functionals, Jellium

1. Introduction

Density functional theory (DFT) is one of the most widely used approaches for theoretical calculations in solid-state physics and quantum chemistry [1]. In its original orbital-free (OF) formulation [2, 3], DFT allows one to describe the ground state of a many-electron system [4] as a function of the electron density (ρ) alone, through the solution of the Euler equation [5]. The Euler equation is obtained minimizing the equation of the ground state energy of a system with N electrons:

$$E[\rho] = T_s[\rho] + E_H[\rho] + \int d\mathbf{r} \nu_{ext}(\mathbf{r})\rho(\mathbf{r}) + E_{xc}[\rho] \quad (1)$$

where $T_s[\rho]$ is the noninteracting kinetic energy (KE); $\nu_{ext}(\mathbf{r})$ is the external (i.e. nuclear) potential; $E_{xc}[\rho]$ is the exchange correlation (XC) energy; $E_H[\rho]$ is the Hartree energy. If in Euler equation we put the exact $T_s[\rho]$:

$$T_s[\rho] = \langle \phi_n^{min} | \hat{T} | \phi_n^{min} \rangle = \int d\mathbf{r} \phi_n^{min}(\mathbf{r}) \hat{T} \phi_n^{min}(\mathbf{r}) \quad (2)$$

we obtain the Kohn-Sham self-consistent equations [6]

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + v_{KS}[\rho](\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon \phi_i(\mathbf{r}),$$

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2, \quad (3)$$

$$v_{KS}[\rho](\mathbf{r}) = \nu_{ext}(\mathbf{r}) + v_H[\rho](\mathbf{r}) + v_{xc}[\rho](\mathbf{r})$$

If in Euler equation we put an approximate $T_s[\rho]$ we obtain orbital-free DFT [2, 7-9].

Different semilocal or nonlocal approximations were developed in recent years for the KE. Non-local KE

functionals are rather accurate, but they are derived mainly from the linear response of the homogeneous electron gas the Lindhard function [2] and are thus only suitable for solid-state simulations. The GGAs are the most popular KE approximations also known as semilocal [10–13]:

$$T_s^{GGA}[\rho] = \int \tau^{TF} F_s(s(\mathbf{r})) d\mathbf{r} \quad (4)$$

where F_s , called *enhancement factor*, is an appropriate function of the *reduced gradient*:

$$s = \frac{|\nabla\rho|}{2(3\pi^2)^{1/3}\rho^{4/3}} \quad (5)$$

and for $F_s = 1$ get the Thomas-Fermi (TF) KE functional. In solid-state physics, DFT has always been more popular than traditional approaches to the Schrödinger equation, because the Hartree-Fock approximation has unpleasant singularities for zero-gap materials, i.e., metals. The next logical step beyond the standard approximations are meta-GGAs, which include the kinetic energy density as an input, and can yield accurate ground-state energies simultaneously for molecules, solids, and surfaces [14]. Another step is obtained including a new ingredient in the kinetic enhancement factor [15, 16]: the laplacian of the density yielding the class of Laplacian-Level meta-GGAs (LL-meta-GGAs) [17]

$$T_s^{LL}[\rho] = \int \tau^{TF} F_s(\rho, \nabla\rho, \nabla^2\rho) d\mathbf{r} \quad (6)$$

Under a uniform scaling of the density

$$\rho_\lambda(\mathbf{r}) = \lambda^3\rho(\lambda\mathbf{r}), \quad \lambda \geq 0 \quad (7)$$

the exact non-interacting kinetic energy behaves as

$$T_s[\rho_\lambda] = \lambda^2 T_s[\rho] \quad (8)$$

i.e. as the Thomas-Fermi KE. Therefore, to have eq.(6) satisfy this constraint, $F_s(\rho, \nabla\rho, \nabla^2\rho, \dots)$ must be invariant under the uniform density scaling. Such a goal can be achieved by considering the following dimensionless reduced gradient and laplacian

$$p = \frac{|\nabla\rho|^2}{4(3\pi^2)^{2/3}\rho^{8/3}}, \quad q = \frac{\nabla^2\rho}{4(3\pi^2)^{2/3}\rho^{5/3}} \quad (9)$$

