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Approach to kinetic energy density functionals: Nonlocal terms with the structure of the von Weizsäcker functional

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We propose a kinetic energy density functional scheme with nonlocal terms based on the von Weizsäcker functional, instead of the more traditional approach where the nonlocal terms have the structure of the Thomas-Fermi functional. The proposed functionals recover the exact kinetic energy and reproduce the linear response function of homogeneous electron systems. In order to assess their quality, we have tested the total kinetic energies as well as the kinetic energy density for atoms. The results show that these nonlocal functionals give as good results as the most sophisticated functionals in the literature. The proposed scheme for constructing the functionals means a step ahead in the field of fully nonlocal kinetic energy functionals, because they are capable of giving better local behavior than the semilocal functionals, yielding at the same time accurate results for total kinetic energies. Moreover, the functionals enjoy the possibility of being evaluated as a single integral in momentum space if an adequate reference density is defined, and then quasilinear scaling for the computational cost can be achieved.

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I. INTRODUCTION

Modern density functional theory (DFT) was originally developed by Hohenberg and Kohn (HK) [1], who proved that the density contains all the information needed for the ground state of an electron system, and that the total energy functional $E[n]$ could be minimized by using the Euler equation

$$\delta E[n]/\delta n = 0. \tag{1}$$

As $E[n]$ is unknown, DFT usually follows the Kohn and Sham (KS) [2] method, which relies on the concept of a noninteracting system of KS orbitals that yields the same electron density as the interacting one and allows one to write

$$E[n] = T_S[n] + V[n] + J[n] + E_{XC}[n], \tag{2}$$

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 energy of the charge distribution (Hartree energy), and finally $E_{XC}[n]$ is the so-called exchange-correlation (XC) energy. We will use atomic units in this paper.

There is a close relation between the response function of an electron system and the KEDF, because the second functional derivative of $E[n]$ yields the total response function [1]. For a homogeneous gas this second derivative equals the linear response function of the free electron gas, and can be written in the momentum space as

$$\mathcal{F}\left(\left. \frac{\delta T_S[n(\mathbf{r})]}{\delta n(\mathbf{r}_1)\,\delta n(\mathbf{r}_2)} \right|_{n_0} \right) = -\frac{1}{\tilde{\chi}_{\mathrm{Lind}}(q)} = \frac{\pi^2}{k_F} F_{\mathrm{Lind}}(\eta), \tag{3}$$

where $\mathcal{F}$ indicates the Fourier transform. The function $F_{\mathrm{Lind}}(\eta)$, known as the Lindhard function [3], has the analytical expression

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

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

On the other hand, the evaluation of *fully nonlocal* KEDFs (i.e., those that use the density of the whole system for calculating the contribution to the kinetic energy from each point of the space) usually needs two integrations in real space because it is assumed that the contributions come from every pair of points $\mathbf{r}$ and $\mathbf{r}'$ (see [4]). The general form of these nonlocal functionals is

$$F[n] = \int d\mathbf{r} \left[f_1(n(\mathbf{r})) f_{12}\left(\int d\mathbf{r}' f_2(n(\mathbf{r}), n(\mathbf{r}'), \mathbf{r}, \mathbf{r}') \right) \right], \tag{5}$$

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 requirement that they have all together the correct dimensionality for $F[n]$. The Chacón-Alvarellos-Tarazona (CAT) functional [5] was the first constructed along these lines.

Another useful and simpler expression for fully nonlocal functionals is

$$F[n] = \int d\mathbf{r} \int d\mathbf{r}' f(n(\mathbf{r}), n(\mathbf{r}'), \mathbf{r}, \mathbf{r}'), \tag{6}$$

where $f(n(\mathbf{r}), n(\mathbf{r}'), \mathbf{r}, \mathbf{r}')$ is a function with the correct dimensionality. The Thomas-Fermi (TF) functional [6,7] can be rewritten in this way as

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$$T_{\rm TF}[n] = C_{\rm TF}\int d\mathbf{r}\int d\mathbf{r}' n^{5/3-\beta}(\mathbf{r})\,\delta(\mathbf{r}-\mathbf{r}')\,n^{\beta}(\mathbf{r}'), \qquad (7)$$

where $C_{\rm TF}=\frac{3}{10}(3\pi^2)^{2/3}$ is the TF constant. We have recently proposed a family of functionals which includes a nonlocal simplified term with a TF-like structure (NLS-TF functionals) [4], by introducing a kernel for linking the contributions at $\mathbf{r}$ and $\mathbf{r}'$:

$$T_{\rm nl}^{\rm NLS\text{-}TF}[n] = C_{\rm TF}\int d\mathbf{r}\int d\mathbf{r}' n^{5/3-\beta}(\mathbf{r}) \times\Omega(\zeta(\mathbf{r},\mathbf{r}'),|\mathbf{r}-\mathbf{r}'|)\,n^{\beta}(\mathbf{r}'). \qquad (8)$$

The kernel Ω is constructed by forcing the functional to reproduce the linear response of the free electron gas.

