Nonlocal kinetic energy functionals in real space using a Yukawa-potential kernel: Properties, linear response, and model functionals

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In the quest for accurate approximations of the noninteracting kinetic energy functional as a functional of the electronic density, two different paths are usually employed: semilocal functionals based on the derivatives of the electronic density (mainly the gradient and the Laplacian) or nonlocal functionals based on the linear response of the homogeneous electron gas, i.e., the Lindhard function. While the former are defined in real space but fail to reproduce the Lindhard function, the latter cannot be expressed exactly in real space (being defined only in the reciprocal space), so applications to finite systems are complicated. In this paper we introduce a nonlocal ingredient (y_{α}) based on the Yukawa potential, i.e., the screened Hartree potential, which can be combined with other semilocal ingredients to obtain a more accurate description of the Lindhard function for both small and large wave vectors. We show and analyze the different properties of y_{α} and introduce a class of density functionals, the Yukawa-generalized gradient approximation (yGGA). We show that both the total energy and the first functional derivative (the kinetic potential) of yGGA functionals can be easily computed in real space. We present model yGGA functionals which well approximate the Lindhard function for both small and large wave vectors and can accurately describe jellium clusters and their perturbations.

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I. INTRODUCTION

Several linear scaling methods attractive for large-scale calculations of electronic systems, such as orbital-free density functional theory (OF-DFT) [1–4], subsystem DFT [5–10], and quantum hydrodynamic theory [11–14], strongly relay on noninteracting kinetic energy (KE) functional approximations [15–58].

However, such approximations are still rather difficult to express as pure density functionals $T_s[n(\mathbf{r})] = \int \tau(\mathbf{r}) d^3 \mathbf{r}$, with $\tau(\mathbf{r})$ being the KE density; despite the noninteracting KE, T_s , is exactly known as a function of occupied Kohn-Sham (KS) orbitals $\phi_i(\mathbf{r})$, i.e., $T_s = (1/2) \sum_i^N \int |\nabla \phi_i(\mathbf{r})|^2 d^3 \mathbf{r}$.

Considering the importance of the KE as an observable and as a key ingredient for electronic structure methods, different KE approximations have been developed during the last 30 years. Currently, they can, in general, be divided into two classes: semilocal functionals [15–37], such as the generalized gradient approximations (GGAs) [15,16,18–26,37] and the Laplacian-level meta-GGAs (mGGA) [27–34], and nonlocal functionals [38–54]. In semilocal functionals, the KE density is written

$$\tau^{\text{semilocal}}(\mathbf{r}) = \tau(n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla^2 n(\mathbf{r})), \qquad (1)$$

such that the KE density is completely defined by the value of the electron density and its derivatives at each single point in space. This makes this approach very efficient from a computational point of view and quite easily transferable between systems with different natures (localized or extended periodic systems). In fact, even rather simple semilocal KE functionals have shown good accuracy for the description of equilibrium lattice constants, bulk moduli, total, kinetic, and vacancy energies of bulk solids in the context of solid-state OF-DFT calculations [25,32,33] and a good ability to describe noncovalent interactions between molecular complexes in the context of subsystem DFT calculations [10,19,29,34,59,60]. However, because the KE density is constructed only from the density information contained in an infinitesimal volume around the point \mathbf{r} , semilocal KE functionals, in general, cannot correctly describe some of the strong nonlocal effects of the exact KE functional.

Nonlocal KE functionals, on the other hand, have the general form

^{non-local}(
$$\mathbf{r}$$
) = $\tau^{\text{semilocal}}(\mathbf{r})$
+ $\int n^{\alpha}(\mathbf{r})K(\zeta(\mathbf{r},\mathbf{r}'),\mathbf{r}-\mathbf{r}')n^{\beta}(\mathbf{r}')d^{3}\mathbf{r}',$ (2)

where α and β are parameters and $K(\zeta(\mathbf{r}, \mathbf{r}'), \mathbf{r} - \mathbf{r}')$ is a nonlocal kernel designed to exactly reproduce the linear response of the noninteracting uniform electron gas, i.e., the Lindhard function [1]. The kernel *K* depends on an effective Fermi wave vector $\zeta(\mathbf{r}, \mathbf{r}')$ [49] that can be chosen in several ways. In particular, it can be a constant, making the kernel density independent [38–40,44,51], or it can depend on the electron

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density at **r** and **r**', making the kernel density dependent [41-43,45-50,52]. These functionals, thanks to the presence of the nonlocal kernel, are able to provide a very accurate description of the KE features. However, they display several disadvantages:

(1) The most evident one is related to the computational cost, due to the nonlocal nature and the complicated expressions of the nonlocal kernel [49,50], which is much higher than the one required for semilocal functionals [61,62].

(2) A second significant drawback is related to the fact that the kernel is based on the Lindhard function, which is only defined in the reciprocal space, while its Fourier transform function does not have an analytical expression in real space. Several methods have been presented in literature [38,63–66] to represent the Lindhard function in real space, which have been used in real-space finite-element implementations of OF-DFT [67–70]. However, most of these methods yield only an approximate description of the Lindhard function and with a quite complicated numerical implementation. Therefore, an exact real-space description of the Lindhard function remains problematic and Lindhard-based nonlocal functionals are much better suited for extended periodic systems.

(3) Moreover, density-independent nonlocal KE functionals [38–40,45,51] cannot be properly applied to finite systems or surfaces [45]. A local density approximation has been introduced in Ref. [53] and recently in Ref. [54], allowing accurate calculations of finite systems with density-independent nonlocal KE functionals. Yet, calculations for isolated systems can only be performed in the periodic space with the use of a large supercell approach (to avoid interactions of periodic replicas).

(4) Another important feature of most nonlocal KE functionals is that, by construction, they are developed considering small perturbations of the homogeneous electron gas (HEG), with the density close to the bulk density. Therefore, they perform best for slowly varying systems, such as bulk solids, but may also be accurate for rapidly varying density regions. Note also that the accuracy of many nonlocal functionals originates from the use of system-dependent parameters [49–52].

The construction of a good KE approximation therefore poses a dilemma, since both classes display advantages and disadvantages. To try to solve this problem, preserving on one side the simplicity and universality of the semilocal functional development and seeking on the other side for the good accuracy typical of the nonlocal functionals, we have recently proposed a simple u-mGGA approximation [71,72]

$$\tau^{u-mGGA}(\mathbf{r}) = \tau(n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla^2 n(\mathbf{r}), u(\mathbf{r})).$$
(3)

which has the general form of a meta-GGA functional but uses as additional input ingredient the Hartree potential:

$$u(\mathbf{r}) = \int n(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'|d^3\mathbf{r}'.$$
 (4)

This is a nonlocal ingredient that can be easily computed in real space [indeed, $u(\mathbf{r})$ is already computed anyway in any electronic structure method] and provides nonlocal features to the functional. In fact, the u-mGGA functional can be seen as a semilocal functional with a nonlocal input ingredient or, equivalently, as a generalization of nonlocal functionals, with a Coulomb-like kernel. In fact, if we consider a u-mGGA functional of the type $\tau \propto n^{5/3} F[n(\mathbf{r})] u(\mathbf{r})$, then

$$\tau(\mathbf{r}) \propto \int n^{5/3}(\mathbf{r}) \frac{F[n(\mathbf{r})]}{|\mathbf{r} - \mathbf{r}'|} n(\mathbf{r}') d^3 \mathbf{r}' , \qquad (5)$$

which is analogous to Eq. (2) with $\alpha = 5/3$ and $\beta = 1$.

The u-mGGA KE functionals therefore have important potentialities in the field of KE approximations. Nevertheless, in view of a general application of the method, they also show a major limitation. In fact, this approach is constrained only to finite systems because the Hartree potential diverges for extended systems. For this reason, in this paper, we improve this method of functional development by considering an ingredient (y_{α}) based on the Yukawa potential, i.e., the screened Hartree potential. This preserves the good features of the u-mGGA method and overcomes the limitations due to the divergence of the Hartree potential for extended systems. Moreover, we show that using the ingredient y_{α} , an accurate description of the Lindhard function can be obtained in real space. As a result, we can construct semilocal functionals with nonlocal features that are efficiently computed in real space and can accurately describe different properties of electronic systems.

In detail, the paper is organized as follows. In Sec. II, we introduce the ingredient y_{α} , its properties, and the class of Yukawa-based functionals, showing how to compute the KE and the kinetic potential. In Sec. III, we present computational details of our implementation for spherical systems. In Sec. IV, we present results for total energy and perturbation of jellium clusters, taken as examples. In Sec. V, conclusions are drawn and possible extensions of this paper are discussed.

II. THEORY

For a given approximate KE functional $(T_s^{app}[n])$ of the electron density $n(\mathbf{r})$, we can compute the Thomas-Fermi (TF) normalized linear response of the HEG in reciprocal space (simply linear response in the following),

$$\frac{\chi^{\operatorname{app}}(\eta)}{\chi^{\operatorname{TF}}(\eta)} = \frac{1}{F^{\operatorname{app}}(\eta)} = \frac{\pi^2}{k_F} \hat{\mathcal{F}} \left[\frac{\delta^2 T_s^{\operatorname{app}}[n]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} \right]^{-1}, \quad (6)$$

where $\hat{\mathcal{F}}$ denotes the Fourier transform, $\eta = k/(2k_F)$ is the renormalized wave vector, the Fermi wave vector is $k_F = (3\pi^2 n)^{1/3}$, and $\chi^{\text{TF}} = -k_F/\pi^2$ is the TF linear response.

The exact linear response for the HEG is

$$\frac{\chi(\eta)}{\chi^{\rm TF}(\eta)} = \frac{1}{F^{\rm Lind}(\eta)} = \frac{1}{2} + \frac{1-\eta^2}{4\eta} \ln \left| \frac{1+\eta}{1-\eta} \right|, \quad (7)$$

which has two important limits:

$$1/F^{\text{Lind}}(\eta) \to 1 - \frac{\eta^2}{3} - \frac{\eta^4}{15} + \cdots \text{ for } \eta \to 0,$$
 (8)

$$1/F^{\text{Lind}}(\eta) \to \frac{1}{3\eta^2} + \frac{1}{15\eta^4} + \cdots \text{ for } \eta \to \infty.$$
 (9)

Note that sometimes in literature series expansions of F^{Lind} instead of $1/F^{\text{Lind}}$ are reported [1,24]. Other important properties of the Lindhard function are [1,73] the derivative singularity at $\eta = 1$, i.e., $d(1/F)/d\eta = -\infty$ and its value, i.e., 1/F(1) = 1/2, see first line of Table I.