The enhancement factor becomes therefore

$$F_s(\rho, \nabla\rho, \nabla^2\rho) = F_s(p, q) \quad (10)$$

2. Computational Details

The results of this work were obtained with the same computational methods used in the two previous works [18, 19] and so all the required numerical calculations have been performed using the electronic structure program:

JELLCODE. This program performs DFT simulations, both at the KS and the OF-DFT level, for spherical systems on a radial semi-logarithmic grid. A careful calibration of the quadrature grid has been performed to ensure that all calculations are well converged. Varying the external potential, both atoms and jellium spheres can be considered.

3. Results

The systems I worked on are the same as the two previous jobs [18]. The uniform electron gas or homogeneous electron gas (HEG), also known as jellium [20], is one of the most fundamental models for understanding electronic properties in simple metals and semiconductors (see Figure 1). Knowledge of its ground state properties and, in particular, of modifications due to electron correlation is at the heart of all approximate approaches to the many-electron problem in realistic models [21]. It can qualitatively reproduce features of real metals such as screening, plasmons, Wigner crystallization and Friedel oscillations. At zero temperature, the properties of jellium depend solely upon the constant electronic density. This lends it to a treatment within DFT.

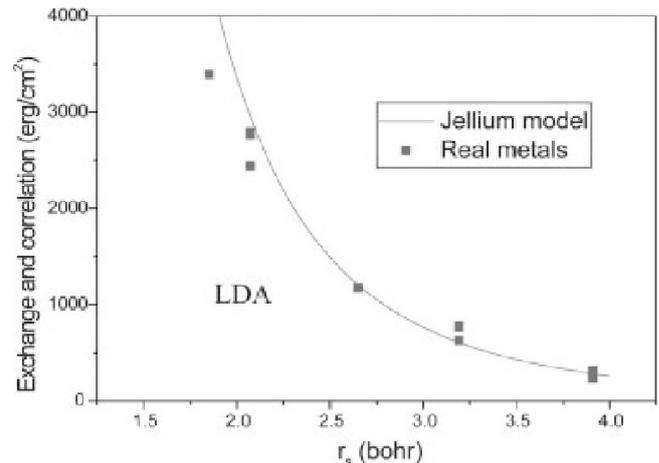


Figure 1. Jellium and real metals in a picture take from [22].

The energy studies are exposed in the work [18] and those on ionization are exposed in the work [19], from these graphs it can be seen that functionals based on gradient expansions, e.g. the second-order one (GE2) and above all the fourth-order (GE4) have been found to work at best; in particular, in Figure 4 and Figure 5 of my work [18] for noble atoms and for the jellium spheres, respectively. From Figure 6 of my work [18] it can be seen that the GGA approximation is not sufficient for our purposes but the LL-meta-GGA approximation works very well. So, considering that the GE4 energy is the best, as shown in the Figure 7 [18], but the GE4 potential is divergent, as shown in Figure 8 [18], I have developed new analytical formulas to eliminate this divergence and I have obtained a third functional with the same method of the previous:

$$F_s^{LAP2} = \frac{5}{3}s^2 + \frac{[1 + (A - 40/27)s^2]}{(1 + As^2)} * \frac{[1 + (B + D) * q + (B * D + Q) * q^2]}{(1 + D * q)} \tag{11}$$

This functional has been built according to the exact constraints, i.e. (i) for $s \rightarrow 0$ and $q \rightarrow 0$ (that is the slowly varying density limit) I want obtain the GE2 functional (ii) for $s \rightarrow \infty$ and $q \rightarrow \infty$ (that is the rapidly varying density limit) I want obtain the VW functional.