We can use three different scaling factors $\zeta(\mathbf{r},\mathbf{r}')$ in the kernel of Eq. (8).

(a) References [8–10] use a constant Fermi wave vector, calculated in terms of a reference uniform density; these functionals are labeled *density-independent kernel* functionals.

(b) In Ref. [5], which proposes a functional of the type of Eq. (5), the local Fermi wave vector $k_F(\mathbf{r})$ was used; these functionals have a *density-dependent kernel*.

(c) References [11–16] use a two-body Fermi wave vector defined as the simple form

$$\zeta(\mathbf{r},\mathbf{r}') = \left(\frac{k_F^{\gamma}(\mathbf{r})+k_F^{\gamma}(\mathbf{r}')}{2}\right)^{1/\gamma}. \qquad (9)$$

These functionals have *double density-dependent kernels*.

Some of these nonlocal KEDFs reproduce the linear response function of the free electron gas and include both the von Weizsäcker (vW) term [17] and a fully nonlocal term with the mathematical structure of the TF functional. The vW functional appears because it is needed to reproduce the linear response of the electron gas—see the discussion in [5]—and the fully nonlocal term is introduced following the classical extension of the TF functional, by including the electron densities powered to $\frac{5}{3}$: the density itself (as in the TF approach), some weighted density ([18–20], though this functional does not reproduce the linear response; see [21]), or averaged or generalized densities (see [5,14]).

Trying to go a step ahead in the development of fully nonlocal KEDFs we can ask if the TF functional is the only mathematical form adequate to construct nonlocal terms for KEDFs. An obvious candidate for this role is the vW functional. The aim of this paper is to study whether nonlocal terms with the structure of the vW functional are adequate for constructing KEDFs. A very preliminary scheme of this study was presented in Ref. [22].

II. THE VON WEIZSÄCKER FUNCTIONAL

The von Weizsäcker functional [17] was originally presented as a correction to the TF functional. Later on, it was conjectured that it must appear multiplied by a factor of $\frac{1}{9}$, to make the correction consistent with the limit of small moments in the linear response function of the free electron gas. This functional, the TF+$\frac{1}{9}$ vW or second-order gradient expansion approximation (GEA2), has been widely applied for estimating the total kinetic energy and yields energies with a relative error of about 1% when applied to atoms and molecules using *good* densities, i.e., those obtained with accurate methods like the Hartree-Fock or KS methods. Despite the success of the GEA2 in the estimation of total energies, many authors have proposed that the full von Weizsäcker functional, without any prefactor, should always appear in the expression of a KEDF [5,10,11,14,15,23–30]. There are several arguments these authors point out in order to justify the vW functional as the starting point in the KEDF (see a general review in [31]): (i) it is the correct one for systems with one or two electrons in the same spatial state; (ii) it gives the correct kinetic energy density in those spatial zones where the contribution of only one spatial orbital is dominant over all the others (these regions are very important in atoms, and include the cusps near the nuclei and the falling density tails far away from them; moreover, it is well know that density decays in those zones are related to the chemical potential of the system); (iii) the full vW functional is needed in order for functionals with a TF-like nonlocal term to reproduce the large-momentum limit of the linear response of the free electron gas; (iv) it naturally arises when the most naive approximation to the density matrix is made, i.e., when the matrix is assumed to be the product of the square root of the electron density evaluated in different points of the space; (v) it is a lower bound to the total kinetic energy of a fermionic system; (vi) it gives the correct kinetic energy for a system of bosons in their ground state; (vii) the vW functional includes derivatives, similar to the evaluation of the kinetic energy density via the KS orbitals.