TABLE I. Values of the linear response function and its first derivative, both calculated in $\eta = 1$, for the different functionals in Fig. 1 as well as for the approximation in Ref. [73].

	$\left(\frac{1}{F}\right) _{\eta=1}$	$\frac{d}{d\eta}(\frac{1}{F}) _{\eta=1}$
Lindhard	0.50	$-\infty$
TFvW	0.25	-0.375
Lind4	0.66	-0.60
PGSL0.25	0.56	-0.78
yuk1	0.31	-0.52
yuk2, yuk3, yuk4	0.39	-0.71
Ref. [73]	0.50	-0.75

We start by considering the general class of mGGA KE functionals of the type

$$T_s^{\text{mGGA}}[n] = \int \tau^{\text{TF}} F_s(p,q) d^3 \mathbf{r} , \qquad (10)$$

where the TF energy density is $\tau^{\text{TF}} = (3/10)k_F^2 n$ and the KE enhancement factor F_s is a general function of the squared reduced gradient $p = s^2 = (\nabla n)^2/(4k_F^2 n^2)$ and the reduced Laplacian $q = (\nabla^2 n)/(4k_F^2 n)$. At the more conventional GGA level of approximation, F_s is a function of p only. The linear response of a general mGGA functional is (see Appendix A)

$$\frac{1}{F^{\text{mGGA}}(\eta)} = \frac{1}{(9/5)D_{qq}\eta^4 + (9/5)D_p\eta^2 + F_s(0,0)}, \quad (11)$$

where $D_{qq} = (1/2)d^2F_s/dq^2$ and $D_p = dF_s/dp$ computed at p = q = 0. Eq. (11) tells us that it is enough to consider a functional of the type $F_s^{\text{mGGA}}(p, q) = F_s(0, 0) + D_p p + D_{qq}q^2$ to describe the linear response, whereas any higher-order term does not contribute to it.

Any GGA or mGGA functional cannot simultaneously satisfy conditions in Eqs. (8) and (9). At the GGA level, the well-known Thomas-Fermi- λ -von Weizsäcker (TF λ vW) functional, i.e., with $F_s = 1 + \lambda(5/3)p$, has a response $1/F^{\text{TF}\lambda vW}(\eta) = 1/(1 + 3\eta^2\lambda)$. When $\lambda = 1$, only Eq. (9) is satisfied (but only up to second order); when $\lambda = 1/9$, only Eq. (8) is satisfied (up to the second order). The TF1vW (simply TFvW in the following) response is reported in Fig. 1: While TFvW is correct at large η , it is quite bad at small η . Moreover, values at $\eta = 1$ are quite incorrect (see Table I).

At the mGGA level of theory, Eq. (8) can be satisfied, with $D_p = 5/27$ and $D_{qq} = 8/81$, i.e., the Lind4 functional [24], but in this case Eq. (9) is largely violated (due to the $D_{qq}\eta^4$ term) and the response at large η is inaccurate (see Fig. 1). The PGSL0.25 functional [32] well reproduces the Lindhard function globally as shown in Fig. 1 and in Table I, but the exact conditions at large wave vectors are not recovered.

With higher-order derivatives, the comparison with the Lindhard function goes even worse [1].

Thus, reproducing the Lindhard function in real space with semilocal ingredients is out of reach. This traces back to the fact that any semilocal ingredient does not generate terms in the numerator of Eq. (11), in contrast to Eq. (7). In Ref. [73], an approximated Lindhard function using a rational polynomial has been presented.



FIG. 1. Linear response (1/F) for different functionals; the inset shows the function F in a log scale. TFvW and yuk1 have an incorrect behavior at small η , whereas Lind4 and PGSL0.25 have incorrect behaviors at large η . Note that the functionals yuk3 and yuk4 have the same response as yuk1.

In this paper, we consider a nonlocal ingredient which can be easily computed in real space:

$$y_{\alpha}(\mathbf{r}) = \frac{3\pi\alpha^2}{4k_F(\mathbf{r})}u_{\alpha}(\mathbf{r}), \text{ with}$$
 (12)

$$u_{\alpha}(\mathbf{r}) = \int \frac{n(\mathbf{r}')e^{-\alpha k_F(\mathbf{r})|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}' .$$
(13)

The quantity $y_{\alpha}(\mathbf{r})$ is proportional to the Yukawa potential (or screened Coulomb potential) u_{α} , with a screening length $\alpha(3\pi^2)^{1/3}n(\mathbf{r})^{1/3}$. The Yukawa potential is widely used in many different applications in physics and chemistry [74–80]. Note that the screening length is fixed for a given \mathbf{r} , i.e., it does not depend on the integration variable \mathbf{r}' . Screening is required (i.e., $\alpha > 0$), otherwise $u_{\alpha}(\mathbf{r})$ diverges as $1/\alpha^2$ for any extended system: When $\alpha \rightarrow 0$, however, $y_{\alpha}(\mathbf{r})$ remains finite thanks to the multiplication by α^2 in Eq. (12). The Yukawa potential can be very easily computed for spherical systems, see Appendix B.

The ingredient y_{α} has the following properties:

(i) y_{α} is positive, adimensional, and invariant under the uniform scaling of the density (see Appendix C).

(ii) When $\alpha \to +\infty$, $u_{\alpha}(\mathbf{r}) \to 4\pi/[\alpha k_F(\mathbf{r})]^2 n(\mathbf{r})$, i.e., there is no nonlocality. In this limit, using Eq. (12), we have that $y_{\alpha} \to 1$.

(iii) y_{α} is unbound in the tail of finite systems: With N electrons (with vanishing density in the tail), we have $u_{\alpha}(\mathbf{r}) \rightarrow (N/r)$ and thus y_{α} diverges as $n(\mathbf{r})^{-1/3}$. This is shown in Fig. 2, e.g., for a jellium cluster with N = 92 electrons, for different values of the α parameter. Increasing α , we have that, inside the cluster, the Yukawa potential decreases while y_{α} approaches 1, see property ii.

(iv) Under the homogeneous scaling $[n(\mathbf{r}) \rightarrow \lambda n(\mathbf{r})]$, we have that $y_{\alpha}(\mathbf{r}) \rightarrow y_{\lambda^{1/3}\alpha}(\mathbf{r})$. Therefore, the limit for large λ (i.e., for a large number of electrons) is the same as the limit



FIG. 2. (a) The Yukawa potential (u_{α}) and (b) the nonlocal ingredient y_{α} versus the scaled radial distance r/R, for different values of α , for a jellium cluster with N = 92 electrons and $r_s = 4$. Also shown is the Hartree potential ($\alpha = 0$). The electronic ground-state density is reported in the inset of panel (b).

for large α , and thus, see point (ii) above, y_{α} is approaching 1 in this limit. On the other hand, for small λ , y_{α} can have a size-dependent behavior. As an example, we consider the model density $n_{jell}(r) = n_0$ inside a sphere of radius R_0 and zero outside, and we obtain at the center of the sphere (see Appendix D),

$$y_{\alpha}(0) = 1 - e^{-\alpha k_F R_0} (1 + \alpha k_F R_0)$$
(14)

$$= 1 - e^{-\frac{\alpha}{2}(18\pi N)^{1/3}} \left(1 + \frac{\alpha}{2} (18\pi N)^{1/3} \right), \quad (15)$$

where $N = n_0 4\pi R_0^3/3$ is the number of electrons. Equation (15) shows that y_{α} assumes different values inside the sphere, depending on the number of electrons N (note that it approaches 1 for an infinite number of electrons, i.e., in the HEG limit). Thus y_{α} shows a system-size dependence, in contrast to the behavior of all semilocal ingredients (reduced gradient and reduced Laplacian) which are, in this case, exactly zero regardless of the number of electrons.

(vi) In the limit $\lambda \to \infty$ of the TF density scaling [81], $n_{\lambda}(\mathbf{r}) = \lambda^2 n(\lambda^{1/3}\mathbf{r})$, which describes the atomic core of the semiclassical atom with an infinite number of electrons [note that $\int d^3\mathbf{r} n_{\lambda}(\mathbf{r}) = \lambda \int d^3\mathbf{r} n(\mathbf{r})$], we have that $y_{\alpha} \to 1$ (see Appendix E for an exponential density).

(v) For an atomic density of the type

$$n_{\rm at}(r) = \frac{2Z^3 f}{\pi} e^{-2Zr}$$
, (16)

which is exact near the nucleus of a large-*Z* neutral atom $[f = \zeta(3)]$, see Ref. [82], we obtain (see Appendix E)

$$y_{\alpha}(r) = \frac{\alpha^2}{\left(\alpha + \left(\frac{4}{3\pi f}\right)^{1/3}\right)^2} + O(Zr)$$
 (17)

Thus the value of y_{α} is less than 1 (namely, 0.343 for $\alpha = 1$) at the nucleus and does not depend on the number of electrons.



FIG. 3. The nonlocal ingredient y_{α} for the radon neutral atom for different values of α . The semilocal ingredients p and q are also reported. The inset shows the electronic density (in a doublelogarithmic scale).

Figure 3 reports y_{α} for several values of the α parameter for the radon atom. For large α , y_{α} approaches 1 everywhere in the space. For $\alpha = 1$, it approaches 0.34 as predicted by Eq. (17). Figure 3 shows also that for α values around 1, the y_{α} indicator contains different information as compared to p and q (which diverge to $-\infty$ at the nucleus).