The best values that I have obtained are $A = 1.60$ and $B = 3$ that allow us to get functionals that approximate the exact one very well both for energy and for potential.

Below are some graphs which show how are obtained this best values of the coefficients A and B and also of the coefficients D and Q .

In the Figure 2 it is possible to see the kinetic energy and the kinetic potential calculated with different functionals in particular the functional proposed in the other work [18] and the new LAP2 with values of the coefficient $A = 1.70$ initially considered the best and later improved.

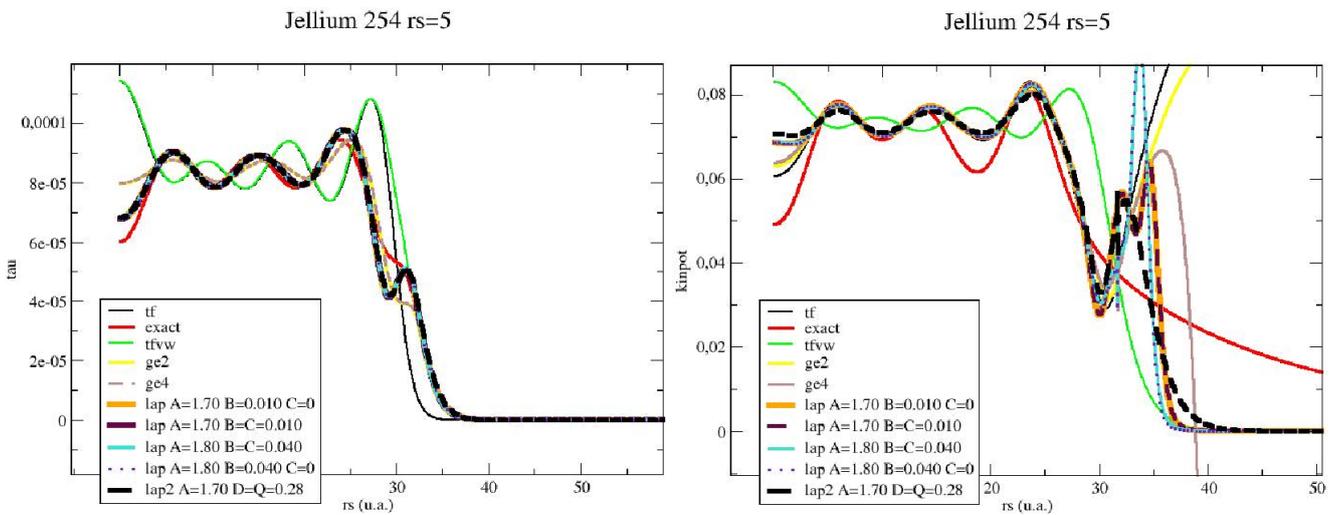


Figure 2. The kinetic energy and the kinetic potential of the previous functionals and the new LAP2.

In the Figure 3 and Figure 4 you can see that the enhancement factor of the new functional has a very different trend from the others precisely to correct the divergence of the potential. The Pauli enhancement factor was used, obtained from the enhancement factor of the exact functional and from the enhancement factor of the VW functional: $F_s^P = F_s^{KS} - F_s^{vW}$.