Giving the deserved importance to these ideas, it can be argued that a functional approximation to the kinetic energy must be written as the full vW functional corrected with additional terms. In this sense Levy, Perdew, and Sahni [32] (see also [5,11,25] and references therein) proposed a final form for the KEDF as

$$T_S[n(\mathbf{r})] = T_{\rm vW}[n(\mathbf{r})] + T_{\theta}[n(\mathbf{r})], \qquad (10)$$

where the unknown $T_\theta[n]$ is the so-called Pauli functional [33,34]. For a boson system, the Pauli functional would be zero, but it appears in any fermion system as a consequence of the Pauli exclusion principle. Defining the Pauli potential as the functional derivative of $T_\theta[n]$, $v_\theta(\mathbf{r})=\delta T_\theta[n]/\delta n(\mathbf{r})$, the Euler equation becomes an equation similar to a KS equation for the square root of the total electron density:

$$\left(-\frac{1}{2}\nabla^2 + v_\theta(\mathbf{r}) + v_{\rm KS}(\mathbf{r})\right)\sqrt{n(\mathbf{r})} = \mu\sqrt{n(\mathbf{r})}. \qquad (11)$$

Here $-\frac{1}{2}\nabla^2$ corresponds to the vW functional, $v_{\rm KS}(\mathbf{r})$ is the KS potential, and μ is the chemical potential.

We define $\varphi(\mathbf{r})=\sqrt{n(\mathbf{r})}$, and call $\varphi(\mathbf{r})$ a *pseudo-orbital* because it shares the following characteristics with regular orbitals (like the KS or Hartree-Fock ones): (i) The squared orbitals, summed over all the occupied states, yield the total electron density; the squared pseudo-orbital gives by itself the total electron density $[\varphi(\mathbf{r})]^2=n(\mathbf{r})$; (ii) the square of the orbitals is normalized to unity, while the square of the pseudo-orbital is normalized to the number of electrons, $\int[\varphi(\mathbf{r})]^2 d\mathbf{r}=\int n(\mathbf{r})d\mathbf{r}=N$.

A. Some different expressions for the von Weizsäcker functional

The vW functional can be written in some different ways. The most common in the literature is

$$T_{\text{vW}}[n]=\frac{1}{8}\int d\mathbf{r}\frac{|\boldsymbol{\nabla} n(\mathbf{r})|^2}{n(\mathbf{r})}, \tag{12}$$

which is not adequate for its manipulation to get a fully nonlocal form. But $T_{\text{vW}}[n]$ can be written as

$$T_{\text{vW}}^{\text{Is}}[n]=\frac{1}{2}\int|\boldsymbol{\nabla}\varphi(\mathbf{r})|^2 d\mathbf{r}=\frac{1}{2}\int|\boldsymbol{\nabla}\varphi(\mathbf{r})||\boldsymbol{\nabla}\varphi(\mathbf{r})|d\mathbf{r}, \tag{13}$$

or, keeping the scalar product of the gradients of $\varphi(\mathbf{r})$,

$$T_{\text{vW}}^{\text{Iv}}[n]=\frac{1}{2}\int\boldsymbol{\nabla}\varphi(\mathbf{r})\cdot\boldsymbol{\nabla}\varphi(\mathbf{r})d\mathbf{r}. \tag{14}$$

On the other hand, the Laplacian of $n(\mathbf{r})$ has the correct dimensionality and the scaling properties to be a kinetic energy density, and integrates to zero in the whole space. That allows a new expression for the vW functional:

$$T_{\text{vW}}^{\text{II}}[n]=-\frac{1}{2}\int\varphi(\mathbf{r})\nabla^2\varphi(\mathbf{r})d\mathbf{r}=-\frac{1}{2}\int n^{1/2}(\mathbf{r})\nabla^2 n^{1/2}(\mathbf{r})d\mathbf{r}. \tag{15}$$

B. Relation to the kinetic energy density

The integrand of the first functional form $T_{\text{vW}}^{\text{I}}[n]$ is positive definite but that corresponding to the second $T_{\text{vW}}^{\text{II}}[n]$ is not—their difference is one-fourth of the Laplacian of the electron density—but both expressions always yield the same kinetic energy. The kinetic energy density (KED) can be defined as any function $t_S(\mathbf{r})$ that integrates to the exact total kinetic energy,

$$T_S[n]=\int d\mathbf{r}\; t_S(\mathbf{r}). \tag{16}$$

The KED of an electron system is not univocally defined (see [35] for a discussion) and two definitions are usually employed:

$$t_S^{\text{I}}(\mathbf{r})=\frac{1}{8}\sum_{i=1}^{N}\frac{|\boldsymbol{\nabla} n_i(\mathbf{r})|^2}{n_i(\mathbf{r})}=\frac{1}{2}\sum_{i=1}^{N}|\boldsymbol{\nabla} n_i^{1/2}(\mathbf{r})|^2 =\frac{1}{2}\sum_{i=1}^{N}\boldsymbol{\nabla} n_i^{1/2}(\mathbf{r})\,\boldsymbol{\nabla}\, n_i^{1/2}(\mathbf{r}), \tag{17}$$

