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Development of Novel Kinetic Energy Functional for Orbital-Free Density Functional Theory Applications-II

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The development of novel Kinetic Energy (KE) functionals is an important topic in density functional theory (DFT). Here, I present a study of Laplacian-Level kinetic energy functionals applied to metallic nanosystems. The nanoparticles are modeled using jellium spheres of different sizes, background densities, and number of electrons. The ability of different functionals to reproduce the correct kinetic energy density and potential of various nanoparticles is investigated and analyzed in terms of semilocal descriptors. Most semilocal KE functionals are based on modifications of the second-order gradient expansion GE2 or GE4. After a series of calculations and analyzes on the second and fourth order gradient expansion and respecting the exact constraints, I propose a new functional LAP1 which allows to remove the divergence of the potential of the functional GE4 and to obtain lower errors of both energy and potential.

Keywords: DFT, kinetic energy functional, jellium spheres.

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I. 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]:

$$\frac{\delta T_s[\rho]}{\delta\rho(\mathbf{r})} + \nu_{ext}(\mathbf{r}) + \nu_J(\mathbf{r};[\rho]) + \frac{\delta E_{xc}[\rho]}{\delta\rho(\mathbf{r})} = \mu \qquad (1)$$

where $T_s[\rho]$ is the noninteracting kinetic energy (KE) density functional; $\nu_{ext}(\mathbf{r})$ and $\nu_J(\mathbf{r};[\rho])$ are the external (i.e. nuclear) and Coulomb potentials, respectively; $E_{xc}[\rho]$ is the exchange correlation (XC) energy functional; and the Lagrange multiplier μ is the chemical potential, which takes into account that the number of electrons is fixed. Equation (1) is of limited practical utility, since only $\nu_J(\mathbf{r};[\rho])$ is known its exact functional form, while $T_s[\rho]$ and $E_{xc}[\rho]$ are not known as explicit functionals of electron density. For the term XC, many different useful approximations have been developed for different types of systems (molecules, solids, surfaces, atoms, etc.) considering the fact that Exc [] is by far the smallest term in Eq. (1). For the functional non-interacting kinetic energy, there are still no reliable approximations. DFT it is conventionally implemented in the Kohn-Sham[6] scheme by introducing an auxiliary set of non-interacting particles to describe the density of the ground state. Alternative methods are: i) Free Orbital DFT (OF-DFT) methods, including the hydrodynamic model to describe the absorption spectra of nanoparticles[7] ; ii) Embedding methods (e.g. subsystem[8] DFT, partition[9] DFT), included their linear response extensions[10]. These methods consist in dividing the main system in smaller interacting fragments, allowing a reduced computational cost.

All of these methods have in common that they need an explicit density functional expression for the kinetic energy (KE) 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 $T_s[\rho]$, as a functional of the electron density, is known only for

- the homogeneous electron gas (HEG), i.e., the Thomas-Fermi (TF) local functional[5,11]

  $$T_s^{TF}[\rho] = \int \tau^{TF}(\mathbf{r})d\mathbf{r} = \int C_{TF}\rho^{5/3}(\mathbf{r})d\mathbf{r} \qquad (2)$$

  with $C_{TF} = 3/10(3\pi^2)^{2/3} \simeq 2.8712$, the TF constant.

- 1 and 2 electron systems, i.e., the von Weizsacker (VW) functional

  $$T_s^{VW}[\rho] = \int \tau^{VW}(\mathbf{r})d\mathbf{r} = \int \frac{|\nabla\rho(\mathbf{r})|^2}{8\rho(\mathbf{r})}d\mathbf{r} \qquad (3)$$

The same holds for the kinetic kernel. In between these two extreme cases, different semilocal or nonlocal approximations were developed in recent years. Non-local KE functionals are rather accurate, but they are derived mainly from the linear response of the homogeneous electron gas (the Lindhard function[12]) and are thus only suitable for solid-state simulations. Semilocal KE functionals are instead usually developed on the basis of the generalized gradient expansion or its resummation.

