

# Kinetic-energy density functionals with nonlocal terms with the structure of the Thomas-Fermi functional

David García-Aldea\* and J. E. Alvarillos†

*Departamento de Física Fundamental, Universidad Nacional de Educación a Distancia (UNED),  
Apartado 60.141, E-28080 Madrid, Spain*

(Received 8 August 2007; published 7 November 2007)

We study two families of approximate nonlocal kinetic-energy functionals that include a full von Weizsäcker functional, and that have nonlocal terms with the mathematical structure of the Thomas-Fermi functional. The functionals recover the exact kinetic energy and the linear response function of a homogeneous electron system. The first family is a generalization of a successful previous nonlocal functional. The second family is proposed in the paper, and is designed to obtain functionals suitable for use in both localized and extended systems. Furthermore, this family has been designed to be evaluated by a single integration in momentum space when a constant reference density is used. The atomic total kinetic energies are in good agreement with the exact calculations. The kinetic-energy density corresponding to each functional has been assessed to control its quality. The results show that, in general, these functionals behave better than both the Thomas-Fermi and all semilocal generalized gradient approximation functionals when describing the kinetic-energy density of atoms, providing a better description of the nonlocal effects of the kinetic energy of electron systems.

DOI: [10.1103/PhysRevA.76.052504](https://doi.org/10.1103/PhysRevA.76.052504)

PACS number(s): 31.15.Ew, 31.15.Bs, 31.15.-p, 71.10.Ca

## I. INTRODUCTION

Density functional theory (DFT) has advantages over other methods for calculating the electronic structure in both computational efficiency and the precision of the results [1–3]. DFT was originally developed by Hohenberg and Kohn [4] and replaces the principal role of the wave function with the electron density, proving that the density has all the information needed to describe the ground state of an electron system through the functional of the exact total energy  $E[n]$ . When  $E[n]$  is minimized, the electron density and the energy of the ground state can be found. The functional for the total energy is unknown, and DFT is usually applied following the Kohn and Sham (KS) [5] method, where the energy functional is divided into four parts, via the concept of a noninteracting system of KS orbitals that yields the same electron density as the interacting one,

$$E[n] = T_S[n] + V[n] + J[n] + E_{XC}[n], \quad (1)$$

where  $T_S[n]$  is the kinetic-energy density functional (KEDF) of the KS noninteracting system,  $V[n]$  is the interaction energy of the electron density with the external potential,  $J[n]$  is the classical electrostatic repulsion energy of the charge distribution (Hartree energy), and finally  $E_{XC}[n]$  is the so-called exchange-correlation (XC) energy. This last functional includes all the quantum effects not described by the other three terms, and usually is an order of magnitude smaller than them. So the KS scheme allows one to exactly calculate the main pieces of the energy except the XC functional, for which a number of approximations have been formulated.

Despite the success of the KS formulation of DFT, there are important reasons to study the functional of the total

energy. Beyond the obvious theoretical interest, using a density functional which depends only on the total electron density and not on the individual KS orbitals—the *orbital-free* scheme—gives a three-dimensional functional space instead of the  $3N$  coordinates of an  $N$ -electron system within the KS scheme. In that case,  $E[n]$  can be minimized by using the Euler equation

$$\delta E[n]/\delta n = 0. \quad (2)$$

Moreover, the orbital-free scheme scales with  $N$ , better than the  $O(N^3)$  scaling characteristic of the orthogonalization of the KS orbitals and, for extended systems, the use of the  $k$ -point sampling is not needed.

The Hartree energy  $J[n]$  and  $V[n]$  in Eq. (1) are explicit functionals of the electron density. Both energies and  $T_S[n]$  usually have the same order of magnitude as the total energy. As the XC energy is usually much smaller, approximations developed for it within the KS scheme may also be employed in the orbital-free scheme: the key issue for orbital-free DFT is then to have a good approximation for  $T_S[n]$ . Formulation of approximate KEDFs is much older than the origin of the modern DFT. The first approximate KEDF was the Thomas-Fermi (TF) [6,7] functional (atomic units will be used in this paper),

$$T_{TF}[n] = C_{TF} \int n(\mathbf{r})^{5/3} d\mathbf{r}, \quad (3)$$

where  $C_{TF}$  is the Thomas-Fermi constant  $C_{TF} = \frac{3}{10}(3\pi^2)^{2/3}$ , constructed to yield the exact kinetic energy of a homogeneous system—i.e., the free-electron gas—and corresponds to the local density approximation. Another old functional is the von Weizsäcker (vW) [8] functional,

\*dgaldea@fisfun.uned.es

†jealvar@fisfun.uned.es

$$T_{\text{vW}}[n] = \frac{1}{8} \int \frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})} d\mathbf{r}, \quad (4)$$

constructed to be exact for one or two electrons in the same spatial state. The TF functional usually underestimates the kinetic energy by around 10%, and very large errors are obtained with the von Weizsäcker functional in many-electron systems. The second-order gradient expansion approximation (GEA2) arises as a combination of the two previous functionals:

$$\begin{aligned} T_S^{\text{GEA2}}[n] &= T_{\text{TF}}[n] + \frac{1}{9} T_{\text{vW}}[n] \\ &= C_{\text{TF}} \int n(\mathbf{r})^{5/3} d\mathbf{r} + \frac{1}{72} \int \frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})} d\mathbf{r}. \end{aligned} \quad (5)$$

This gives total errors close to 1% when applied to atoms and molecules using *good* densities, i.e., those obtained with accurate methods like the Hartree-Fock or KS ones.

Functionals within the generalized gradient approximation (GGA) [9] depend only on the electron density and its gradients (a summary of those semilocal functionals can be found in Refs. [10,11]; see also a recent review in [12]). The GEA2 functional, as well as the TF and vW functionals, can be formulated as particular GGA ones. When using good densities, those GGA functionals that are similar to the GEA2 functionals usually yield results for the total kinetic energy also close to those obtained with the GEA2. The relative errors of the GGA functionals are too big for chemical precision but they are the smallest errors found for orbital-free approximations to the kinetic energy. But when the Euler equations corresponding to the GGA functionals are solved variationally, some unphysical results are obtained: the quantum effects are lost and no shell structure appears in the minimized density profiles for atoms. Only more sophisticated functionals, the fully nonlocal functionals, can yield shell structure for atoms and reproduce the quantum effects, even though their relative errors—among the smallest found for any orbital-free approximation—are also too big for chemical precision.

The paper is structured as follows. In Sec. II a generalization of the mathematical form of some nonlocal density functionals is presented. In Sec. III two families of nonlocal KEDFs with density-independent kernels are developed. Section IV presents the construction of more sophisticated cases, functionals with double-density-dependent kernels, which are studied in Sec. V (atomic total kinetic energies) and in Secs. VI and VII (kinetic-energy densities). Finally, conclusions are summarized in Sec. VIII.

## II. NONLOCAL FUNCTIONALS WITH TWO INTEGRALS

The GGA functionals can be considered as semilocal functionals because they only use information about the value of the density and its variation at one point in space when calculating the contribution to the kinetic energy from that point. More sophisticated functionals can be developed by introducing nonlocality in such a way that the whole electron density is taken into account when this contribution is

evaluated. We call those functionals that use the density of the whole system to estimate the kinetic-energy density coming from each point of the space *fully nonlocal functionals*. The first fully nonlocal functional was the weighted density approximation, introduced independently by Alonso and Girifalco [13,14] and by Gunnarson, Jonson, and Lundqvist [15], where the contribution of the whole density comes through the normalization of a parametrized XC hole of the free-electron gas.