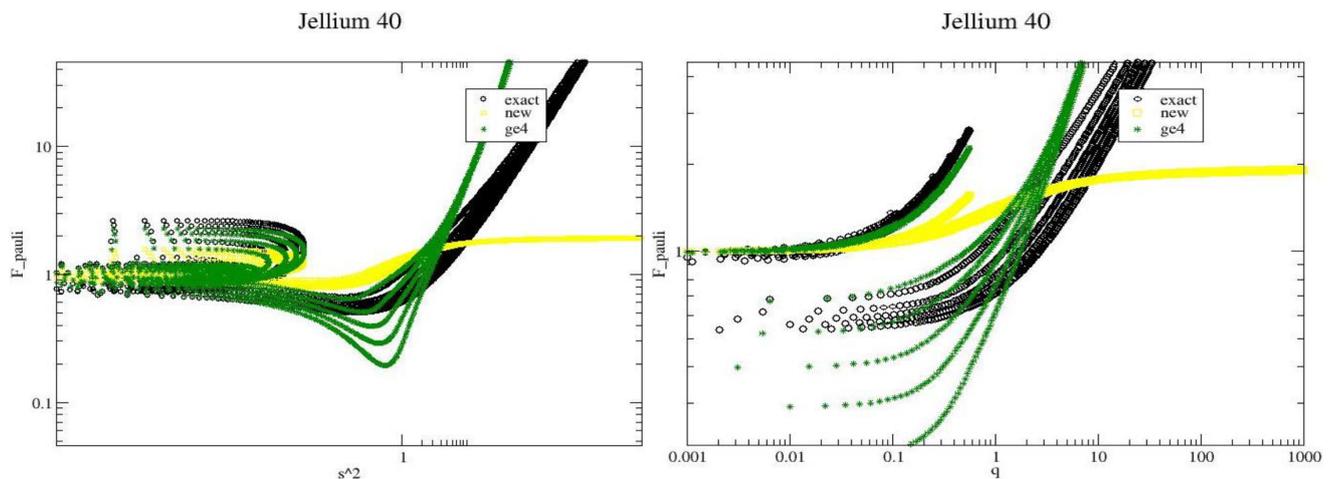


Figure 3. The enhancement factor of Pauli versus s^2 (upper panel) and q (lower panel) of the functionals named in the legend, the new functional LAP2 (in the legend called new) shows a non divergent trend.

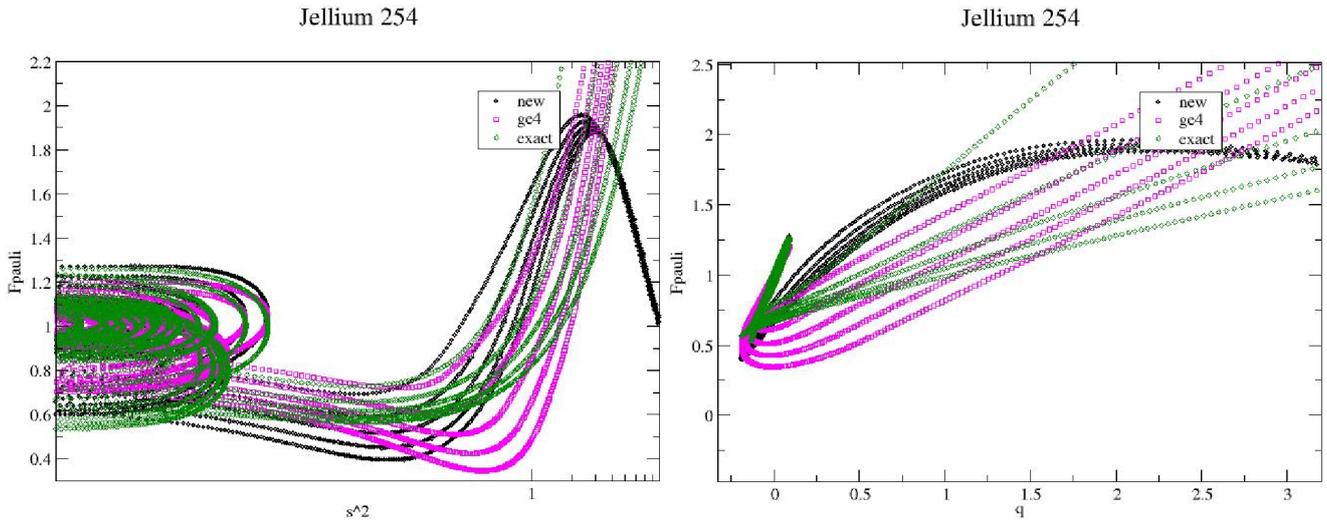


Figure 4. The enhancement factor of Pauli versus s^2 (upper panel) and q (lower panel) of the functionals named in the legend, the new functional LAP2 (in the legend called new) shows a non divergent trend.