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The approximation (2) is not very accurate for real applications but it is the basis to construct generalized gradient approximations (GGAs)[13–16]:

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

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

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

and therefore for $F_s = 1$ I obtain the TF (Thomas-Fermi) KE functional. The GGAs are the most popular KE approximations also known as semilocal. The functional (3) is a lower bound for the kinetic energy and is accurate in nuclear and asymptotic regions, its enhancement factor is:

$$F_s = \frac{5}{3}s^2 \tag{6}$$

Gradient expansions are poweful theoretical tools which describe with accuracy the KE slowly varying density regime of an electronic system, providing an ideal starting point for the development of approximate KE models. One model is obtained including a new ingredient in the kinetic enhancement factor[17,18]: the laplacian of the density yielding the class of Laplacian-Level meta-GGAs (LL-meta-GGAs)[19]

$$T_s^{LL}[\rho] = \int \tau^{TF} F_s(\rho, \nabla\rho, \nabla^2\rho)\, d\mathbf{r} \tag{7}$$

Under a uniform scaling of the density

$$\rho_\lambda(\mathbf{r}) = \lambda^3 \rho(\lambda \mathbf{r}), \quad \lambda \geq 0 \tag{8}$$

the exact non-interacting kinetic energy behaves as

$$T_s[\rho_\lambda] = \lambda^2 T_s[\rho] \tag{9}$$

i.e. as the Thomas-Fermi KE. Therefore, to have eq.(7) satisfy this constraint, $F_s(\rho, \nabla\rho, \nabla^2\rho, ...)$ must be invariant under the uniform density scaling. Such a goal can be achieved by considering the following dimensioneless reduced gradient and laplacian

$$p = \frac{|\nabla\rho|^2}{4(3\pi^2)^{2/3}\rho^{8/3}} \quad , \quad q = \frac{\nabla^2\rho}{4(3\pi^2)^{2/3}\rho^{5/3}} \tag{10}$$

The enhancement factor becomes therefore

$$F_s(\rho, \nabla\rho, \nabla^2\rho) = F_s(p, q) \tag{11}$$

II. THEORY

The Thomas-Fermi (TF) model makes the origin of DFT. The TF model is only exact for the free-electron gas (FEG). Calculations with this model didn't explain the exchange-correlation effects and the kinetic-energy density functional. Using the approximation for realistic systems yields poor quantitative predictions, even failing to reproduce some general features of the density such as shell structure in atoms and Friedel oscillations in solids. It has, however, found modern applications in many fields through the ability to extract qualitative trends analytically and with the ease at which the model can be solved. The kinetic energy expression of Thomas-Fermi theory is also used as a component in more sophisticated density approximation to the kinetic energy within modern orbital-free density functional theory[18] .

Can be calculated the kinetic energy and the kinetic potential of the systems with the 41 kinetic functionals that can be found in Libxc[20], 2 LDA (Local Density Approximation) and 39 GGA (Generalized Gradient Approximation). Libxc is a library of exchange-correlation functionals for density functional theory. In Libxc it can find different types of functionals: LDA, GGA, hydrids, and mGGA. These functionals depend on local information, in the sense that the value of the potential at a given point depends only on the values of the density and the gradient of the density and the kinetic energy density.

In the following there are some of the enhancement factor of the 41 kinetic functionals with particular relevance for the present work:

- 1. LDA, Thomas-Fermi

$$F_s^{TF} = 1 \tag{12}$$

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

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

- 4-8. GGA, PBE-like

$$F_s^{PBEn} = 1 + \sum_{1}^{n-1} C_i^{(n)} \left(\frac{s^2}{1 + a^{(n)} s^2} \right)^i \tag{14}$$