On the other hand, the evaluation of the usual nonlocal energy density functionals relies on two integrations in real space, i.e., a six-dimensional integral. We now propose a generalization of the mathematical expressions on which those functionals are based. The main point is that we assume that the contributions from every pair of points  $\mathbf{r}$  and  $\mathbf{r}'$  to the nonlocal functional depend only on  $\mathbf{r}$  and  $\mathbf{r}'$  and on the densities at them, through a first integration over  $\mathbf{r}'$  and a second integration over  $\mathbf{r}$ . After integrating in  $\mathbf{r}'$ , we must obtain a function that depends only on  $\mathbf{r}$  [and implicitly on the electron density  $n(\mathbf{r})$ ]. The general form can then be written as

$$F^{\text{NL1}}[n] = \int d\mathbf{r} \left[ f_1(n(\mathbf{r})) f_{12} \left( \int d\mathbf{r}' f_2(n(\mathbf{r}), n(\mathbf{r}'), \mathbf{r}, \mathbf{r}') \right) \right], \quad (6)$$

where  $f_1(n(\mathbf{r}))$ ,  $f_{12}(\int d\mathbf{r}' f_2(n(\mathbf{r}), n(\mathbf{r}'), \mathbf{r}, \mathbf{r}'))$ , and  $f_2(n(\mathbf{r}), n(\mathbf{r}'), \mathbf{r}, \mathbf{r}')$  are arbitrary functions with the only requirement that all together must have the correct dimensionality for  $F^{\text{NL1}}[n]$  to be an energy.

All the nonlocal functionals with two integrations in real space can be written in the previous form. But, for convenience, we would like to present a simpler one:

$$F^{\text{NL2}}[n] = \int d\mathbf{r} \int d\mathbf{r}' f(n(\mathbf{r}), n(\mathbf{r}'), \mathbf{r}, \mathbf{r}'), \quad (7)$$

where the new function  $f(n(\mathbf{r}), n(\mathbf{r}'), \mathbf{r}, \mathbf{r}')$  has the same dimensional requirements as before. The main difference now is that integration over  $\mathbf{r}'$  is not included as an argument of any other function. With this simplified form, and when  $f(n(\mathbf{r}), n(\mathbf{r}'), \mathbf{r}, \mathbf{r}')$  is adequately chosen, the functional can be calculated with a single integration in momentum space using the concept of the Fourier transform.

In addition to the mathematical form, it is advisable to enforce some physical limits in order to obtain the final functional. For KEDFs, the kinetic energy of a homogeneous electron system must first be recovered. For the second condition, a common procedure is to take advantage of the close relation between the response function of an electron system and the KEDF [4]: the second functional derivative of  $T_S[n]$  in the homogeneous limit must be equal to the linear response function of the free-electron gas. In momentum space, we have

$$\mathcal{F}\left(\frac{\delta T_s[n(\mathbf{r})]}{\delta n(\mathbf{r}_1)\delta n(\mathbf{r}_2)}\bigg|_{n_0}\right) = -\frac{1}{\tilde{\chi}_{\text{Lind}}(q)} = \frac{\pi^2}{k_F} F_{\text{Lind}}(\eta), \quad (8)$$

where  $\mathcal{F}$  indicates the Fourier transform. The function  $F_{\text{Lind}}(\eta)$ , known as the Lindhard function [16], has the analytical expression

$$F_{\text{Lind}}(\eta) = \left(\frac{1}{2} + \frac{1-\eta^2}{4\eta} \ln\left|\frac{1+\eta}{1-\eta}\right|\right)^{-1}, \quad (9)$$

which depends only on the scaled momentum  $\eta = q/2k_F$ ,  $k_F$  being the Fermi wave vector of the electron gas with density  $n_0$ .

A number of nonlocal functionals were constructed following this procedure. The Chacón-Alvarellos-Tarazona (CAT) functional [17] was formulated in 1985 with a mathematical form used previously in the description of the free energy of classical fluids [18–20] and the XC energy of an electron system [15]. This functional has the form expressed by Eq. (6) and uses an *averaged density* in its formulation. Later on, many authors developed similar functionals suitable for implementation for extended systems. The most remarkable are those of Wang and Teter (WT) [21], Perrot (P), and Smargiassi and Madden (SM) [22], all of which are written in the simpler form given by Eq. (7).

The aforementioned nonlocal functionals always have a TF-like term, i.e., a term with an explicit integration of some different powers of the electron density. But this term also has another factor in the integrand—usually called the *kernel*—that allows one to reproduce the linear response function of the free-electron gas. All these functionals have an intrinsic dependence on the Fermi wave vector through the argument  $\eta$  of the Lindhard function. In position space this dependency must appear as a scaling factor in the argument of the kernel. In the CAT functional [17], and also in its first modification [23], the local Fermi wave vector at the local position  $\mathbf{r}$ ,  $k_F(\mathbf{r})$ , was chosen as the quantity to be used in all scaled magnitudes that appear in the formalism. On the other hand, the WT, P, and SM functionals scale through a constant Fermi wave vector calculated by means of a reference uniform density; the generalizations of those functionals developed by Wang, Govind, and Carter (WGC) [24,25] follow the same procedure. These functionals with a constant scaling are labeled *density-independent kernel* functionals, unlike the CAT functional, which uses a local Fermi wave vector  $k_F(\mathbf{r})$  as the scaling factor and is labeled a *density-dependent kernel*.

In order to improve the description of the intrinsic nonlocality of the KEDF, we can go a step further by extending the scaling factor from the local Fermi wave vector  $k_F(\mathbf{r})$  at one point  $\mathbf{r}$  (i.e., a *one-body Fermi wave vector*) to a two-point scaling function that aims to reflect any connection between the points  $\mathbf{r}$  and  $\mathbf{r}'$  involved in the calculations needed to evaluate the functional. Putting  $\mathbf{r}$  and  $\mathbf{r}'$  on the same footing, a simple *two-body Fermi wave vector* is

$$\zeta(\mathbf{r}, \mathbf{r}') = \left(\frac{k_F^\gamma(\mathbf{r}) + k_F^\gamma(\mathbf{r}')}{2}\right)^{1/\gamma}. \quad (10)$$

This scaling factor  $\zeta(\mathbf{r}, \mathbf{r}')$  can be seen as the mean of a certain power  $\gamma$  of the Fermi wave vector at positions  $\mathbf{r}$  and  $\mathbf{r}'$ . The functionals that include the scaling in this way are said to have a *double-density-dependent kernel*. This kind of scaling factor was first introduced in the so-called symmetrized CAT functional [26], with good results: a shell structure was obtained when the atoms were variationally minimized [26], Friedel oscillations appeared in minimized jellium surfaces [27], and quantum oscillations were found in one-dimensional systems [28]. Thus these double-density-dependent kernel CAT functionals reproduce quantum effects for very different physical situations, unlike the semilocal functionals. On the other hand, other double-density-dependent kernel functionals developed by WGC for extended systems have obtained good results in simple metals, alloys, clusters, and even covalent materials [25,29–32].