In the Figure 5 there are the 2-D scan, for $A = 1.6, B = 3$, over the parameter space $(D, Q) \in [0, 1.4] \times [0, 1.95]$. The value of the coefficient A has been obtained with the same scan over the parameter space $(AD), (AQ)$:

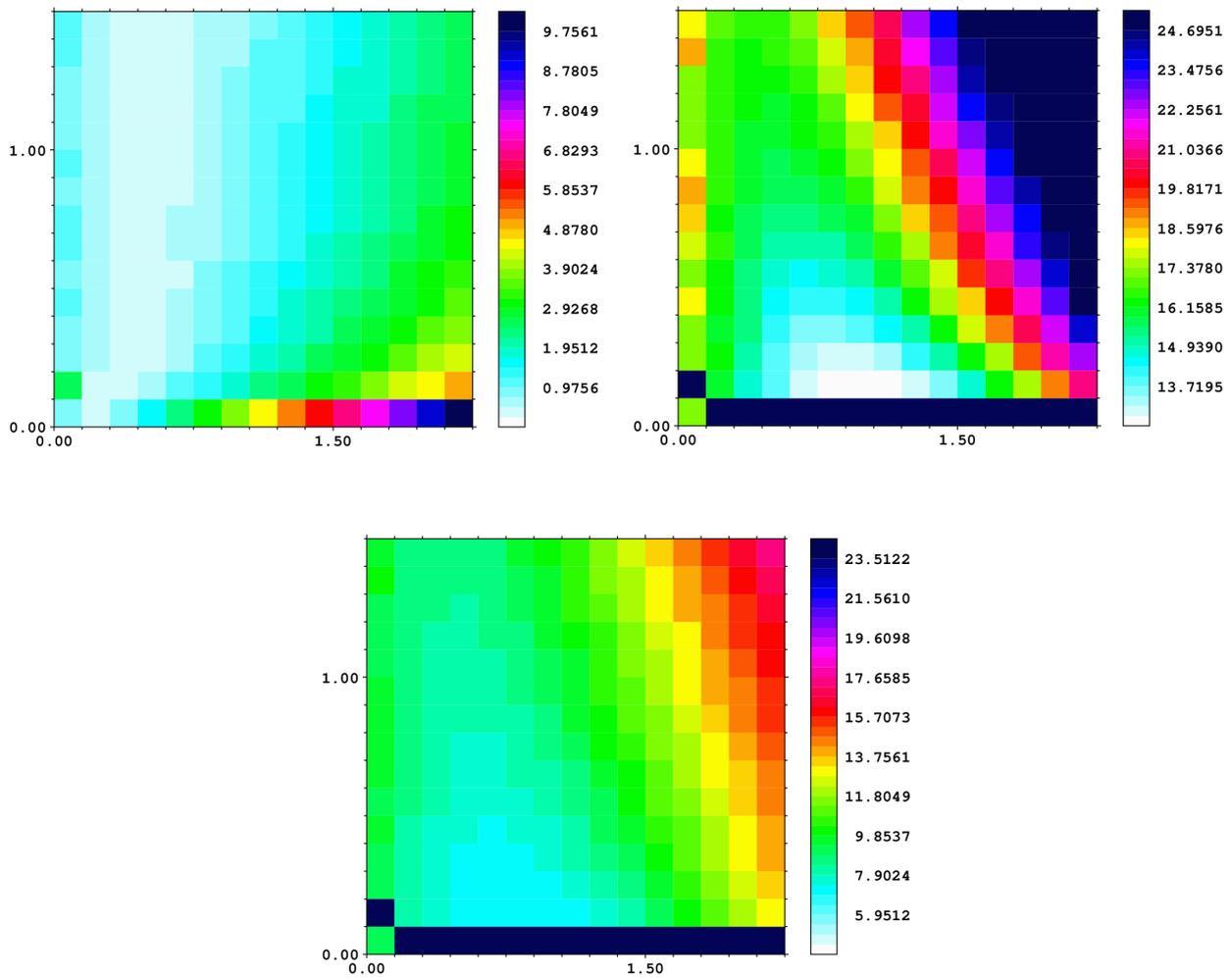


Figure 5. Two dimensional scan for the LAP2 functional over the parameter space D - Q averaged over the 3 jellium's systems for the kinetic energy (first panel) for the kinetic potential (second panel) for kinetic energy + kinetic potential (third panel).

In the Figure 6 there is the plot of the enhancement factor of the functionals with the values of the parameters obtained from the above scans that allow to obtain the minimum errors both for LAP1 (i.e. $B = C = 0$) and for LAP2 (i.e. $D = 1.20, Q = 0.45$) :

Jellium sphere ($N=254, r_s=5$)

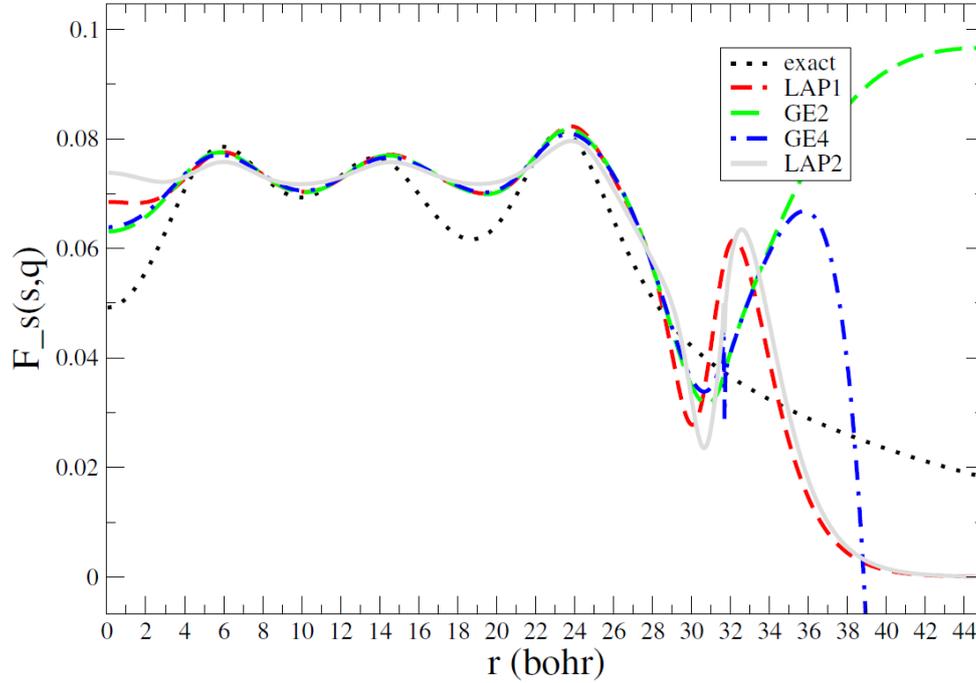


Figure 6. The LAP1 and the LAP2 functionals with their minimum values.

In the table 1 there are the values of the errors on the energy and on the potential of the reference functionals and of the new functionals with the values of the parameters mentioned and plotted above. The new functionals provide errors on the energy and on the potential lower than those existing in the literature:

Table 1. Summary of MARE (Mean absolute relative errors).

Functional	KE error	KP error	total KE
TF	2.9618	24.8706	13.9162
GE2	0.954567	21.7619	11.3582
GE4	0.435183	10.6*10exp13	53.2*10exp13
NEWab	4.8922	24.3191	14,6056
LAP1	0.430675	16.3654	8.39804
LAP2	0.3809	16.3211	8.3510

4. Conclusions

LAP2 with the coefficient $A = 1.60, B = 3$ and $D = 1.20$ and $Q = 0.45$ works better of the two previous and I managed to obtain in the denominator, which is the crucial part that eliminates the divergence, the two quantities s^2 and q , reduced gradient and laplacian, and not just s^2 or s^2 and q^2 as in the previous ones. These new features, still unused, represent a

state of the art and a showcase of what could become standard procedures in the near future.