- 11. GGA, Tran and Wesolowski TW02

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

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

- 13. GGA, von Weiszaecker corretion to Thomas-Fermi

$$F_s^{vW} = \frac{5}{3}s^2 \tag{16}$$

- 14. GGA, second-order gradient expansion

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

- 15-18. GGA, TFλvW

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

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

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

- 30. GGA, Perdew

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

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

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

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

- 33. GGA, Ernzerhof

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

- 41. GGA, TB3

$$F_s^{TB3} = 1.20243339s^{0.2} \tag{23}$$

When I use the semilocal approximation, I have the following enhancement factor based on modifications of the second-order gradient expansion GE2

$$F_s^{GE2} = 1 + \frac{5}{}s^2 + \frac{20}{27}q \quad 9 \tag{24}$$

or fourth-ordeer gradient expansion GE4

$$F_s^{GE4} = F_s^{GE2} + \Delta \tag{25}$$

where Δ is

$$\Delta = \frac{8}{81}q^2 - \frac{1}{9}s^2q + \frac{8}{243}s^4 \tag{26}$$

GE4 functional, that is the simplest LL-meta-GGA functional, allows us to obtain better results for energy but the kinetic potential is divergent.

III. COMPUTATIONAL DETAILS

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 carefull 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.

IV. RESULTS

The main goal of mine is the development of new kinetic functionals which can be applied in different DFT applications. To reach this target, I have done several analysis with newly developed benchmark sets, which extend the previous ones; in the case:

- Jellium Cluster of 40 electrons,
- Jellium Cluster of 138 electrons,
- Noble Atoms (Ne, Ar, Kr, Xe, Rn, Og).

The Jellium Clusters of 40 and 138 electrons have type HOMO (highest occupied molecular orbital) p, later I have worked with Jellium Cluster of 92 electrons with type HOMO s and with Jellium Cluster of 254 electrons with type HOMO h. The noble atoms (He-Og) are used as representative of rapidly varying density systems. The jellium spheres (N=40e,138e) are used as representative of the slowly-varying density regime. The use of atoms and jellium spheres with varying numbers of electrons allows the consideration of both high- and low-density regime. After the energy studies exposed in the work[21], I also carried out studies on ionization, I plotted the ionization versus r_s, and I analyzed the trend of everyone functionals, as shown in Fig.1.

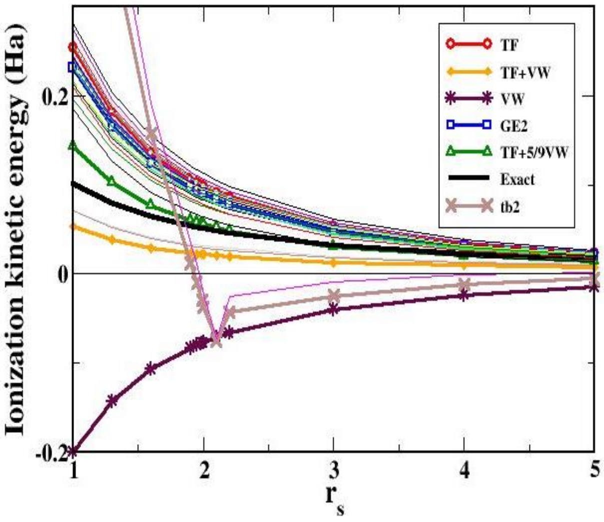

Fig. 1: The kinetic ionization calculated by the 41 kinetic functionals.

I have calculated the energy, the ionization and the potential for jellium clusters having different values of the bulk parameter, Wigner Seitz radius r_s,

$$r_s = (\frac{3}{4\pi\rho})^{1/3} \tag{27}$$

in particular in the range $r_s = [1, 5]$ which corresponds to most metals and semiconductors[22]. The range [1,5] of values is expressed in atomic units that is, in units of the Bohr radius (as already done in Fig. 1).