$$t_S^{\text{II}}(\mathbf{r})=\frac{1}{2}\sum_{i=1}^{N}n_i^{1/2}(\mathbf{r})\nabla^2 n_i^{1/2}(\mathbf{r})=\frac{1}{8}\sum_{i=1}^{N}\frac{|\boldsymbol{\nabla} n_i(\mathbf{r})|^2}{n_i(\mathbf{r})}-\frac{1}{4}\sum_{i=1}^{N}\nabla^2 n_i(\mathbf{r}) =t_S^{I}(\mathbf{r})-\frac{1}{4}\nabla^2 n(\mathbf{r}), \tag{18}$$

where $n_i(\mathbf{r})=|\phi_i(\mathbf{r})|^2$ is the partial density corresponding to the ith KS orbital ϕ_i of an N-electron system. The first definition of the KED, $t_S^{\text{I}}(\mathbf{r})$, is related to $T_{\text{vW}}^{\text{I}}[n]$, and can be seen as the application of $T_{\text{vW}}^{\text{I}}[n]$ to each of the partial densities $n_i(\mathbf{r})$ of the electrons of the system. By simple inspection, the second definition $t_S^{\text{II}}(\mathbf{r})$ has a close relation to the second form $T_{\text{vW}}^{\text{II}}[n]$ of the vW functional. We will use these two forms to propose fully nonlocal terms for the KEDF, with a vW-like structure and closely related to the usual definitions of the KED.

III. KINETIC ENERGY FUNCTIONALS WITH NONLOCAL SIMPLIFIED TERMS THAT HAVE THE VON WEIZSÄCKER STRUCTURE: DENSITY-INDEPENDENT KERNEL

In this work we are going to present, following the simplified expression suggested by Eq. (8), three families of KEDFs, all with fully nonlocal terms with the structure of the vW functional. In order to simplify the discussion, and even though we are not going to develop any functional of this type here, we first show how to construct the simpler density-independent kernel functionals. We will extend these ideas for the construction of KEDFs with density-dependent kernels in Sec. IV.

A. First nonlocal functional (vectorial)

The first form of the fully nonlocal term with the vW structure is vectorial (NLS-vW-Iv functional) and can be constructed by introducing in Eq. (14) a second integral that couples the gradients of the pseudo-orbital through a Dirac delta function:

$$T_{\text{vW}}^{\text{Iv}}[n]=\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\;\boldsymbol{\nabla}\,\varphi(\mathbf{r})\cdot\boldsymbol{\nabla}\varphi(\mathbf{r}')\delta(\mathbf{r}-\mathbf{r}'), \tag{19}$$

and the nonlocal term is obtained by substituting the δ function by a kernel:

$$T_S^{\text{NLS-vW-Iv}}[n]=\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\;\boldsymbol{\nabla}\,\varphi(\mathbf{r})\cdot\boldsymbol{\nabla}\varphi(\mathbf{r}')\Omega(n_0,|\mathbf{r}-\mathbf{r}'|). \tag{20}$$

In order to be sure that the functional reproduces the linear response of the free electron gas, the second functional derivative must be calculated and the resulting expression evaluated at the homogeneous limit. We can save a lot of work by making the analysis presented in the Appendix. When the homogeneous limit is taken, several terms (those with any differential or gradient factor) yield a zero value and only two terms remain: those that have the two functional derivatives applied over the pseudo-orbital in two different points of space. Due to the symmetry of those terms it is possible to rewrite them as a double convolution product:

$$\left.\frac{\delta^2 T_S^{\text{NLS-vW-Iv}}[n]}{\delta n(\mathbf{r}_1)\delta n(\mathbf{r}_2)}\right|_{n_0} = \frac{1}{8n_0}\int d\mathbf{r}\int d\mathbf{r}'\,\nabla\,\delta(\mathbf{r}-\mathbf{r}_1)\cdot\nabla\delta(\mathbf{r}'-\mathbf{r}_2)\Omega(n_0,|\mathbf{r}-\mathbf{r}'|) + \frac{1}{8n_0}\int d\mathbf{r}\int d\mathbf{r}'\,\nabla\,\delta(\mathbf{r}-\mathbf{r}_2)\cdot\nabla\delta(\mathbf{r}'-\mathbf{r}_1)\Omega(n_0,|\mathbf{r}-\mathbf{r}'|) = \frac{1}{4n_0}\{\nabla\delta*\{\Omega*\nabla\delta\}\}. \tag{21}$$

The scaling of the Lindhard function imposes a scaling on the kernel of any functional constructed to reproduce the free electron linear response. The kernels of any of these functionals must scale with $2k_F$, so their dependence on the position vector $\mathbf{r}$ must be written as $2k_F\mathbf{r}$, i.e.,

$$\Omega(k_F,|\mathbf{r}-\mathbf{r}'|) = [2k_F]^3\omega(2k_F|\mathbf{r}-\mathbf{r}'|), \tag{22}$$

and using the properties of the Fourier transform it is easy to see that

$$\mathcal{F}[\Omega(k_F,|\mathbf{r}_1-\mathbf{r}_2|)] = \omega\left(\frac{|\mathbf{q}|}{2k_F}\right) = \omega(\eta), \tag{23}$$

where $\eta=|\mathbf{q}|/2k_F$ is the natural scaled variable in momentum space. Only with that scaling is the second functional derivative of the functional able to reproduce the Lindhard function.