Conflicts of Interest

The authors declare no conflicts of interest.

Appendix: Functionals

Below are some of the enhancement factors, relevant to the present work, with the corresponding number with which they can be found among the 41 existing kinetic functionals in libxc [23]:

1. A-1. LDA, Thomas-Fermi

$$F_s^{TF} = 1 \quad (12)$$

2. A-3. GGA, Thomas-Fermi plus von Weiszaecker correction

$$F_s^{TF} = 1 + \frac{5}{3}s^2 \quad (13)$$

3. A-4-8. GGA, PBE-like

$$F_s^{PBE^n} = 1 + \sum_1^{n-1} C_i^{(n)} \left(\frac{s^2}{1 + a^{(n)}s^2} \right)^i \quad (14)$$

4. A-11. GGA, Tran and Wesolowski TW02

$$F_s^{TW02} = 1 + \kappa - \frac{\kappa}{1 + \frac{\mu}{\kappa} s^2} \quad (15)$$

where $\kappa = 0.8438$ and $\mu = 0.2319$.

5. A-13. GGA, von Weiszaecker correction to Thomas-Fermi

$$F_s^{vW} = \frac{5}{3} s^2 \quad (16)$$

6. A-14. GGA, second-order gradient expansion

$$F_s^{GE2} = 1 + \frac{5}{27} s^2 \quad (17)$$

7. A-15-18. GGA, TF λ vW

$$F_s^{TF} = 1 + \lambda \frac{5}{3} s^2 \quad (18)$$

8. A-25. GGA, Ou-Yang and Levy v.1

$$F_s^{OL1} = 1 + \frac{5}{27} s^2 + 0.00677 \frac{20}{3} (3\pi^2)^{-1/3} s \quad (19)$$

9. A-30. GGA, Perdew

$$F_s^{P92} = \frac{1 + 88.396s^2 + 16.3683s^4}{1 + 88.2108s^2} \quad (20)$$

10. A-31. GGA, Vitos, Skriver, and Kollar (VSK)

$$F_s^{VSK98} = \frac{1 + 0.95x + 3.56x^3}{1 - 0.05x + 0.396x^2} \quad (21)$$

with $x = (5/27)s^2$.

11. A-33. GGA, Ernzerhof

$$F_s^{E00} = \frac{135 + 28s^2 + 5s^4}{135 + 3s^2} \quad (22)$$

Cambridge Philosophical Society. Vol. 23, Cambridge University Press; 1927, 542-548.

- [6] Percus J. K. The role of model systems in the few-body reduction of the N-fermion problem. *International Journal of Quantum Chemistry*. 1978, 13(1), 89-124. <https://doi.org/10.1002/qua.560130108>

- [7] Pope T., Hofer W. Exact orbital-free kinetic energy functional for general many-electron systems. *Frontiers of Physics*. 2020, 15, 23603. <https://doi.org/10.1007/s11467-019-0948-6>

- [8] Kohn W., Sham L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Physical Review Journals Archive*. 1965, 140(4A), A1133-A1138. <https://doi.org/10.1103/PhysRev.140.A1133>

- [9] Neugebauer J. Couplings between electronic transitions in a subsystem formulation of time-dependent density functional theory. *The Journal of Chemical Physics*. 2007, 126(13), 134116. <https://doi.org/10.1063/1.2713754>

- [10] Karasiev V. V., Jones R. S., Trickey S. B., Harris F. E. Properties of constraint-based single-point approximate kinetic energy functionals. *Phys. Rev. B*. 2009, 80(24), 245120-245136. <https://doi.org/10.1103/PhysRevB.80.245120>