From these graphs it can be seen that functional based on gradient expansions, e.g. the second-order one, GE2 have been found to work at best, see the Fig.1 and also in the Fig.2

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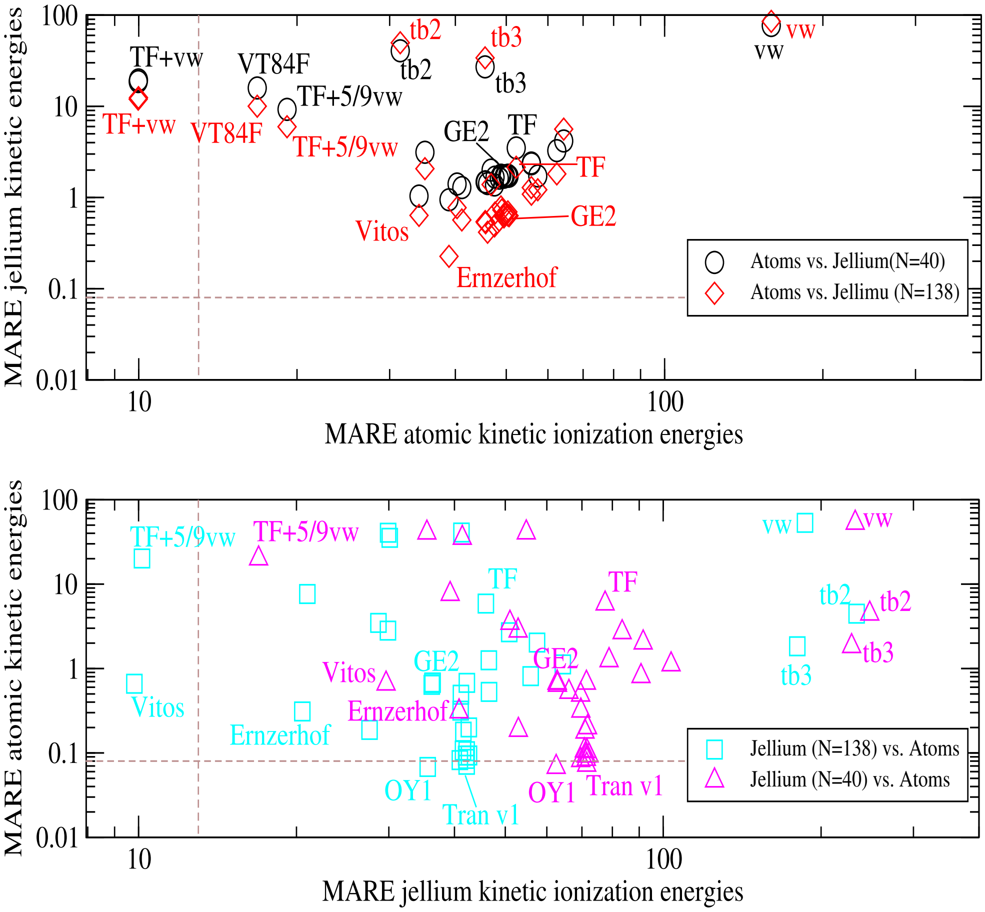

Fig. 2: Top: Mean Absolute Relative Error (MARE) of jellium kinetic energy (circle=sphere-40, rombus=sphere- 138) vs. MARE of noble atoms ionization kinetic en- ergy. Bottom: MARE of jellium ionization kinetic energy (square=sphere=138, triangle=sphere-40) vs. MARE of no- ble atoms kinetic energy.

This has motivated a further study, aimed at investigating the performance of the family of functionals

$$\lambda TF + \mu VW \tag{28}$$

with λ and μ being parameters.

The results of this study can be found in Figs. 4 and 5 of my work^{21} for noble atoms and for the jellium spheres, respectively.

The following formulas are used for the relative errors

$$RelativeError_{energy} = \frac{Energy - Energy_{exact}}{Energy_{exact}} \tag{29}$$

$$RelativeError_{potential} = \frac{Potential - Potential_{exact}}{Potential_{exact}} \tag{30}$$

$$Kinetic\,Ionization\,Energy = T_{ion}[n] - T_{neutral}[n] \tag{31}$$

$$RelativeError_{ionization} = \frac{ionization - ionization_{exact}}{ionization_{exact}} \tag{32}$$

Plotting the enhancement factors both in GGA approximation and in LL-meta-GGA approximation (with GNUPLOT), I obtained the results shown in the Fig. 6 of my work^{21} and this confirms that the GGA approximation is not sufficient for our purposes but the LL-meta-GGA approximation works very well.