### III. KINETIC FUNCTIONALS WITH NONLOCAL TERMS WITH THE STRUCTURE OF THE THOMAS-FERMI FUNCTIONAL (DENSITY-INDEPENDENT KERNEL)

Following the ideas of WGC [25], first we are going to present functionals with a density-independent kernel, i.e., with a kernel scaled through a constant Fermi wave vector. It is not the aim of this work to present new density-independent kernel functionals, but we think they are useful for understanding the development of nonlocal functionals with density-dependent kernels.

#### A. Chacón-Alvarellos-Tarazona family of functionals

By extending the formulation of the CAT functionals, we can construct an entire family of functionals. The functionals of that family share a few fundamental properties and requirements that reflect the physical limits we are imposing on them, their mathematical structure and the form of their weight function (in this case the kernel can be identified as a weight function for the definition of the *averaged density*)—a key quantity for these functionals as can be seen below.

We can characterize a functional of this family with these three requirements:

(i) The functional includes a nonlocal term that has a mathematical structure similar to that of the TF functional, where the kinetic energy density per particle is calculated with the help of an averaged density, defined as the convolution of a weight function (kernel) with a certain power of the electron density.

(ii) The functional reproduces the linear response function of the free-electron gas. As a consequence, both TF and vW contributions appear naturally. Obviously, the functional must also give the correct kinetic energy for the free-electron gas.

(iii) The weight function has to be normalized to unity in the homogeneous limit. To avoid large-range effects in the weight function, and therefore allow the functional to be ap-

plicable to localized systems, prefactors in the TF functional and in the nonlocal term are required, and the weight function in momentum space reaches a value of 1 when  $q \rightarrow 0$ —a consequence of the normalization—and goes asymptotically to 0 when  $q \rightarrow \infty$ .

The CAT family of functionals,  $T_S^{\text{CAT}}[n]$ , with a density-independent kernel can be defined as [requirement (i)]

$$T_S^{\text{CAT}}[n] = T_{\text{vW}}[n] - \alpha T_{\text{TF}}[n] + (1 + \alpha) T_{\text{CAT}}^{\text{NL}}[n], \quad (11)$$

where the nonlocal term  $T_{\text{CAT}}^{\text{NL}}[n]$  has the structure of the TF functional, but using an averaged density  $\tilde{n}_\beta(\mathbf{r})$  for the kinetic-energy density per particle,

$$T_{\text{CAT}}^{\text{NL}}[n] = C_{\text{TF}} \int d\mathbf{r} n(\mathbf{r}) [\tilde{n}_\beta(\mathbf{r})]^{2/3\beta}. \quad (12)$$

In general,  $\tilde{n}_\beta(\mathbf{r})$  is an average of the power  $\beta$  of the electron density, where the nonlocal effects are supposedly included through a weight function  $\Omega$ ,

$$\tilde{n}_\beta(\mathbf{r}) = \int d\mathbf{r}' n^\beta(\mathbf{r}') \Omega(k_F, |\mathbf{r} - \mathbf{r}'|). \quad (13)$$

Note that we are now constructing a density-independent kernel functional with a constant  $k_F$  in  $\Omega$ , instead of the

scaling factor of the original CAT functional [17],  $k_F(\mathbf{r})$ . Due to the scaling properties of the Lindhard function, we can rewrite the weight function in a more convenient way,  $\Omega(k_F, |\mathbf{r} - \mathbf{r}'|) = (2k_F)^3 \omega(2k_F |\mathbf{r} - \mathbf{r}'|)$ , and the average density is then calculated as

$$\tilde{n}_\beta(\mathbf{r}) = (2k_F)^3 \int d\mathbf{r}' n^\beta(\mathbf{r}') \omega(2k_F |\mathbf{r} - \mathbf{r}'|). \quad (14)$$

Normalization in the uniform limit means that  $\int d\mathbf{r}' \Omega(k_F, |\mathbf{r} - \mathbf{r}'|) = 1$ .

With this formulation we have, in principle, two degrees of freedom to be fixed in the formulation of the functional: the parameters  $\alpha$  and  $\beta$ . Following requirement (ii), the kernel is obtained by the enforcement of Eq. (8). Since the kernel is not density dependent, we obtain an algebraic equation,

$$10 \frac{F_{\text{Lind}}(\eta) - 3\eta^2 + \alpha}{1 + \alpha} = 12\omega(\eta) + 2(2 - 3\beta)[\omega(\eta)]^2 + 6(\beta - 1), \quad (15)$$

where  $\omega(\eta) = \mathcal{F}[\Omega(|\mathbf{R}|)]$ . Rewriting it as a quadratic equation, the explicit form of the kernel  $\omega(\eta)$  in momentum space becomes

$$\omega(\eta) = \frac{1}{(2 - 3\beta)} \left( -3 + \sqrt{9 - 5 \frac{F_{\text{Lind}}(\eta) - 3\eta^2 + \alpha}{1 + \alpha} (2 - 3\beta) + 3(2 - 3\beta)(\beta - 1)} \right).$$

In order to verify requirement (iii), and because  $F_{\text{Lind}}(0) = 1$  and  $F_{\text{Lind}}(\infty) = -3/5$ , an explicit relation between the parameters  $\alpha$  and  $\beta$  appears,

$$\alpha = 3\beta/(8 - 3\beta), \quad (16)$$

and only one parameter is needed to specify these CAT kinetic functionals. Since  $\beta$  is the power of the electron density to be averaged in Eq. (14), we can first fix  $\beta$  and then get the corresponding value of  $\alpha$ . As  $k_F$  is related to the electron density through a power 1/3, we are going to choose values of  $\beta$  that yield integer powers of the Fermi wave vector. The values of  $\beta$  chosen and their corresponding values of  $\alpha$  are listed in Table I. Note that for  $\beta = 1$  we get the density-

TABLE I. Values of the parameters  $\alpha$  and  $\beta$  for CAT and NLS-TF functionals. For the NLS-TF cases, we have written out those values of  $\beta$  that yield the same functional (e.g.,  $\beta = 2/3$  or 1 for  $\alpha = 1/3$ ).

CAT	$\alpha$	1/7	1/3	3/5	1
	$\beta$	1/3	2/3	1	4/3
NLS-TF	$\alpha$	1	1/3	3/5	7/25
	$\beta$	1/3, 4/3	2/3, 1	5/6 $\pm$ $\sqrt{5}/6$	5/6

independent version of the original CAT functional, a functional that includes the terms  $T_{\text{vW}}[n] - \frac{3}{5} T_{\text{TF}}[n]$  which come from the correct expansion of the Lindhard function for large values of the scaled moment  $\eta$ . On the other hand, the value  $\alpha = 1$ , corresponding to a value of  $\beta = 4/3$ , gives a full negative Thomas-Fermi contribution. For  $\beta = 2/3$  we have a special case, because in this case the averaged density—and thus the second integral in Eq. (6)—has the power 1, and we get a simplified functional that can be written in the form of Eq. (7).

## B. Functionals with nonlocal simplified terms with Thomas-Fermi structure

While the CAT functional has an adequate mathematical form to be applied to localized systems in real space, WGC functionals are constructed with a mathematical structure according to Eq. (7) that allows quasilinear scaling of their computational cost. Unfortunately, the kernels of those functionals make them inapplicable to localized systems. It would be interesting to generate a KEDF able to keep the main benefits of both types of functional: the possibility of linear scaling in momentum space—like the WGC functionals—and a kernel suitable for working in position space for localized systems—like the CAT ones. To develop

such functionals, which we will call nonlocal simplified functionals with Thomas-Fermi structure (NLS-TFs), we are going to impose the requirements (ii) and (iii) from the CAT functional. So we write the functional  $T_S^{\text{NLS-TF}}[n]$  in the same way as in Eq. (11) but we change the first requisite to the following one.