In conclusion, we have shown that the y_{α} ingredient satisfies all the properties required to be a valid indicator in the construction of a generalized class of u-mGGA functionals [72], which we define here as the Yukawa-GGA (yGGA) functional. A yGGA functional has a KE of the type

$$T_{s}^{\text{yGGA}} = \int \tau(n, \nabla n, \nabla^{2} n, u_{\alpha}) d^{3} \mathbf{r}$$
(18)

$$=\int \tau^{TF} F_s(p,q,y_\alpha) d^3 \mathbf{r}.$$
 (19)

As shown in Figs. 2 and 3, the value of the α parameter should be around 1 to carry significant information in the high-density region.

A. Kinetic potential of yGGA functionals

Having defined the yGGA energy functional, the next fundamental step is to define the kinetic potential (its first functional derivative), which is the most important quantity in OF-DFT calculations.

The yGGA kinetic potential is (see Appendix F):

$$\frac{\delta T_s^{\text{yGGA}}}{\delta n(\mathbf{r})} = v_k^{\text{mGGA}}(\mathbf{r}) + v_k^{\text{yGGA},1}(\mathbf{r}) + v_k^{\text{yGGA},2}(\mathbf{r}) , \quad (20)$$

where the first term,

$$v_k^{\text{mGGA}}(\mathbf{r}) = \frac{\partial \tau}{\partial n}(\mathbf{r}) - \nabla \cdot \frac{\partial \tau}{\partial \nabla n}(\mathbf{r}) + \nabla^2 \frac{\partial \tau}{\partial \nabla^2 n}(\mathbf{r}), \quad (21)$$

is the kinetic potential of a mGGA-type functional [28,83], whereas

$$v_k^{\text{yGGA},1}(\mathbf{r}) = \frac{3k_F(\mathbf{r})^2}{10}\tilde{y}_\alpha(\mathbf{r}),$$
(22)

$$v_k^{\text{yGGA,2}}(\mathbf{r}) = -\frac{2k_F(\mathbf{r})^2}{10}e_\alpha(\mathbf{r}), \qquad (23)$$

with

$$\tilde{y}_{\alpha}(\mathbf{r}) = \frac{3\pi\alpha^2}{4k_F(\mathbf{r})n^{1/3}(\mathbf{r})} \times \int n(\mathbf{r}')^{4/3} \frac{\partial F_s}{\partial y_{\alpha}}(\mathbf{r}') \frac{e^{-\alpha k_F(\mathbf{r}')|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}', \quad (24)$$

$$e_{\alpha}(\mathbf{r}) = \frac{3\pi\alpha^3}{8} \frac{\partial F_s}{\partial y_{\alpha}}(\mathbf{r}) \int n(\mathbf{r}') e^{-\alpha k_F(\mathbf{r})|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}', \quad (25)$$

are the additional terms due to the dependence on y_{α} . The functions \tilde{y}_{α} and $e_{\alpha}(\mathbf{r})$ have been renormalized to be adimensional and recovering 1 in the HEG limit (when $dF_s/dy_{\alpha} = 1$, see Appendix I).

The integrals appearing in Eqs. (24) and (25) can also be easily computed for spherical systems, see Appendix B. The form of the yGGA potential thus depends on the specific form of the enhancement factor. In the following section, some model functionals will be analyzed.

B. Model yGGA functionals

The simplest yGGA functional is

$$F_s^{\text{yukl}}(p, q, y_\alpha) = (5/3)p + y_\alpha , \qquad (26)$$

which is a generalization of the TFvW one and satisfies the condition [27,84]

$$F_{\theta} = F_s - (5/3)p > 0 , \qquad (27)$$

where F_{θ} is the Pauli enhancement factor. The yuk1 functional is defined with $\alpha = 1$ and its linear response is (see Appendix G)

$$\frac{1}{F^{\text{yuk1}}(\eta)} = \left(3\eta^2 + \frac{-16\eta^4 + 40\eta^2 + 5}{80\eta^4 + 40\eta^2 + 5}\right)^{-1}.$$
 (28)

Note that in this case a fourth-order polynomial in η is present in the numerator, which is a striking difference with respect to TFvW and also the to mGGAs. For $\eta \to \infty$, we have that $F^{\text{yuk1}} \to 3\eta^2 - 1/5 + \cdots$ which is close to the exact result $F^{\text{Lind}} \to 3\eta^2 - 3/5 + \cdots$ [1]. For $\eta \to 0$, we have a $F^{\text{yuk1}} \to 3\eta^2 + 1 + \cdots$ which is like the TFvW functional.

If we consider the model density $n_{jell}(r) = n_0$ inside a sphere of radius R_0 and zero outside, we obtain the kinetic potential components, i.e., Eqs. (21)–(23) reported in Fig. 4. The values at r = 0 are discussed in Appendix I: For $R_0 \rightarrow \infty$, the sum of all contributions converges to the TF potential. Outside the sphere, where the density is zero, we have that all contributions are zero but $v_k^{yGGA,1}$, which decays proportionally to $e^{-\alpha k_F r}/r$, showing again the nonlocal features of yGGA functionals (i.e., the potential is nonzero where the density is exactly zero).



FIG. 4. Components of the yukl kinetic potential for a model density (see text). For v_k^{mGGA} , the vW part is not considered.

If we consider the model atomic density of Eq. (16), we have at r = 0 [see Eq. (17) and Appendix I],

$$F_{\theta}^{\text{yuk1}} = y_{\alpha=1}(0) = 0.343 , \qquad (29)$$

$$v_{\theta}^{\text{yuk1}}(0) = 1.77Z^2$$
, (30)

where $v_{\theta} = v_k - v_k^{\text{vW}}$ is the Pauli potential [84]. These results can be be compared with the exact results [82,85]:

$$F_{\theta} = 0.0286$$
, (31)

$$v_{\theta}(0) = Z^2/2$$
. (32)

Thus, the yuk1 functional gives a kinetic potential at the nucleus about three times larger than the exact one. This is a very good result considering that TFvW overestimates it by eight times $[v_{\theta}^{\text{TFvW}}(0) = 4.003Z^2]$, as also shown in Fig. 5 where we report the Pauli potential for the radon atom. Thus, the yuk1 functional is quite accurate at the nucleus, considering that, in general, GGA and mGGA functionals diverge at



FIG. 5. Pauli potential for the Radon atom from different KE functionals.

the nucleus [28], as also shown in Fig. 5 for, e.g., PG1 [32] and GE4 functionals. Although the reproduction of the exact Pauli potential is challenging [28,55,56,86–89], the yuk1 has some novel features.

Despite the yuk1 being quite correct at the atomic nucleus, the yuk1 functional does not recover the properties of Eqs. (8) and (9), and the linear response is not very different from the TFvW functional, see Fig. 1 and Table I. Note, in fact, that the nuclear region is a very rapidly varying density region, which is thus not related to the HEG linear-response properties. In other words, KE functionals which are accurate for the HEG linear response may largely fail for the nuclear region. In general, the accuracy for atoms is related to the semiclassical atom theory [18] and not to the HEG. In fact, consider, for example, that already the coefficients for the second-order gradient expansion are different for atoms and HEG [18]. In this paper, we focus on yGGA functionals which are accurate for the HEG.

While a generic enhancement factor, see Eq. (19), can be considered, we found that all the main properties of the Lindhard function, i.e., Eqs. (8) and (9), can be obtained considering a functional which is linear in y_{α} and nonlinear in p and q, i.e.,

$$F_s^{\text{linyuk}} = (5/3)p + y_\alpha G(p,q)$$
. (33)

The corresponding linear response is (see Appendix G)

$$\frac{1}{F_s^{\text{linyuk}}} = \left(3\eta^2 + \frac{C_8\eta^8 + C_6\eta^6 + C_4\eta^4 + C_2\eta^2 + C_0}{80\eta^4 + 40\eta^2\alpha^2 + 5\alpha^4}\right)^{-1},$$
(34)

with

$$C_8 = 72D_{qq},\tag{35}$$

$$C_6 = 36D_{qq}\alpha^2 + 144D_p + 144D_q, \tag{36}$$

$$C_4 = (9/2)D_{qq}\alpha^4 + (72D_p + 36D_q)\alpha^2 - 16G_0, \quad (37)$$

$$C_2 = 9\alpha^4 D_p + 40\alpha^2 G_0, (38)$$

$$C_0 = 5G_0\alpha^4 , \qquad (39)$$

where $D_q = dG/dq$, $D_{qq} = d^2G/dq^2$, and $D_p = dG/dp$, computed at p = q = 0, and $G_0 = G(0, 0)$. Thus the linear response of a linyuk functional is completely described by a function $G(p, q) = G_0 + D_p p + D_q q + D_{qq} q^2/2$ whereas higher-order terms do not contribute. Note that while in mGGA functionals a linear term in q in F_s is vanishing for both energy and potential [90], in linyuk functionals we have a linear term in q in G which is not vanishing. This is another fundamental difference between yGGA and mGGA functionals.

As shown in Appendix H, the Lindhard conditions can be (almost) recovered with

$$G_0 = 1, \quad D_{qq} = 0, \quad D_q = 40/27 = -D_p; \quad \alpha = 1.3629,$$
(40)

which defines the yuk2 functional:

$$F_s^{\text{yuk2}} = (5/3)p + y_\alpha \left(1 + \frac{40}{27}(q-p) \right). \tag{41}$$



FIG. 6. The function $T_a(x)$ for different values of *a*.

The normalized linear response for the yuk2 functional is shown in Fig. 1: The agreement with the Lindhard response is very good. Values at $\eta = 1$ for the yuk2 functional are also better and closer to the best functionals, i.e., PGSL0.25 and the approximation in Ref. [73]. Clearly, all the functionals in Table I do not reproduce the derivative discontinuity at $\eta = 1$, which is very difficult to obtain in real space.