So, I have plotted the kinetic energy and the kinetic potential versus r of the functionals in approximation LL-meta-GGA and I found that the GE4 energy is the best, as shown in the Fig. 7^{21}, but the GE4 potential is divergent, as shown in Fig. 8^{21} so I have developed new analytical formulas to eliminate this divergence.

Starting from the same functional form of the previous work:

$$F(s, q) = FW + FQ \tag{33}$$

I have obtained the following formula

$$F_s^{LAP1} = \frac{5}{3}s^2 + \frac{[1 + (A - 40/27)s^2]}{1 + As^2} * \frac{1 + 3q + Cq^2}{1 + Bq^2} \tag{34}$$

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this functional has been built according to the exact constraints, i.e.

- for $s \to 0$ and $q \to 0$ (that is the slowly varying density limit) I want obtain the GE2 functional
- for $s \to \infty$ and $q \to \infty$ (that is the rapidly varying density limit) I want obtain the VW functional

The best values that I have obtained are

$$A = 1.70 \quad \text{and} \quad B = C \in [0, 0.10] \tag{35}$$

that allow us to get functionals that approximate the exact one very well both for energy and for potential

To obtain the coefficient A I have performed some scans with xfarbe program of the functional GE2 of which I know the energy and potential values, which are indicated below:

GE2	$40e^-$	$92e^-$	$254e^-$
energy	1.477	0.629	0.649
potential	10.974	9.602	6.7

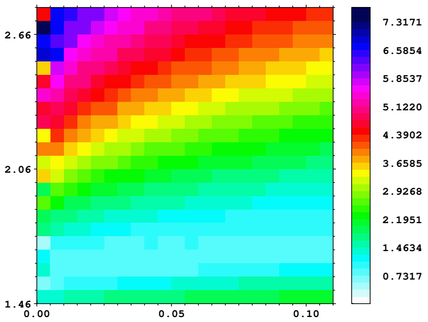

Fig. 3: Two dimensional scan for the GE2 functional over the parameter space A-B=C for the jellium of N=40e (mediated on rs=[1,5]) for the kinetic energy.

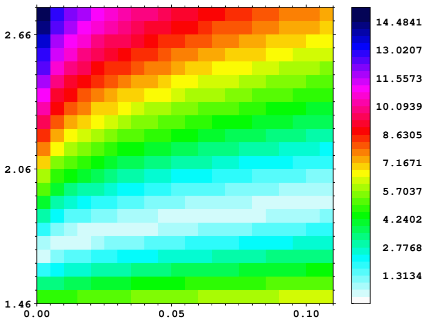

Fig. 4: Two dimensional scan for the GE2 functional over the parameter space A-B=C for the jellium of N=92e (mediated on rs=[1,5]) kinetic energy.

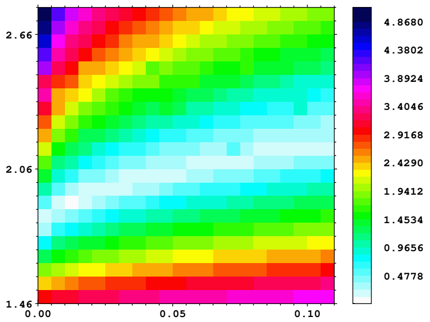

Fig. 5: Two dimensional scan for the GE2 functional over the parameter space A-B=C for the jellium of N=254e (mediated on rs=[1,5]) kinetic energy.