(i)' The mathematical form of the nonlocal term is based on an expression similar to the TF functional, written in terms of a double integration of a product of two different powers of the density,  $n^{5/3-\beta}(\mathbf{r})$  and  $n^\beta(\mathbf{r}')$ , evaluated at  $(\mathbf{r})$  and  $\mathbf{r}'$ , and coupled by the kernel (note that we have assumed the sum of these powers to be  $5/3$ , in order to have the correct dimensionality and scaling of the TF functional). Writing

$$T_S^{\text{NLS-TF}}[n] = T_{\text{vW}}[n] - \alpha T_{\text{TF}}[n] + (1 + \alpha) T_{\text{NLS-TF}}^{\text{NL}}[n], \quad (17)$$

the nonlocal term  $T_{\text{NLS-TF}}^{\text{NL}}[n]$  of this functional is then a double convolution of the densities with a kernel  $\Omega(k_F, |\mathbf{r} - \mathbf{r}'|)$  that has a constant Fermi wave vector as a scaling factor,

$$T_{\text{NLS-TF}}^{\text{NL}}[n] = \int d\mathbf{r} \int d\mathbf{r}' n^{5/3-\beta}(\mathbf{r}) n^\beta(\mathbf{r}') \Omega(k_F, |\mathbf{r} - \mathbf{r}'|), \quad (18)$$

similar to the WGC one. The functional fits into the general mathematical form given by Eq. (7) and a linear scaling in momentum space could be implemented. Moreover, the functional retains the properties of the CAT functional because the kernel satisfies requirement (iii). We now have a new set of parameters  $\alpha$  and  $\beta$ , related through the conditions that the kernel must satisfy. The kernel is also fixed by the second functional derivative of  $T_S^{\text{NLS-TF}}[n]$ ; its relation with the Lindhard function gives again an algebraic equation

$$10 \frac{F_{\text{Lind}}(\eta) - 3\eta^2 + \alpha}{1 + \alpha} = 18\beta(5/3 - \beta)\omega(\eta) + 18\beta^2 - 30\beta + 10, \quad (19)$$

and the explicit expression of the kernel is

$$\omega(\eta) = \frac{1}{18\beta(5/3 - \beta)} \left( 10 \frac{F_{\text{Lind}}(\eta) - 3\eta^2 + \alpha}{1 + \alpha} - 18\beta^2 + 30\beta - 10 \right). \quad (20)$$

The mentioned asymptotic condition on the kernel (iii) gives a relation between  $\alpha$  and  $\beta$ ,

$$\alpha = \frac{[(9\beta^2/5) - 3\beta + 8/5]}{[-(9\beta^2/5) + 3\beta]}. \quad (21)$$

When this value of  $\alpha$  is substituted in the expression of the kernel, Eq. (20), we obtain

$$\omega(\eta) = \frac{1}{8} \{5[F_{\text{Lind}}(\eta) - 3\eta^2] + 3\}, \quad (22)$$

which is the same for all the functionals of the family. This is an elegant result: to have the required asymptotic behavior, the kernel is independent of the parameters  $\alpha$  and  $\beta$ . Note that, even though they share the same kernel, each functional of the family obviously yields different values of the kinetic energy.

Table I also summarizes the values of the parameters corresponding to the NLS-TF functionals. The first two values of  $\beta$  are chosen to yield integer powers of the Fermi wave vector. We have also included  $\beta=5/6$  due to the symmetry of the final form of the functional. Choosing  $\alpha=3/5$ —in order to obtain an adequate linear combination of the TF and vW functionals for large values of  $\eta$ — $\beta$  is  $5/6 \pm \sqrt{5}/6$  (a similar result was obtained by WGC for their functional [25]). We must remark that the NLS-TF functional is highly symmetric and the choice of a value for  $\beta$  gives the same functional choosing  $5/3 - \beta$ , as reflected in Table I.

#### IV. KINETIC FUNCTIONALS WITH NONLOCAL TERMS WITH THE STRUCTURE OF THE THOMAS-FERMI FUNCTIONAL (DENSITY-DEPENDENT KERNEL)

##### A. Chacón-Alvarelos-Tarazona family of functionals

The CAT family of functionals with density-dependent kernels is defined with the same expression as their density-independent kernel counterparts, Eq. (11), but now the averaged density is calculated as

$$\tilde{n}_\beta(\mathbf{r}) = \int d\mathbf{r}' n^\beta(\mathbf{r}') \Omega[\zeta(\mathbf{r}, \mathbf{r}'), |\mathbf{r} - \mathbf{r}'|], \quad (23)$$

where the scaling is now introduced through the two-body wave vector  $\zeta(\mathbf{r}, \mathbf{r}')$ . This is a generalization of the mentioned symmetrized CAT functional [26].

We must now remark that the behavior of the weight function when  $q \rightarrow 0$  and  $q \rightarrow \infty$  does not depend on the derivatives of the kernel. As a consequence, the previous discussion about the parameters  $\alpha$  and  $\beta$  is valid, and we can use the same sets of parameters  $\alpha$  and  $\beta$  as in the density-independent case (i.e., those given in Table I).

On the other hand, the relationship between the kernel and the Lindhard function, obtained through the second functional derivative of  $T_S^{\text{CAT}}[n]$ , is now not algebraic but a complicated second-order differential equation. In momentum space we obtain

$$\begin{aligned} & 10 \frac{F_{\text{Lind}}(\eta) - 3\eta^2 + \alpha}{1 + \alpha} \\ &= 12\omega(\eta) + 2(2 - 3\beta)[\omega(\eta)]^2 + \frac{1}{36} \frac{2}{\beta} \left( \frac{2}{\beta} - 3 \right) [\omega'(\eta)\eta]^2 \\ & \quad - 2 \left( \frac{2}{3\beta} - 1 \right) \omega(\eta)\omega'(\eta)\eta + 6(\beta - 1) \\ & \quad + \frac{1}{3\beta} \omega''(\eta)\eta^2 + \left( -\frac{2}{\beta} - 2 + \frac{1 + \gamma}{3\beta} \right) \omega'(\eta)\eta. \end{aligned} \quad (24)$$

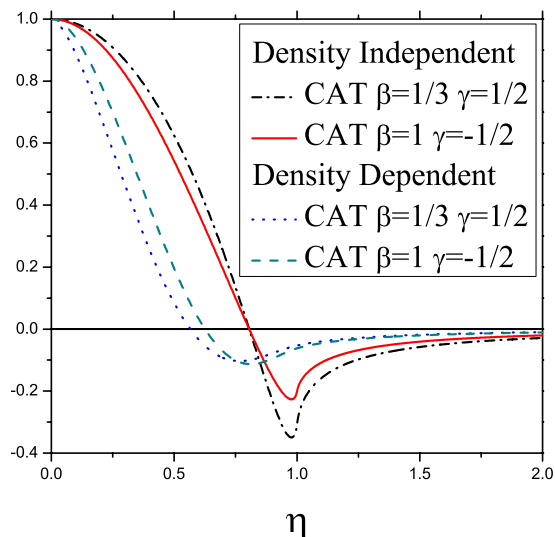


FIG. 1. (Color online) Kernels for the CAT functionals as a function of the scaled momentum  $\eta$ .