For general applications to finite systems, q and p can be very far from zero, thus a KE functional with broad applicability must not only satisfy the Lindhard response but also other properties, in particular Eq. (27), which is not the case for the yuk2 functional (as q can be negative or |q| < p). More generally, we can consider a functional in which

$$G(p,q) = h(x)$$
, with $x = \frac{40}{27}(q-p)$, (42)

where h(x) > 0 is a positive function, so Eq. (27) is satisfied and

$$h(x) \to 1 + x + O(x^3)$$
 for $x \to 0$, (43)

i.e., with a null quadratic term, so yuk2 is recovered for small p and q. A different linear combination between p and q has been used in Ref. [30], as an approximation of the electron localization. Here, the quantity x appears directly from the Lindhard function analysis. Note that x is usually negative and, in the tail of an exponentially decaying density, is proportional to $-s^2/r$ [10] and thus it approaches $-\infty$. Also, at the core of an atom, where $q \to -\infty$ and $p \approx 0.13 - 0.14$, we have $x \to -\infty$.

In this paper, we consider a very simple one-parameter function,

$$h^{\text{yuk3}}(x) = T_a(x) = \frac{4}{a} \frac{e^{ax}}{(e^{ax} + 1)} + \frac{a - 2}{a},$$
 (44)

which is always positive for a > 2, satisfies Eq. (43), approaches 1 - 2/a for $x \to -\infty$ and 1 + 2/a for $x \to +\infty$, as shown in Fig. 6.

We fix a = 4 from optimization of jellium clusters, as described in Sec. III. Note that for jellium clusters, *a* describes the details of the tail region, where the gradient expansion cannot be applied and thus no exact constraint can be used.

Another option to satisfy Eq. (43) is

$$G^{\text{yuk4}}(p,q) = T_a(-40p/27)T_2(40q/27), \qquad (45)$$

i.e., using a product of separated functions in p and q. For the function in q, we used a = 2 so, at the atomic core, where $q \rightarrow -\infty$, we have $G^{\text{yuk4}} \rightarrow 0$ and thus $F_{\theta}^{\text{yuk4}} \rightarrow 0$. This is a quite correct condition, considering that the exact result, see Eq. (31), is also close to zero. More importantly, with this choice we have that the mGGA contribution to the potential vanishes at the nucleus (see Appendix J) and thus only the Yukawa terms in Eqs. (22) and (23) contribute to the potential.

The yuk4 functional thus has just one parameter as yuk3. We fixed a = 3.3 from optimization of jellium clusters, as described in Sec. III. The yuk3 and yuk4 functionals are close to each other and have the same linear response as yuk2. However, the yuk3 functional cannot distinguish between the atomic core and the density tail ($G^{yuk3} = 1/2$ for both cases), while $G^{yuk4} = 0$ in the former and $G^{yuk4} \approx 1.67$ in the latter.

In Sec. IV, we will analyze the performances of yuk1, yuk3, and yuk4 for jellium clusters and noble atoms.

III. COMPUTATIONAL DETAILS

Jellium cluster calculations for kinetic energies and potentials were performed using an in-house developed code, in which all the kinetic functionals appearing in this paper have been implemented. The reference values for the kinetic energies and potentials were obtained by self-consistent KS LDA calculations [12]. The external potential of a jellium cluster with N electrons and Wigner-Seitz radius r_s is

$$v_{\text{ext}}^{\text{jell}}(r) = \begin{cases} N\left(-\frac{3}{2R} + \frac{r^2}{2R^3}\right), & r < R = r_s N^{1/3} \\ -N/r, & r \ge R = r_s N^{1/3}. \end{cases}$$
(46)

The errors for the Pauli potential for jellium clusters are obtained by using the formula

$$\epsilon_{\rm pot} = \frac{\int 4\pi r^2 n^\beta \left| v_\theta(r) - v_\theta^{\rm ref}(r) \right| dr}{\int 4\pi r^2 n^\beta v_\theta^{\rm ref}(r) dr} , \qquad (47)$$

where we indicated by v_{θ}^{ref} the exact Pauli potential from KS calculation [i.e., $\mu - v_{\text{KS}}(\mathbf{r}) - v_k^{\text{vW}}(\mathbf{r})$] [86]. The weight function $n(r)^{\beta}$ is required because we are also considering functionals which contain a term q^2 in their enhancement factor (e.g., GE4 and PGSL0.25) so the corresponding kinetic potential diverges in the tail as $n(\mathbf{r})^{-2/3}$. Thus the term $n(r)^{\beta}$ with $\beta > 2/3$ is required to obtain a finite value of the error: We choose $\beta = 0.7$ (for larger values, the tail region becomes not relevant for the error). The denominator normalizes to one the value of ϵ_{pot} for the vW functional.

Optimization of the yuk3 and yuk4 functional has been done considering the error

$$E = \sum_{N} \sum_{r_s} \text{MARE}_{\text{ene}} + \epsilon_{\text{pot}}$$
(48)

where MARE_{ene} is the mean absolute relative error for the energy, *N* runs over the number of electrons considered (40, 92, 138, 254, 438), and r_s over the Wigner-Seitz radius considered (2, 3, 4, 5). For both yuk3 and yuk4, we performed a scan from a = 2 to a = 5 and the resulting minima is a = 4 for yuk3 and a = 3.3 for yuk4.

TABLE II. Mean absolute relative errors (MAREs), in percent, for the KEs (kinetic energies) of jellium clusters of different sizes (N = 40, 92, 138, 254, 438) averaged over five different values of the Wigner-Seitz radius ($r_s = 2, 3, 4, 5, 6$). The last column contains the value averaged over the number of electrons N. Best results (among functionals with the full vW term) are in bold.

N	40	92	138	254	438	Average
TFvW	20.47	16.50	13.77	11.09	8.87	14.14
VT84f	16.70	13.38	11.16	8.86	7.08	11.44
PG1	12.19	9.92	8.18	6.47	5.11	8.37
PGS	9.89	8.02	6.56	5.11	4.00	6.72
PGSL0.25	24.33	18.96	15.46	12.17	9.51	16.10
yuk1	8.60	7.37	6.11	4.93	3.94	6.19
yuk3	1.02	0.86	1.09	1.15	1.15	1.06
yuk4	1.57	1.12	1.32	1.25	1.30	1.29
GE4	1.29	0.25	0.38	0.27	0.33	0.50
uGE4m	2.50	0.55	0.35	0.05	0.17	0.74

IV. RESULTS

In this section, we will present results for the yGGA functionals introduced in Sec. II for jellium clusters and noble atoms. We compare our yGGA functionals only with other GGA and mGGA functionals which, correctly, use the full vW term [i.e., satisfy Eq. (27)] and thus can have a correct Pauli potential. At the semilocal level, we considered TFvW, PG1 [32], PGS [32], PGSL025 [32], and VT84f [20]. Other functionals based on the gradient expansion (e.g., GE2 and GE4) or on the modified gradient expansion from the semiclassical atom theory [18,19,91] employ just a fraction of the vW and thus cannot correctly describe the electronic density in OF-DFT calculations [12,20]. This is not really a problem when these functionals are applied in the solid state but can be a major shortcoming for finite systems. In literature, there are other mGGA functionals with the full vW term [27,28], which can be very accurate for total energies, but they have a very bad and oscillating potential, thus they are not considered in the following.

A. Total energies of jellium clusters

In Table II, we report the performance of different KE functionals for the description of jellium clusters. We considered functionals with the full vW term (upper part of the table) and compared with GE4 and the uGE4m [72], which is a u-mGGA functional: Both functionals are very accurate for jellium clusters [72]. Recall that total KE energies are computed non-self-consistently from the KS density. The yuk1 functional has an average error of 6% which is lower (more than a factor of 2) than the related TFvW functional with errors 14%, showing the importance of the y_{α} ingredient. The yuk3 functional, which approximates well the Lindhard function, is by far the best functional among the ones considered, with an average error of about 1%. The yuk4 functional is also very accurate, with an average error of only 1.29%. The yuk3 also compares well with the GE4 and uGE4m functionals (with average errors of 0.5% and 0.7%), which are the most accurate ones, but do not employ the full vW and have a potential which diverges in the tail.



FIG. 7. Exact and approximate Pauli potential v_{θ} for a jellium cluster with 254 electrons and $r_s = 4$, versus the scaled radial distance r/R (R = 25.33 a.u. is the radius of the cluster).

In Fig. 7, we report the Pauli potential for a jellium cluster with 254 electrons and $r_s = 4$ as computed from different KE functionals. None of the functionals is able to reproduce the exact Pauli potential accurately, which is a very challenging task [28,55,56,86–89]. The GE4 functional, which is reputed among the best ones for jellium systems and is very accurate for the total energy, reproduces the oscillations of the exact KS result inside the cluster only qualitatively (the magnitude of the oscillations cannot be reproduced), shows a large bump outside the jellium sphere, and diverges in the tail. The TFvW potential cannot even reproduce qualitatively the KS oscillations, showing maxima and minima out of phase with respect to the exact potential. However, the TFvW potential does not diverge asymptotically, despite it decays too fast. The yuk1, yuk3, and yuk4 functionals are all quite similar to the GE4 one inside the jellium sphere (except at the origin, which has zero measure, thus it is not very relevant), suggesting that they can be reasonably accurate in this region even if they cannot closely reproduce all the features of the exact potential. Also, on the edge of the jellium sphere $(0.7 \leq r/R \leq 1)$, they are rather accurate, being close to GE4 and the exact potentials. At the border of the sphere (r/R = 1), the yuk3 and yuk4 potentials show a discontinuity due to a discontinuity of the second (radial) derivative of q, which in turn depends on the discontinuity of the fourth derivative of the density at this point (because of the discontinuous positive background). Note that the GE4 potential also has a discontinuity at the jellium edge even if it cannot be seen on the actual plot scale. Outside the jellium sphere, the yuk1, yuk3, and yuk4 potentials show a bump similar to the GE4 one, but then they decay correctly in the long-range limit, which is a very important requirement [12,20,86,89,92].

In Table III, we report the error in potential as computed by Eq. (47). We recall that the error ϵ_{pot} mainly considers the difference with respect the KS one, mostly inside the jellium cluster. The ϵ_{pot} for yuk1, yuk2, and yuk3 are all quite small, in the range of 11%-12%, with an accuracy better than the best GGA functional (i.e., PGS). The yuk3 is the best functional with an average error of only 11%. As previously discussed, GE4 and uGE4m, which are accurate for total energy are instead much worse for the potential.