From these scans we can deduce that a good value for the coefficient A is $A = 1.70$, with which the following errors were calculated

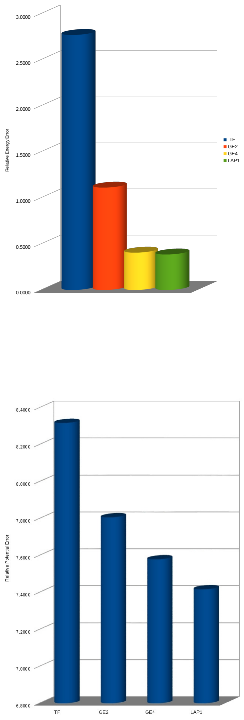

Fig. 6: Histogram of kinetic energy and kinetic potential errors, the new LAP1 functional with A=1.70 work very well.

Below are the 2D scans for the LAP1 functional in the B-C space with the coefficient $A = 1.70$. It can be seen that the right values for B and C are very small.

In the following plots 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[21] and the new LAP1 with a value of the co-

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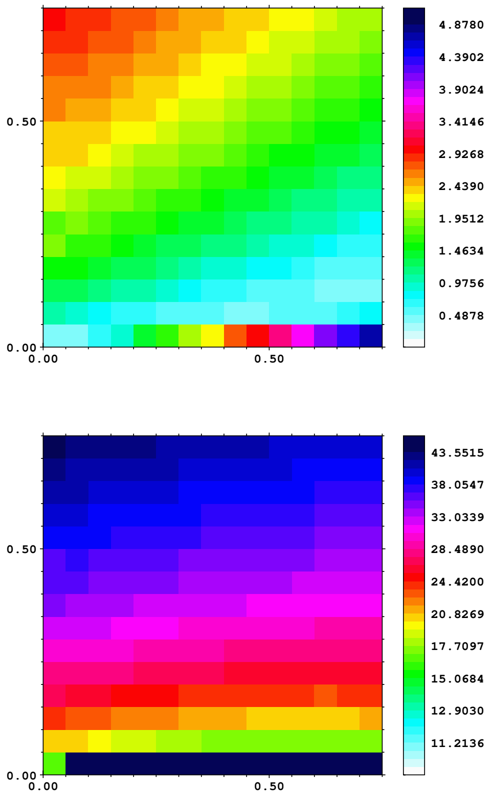


Fig. 7: Two dimensional scan for the LAP1 functional over the parameter space B-C for the 3 jellium's systems with A = 1.70: kinetic energy (in the upper panel) and kinetic potential (in the lower panel).

efficient $A = 2.06$ initially considered good but later improved.

In the following table there are the values of the errors on the energy and on the potential of the reference functionals and of the new functionals

Table I: 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

In the following plots 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[21] and the new LAP1 with values of the coefficient $A = 1.70; 1.80$

In the following there are the 2D scans of the energy and potential above the space of the parameters $A - B = C$