As the kernel is now double-density-dependent through the two-body Fermi wave vector, an additional degree of freedom in the final form of the functional appears—the power  $\gamma$  for averaging the scaling function in Eq. (10)—and the differential equation depends also on  $\gamma$ . This differential equation must be solved numerically; we have chosen a Runge-Kutta method, starting the integration at infinity to avoid numerical problems. In Fig. 1 the kernel in momentum space is represented for both the density-dependent and density-independent versions of the CAT functional. The density-dependent kernel has a softer structure than the density-independent one. The shape of the kernel depends greatly on the value of  $\beta$  but is almost independent of the value of  $\gamma$ . For that reason, in this paper we have used  $\gamma = \frac{1}{2}$  and  $\gamma = -\frac{1}{2}$ , following the discussion of the original formulation of the symmetrized CAT functional [26], and the values of the parameters given in Table I.

### B. Functionals with nonlocal simplified terms with Thomas-Fermi structure

This family of functionals is obtained in the same way as in the density-independent case, Eq. (17), but the nonlocal term is now calculated with the two-body Fermi wave vector  $\zeta(\mathbf{r}, \mathbf{r}')$  in the kernel:

$$T_{\text{NLS-TF}}^{\text{NL}}[n] = \int d\mathbf{r} \int d\mathbf{r}' n^{5/3-\beta}(\mathbf{r}) n^{\beta}(\mathbf{r}') \Omega[\zeta(\mathbf{r}, \mathbf{r}'), |\mathbf{r} - \mathbf{r}'|], \quad (25)$$

instead of Eq. (18). As commented before, we can have the same discussion about the choice of the sets of parameters as in the density-independent functionals.

The final form of the kernel is given by a much simpler differential equation than for the CAT functionals:

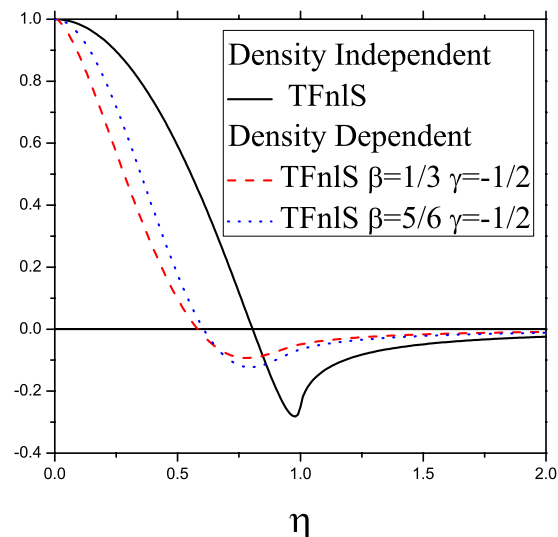


FIG. 2. (Color online) Kernels for the NLS-TF functionals as a function of the scaled momentum  $\eta$ .

$$\begin{aligned} & 10 \frac{F_{\text{Lind}}(\eta) - 3\eta^2 + \alpha}{1 + \alpha} \\ &= 18\beta \left( \frac{5}{3} - \beta \right) \omega(\eta) + \frac{1}{2} \omega''(\eta) \eta^2 + \left( \frac{\gamma+1}{2} - 5 \right) \omega'(\eta) \eta \\ &+ 18\beta^2 - 30\beta + 10, \end{aligned} \quad (26)$$

where there are no products of the kernel and its derivatives.

This differential equation can be solved numerically in the same way we did previously. The kernels are represented in Fig. 2, and similar conclusions about the structure and the dependence of the kernels on the values of  $\beta$  and  $\gamma$  can be obtained. We chose the same values for  $\alpha$  and  $\beta$  as in the density-independent case (see Table I), and also used  $\gamma = \frac{1}{2}$  and  $\gamma = -\frac{1}{2}$ .

### V. ACCURATE TOTAL KINETIC ENERGIES FOR CLOSED-SHELL ATOMS

In order to test the quality of our proposed fully nonlocal functionals with double-density-dependent kernels, i.e., the CAT family defined by Eqs. (11), (18), and (23) and the NLS-TF family defined by Eqs. (17) and (25), we have performed total energy calculations for some closed-shell atoms, from He to Xe. The kinetic energy was evaluated using the output densities obtained by the variational minimization of the KS scheme through the GAUSSIAN package [33], with a 6-311++G(d,p) basis set for all atoms, except for Sr and Xe, where the basis 3-21G\*\* was used instead. The sizes of these basis sets are big enough to ensure quality electronic densities and energies after solution of the KS method, within the local density approximation for the XC.

In Table II we present the relative errors of the total kinetic energies obtained with the CAT functionals, compared with the KS *exact* results, with an additional column for the average of the absolute values of the errors. These results show that, in general, when we choose a negative value for

TABLE II. Relative errors in the total kinetic energy for the CAT functionals, when using the KS densities. The average of the relative errors is made over their absolute values. In the last row the KS values of the total energies are presented.

$\beta$	$\gamma$	He	Be	Ne	Mg	Ar	Ca	Kr	Sr	Xe	Av.
1/3	1/2	0.035	0.033	0.006	0.010	0.009	0.008	0.003	0.000	-0.002	0.012
1/3	-1/2	-0.056	0.031	0.054	0.122	0.089	0.093	0.055	0.049	0.044	0.066
2/3 <sup>a</sup>	1/2	0.053	0.038	0.014	0.016	0.017	0.016	0.009	0.006	0.004	0.019
2/3 <sup>a</sup>	-1/2	-0.014	-0.008	-0.003	0.008	0.014	0.014	0.006	0.002	0.001	0.008
3/3	1/2	0.079	0.065	0.034	0.035	0.033	0.032	0.021	0.018	0.014	0.037
3/3	-1/2	0.014	0.017	0.015	0.022	0.027	0.027	0.017	0.013	0.011	0.018
4/3	1/2	0.085	0.094	0.083	0.084	0.082	0.080	0.067	0.063	0.056	0.077
4/3	-1/2	0.010	0.065	0.079	0.087	0.089	0.087	0.076	0.072	0.067	0.070
KS total energy											
		2.761	14.350	128.155	198.885	524.829	675.535	2749.055	3123.615	7174.034	

<sup>a</sup>This functional belongs to both the CAT and NLS-TF families.

the parameter  $\gamma$  we get lower relative errors—except for the functional with  $\beta=1/3$  and  $\gamma=1/2$ , which yields values with an average error of about 1%. For  $\beta=4/3$  we get relative errors greater than 7%, so this parameter appears to be inadequate for use in a dependable KEDF. The best relative errors are obtained for  $\beta=2/3$  and  $\gamma=-1/2$ , with similar values (average value of 0.8%) to those obtained by usual semilocal functionals [10–12].

Results for the NLS-TF family of functionals are shown in Table III, where we have labeled with 5/6+ the rows for  $\beta=5/6+\sqrt{5}/6$ . Large errors are obtained for  $\beta=1/3$ , the best results being those corresponding to  $\gamma=-1/2$  and a value of  $\beta$  equal to 5/6 or 2/3 (as remarked in Secs. III and IV, when  $\beta=2/3$  this functional coincides with the CAT one). Consequently, we can choose that functional with  $\gamma=-1/2$  and  $\beta=5/6$  as the prototypical NLS-TF one—a symmetric functional, because the densities at different points have the same exponent in Eq. (25)—that yields the best results for this set of atoms.