TABLE III. Error in the potential, ϵ_{pot} , see Eq. (47), in percent, of jellium clusters of different sizes (N = 40, 92, 138, 254, 438) averaged over five different values of the Wigner-Seitz radius ($r_s = 2, 3, 4, 5, 6$). The last column contains the value averaged over the number of electrons *N*. Best results (among functionals with the full vW term) are in bold.

N	40	92	138	254	438	Average
TFvW	22.3	39.8	20.6	21.2	15.3	21.9
VT84f	29.7	32.6	23.2	21.9	16.1	24.7
PG1	15.7	23.0	14.8	15.4	10.6	15.9
PGS	18.1	22.0	14.0	14.4	9.8	15.6
PGSL0.25	615.1	392.1	256.0	178.0	122.4	312.7
yuk1	11.5	17.7	11.6	12.9	9.2	12.6
yuk3	16.4	12.2	9.2	9.7	7.7	11.1
yuk4	18.4	13.3	10.7	11.2	8.8	12.5
GE4	33	26.0	17.4	14.3	10.5	20.6
uGE4m	206	128.0	84.3	58.3	41.5	100.8

B. Perturbation of jellium clusters

We tested jellium clusters with N = 40 and 92 electrons, and $2 \le r_s \le 6$ in a perturbed external potential of the following form [89]:

$$v_{\text{ext},\kappa}(r) = v_{\text{ext}}^{\text{jell}}(r) \left(1 + \frac{1}{m} \sin(\kappa r) \right), \tag{49}$$

In Eq. (49), *m* is a parameter that can vary the amplitude of the perturbation and κ is the wave vector of the perturbation. We fix m = 50, such that the amplitude of the perturbation is small. Then, we vary $0 \le \kappa \le 2.1$, capturing both the long-wavelength perturbations ($\kappa \to 0$) and the rapidly oscillating perturbations ($\kappa \ge 2\pi/R$), where *R* is the radius of the cluster. For all these cases, we calculate the KE response of the KE functional T_s^{app} as

$$\delta_{\kappa} T_s^{\text{app}} = T_s^{\text{app}} [v_{\text{ext},\kappa}] - T_s^{\text{app}} [v_{\text{ext}}^{\text{jell}}].$$
(50)

We also considered the relative KE response defined as $\bar{\delta}_{\kappa} T_s^{\text{app}} = \delta_{\kappa} T_s^{\text{app}} / T_s^{\text{KS}} [v_{\text{ext}}^{\text{jell}}].$

Then we measure its κ -averaged KE response error as

$$\Delta T_s^{\text{app}} = \int_{\kappa^{\min}}^{\kappa^{\max}} d\kappa \left| \delta_{\kappa} T_s^{\text{app}} - \delta_{\kappa} T_s^{\text{KS}} \right| / (\kappa^{\max} - \kappa^{\min}), \quad (51)$$

where $\kappa^{\min} = 0$ and $\kappa^{\max} = 2.1$ bohr⁻¹ (and we use a step of 0.05 for the integration over κ). A similar definition is used for the κ -averaged relative KE response error, $\bar{\Delta}T_s^{app} = \Delta T_s^{app}/T_s^{KS}[v_{ext}^{\text{ell}}]$.

In Table IV, we report ΔT_s , see Eq. (51), for several selected KE functionals, for the jellium clusters with 40 and 92 electrons in the case of several bulk parameters ($2 \leq r_s \leq 6$). The second to last column reports ΔT_s averaged among all r_s whereas the last column considers the r_s -averaged $\overline{\Delta}T_s$, which takes into account the different KE total energies for different r_s . For all clusters, we observe that ΔT_s follows the trend TF > GE2 > u-mGGA > GE4, that agrees with Table 4 of Ref. [72]. The first five functionals in Table IV (i.e., all functionals with the full vW term, but yuk4) display a significant dependence on the value of r_s , being much more accurate

TABLE IV. The κ -averaged KE response errors [ΔT_s of Eq. (51) in mH] of various KE functionals for the jellium clusters with 40 and 92 electrons in the case of several bulk parameters ($2 \leq r_s \leq 6$). The second-last column shows the overall accuracy (averaged over r_s), whereas the last column considers the r_s -averaged $\overline{\Delta}T_s$ in percent. The best two results of each column are highlighted in bold.

			Overall						
	2	3	4	5	6	ΔT_s	$\bar{\Delta}T_s$		
Jellium cluster with 40 e ⁻									
TFvW	168	98	62	43	33	81.0	2.4%		
PG1	102	47	32	24	19	44.8	1.3%		
PGSL025	243	158	113	90	78	136.5	4.5%		
yuk1	77	44	27	19	14	36.5	1.1%		
yuk3	69	50	39	32	27	43.4	1.5%		
yuk4	53	33	27	28	28	34.0	1.3%		
TF	99	101	88	76	67	86.2	3.4%		
GE2	72	80	72	63	55	68.2	2.8%		
GE4	57	63	54	45	38	51.4	2.0%		
uGE4m	70	73	62	53	44	60.2	2.3%		
	Jelli	um clus	ter with	92 e ⁻					
TFvW	1039	575	373	262	195	488.8	6.0%		
PG1	477	259	190	152	128	241.1	3.3%		
PGSL025	785	438	351	337	338	449.8	6.9%		
yuk1	552	279	173	117	85	241.2	2.8%		
yuk3	250	109	90	88	80	123.6	1.8%		
yuk4	263	312	298	258	219	269.9	4.7%		
TF	528	565	513	455	403	429.8	8.5%		
GE2	387	449	419	376	337	393.7	6.9%		
GE4	301	348	314	268	227	291.7	5.0%		
uGE4m	334	376	338	291	250	317.9	5.4%		

(in absolute value) for large r_s than for small r_s . The PG1 functional is the most accurate among the considered semilocal functionals, whereas GE2 and GE4 are significantly less accurate. Recall that, see Table II, GE4 is very accurate for total energy (MARE is 1.29% and 0.25% for N = 40 and N = 92, respectively), but when a perturbation is considered the accuracy largely decreases (down to 2.0% and 5.0%, respectively).

The yGGA functionals have the best accuracy for most of the clusters. In particular, yuk1 is the best functional for N = 40, while yuk3 is for N = 90.

To better clarify the performances reported in Table IV, we show in Fig. 8 the relative KE response $(\bar{\delta}_{\kappa}T_s)$ versus κ for several KE functionals for the considered jellium clusters with $r_s = 3$. We observe that the exact KS energy changes significantly with κ (about 10–20%) despite the perturbing potential being small (m = 50). All the functionals follow the KS oscillations versus κ but TFvW (GE4) largely overestimates (underestimates) them. For N = 40 (N = 92), we see that yuk4 (yuk3) matches very well the KS results, correspondingly yielding the lowest errors in Table IV. A more detailed analysis of the performances of the yGGA functionals for different cluster sizes and different values of m will be presented elsewhere.

C. Atoms

Finally, in this section we briefly report results for some closed-shell neutral noble atoms, up to 290 electrons. We



FIG. 8. Relative kinetic response errors $(\bar{\delta}_{\kappa} T_s)$ versus κ of several KE functionals for the jellium clusters with N = 40 (upper panel) and N = 92 (lower panel), and $r_s = 3$.

recall that, as already discussed in Sec. II B, atoms are not slowly varying systems; thus a functional that satisfies the Lindhard response may not be accurate for atoms.

In Table V, we report the error for the total KE. Results show that yuk1 is significantly more accurate than the related TFvW. The accuracy of the yuk3 functional is also quite interesting considering that it recovers the Lindhard function with great accuracy and does not diverge at the nucleus in contrast to the PG1, PGS, and PGSL0.25 functionals. The VT84f functional does not diverge at the nucleus, too, but its accuracy is very close to the TFvW. The best results are

TABLE V. Kinetic energy relative errors (in percent) for different noble atoms and functionals. Best results are in bold.

	Ne	Ar	Kr	Xe	Rn	118	290	Average
TFvW	61.4	51.3	40.4	35.3	30.0	27.0	19.8	37.9
VT84f	55.0	46.1	35.4	30.0	24.3	21.2	14.3	32.2
PG1	29.8	23.3	17.2	14.6	12.0	10.7	7.6	16.5
PGS	19.8	13.8	8.6	6.7	5.0	4.2	2.7	8.7
PGSL0.25	23.9	16.6	10.4	8.2	6.2	5.3	3.4	10.6
yuk1	33.0	27.7	22.4	20.1	17.7	16.2	12.5	21.4
yuk3	18.1	13.8	10.1	8.7	7.2	6.3	4.5	10.6
yuk4	13.1	8.2	5.0	4.1	3.4	3.1	2.3	5.6

obtained with the yuk4 functional. Recall that yuk4 (as well as yuk3) does not use any parameter fitted from atoms (the *a* parameter is fitted from jellium clusters). Note, however, that GE4 and uGE4m show a much better accuracy (below 1% for all the noble atoms considered) but their potential diverges both at the nucleus and in the tail [72]. Further investigations on (optimized) yGGA functionals for atoms will be presented elsewhere.

V. CONCLUSIONS AND FUTURE PERSPECTIVES

In this paper, we have introduced an ingredient y_{α} which can be used in the construction of a class of kinetic functionals, the yGGA. The ingredient y_{α} is adimensional, invariant under the uniform scaling of the density, and can be used both for finite systems as well as for extended systems, approaching 1 for the HEG. The ingredient y_{α} is finite at the atomic nucleus and diverges in the tail of finite systems: This feature resembles the one of the reduced gradient but y_{α} shows a size-dependent behavior.

The most relevant property of the y_{α} ingredient is that it can be combined with the reduced gradient and reduced Laplacian to obtain an improved approximation of the linear response of the HEG, both for small and large wave vectors, which is out of reach for GGA and meta-GGA functionals (and also for the recent class of u-mGGA functionals, which cannot be applied to extended systems). We present two very simple and nonempirical model functionals (yuk3 and yuk4) which are linear in the y_{α} ingredient. These functionals yield an improved description of the Lindhard function and the Pauli potential of jellium clusters with respect to mGGAs and give accurate total and perturbation energies of jellium clusters. The simultaneous satisfaction of these properties is out of reach for all the previous mGGA and u-mGGA class of functionals. Results indicate that the class of yGGA functionals can be very promising due to its novel features.