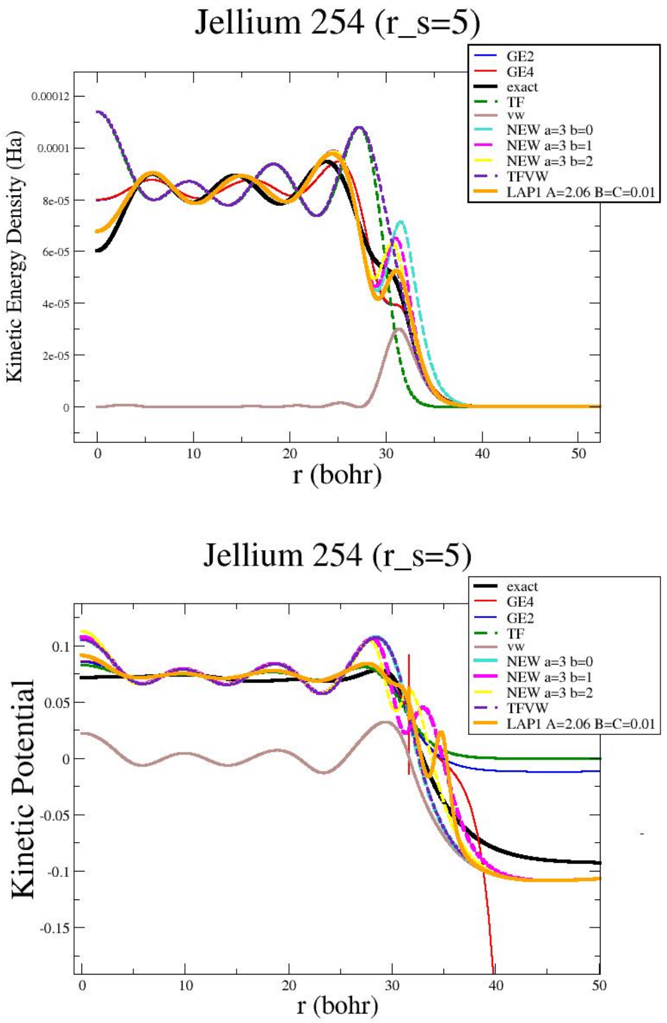
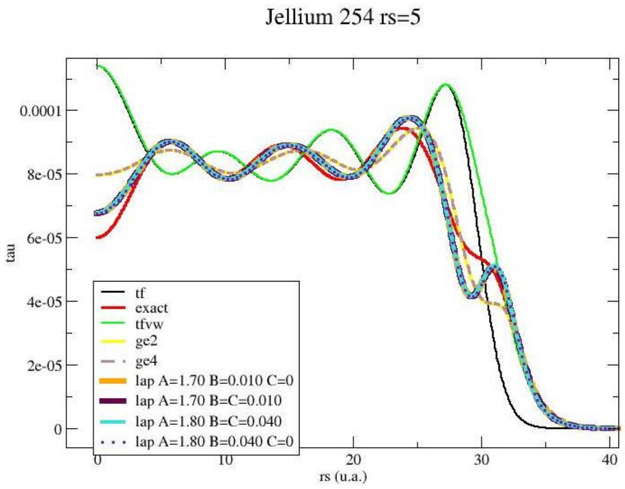


Fig. 8: In the upper panel there is the plot of the kinetic energy of some functionals and the new LAP1 one, in the lower panel there is the plot of the kinetic potential of same functionals and the new LAP1 one.



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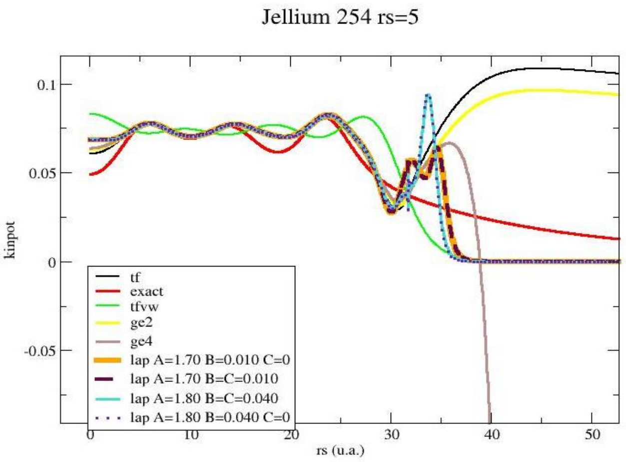

Fig. 9: The kinetic energies and the kinetic potential of some functionals and the LAP1 one.

for the function LAPI

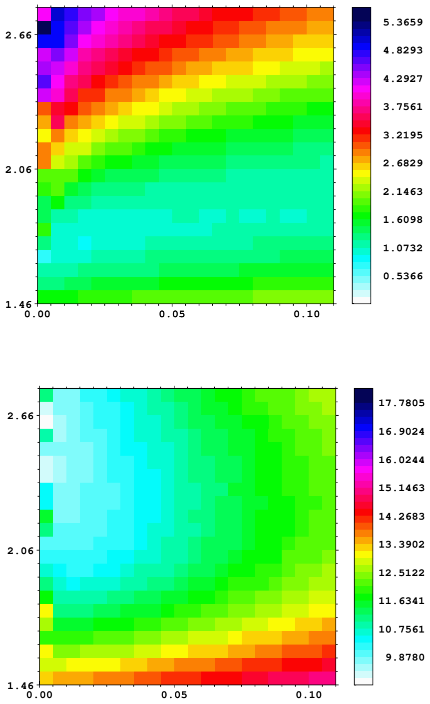

Fig. 10: Two dimensional scan for the LAP1 functional over the parameter A-B=C space for the jellium of 92e−, energy (in the upper panel) and potential (in lower panel).