- [11] Laricchia S., Fabiano E., Constantin L., Della Sala F. Generalized Gradient Approximations of the Noninteracting Kinetic Energy from the Semiclassical Atom Theory: Rationalization of the Accuracy of the Frozen Density Embedding Theory for Nonbonded Interactions. *Journal of chemical theory and computation*. 2011, 7(8), 2439-2451. <https://doi.org/10.1021/ct200382w>

- [12] Lembarki A., Chermette H. Obtaining a gradient-corrected kinetic-energy functional from the Perdew-Wang exchange functional. *Phys. Rev. A*. 1994, 50(6), 5328-5331. <https://doi.org/10.1103/PhysRevA.50.5328>

- [13] Thakkar A. J. Comparison of kinetic-energy density functionals. *Phys. Rev. A*. 1992, 46(11), 6920-6924. <https://doi.org/10.1103/PhysRevA.46.6920>

- [14] Burke K. Perspective on density functional theory. *The Journal of Chemical Physics*. 2012, 136(15), 150901. <https://doi.org/10.1063/1.4704546>

- [15] Perdew J. P., Wang Y. Accurate and simple analytic representation of the electron-gas correlation energy. *Phys. Rev. B*. 1992, 45(23), 13244-13249. <https://doi.org/10.1103/PhysRevB.45.13244>

- [16] Yang W. Gradient correction in Thomas-Fermi theory. *Physical Review A*. 1986, 34(6), 4575. <https://doi.org/10.1103/PhysRevA.34.4575>

References

- [1] Engel E., Dreizler R. M. *Density functional theory*. Springer; 2013, <https://doi.org/10.1007/978-3-642-14090-7>
- [2] Wang Y. A., Carter E. A. Orbital-free kinetic-energy density functional theory. In *Theoretical Methods in Condensed Phase Chemistry*, edited by S. D. Schwartz. Netherlands, Dordrecht: Springer; 2002, 117-184.
- [3] Wesolowski T. A., Wang Y. A. *Recent progress in orbital-free density functional theory*, Vol. 6. World Scientific; 2013.
- [4] Bruus H., Flensberg K. *Many-body quantum theory in condensed matter physics: an introduction*. Oxford university press; 2004.
- [5] Thomas L. H. In *Mathematical Proceedings of the*

- [17] Laricchia S., Constantin L. A., Fabiano E., Della Sala F. Laplacian-Level Kinetic Energy Approximations Based on the Fourth-Order Gradient Expansion: Global Assessment and Application to the Subsystem Formulation of Density Functional Theory. *Journal of chemical theory and computation*. 2014, 10(1), 164-179. <https://doi.org/10.1021/ct400836s>
- [18] Urso V. Development of novel kinetic energy functional for orbital-free density functional theory applications. *International Journal of Modern Physics C*. 2021, 33(04), 2250044. <https://doi.org/10.1142/S0129183122500449>
- [19] Urso V. Development of novel kinetic energy functional for orbital-free density functional theory applications II. *London Journals Press*. 2022, 22(12), 1-8. DDC Code: 530.41 LCC Code: QC176.8.E4.
- [20] Mahan G. D., Subbaswamy K. *Local density theory of polarizability*. New York: Springer; 1990.
- [21] Loos P.-F., Gill P. M. W. The uniform electron gas. *Wiley Interdisciplinary Reviews: Computational Molecular Science*. 2016, 6. <https://doi.org/10.1002/wcms.1257>
- [22] Fiolhais C., Almeida L. M. Surface energies of simple metals from slabs: Comparison of exchange-correlation density functionals. *International Journal of Quantum Chemistry*. 2005, 101(6), 645-650. <https://doi.org/10.1002/qua.20321>
- [23] Lehtola S., Steigemann C., Oliveira M. J., Marques M.A. Recent developments in libxc - A comprehensive library of functionals for density functional theory. *SoftwareX*. 2018, 7, 1-5.