Different paths can be followed in the future: performing fully self-consistent OF-DFT calculations (in this paper, we only used the exact KS density), development of functionals which depend in a nonlinear way from y_{α} , as well as functionals which are also accurate for atoms. In this paper, we have indeed shown that yGGA functionals can have both a finite KE density and kinetic potential at the nucleus, which is an important prerequisite. Moreover, implementation of the functionals for molecular and extended systems is required (in this paper, we considered only spherical systems) to further check the accuracy of the yGGA functionals for those systems. Finally, the yGGA class of functionals can be further extended, considering other quantities instead of the electronic density in Eq. (13), e.g., $n(\mathbf{r})$ to some power, as well as a different screening function, e.g., which depends also on the density gradient [82].

APPENDIX A: LINEAR RESPONSE OF A MGGA FUNCTIONAL

Following Ref. [93], we can calculate the linear response function for a generic mGGA kinetic functional defined in Eq. (10). We start from considering a perturbed density $n(\mathbf{r}) = n_0 + n_k e^{-i\mathbf{k}\cdot\mathbf{r}}$ (with n_0 and n_k constants) and, evaluating in

 $\mathbf{r} = 0$, we have $n = n_0 + n_k$, $|\nabla n|^2 = n_k^2 k^2$ and $\nabla^2 n = -n_k k^2$. We write *p* and *q* in terms of these new expressions and use them in the generic mGGA kinetic energy density obtaining

$$\tau = \tau^{TF} F_s(p,q) = \frac{3}{10} k_0^2 (n_0 + n_k)^{5/3} \\ \times F_s \left(\frac{n_k^2 k^2}{4k_0^2 (n_0 + n_k)^{8/3}}, -\frac{n_k k^2}{4k_0^2 (n_0 + n_k)^{5/3}} \right), \quad (A1)$$

with $k_0 = (3\pi^2)^{1/3}$. If we expand Eq. (A1) in powers of n_k , we have

$$\begin{aligned} \tau &= \frac{3}{10} k_0^2 n_0^{5/3} F_s(0,0) \\ &+ \frac{1}{40} \Big(20 k_0^2 n_0^{2/3} F_s(0,0) - 3k^2 D_q \Big) n_k \\ &+ \frac{1}{2} \frac{1}{240 k_0^2 n_0^{5/3}} \Big(80 F_s(0,0) k_0^4 n_0^{4/3} \\ &+ 36 D_p k_0^2 k^2 n_0^{2/3} + 9 D_{qq} k^4 \Big) n_k^2 + O\big(n_k^3 \big), \end{aligned}$$
(A2)

where $D_{qq} = (1/2)d^2F_s/dq^2$ and $D_q = dF_s/dp$ computed at p = q = 0.

The linear response $\chi(\eta)$ is the negative of the half of the reciprocal of coefficient of the n_k^2 term [93], and using $k = 2\eta k_F$:

$$\chi(\eta) = -\frac{15n_0^{1/3}}{k_0^2} \frac{1}{9D_{qq}\eta^4 + 9D_p\eta^2 + 5F_s(0,0)} \,. \tag{A3}$$

Multiplying this expression by $1/\chi^{TF} = -\pi^2/(k_F)$, we finally obtain Eq. (11).

APPENDIX B: SPHERICAL INTEGRALS

The screened Coulomb integral can be easily computed for any system with spherical symmetry. Let us consider two generic functions with spherical symmetry, $f(\mathbf{r})$ and $a(\mathbf{r})$, and define

$$u[a](\mathbf{r}) = \int f(\mathbf{r}') \frac{e^{-a(\mathbf{r})|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}'.$$
 (B1)

Equation (13) can be obtained using $f(\mathbf{r}) = n(\mathbf{r})$ and $a(\mathbf{r}) = \alpha k_F(\mathbf{r})^{1/3}$. Due to the spherical symmetry, it is enough to compute $u[a](\mathbf{r})$ along the *z* axis:

$$u[a](z) = \int_0^\infty \int_0^\pi 2\pi r^2 \sin(\theta) f(r)$$
$$\times \frac{e^{-a(z)\sqrt{r^2 + z^2 - 2rz\cos(\theta)}}}{\sqrt{r^2 + z^2 - 2rz\cos(\theta)}} dr d\theta.$$
(B2)

The integral over θ can be easily computed,

$$\frac{2\pi f(r)r e^{-a(z)|z-r|}}{za(z)} - \frac{2\pi f(r)r e^{-a(z)(r+z)}}{za(z)}, \qquad (B3)$$

and thus we finally have

$$u[a](z) = \frac{2\pi}{za(z)} \int_0^\infty r' f(r') \times (e^{-a(z)|z-r'|} - e^{-a(z)|z+r'|}) dr'.$$
(B4)

For z = 0, we have (expanding the exponential functions in series)

$$u[a](0) = 4\pi \int_0^\infty r' f(r') e^{-a(0)r'} dr'.$$
 (B5)

For the calculation of the kinetic potential, two different integrals are present, see Eqs. (24) and (25). In Eq. (24), the screening coefficient depends on the integration variable, i.e., $a(\mathbf{r}')$ instead of $a(\mathbf{r})$:

$$\tilde{u}[a](\mathbf{r}) = \int f(\mathbf{r}') \frac{\mathrm{e}^{-a(\mathbf{r}')|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}'.$$
(B6)

In this case, Eq. (B3) is still valid with $a(z) \rightarrow a(r)$ and we obtain

$$\tilde{u}[a](z) = \frac{2\pi}{z} \int_0^\infty \frac{r'f(r')}{a(r')} \times (e^{-a(r')|z-r'|} - e^{-a(r')|z+r'|})dr', \quad (B7)$$

where we can use $f(\mathbf{r}') = \frac{\partial \tau}{\partial u_{\alpha}}(\mathbf{r}')$ and $a(\mathbf{r}') = \alpha k_F(\mathbf{r}')$ to obtain Eq. (24). For z = 0, we have

$$\tilde{u}[a](0) = 4\pi \int_0^\infty r' f(r') e^{-a(r')r'} dr'.$$
 (B8)

This expression does not have an analytical solution but can be computed in series as we will show in Appendix I.

For Eq. (25), we have an expression of the type

$$h[a](\mathbf{r}) = \int f(\mathbf{r}') e^{-a(\mathbf{r})|\mathbf{r}-\mathbf{r}'|} d^3 \mathbf{r}', \qquad (B9)$$

where we can use again $f(\mathbf{r}) = n(\mathbf{r})$ and $a(\mathbf{r}) = \alpha k_F(\mathbf{r})$. After similar algebra, we obtain

$$h[a](z) = \frac{2\pi}{za(z)^2} \int_0^\infty r' f(r')$$

× $(e^{-a(z)|z-r'|}(1+a(z)|z-r'|))$
 $- e^{-a(z)|z+r'|}(1+a(z)|z+r'|))dr'.$ (B10)

For z = 0, we have

$$h[a](0) = 4\pi \int_0^\infty r'^2 f(r') \mathrm{e}^{-a(0)r'} dr' \,. \tag{B11}$$

APPENDIX C: UNIFORM SCALING BEHAVIOR

The quantity y_{α} is invariant under the uniform scaling of the density [i.e., $n(\mathbf{r}) \rightarrow n_{\lambda} = \lambda^3 n(\lambda \mathbf{r})$]. In fact, under such a scaling we have that $k_F(\mathbf{r}) \rightarrow \lambda k_F(\lambda \mathbf{r})$; this implies that the Yukawa potential becomes

$$u_{\alpha}(\mathbf{r}) \rightarrow \int \frac{\lambda^{3} n(\lambda \mathbf{r}') \mathrm{e}^{-\alpha \lambda k_{F}(\lambda \mathbf{r}) |\mathbf{r} - \mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|} d^{3}\mathbf{r}'$$

= $\lambda \int \frac{n(\lambda \mathbf{r}') \mathrm{e}^{-\alpha k_{F}(\lambda \mathbf{r}) |\lambda \mathbf{r} - \lambda \mathbf{r}'|}}{|\lambda \mathbf{r} - \lambda \mathbf{r}'|} d^{3}(\lambda \mathbf{r}')$
= $\lambda u_{\alpha}(\lambda \mathbf{r})$. (C1)

Hence, for the quantity $y_{\alpha}(\mathbf{r})$, we find

$$y_{\alpha}(\mathbf{r}) \rightarrow \frac{3\pi\alpha^2}{4\lambda k_F(\lambda \mathbf{r})} \lambda u_{\alpha}(\lambda \mathbf{r}) = y_{\alpha}(\lambda \mathbf{r}) .$$
 (C2)

APPENDIX D: HOMOGENEOUS SPHERE DENSITY AT THE ORIGIN

If we consider a homogeneous sphere of radius R_0 and with density n_0 inside and zero outside, Eqs. (B5) and (B11) become at r = 0,

$$u^{S}[a](0) = \frac{4\pi n_{0}}{a_{0}^{2}} [1 - e^{-a_{0}R_{0}}(1 + R_{0}a_{0})], \quad (D1)$$
$$h^{S}[a](0) = \frac{8\pi n_{0}}{a_{0}^{3}} \{1 - e^{-a_{0}R_{0}} [1 + R_{0}a_{0} + (1/2)R_{0}^{2}a_{0}^{2}]\}, \quad (D2)$$

where $a_0 = a(0)$ and in both expressions we use $f(\mathbf{r}) = n(\mathbf{r})$.