## VI. KINETIC-ENERGY DENSITIES

In a previous paper, we presented a comparative study of the quality of the *kinetic-energy density* (KED) of semilocal

functionals within the GGA scheme [12], proposing a *quality factor*  $\sigma$  that measures the local differences between KED distributions. We showed that all the semilocal functionals but those with a full vW term give total kinetic energies within 2% of the exact one (i.e., they greatly improve the TF results), but they place the additional KED (i.e., the KED not included in the TF functional) in wrong regions of space. So semilocal GGA functionals yield total kinetic energies better than the TF functional by canceling the global errors in the evaluation, but the local behavior of their KEDs becomes worse than the TF behavior. Semilocal functionals that include higher density derivatives (see, e.g., [34–36]) deserve additional study.

We have just shown in Sec. V that the fully nonlocal families of functionals CAT and NLS-TF give good results for the total kinetic energies in atomic systems. But, in order to assess their quality, we must pay attention not only to the results for the total kinetic energies but also to the results of the KED generated by the functionals. For that reason, we have also calculated the quality factor  $\sigma$  for the functionals we are presenting in this paper. Following Ref. [12], we use an infinite set of valid KEDs  $t_S^L(\mathbf{r})$  through (see, e.g., Ref. [37])

TABLE III. Relative errors in the total kinetic energy for the NLS-TF functionals, when using the KS densities. The average of the relative errors is made over their absolute values. In the last row the KS values of the total energies are presented.

$\beta$	$\gamma$	He	Be	Ne	Mg	Ar	Ca	Kr	Sr	Xe	Av.
1/3	1/2	-0.179	-0.116	-0.066	-0.053	-0.039	-0.037	-0.029	-0.031	-0.027	0.064
1/3	-1/2	-0.404	-0.117	-0.011	0.062	0.044	0.048	0.030	0.026	0.026	0.085
2/3 <sup>a</sup>	1/2	0.053	0.038	0.014	0.016	0.017	0.016	0.009	0.006	0.004	0.019
2/3 <sup>a</sup>	-1/2	-0.014	-0.008	-0.003	0.008	0.014	0.014	0.006	0.002	0.001	0.008
5/6	1/2	0.073	0.053	0.021	0.022	0.021	0.020	0.012	0.009	0.006	0.026
5/6	-1/2	0.016	0.006	0.000	0.008	0.014	0.014	0.006	0.003	0.001	0.007
5/6+	1/2	-0.042	-0.029	-0.019	-0.012	-0.005	-0.005	-0.006	-0.008	-0.007	0.015
5/6+	-1/2	-0.164	-0.065	-0.010	0.020	0.021	0.022	0.010	0.006	0.006	0.036
KS total energy											
		2.761	14.350	128.155	198.885	524.829	675.535	2749.055	3123.615	7174.034	

<sup>a</sup>This functional belongs to both the CAT and NLS-TF families.

TABLE IV. Values of the Slater orbital exponents.

Orbital	Atom						
	He	Be	N	Ne	Mg	P	Ar
1s	1.6875	3.6848	6.6651	9.6421	11.6089	14.5578	17.5075
2s		0.9560	1.9237	2.8792	3.6960	4.9125	6.1152
2p			1.9170	2.8792	3.9129	5.4806	7.0041
3s					1.1025	1.8806	2.5856
3p						1.6288	2.2547

$$t_S^L(\mathbf{r}) = \frac{1}{2} \sum_{i=1}^N |\nabla \phi_i(\mathbf{r})|^2 + a \nabla^2 n(\mathbf{r}), \quad (27)$$

$t_S^L(\mathbf{r})$  being constructed as an orbital-based KED plus the Laplacian of the electron density multiplied by a prefactor  $a$  that can have any real value. For each  $a$  we have a different value of the quality factor,

$$\sigma = \frac{\int d\mathbf{r} |t_S^L(\mathbf{r}) - t_S^{\text{func}}(\mathbf{r})|}{T_S[n]}, \quad (28)$$

where  $t_S^{\text{func}}(\mathbf{r})$  is the approximate KED for the given functional. The value of  $\sigma$  can be interpreted as the amount of the approximated KED that is misplaced when compared to the distribution of the orbital-based KED. To test every functional in the appropriate conditions for that functional, we have compared its approximate KED with its closest  $t_S^L(\mathbf{r})$ , choosing among all possible values of the parameter  $a$ , i.e., minimizing the value of  $\sigma$  when varying the parameter  $a$ . The best fit of the distribution  $t_S^L(\mathbf{r})$  to the approximated KED is obtained by a *golden search* algorithm [38]. After the minimization process, each functional has a value  $a_{\text{min}}$  corresponding to the lowest value of  $\sigma$ ; the KED  $t_S^L(\mathbf{r})$  closest to  $t_S^{\text{func}}(\mathbf{r})$  is evaluated by using  $a_{\text{min}}$  in Eq. (27).

As commented in Ref [12], in order to get good enough atomic electron densities and orbital-based KEDs, the use of properly orthogonalized Slater orbitals is very advisable, because they approximately describe the KS orbitals without adding spurious behavior when the Laplacian of the density is evaluated, and the correct cusp conditions and the density decay for  $r \rightarrow \infty$  can be achieved. The values of the Slater orbital exponents used in this paper are shown in Table IV

[39,40].

In order to simplify the presentation, in this work we will only discuss atoms with complete shells and complete half shells up to Ar, using those functionals that obtained the best total kinetic energies in Sec. V. As commented previously, the parameter  $\beta=2/3$  makes the KEDF belong to both the CAT and the NLS-TF families, and has been proven to be an accurate functional for both families. We must remark that only double-density-dependent functionals have been used in our calculations.

*CAT family of functionals.* In Table V we present the percent relative errors for the total kinetic energies as evaluated with the CAT family with orthogonalized Slater orbitals. As a general trend, those functionals that gave small errors for the total kinetic energies (when the KS electron density that comes from the GAUSSIAN package was used) also yield almost the same small errors in this case. For the best functionals, the errors (and their average values) are close to those obtained with semilocal functionals [12]. Some functionals—e.g., those with  $\beta=2/3$  and  $\gamma=-1/2$ —yield errors smaller than 1%, the same level of accuracy as the best semilocal functionals.

We present the values for the quality factor  $\sigma$  in Table VI, after fitting  $t_S^{\text{func}}(r)$  to the KED  $t_S^L(r)$  of Eq. (27). The results clearly show that CAT functionals give in general smaller values of  $\sigma$  than the TF functional. As a consequence, unlike any semilocal functional studied in Ref. [12], these fully nonlocal functionals give a better description of the KED than the TF functional. Again, the parameters  $\beta=2/3$  and  $\gamma=-1/2$  correspond to the CAT functional with the best value of  $\sigma$ : on the average this functional misplaces about 13% of the KED.

*NLS-TF family of functionals.* Table V also includes the relative errors for the kinetic energies when evaluated with

TABLE V. Relative errors in the total kinetic energy for the fully nonlocal functionals, when using the densities that come from the orthogonalized Slater orbitals. The average is made over the absolute values of the relative errors.