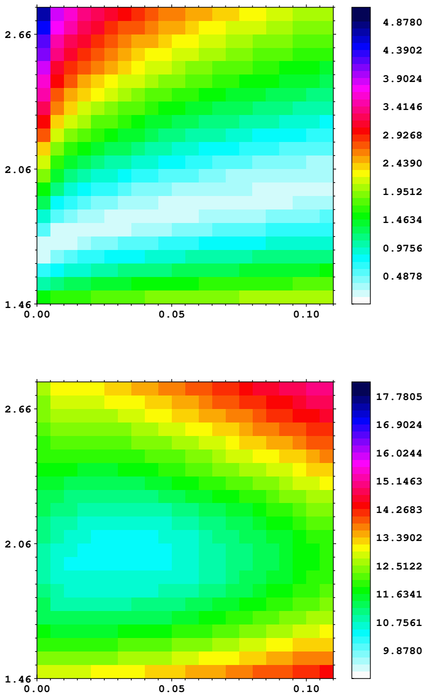

Fig. 11: Two dimensional scan for the LAP1 functional over the parameter A-B=C space for the jellium of 92e−, energy (in the upper panel) and potential (in lower panel).

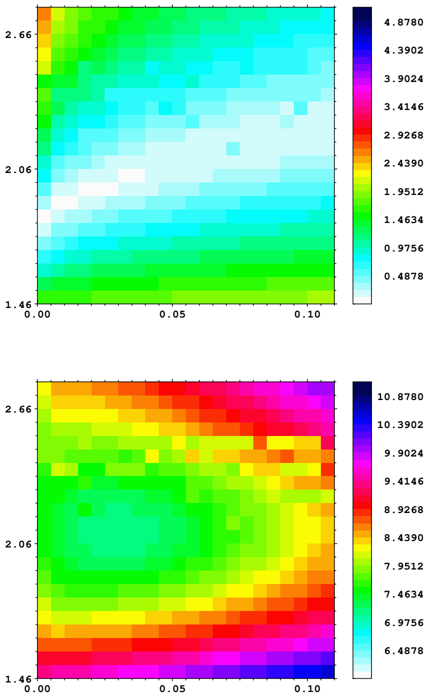

Fig. 12: Two dimensional scan for the LAP1 functional over the parameter A-B=C space for the jellium of 254e−, energy (in the upper panel) and potential (in lower panel).

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V. CONCLUSIONS

The results that I obtained indicate the no GGA ki- netic energy functional available in literature is able to describe with good accuracy even simple systems such as noble gas atoms and jellium spheres. Nevertheless, gradi- ent expansions clearly include important features to approximate the kinetic energy functional. Thus, I have in- vestigated the kinetic functionals beyond the GGA level of the theory, with special attention to LL-meta-GGAs, which can not only recover exactly gradient expansions but also describe rapidly-varying density regions, thanks to their ability to distinguish different density regions by virtue of the sue of both s and q. The results that I ob- tained, at a later time, indicate that no LL-meta-GGA ki- netic functional available in literature is able to describe with good accuracy the systems previously considered, in particular the potential of these systems. Nevertheless, with appropriate analyzes, functional devices can be ob- tained that are able to remove the divergences (where they exist), respecting the exact constraints and finding those parameters that can improve the errors of both energy and potential and eliminate oscillations, such as the functional LAP1 with the coefficient $A = 1.70$ and $B = C \in [0, 0.10]$.

VI. DATA AVAILABILITY STATEMENT

All data generated or analysed during this study are included in this published article.

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