When using $a_0 = \alpha k_F = \alpha (3\pi^2)^{1/3} n_0^{1/3}$, we also obtain simple expressions for Eqs. (12) and (25):

$$y_{\alpha}^{S}(0) = \frac{3\pi\alpha^{2}}{4k_{F}}u^{S}[\alpha k_{F}](0)$$
 (D3)

$$= [1 - e^{-\alpha k_F R_0} (1 + \alpha k_F R_0)],$$
(D4)

$$e^{S}(0) = \frac{3\pi\alpha^{3}}{8} \frac{\partial F_{s}}{\partial y_{\alpha}}(0)h^{S}[\alpha k_{F}](0)$$
(D5)

$$= \frac{\partial F_s}{\partial y_{\alpha}}(0) \left\{ 1 - e^{-\alpha k_F R_0} \right.$$
$$\times \left[1 + \alpha k_F R_0 + (1/2) \alpha^2 k_F^2 R_0^2 \right] \left\}.$$
(D6)

APPENDIX E: EXPONENTIAL ATOMIC DENSITY AT THE ORIGIN

If we consider an exponential density $n(r) = Ae^{-\zeta r}$ and a screening function a(r), Eqs. (B5) and (B11) become at r = 0:

$$u^{A}[a](0) = \frac{4\pi A}{[\zeta + a(0)]^{2}},$$
(E1)

$$h^{A}[a](0) = \frac{8\pi A}{[\zeta + a(0)]^{3}}.$$
 (E2)

Using the screening function $a(0) = \alpha k_F = \alpha (3\pi^2)^{1/3} A^{1/3}$, we obtain for Eqs. (12) and (25):

$$y_{\alpha}^{A}(0) = \frac{3\pi\alpha^{2}}{4k_{F}}u^{A}[\alpha k_{F}](0) = \frac{\alpha^{2}}{\left(\alpha + \frac{\zeta}{(3\pi^{2})^{1/3}A^{1/3}}\right)^{2}}, \quad (E3)$$
$$e^{A}(0) = \frac{\partial F_{s}}{\partial y_{\alpha}}(0)\frac{3\pi\alpha^{3}}{8}h^{A}[\alpha k_{F}](0)$$
$$= \frac{\partial F_{s}}{\partial y_{\alpha}}(0)\frac{\alpha^{3}}{\left(\alpha + \frac{\zeta}{(3\pi^{2})^{1/3}A^{1/3}}\right)^{3}}. \quad (E4)$$

Using the density from Eq. (16), we have that $\zeta/[(3\pi^2)^{1/3}A^{1/3}] = [4/(3\pi f)]^{1/3}$ and thus Eq. (17) is obtained.

For a TF scaling, we can consider $A \to A_{\lambda} = \lambda^2 A$ and $\zeta \to \zeta_{\lambda} = \lambda^{1/3} \zeta$, so the second term in the denominator of Eq. (E3) becomes $\zeta_{\lambda}/A_{\lambda}^{1/3} \propto 1/\lambda^{1/3}$, which vanishes for $\lambda \to \infty$. Thus, $y_{\alpha}^{\alpha}(0) \to 1$ for $\lambda \to \infty$.

APPENDIX F: DERIVATION OF THE FUNCTIONAL DERIVATIVE OF YGGA FUNCTIONALS

The functional derivative of T_s^{yGGA} is defined by the identity

$$\int \frac{\delta T_s^{\text{yGGA}}}{\delta n(\mathbf{r})} g(\mathbf{r}) d^3 \mathbf{r} = \frac{d}{d\lambda} \left[\int \tau(n + \lambda g, \nabla(n + \lambda g), \nabla^2(n + \lambda g), u'_{\alpha}) d^3 \mathbf{r} \right]_{\lambda = 0},$$
(F1)

where

$$u'_{\alpha} = \int \frac{(n(\mathbf{r}') + \lambda g(\mathbf{r}'))}{|\mathbf{r} - \mathbf{r}'|} e^{-k_0 \alpha (n(\mathbf{r}) + \lambda g(\mathbf{r}))^{1/3} |\mathbf{r} - \mathbf{r}'|} d^3 \mathbf{r}',$$
(F2)

with $k_0 = (3\pi^2)^{1/3}$ and λg (λ is a real positive number and g is an arbitrary function) is the variation of the density. Expanding τ according to its Taylor series allows us to write

$$\int \frac{\delta T_s^{\text{yGGA}}}{\delta n(\mathbf{r})} g(\mathbf{r}) d^3 \mathbf{r} = \int \frac{\partial \tau}{\partial n} g d^3 \mathbf{r} + \int \frac{\partial \tau}{\partial \nabla n} \nabla g d^3 \mathbf{r} + \int \frac{\partial \tau}{\partial \nabla^2 n} \nabla^2 g d^3 \mathbf{r} + \int \frac{\partial \tau}{\partial u_\alpha} \left(\frac{du'_\alpha}{d\lambda}\right)_{\lambda=0} d^3 \mathbf{r}.$$
 (F3)

Using the first Green's identity [94], the second integral can be written as

$$\int \frac{\partial \tau}{\partial \nabla n} \nabla g(\mathbf{r}) d^3 \mathbf{r} = -\int \left(\nabla \cdot \frac{\partial \tau}{\partial \nabla n} \right) g(\mathbf{r}) d^3 \mathbf{r} .$$
 (F4)

Similarly, using the second Green's identity [94], we have

$$\int \frac{\partial \tau}{\partial \nabla^2 n} \nabla^2 g(\mathbf{r}) d^3 \mathbf{r} = \int \nabla^2 \left(\frac{\partial \tau}{\partial \nabla^2 n} \right) g(\mathbf{r}) d^3 \mathbf{r} .$$
(F5)

For the last integral in Eq. (F3), we can calculate

$$\left(\frac{du'_{\alpha}}{d\lambda}\right)_{\lambda=0} = \int \frac{d}{d\lambda} \left(\frac{n(\mathbf{r}') + \lambda g(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} e^{-k_0 \alpha (n(\mathbf{r}) + \lambda g(\mathbf{r}))^{1/3} |\mathbf{r} - \mathbf{r}'|}\right)_{\lambda=0} d^3 \mathbf{r}'$$

$$= \left(\int \frac{1}{|\mathbf{r} - \mathbf{r}'|} e^{-k_0 \alpha (n(\mathbf{r}) + \lambda g(\mathbf{r}))^{1/3} |\mathbf{r} - \mathbf{r}'|} g(\mathbf{r}') d^3 \mathbf{r}' + \frac{\alpha k_0}{3} (n(\mathbf{r}) + \lambda g(\mathbf{r}))^{-2/3} \int (n(\mathbf{r}') + \lambda g(\mathbf{r}')) e^{-k_0 \alpha (n(\mathbf{r}) + \lambda g(\mathbf{r}))^{1/3} |\mathbf{r} - \mathbf{r}'|} g(\mathbf{r}) d^3 \mathbf{r}'\right)_{\lambda=0}$$

$$= \int \frac{1}{|\mathbf{r} - \mathbf{r}'|} e^{-\alpha k_F(\mathbf{r})|\mathbf{r} - \mathbf{r}'|} g(\mathbf{r}') d^3 \mathbf{r}' + -\frac{\alpha k_0}{3} n^{-2/3} (\mathbf{r}) \int n(\mathbf{r}') e^{-\alpha k_F(\mathbf{r})|\mathbf{r} - \mathbf{r}'|} g(\mathbf{r}) d^3 \mathbf{r}' \tag{F6}$$

Inserting Eq. (F6) in the last integral of Eq. (F3), and interchanging the integration variables so that the function $g(\mathbf{r})$ appears in each term, we have

$$\int \left(g(\mathbf{r}) \int \frac{\partial \tau}{\partial u_{\alpha}} (\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} e^{-\alpha k_F(\mathbf{r}')|\mathbf{r} - \mathbf{r}'|} d^3 \mathbf{r}' \right) d^3 \mathbf{r} + \int g(\mathbf{r}) \left(\frac{\partial \tau}{\partial u_{\alpha}} (\mathbf{r}) \frac{\alpha k_0}{3} n^{-2/3} (\mathbf{r}) \int n(\mathbf{r}') e^{-\alpha k_F(\mathbf{r})|\mathbf{r} - \mathbf{r}'|} d^3 \mathbf{r}' \right) d^3 \mathbf{r}$$
(F7)

Recalling Eq. (20), we finally obtain

$$v_k^{\text{yGGA},1}(\mathbf{r}) = \int \frac{\partial \tau}{\partial u_\alpha}(\mathbf{r}') \frac{e^{-\alpha k_F(\mathbf{r}')|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}',$$
(F8)

$$v_k^{\text{yGGA},2}(\mathbf{r}) = -\frac{\alpha k_F(\mathbf{r})}{3n(\mathbf{r})} \frac{\partial \tau}{\partial u_\alpha}(\mathbf{r}) \int n(\mathbf{r}') e^{-\alpha k_F(\mathbf{r})|\mathbf{r}-\mathbf{r}'|} d^3 \mathbf{r}'.$$
(F9)

The final expression in Eqs. (22) and (23) in the paper can be obtained using that

$$\frac{\partial \tau}{\partial u_{\alpha}}(\mathbf{r}) = \frac{9\pi \alpha^2 k_F(\mathbf{r}) n(\mathbf{r})}{40} \frac{\partial F_s}{\partial y_{\alpha}}(\mathbf{r}).$$
(F10)

APPENDIX G: LINEAR RESPONSE OF LINYUK FUNCTIONALS

We can employ the method presented in Appendix A to calculate the linear response of the kinetic functional with $\tau = \tau^{\text{TF}} y_{\alpha}(\mathbf{r}) G(p, q)$.