Functional	$\beta$	$\gamma$	He	Be	N	Ne	Mg	P	Ar	Av.
CAT	1/3	1/2	0.026	0.033	0.000	0.016	0.018	0.014	0.012	0.017
CAT	1	-1/2	0.035	0.023	0.006	0.024	0.028	0.029	0.030	0.025
NLS-TF	5/6	-1/2	0.030	0.010	-0.009	0.012	0.015	0.016	0.017	0.016
CAT/NLS-TF	2/3	-1/2	-0.001	-0.005	-0.017	0.006	0.014	0.016	0.017	0.011
TF	-	-	-0.082	-0.091	-0.102	-0.076	-0.074	-0.072	-0.069	0.081
GEA2	-	-	0.029	0.013	-0.012	0.004	0.001	-0.003	-0.003	0.009



TABLE VI. Values of  $\sigma$  for the nonlocal functionals with a nonlocal term with TF structure.

Functional	$\beta$	$\gamma$	He	Be	N	Ne	Mg	P	Ar	Av.
CAT	1/3	1/2	0.030	0.110	0.160	0.155	0.163	0.165	0.161	0.135
CAT	1	-1/2	0.069	0.129	0.157	0.179	0.185	0.184	0.182	0.155
NLS-TF	5/6	-1/2	0.042	0.099	0.133	0.157	0.165	0.167	0.166	0.133
CAT/NLS-TF	2/3	-1/2	0.021	0.090	0.138	0.161	0.172	0.175	0.174	0.133
TF	-	-	0.166	0.168	0.172	0.160	0.155	0.148	0.141	0.158
GEA2	-	-	0.187	0.190	0.190	0.186	0.180	0.171	0.163	0.181

the NLS-TF family of functionals. As for the CAT family, we again find better results for the functionals that gave smaller errors when the kinetic energy was evaluated with the KS densities.

The results for the quality factor of the KED, i.e., the minimized values of  $\sigma$  after varying  $a$ , are shown in Table VI. For the parameters we have used— $\beta=2/3$ ,  $\gamma=-1/2$  and  $\beta=5/6$ ,  $\gamma=-1/2$ —about 13% of the KED is misplaced on the average. As a general trend, we again obtain smaller values of  $\sigma$  than those for the TF functional—the best one among all semilocal functionals; TF misplaces about 16% of the KED.

## VII. QUALITATIVE VIEW OF THE KINETIC-ENERGY DENSITY

As commented in Secs. V and VI, we have found two optimal functionals: for both the CAT and NLS-TF families, that with  $\beta=2/3$  and  $\gamma=-1/2$ ; and for the NLS-TF family, the functional with  $\beta=5/6$  and  $\gamma=-1/2$ .

When CAT and NLS-TF functionals are tested by comparing the approximate KED with that orbital-based KED that is closest to the approximate value (see [12]), and minimizing  $\sigma$  among all possible values of  $a$ , we found small values for  $a$ . That reminds us of the results obtained for the vW functional [12], which gives values of  $a$  very close to

zero for all atoms. Both the CAT and NLS-TF families are constructed with a full vW functional, corrected with nonlocal terms that have the mathematical structure of the TF functional; it seems that the KEDs generated by them are closer to the first term in Eq. (27),  $t_S^I(\mathbf{r}) = \frac{1}{2} \sum_{i=1}^N |\nabla \phi_i(\mathbf{r})|^2$ , directly related to  $T_{vW}$  as written in Eq. (4), and which plays an important role in the theory of atoms in molecules [41]. Thus, our fully nonlocal functionals give results close to  $t_S^I(\mathbf{r})$ , whereas the semilocal functionals have been proved [12] to yield results much closer to the definition of the “classical” KED, which has been proposed to be the mean average of  $t_S^I(\mathbf{r})$  and  $t_S^{II}(\mathbf{r}) = -\frac{1}{2} \sum_{i=1}^N \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r})$  [37,42,43]. Further discussion about the nonuniqueness of the orbital-based definitions of the KED can be seen in Ref. [12].

For the same reason, it can be expected that those functionals with nonlocal simplified terms with TF structure will better describe the KED in the neighborhood of the atomic nucleus. In order to compare our results on the same footing, we are going to compare the KEDs of the Ne atom, because the value of the minimum  $\sigma$  for almost all the functionals is about 0.16 (for GEA2 we have a value of 0.19 instead). In Fig. 3 we present the approximate KEDs for the Ne atom, depicted vs  $t_S^I(\mathbf{r}) = \frac{1}{2} \sum_{i=1}^N |\nabla \phi_i(\mathbf{r})|^2$ . Figure 4, on the other hand, shows the differences among the approximate KEDs and  $t_S^I(\mathbf{r})$ . As expected, it can be clearly seen that the fully

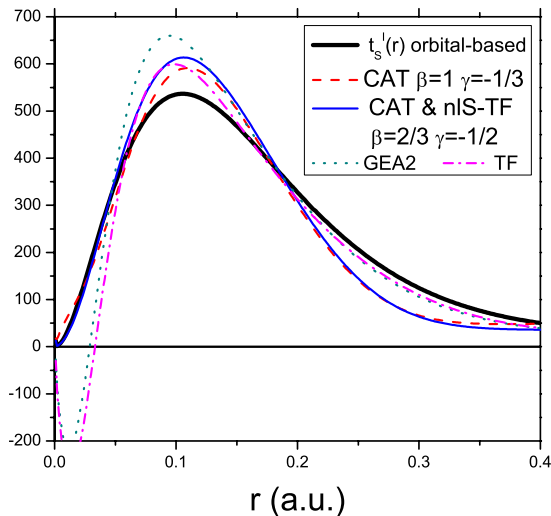


FIG. 3. (Color online) Kinetic-energy density of the Ne atom for some selected functionals.

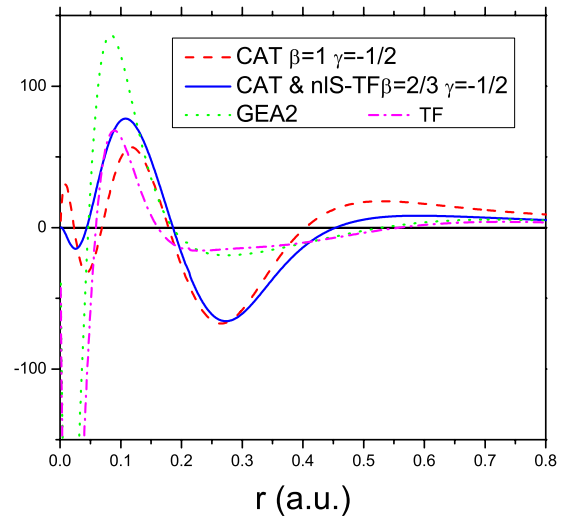


FIG. 4. (Color online) Differences of the kinetic-energy density of the Ne atom for some selected functionals, when compared with the orbital-based kinetic-energy density  $t_S^I$ .

nonlocal functionals describe more adequately the maximum that corresponds to the “core” electrons—those in the region  $r \leq 0.1$ —and the pathologies of the TF functional, exhibiting an excess of KED in the first peak of the density (corresponding to the  $1s$  orbital) as well as a defect of KED near the nucleus, almost disappear. We must recall that these pathologies are always enlarged in the semilocal functionals [12].

### VIII. CONCLUSIONS

The families of KEDFs with double-density-dependent kernels given by Chacón, Alvarillos, and Tarazona and Wang, Govind, and Carter are among the most sophisticated in the literature.

In this paper, a complete CAT family has been generalized and studied. These functionals are defined by Eq. (11), with a nonlocal term (12) calculated with the averaged density (23). The double-density-dependent kernel is obtained through the differential equation (24).

We have also proposed an additional family, which we called nonlocal simplified functionals with Thomas-Fermi structure, which is able to gather the best properties of the CAT and WGC functionals: (a) the mathematical structure of the nonlocal term of the WGC functionals, which allows us to evaluate them by a single integration on momentum space (so the computational cost scales linearly with the number of electrons of the system); (b) the properties of the kernel or weight function of the CAT functionals, which makes them applicable to extended and localized systems.

In this case the functionals are constructed using Eq. (17), with a nonlocal term evaluated as a double convolution (25), whereas the kernel satisfies Eq. (26).

We have paid attention not only to the total kinetic energies but also to the local behavior of the energy densities, by

implementing the method developed in Ref. [12] to test the KEDFs locally. After checking that, using good densities, the functionals give accurate total kinetic atomic energies, we discussed the quantitative measurement of the differences between the KEDs by means of a quality factor  $\sigma$ . Selecting those functionals that give better results for the previous test, both the CAT and NLS-TF families of functionals clearly improve the values of the quality factor  $\sigma$ , getting better KEDs than the TF functional.

The qualitative study of the KED shows that the nonlocal functionals have improved the description of the KED related to the core region, when compared with the results obtained with all the semilocal approximations [12].

Both families ensure a better description of the KED than any available semilocal functional, even if they do not always improve the TF results for each particular atom. We must remark that, in any case, the TF functional has much larger errors for the total kinetic energy than the semilocal and fully nonlocal KEDFs. But the relative errors of these KEDFs, being among the smallest found for any orbital-free approximation, are still far too big for chemical precision.

So, we can conclude that these fully nonlocal models for the KEDF get good enough results for both the energies and the KEDs, showing the positive effects of introducing better nonlocal characteristics on the construction of approximate kinetic functionals.

### ACKNOWLEDGMENTS

We acknowledge the continuous interest in this work of Rafael Almeida, Pablo García-González, and Teresa Martín Blas. This work has been partially supported by the Spanish Ministerio de Educación y Ciencia (Grant No. FIS2004-05035-C03-03).

- 
- [1] R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).
- [2] E. S. Kryachko and E. V. Ludeña, *Energy Density Functional Theory of Many-Electron Systems* (Kluwer Academic, London, 1990).
- [3] W. Koch and M. C. Holthausen, *A Chemist's Guide to Density Functional Theory*, 2nd ed. (Wiley-VCH, Weinheim, 2001).
- [4] P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).
- [5] W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- [6] L. H. Thomas, *Proc. Cambridge Philos. Soc.* **23**, 542 (1927).
- [7] E. Fermi, *Nephrol. Dial Transplant* **6**, 602 (1927).
- [8] C. F. V. Weizsacker, *Z. Phys.* **96**, 431 (1935).
- [9] J. P. Perdew and Y. Wang, *Phys. Rev. B* **33**, 8800 (1986).
- [10] A. J. Thakkar, *Phys. Rev. A* **46**, 6920 (1992).
- [11] D. J. Lacks and R. G. Gordon, *J. Chem. Phys.* **100**, 4446 (1994).
- [12] D. García-Aldea and J. E. Alvarillos, *J. Chem. Phys.* **127**, 144109 (2007).
- [13] J. A. Alonso and L. A. Girifalco, *Solid State Commun.* **24**, 135 (1977).
- [14] J. A. Alonso and L. A. Girifalco, *Phys. Rev. B* **17**, 3735 (1978).
- [15] O. Gunnarsson, M. Jonson, and B. I. Lundqvist, *Phys. Rev. B* **20**, 3136 (1979).
- [16] J. Lindhard, *K. Dan. Vidensk. Selsk. Mat. Fys. Medd.* **28**, 8 (1954).
- [17] E. Chacón, J. E. Alvarillos, and P. Tarazona, *Phys. Rev. B* **32**, 7868 (1985).
- [18] P. Tarazona, *Mol. Phys.* **52**, 81 (1984).
- [19] P. Tarazona and R. Evans, *Mol. Phys.* **52**, 847 (1984).
- [20] P. Tarazona, *Phys. Rev. A* **31**, 2672 (1985).
- [21] L. W. Wang and M. P. Teter, *Phys. Rev. B* **45**, 13196 (1992).
- [22] E. Smargiassi and P. A. Madden, *Phys. Rev. B* **49**, 5220 (1994).
- [23] P. García-Gonzalez, J. E. Alvarillos, and E. Chacón, *Phys. Rev. B* **53**, 9509 (1996).
- [24] Y. A. Wang, N. Govind, and E. A. Carter, *Phys. Rev. B* **58**, 13465 (1998).
- [25] Y. A. Wang, N. Govind, and E. A. Carter, *Phys. Rev. B* **60**, 16350 (1999).
- [26] P. García-Gonzalez, J. E. Alvarillos, and E. Chacón, *Phys. Rev. A* **54**, 1897 (1996).

- [27] P. García-Gonzalez, J. E. Alvarellos, and E. Chacón, *Phys. Rev. B* **57**, 4857 (1998).
- [28] P. García-Gonzalez, J. E. Alvarellos, and E. Chacón, *Phys. Rev. A* **57**, 4192 (1998).
- [29] Y. A. Wang and E. A. Carter, in *Theoretical Methods in Condensed Phase Chemistry*, edited by S. D. Schwartz, Progress in Theoretical Chemistry and Physics (Kluwer, Dordrecht, 2000), Chap. 5, pp. 117–184.
- [30] S. C. Watson and E. A. Carter, *Comput. Phys. Commun.* **128**, 67 (2000).
- [31] K. M. Carling and E. A. Carter, *Modell. Simul. Mater. Sci. Eng.* **11**, 339 (2003).
- [32] B. Zhou, V. L. Ligneres, and E. Carter, *J. Chem. Phys.* **122**, 044103 (2005).
- [33] M. J. Frisch *et al.*, computer code GAUSSIAN 98, Revision A.6 (Gaussian, Inc., Pittsburgh, PA, 1998).
- [34] C. H. Hodges, *Can. J. Phys.* **51**, 1428 (1973).
- [35] D. R. Murphy, *Phys. Rev. A* **24**, 1682 (1981).
- [36] J. P. Perdew and L. A. Constantin, *Phys. Rev. B* **75**, 155109 (2007).
- [37] Z.-Z. Yang, S. Liu, and Y. A. Wang, *Chem. Phys. Lett.* **258**, 30 (1996).
- [38] W. Press, B. Flannery, S. Teukolsky, and W. Vetterling, *Numerical Recipes: The Art of Scientific Computing*, 2nd ed. (Cambridge University Press, Cambridge, UK, 1992).
- [39] P. W. Atkins, *Molecular Quantum Mechanics*, 3rd ed. (Oxford University Press, Oxford, 1997).
- [40] E. Clementi and D. L. Raimondi, *J. Chem. Phys.* **38**, 2686 (1963).
- [41] R. F. W. Bader, *Atoms in Molecules. A Quantum Theory* (Oxford University Press, Oxford, 1990).
- [42] R. J. Lombard, D. Mas, and S. A. Moszkowski, *J. Phys. G* **17**, 455 (1991).
- [43] S. K. Ghosh, M. Berkowitz, and R. G. Parr, *Proc. Natl. Acad. Sci. U.S.A.* **81**, 8028 (1984).