We first consider the ingredient y_{α} only: Inserting the expression of the density perturbation (taking $\mathbf{r} = 0$) in y_{α} , we obtain

$$y_{\alpha}(0) = \frac{3\pi\alpha^2}{4(3\pi^2)^{1/3}(n_0 + n_k)^{1/3}} \\ \times \int \frac{(n_0 + n_k e^{-i\mathbf{k}\cdot\mathbf{r}'})e^{-\alpha(3\pi^2)^{1/3}(n_0 + n_k)^{1/3}r'}}{r'} d^3\mathbf{r}'.$$
(G1)

Let us choose a coordinate system where **k** lays on the *z* axis, so $\mathbf{k} \cdot \mathbf{r}' = kr' \cos(\theta)$ (with θ being the angle between the positive *z* axis and the variable of integration, namely, **r**'). We can thus rewrite the integral, passing from Cartesian to spherical coordinates, as

$$y_{\alpha}(0) = \frac{3\pi\alpha^{2}}{4(3\pi^{2})^{1/3}(n_{0}+n_{k})^{1/3}}(2\pi)\int_{0}^{\pi}\int_{0}^{\infty}r'^{2}\sin(\theta)$$
$$\times \frac{(n_{0}+n_{k}e^{-ikr'\cos(\theta)})e^{-\alpha(3\pi^{2})^{1/3}(n_{0}+n_{k})^{1/3}r'}}{r'}dr'd\theta,$$
(G2)

where the factor 2π takes into account the integration in the angular variable ϕ . This integral can be computed analytically, yielding

$$y_{\alpha}(0) = \frac{\alpha^2 3^{2/3} \pi^{4/3} (n_0 + n_k)^{5/3} + k^2 n_0}{(n_0 + n_k)((n_0 + n_k)^{2/3} \alpha^2 3^{2/3} \pi^{4/3} + k^2)} .$$
 (G3)

We now expand the resulting expression in a Taylor series in powers of n_k :

$$y_{\alpha}(0) = 1 - \frac{k^2}{n_0 \left((3\pi^2)^{2/3} \alpha^2 n_0^{2/3} + k^2 \right)} n_k + \frac{1}{3n_0^2} \frac{k^2 \left(5(3\pi^2)^{2/3} \alpha^2 n_0^{2/3} + 3k^2 \right)}{\left((3\pi^2)^{2/3} n_0^{2/3} \alpha^2 + k^2 \right)^2} n_k^2 + O(n_k^3).$$
(G4)

To obtain the linear response function of the linyuk functional, it is possible to multiply Eq. (G4) by Eq. (A2) (which is obtained by the perturbation of $\tau^{\text{TF}}G(p, q)$) and to take half of the reciprocal of the coefficient of the n_k^2 term in the resulting expression. After some algebra, the expression in Eq. (34) is obtained.

APPENDIX H: COEFFICIENTS FOR THE YUK2 FUNCTIONAL

In this Appendix, we derive the coefficients of the yuk2 functional, a linyuk functional which correctly reproduces the expansion of Lindhard function for small and large wave vectors.

The series expansion of a general linyuk functional for $\eta \rightarrow 0$ taking $D_{qq} = 0$ is, see Eq. (34),

$$\frac{1}{F^{\text{linyuk}}} \to \frac{1}{G_0} - \frac{9D_p + 15}{5G_0^2}\eta^2 + C_0\eta^4 + O(\eta^6), \quad (\text{H1})$$

with

$$C_0 = \frac{81(D_p + \frac{5}{3})^2 \alpha^4 - 180D_q G_0 \alpha^2 + 480G_0^2}{25G_0^3 \alpha^4}.$$
 (H2)

From the first two terms of Eq. (H1), we have that $G_0 = 1$ and $D_p = -40/27$ to satisfy the first two terms in Eq. (8).

For $\eta \to \infty$, we have, setting $D_{qq} = 0$,

$$\frac{1}{F^{\text{linyuk}}} \to \frac{5}{(9D_p + 9D_q + 15)\eta^2} + \frac{C_{\infty}}{\eta^4} + O(\eta^{-6}), \quad (\text{H3})$$

with

$$C_{\infty} = \frac{5}{36} \frac{9D_q \alpha^2 + 4G_0}{(3D_p + 3D_q + 5)^2}.$$
 (H4)

From the first term of Eq. (H3), we have that $D_q = -D_p = 40/27$ to recover the first term of Eq. (9). With the above settings, the coefficients of the fourth-order term in Eqs. (H1) and (H3) become

$$C_0 = \frac{5\alpha^4 - 480\alpha^2 + 864}{45\alpha^4} = -1/15,$$
 (H5)

$$C_{\infty} = \frac{2\alpha^2}{27} + \frac{1}{45} = 1/15$$
. (H6)

As there is just one parameter (α), the above two equations cannot be satisfied simultaneously. In general, it is much more important to have the correct response to small η , whereas details for large η are less relevant. Thus, we solve Eq. (H5), which has two positive solutions, $\alpha_1 = 1.362903313$ and $\alpha_2 = 7.625122593$, the corresponding C_{∞} values being 0.1598 and 4.329, respectively. The α_2 value generates a too large C_{∞} coefficient (64 times larger) and must be disregarded. Thus we select $\alpha = \alpha_1$, which gives a quite correct (only about two times larger) C_{∞} .

APPENDIX I: KINETIC POTENTIAL OF THE YUK1 FUNCTIONAL

In this Appendix, we derive expressions for the Pauli potential for the yuk1 functional (the vW term can be considered separately). For a KE density of the form $\tau = \tau^{TF} y_{\alpha}$, the mGGA potential, see Eq. (21), is

$$v_k^{\text{mGGA}}(\mathbf{r}) = \frac{\partial \tau}{\partial n}(\mathbf{r}) = \frac{3\pi}{10} (3\pi^2)^{1/3} \alpha^2 n(\mathbf{r})^{1/3} u_\alpha(\mathbf{r})$$
$$= \frac{4}{10} k_F(\mathbf{r})^2 y_\alpha(\mathbf{r}) \,. \tag{I1}$$

Using that $dFs/dy_{\alpha} = 1$, Eqs. (24) and (25) become

$$\tilde{y}_{\alpha}(\mathbf{r}) = \frac{3\pi\alpha^2}{4k_F(\mathbf{r})n^{1/3}(\mathbf{r})} \times \int n(\mathbf{r}')^{4/3} \frac{e^{-\alpha k_F(\mathbf{r}')|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}', \qquad (I2)$$

$$e_{\alpha}(\mathbf{r}) = \frac{3\pi\alpha^3}{8} \int n(\mathbf{r}') e^{-\alpha k_F(\mathbf{r})|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}', \qquad (I3)$$

which can be used in Eqs. (22) and (23) to obtain the potential terms.

The yuk1 potential terms at the center (r = 0) of an uniform sphere with density n_0 inside and zero outside, are

$$v_k^{\text{mGGA}}(0) = \frac{4}{10} k_F^2 y_\alpha^S(0) \,, \tag{I4}$$

$$v_k^{\text{yGGA,1}}(0) = \frac{3}{10} k_F^2 \tilde{y}_\alpha^S(0) \,, \tag{I5}$$

$$v_k^{\text{yGGA},2}(0) = -\frac{2}{10}k_F^2 e_\alpha^S(0)$$
, (I6)

where we used Eqs. (I1), (22), and (23). Considering Eqs. (D3) and (D5) and that

$$\tilde{y}_{\alpha}^{S}(0) = \frac{3\pi\alpha^{2}}{4k_{F}}u^{S}[\alpha k_{F}](0)$$
$$= [1 - e^{-\alpha k_{F}R_{0}}(1 + \alpha k_{F}R_{0})], \qquad (I7)$$

we have, summing up all potential terms, in the limit of a large number of electrons, $v_k^{\text{yuk1}}(0) = 5/10k_F^2$, which is the TF potential.

For an atomic exponential density, let us first consider the term in Eq. (12) which at r = 0 becomes

$$\tilde{y}_{\alpha}(0) = \frac{3\pi\alpha^2}{4(3\pi^2)^{1/3}A^{2/3}}\tilde{u}[a = \alpha k_F; f = n^{4/3}](0), \quad (I8)$$

where we used the definition in Eq. (B6). We found that we can approximate Eq. (I8), computing the Taylor expansion of $\tilde{y}_{\alpha}(0)^{-1}$ for small α : Using the density of Eq. (16), we obtained

$$\tilde{y}_{\alpha}^{\text{app}}(0) = \frac{1.02916\alpha^2}{\frac{1.033}{f^{2/3}} + \frac{1.056\alpha}{f^{1/3}} + 0.4693\alpha^2 + 0.1066\alpha^3 f^{1/3}},$$
 (I9)

which has an error less than 1.5% for α up to 3. For $\alpha = 1$, we have $\tilde{y}_{\alpha}^{\text{app}}(0) = 0.41335$. Thus the yuk1 potential terms are

$$v_k^{\text{mGGA}}(0) = \frac{4}{10} k_F^2 \frac{\alpha^2}{\left(\alpha + \left(\frac{4}{3\pi f}\right)^{1/3}\right)^2},$$
 (I10)

$$v_k^{\text{yGGA},1}(0) = \frac{3}{10} k_F^2 \tilde{y}_{\alpha}^{\text{app}}(0),$$
 (I11)

$$v_k^{\text{yGGA,2}}(0) = -\frac{2}{10}k_F^2 \frac{\alpha^3}{\left(\alpha + \left(\frac{4}{3\pi f}\right)^{1/3}\right)^3},$$
 (I12)

where we used Eqs. (I1), (22), and (23) and the definitions in Eqs. (E3) and (E4). Considering that $k_F^2 = 8.007263127Z^2$, for $\alpha = 1$ we finally have

$$v_k^{\text{mGGA}}(0) = 1.099476475 Z^2$$
, (I13)

$$v_k^{\text{yGGA},1}(0) = 0.9929508721 Z^2$$
, (I14)

$$v_k^{\text{yGGA},2}(0) = -0.3220897252 Z^2$$
, (I15)

$$v_k^{\text{yuk1}}(0) = 1.770337622 Z^2$$
 (I16)

APPENDIX J: POTENTIAL OF AN EXPONENTIAL-LAPLACIAN FUNCTIONAL

Let us consider an enhancement factor of the form

$$F_s = e^{\beta q} \tag{J1}$$

for an exponential density of the type $n(r) = Ae^{-ar}$. The corresponding mGGA potential, see Eq. (21), near r = 0 is (after some algebra)

$$v_k(r) \to \frac{3^{2/3} a^2 \beta^3 \exp\left(\frac{\beta^{3^{1/3} a^2}}{12\pi^{4/3} A^{2/3}}\right)}{r^{4} 480 \pi^{8/3} A^{4/3}} \times \exp\left(-\frac{1}{r} \frac{a \beta^{3^{1/3}} \exp\left[(2/3) ar\right]}{6\pi^{4/3} A^{2/3}}\right), \quad (J2)$$

which is null with all derivatives null.

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