Taking advantage of this scaling the aforementioned convolution products in Eq. (21) have a simpler expression in momentum space. After taking the Fourier transform, and using the scaled Fourier transform $\omega(\eta)$ of the kernel Ω, we obtain

$$\mathcal{F}\left(\left.\frac{\delta^2 T_S^{\text{NLS-vW-Iv}}[n]}{\delta n(\mathbf{r}_1)\delta n(\mathbf{r}_2)}\right|_{n_0}\right) = \frac{1}{4n_0}q^2\omega(\eta) = -\frac{1}{\tilde{\chi}_{\text{Lind}}(q)} = \frac{\pi^2}{k_F}F_{\text{Lind}}(\eta), \tag{24}$$

and an explicit relationship between $\omega(\eta)$ and the Lindhard function appears:

$$\omega(\eta) = \frac{F_{\text{Lind}}(\eta)}{3\eta^2}. \tag{25}$$

This expression for the kernel is much simpler than those corresponding to any functional with a TF-like nonlocal term, such as the CAT functional (see [4,11]). It is now necessary to clarify whether this kernel is adequate to perform calculations for both extended and localized systems. This kernel has a very strong singularity in the limit $\eta\to 0$, due to the behavior of the leading factor $1/(3\eta^2)$. The singularity can be eliminated by redesigning the kernel in order to have a finite value in the low-η limit. And if we include a full vW functional in $T_S[n]$, extracting the contribution of the vW term from the nonlocal kernel, its second functional derivative exactly cancels this singularity for $\eta\to 0$. So, as in many other functionals [5,11–14], the full vW term naturally appears in nonlocal functionals if we choose a definite mathematical form and force the functional to reproduce the linear response of the free electron gas. The new kernel $\omega(\eta)$ then becomes

$$\omega(\eta) = \frac{F_{\text{Lind}}(\eta)-1}{3\eta^2}. \tag{26}$$

On the other hand, the asymptotic behavior of the kernel for large values of η is very important for obtaining a kernel suitable for calculations on localized systems. As in the NLS-TF functionals [4], the kernel must go to zero as $\eta\to\infty$. The kernel in Eq. (26) tends to 1 for $\eta\to\infty$, giving a nondesirable Dirac δ contribution in position space. To avoid this inconvenience it is necessary to explicitly include in $T_S[n]$ the complete TF functional, without any prefactor. The final form of the modified kernel is then

$$\omega(\eta) = \frac{F_{\text{Lind}}(\eta)-3\eta^2-1}{3\eta^2}, \tag{27}$$

which has an adequate behavior, without any singularity in the limit $\eta\to 0$ and going to zero as $\eta\to\infty$. This has been accomplished by including both the TF and vW functionals in the fully nonlocal functional.

For the sake of comparison, Fig. 1 shows the behavior of the possible kernels with or without explicitly extracting the TF and the vW contributions, i.e., the kernels given by Eqs. (25)–(27).

As a summary, we require our functional $T_S[n]$ to have the following characteristics (see [4] for a similar discussion of functionals with TF-like nonlocal terms).

(i) $T_S[n]$ includes a nonlocal term that has the structure of the vW functional, coupling the contributions coming from different points of the space through a kernel Ω:

$$T_{\text{nl}}^{\text{NLS-vW-Iv}}[n] = \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\nabla\,\varphi(\mathbf{r})\cdot\nabla\varphi(\mathbf{r}')\Omega(n_0,|\mathbf{r}-\mathbf{r}'|). \tag{28}$$

(ii) The functional must reproduce the linear response of the electron gas (the scaling properties of the kernel are then fixed by the Lindhard function, and are the same as for the CAT functional [5] and for any functional that reproduces the linear response of the electron gas).

(iii) Even though the kernel is not necessarily normalized, we assume $\omega(\eta)$ to have a finite value for $\eta\to 0$ and that $\lim_{\eta\to\infty}\omega(\eta)=0$; with these properties $\omega(\eta)$ becomes an adequate kernel in position space, with no undesirable long-

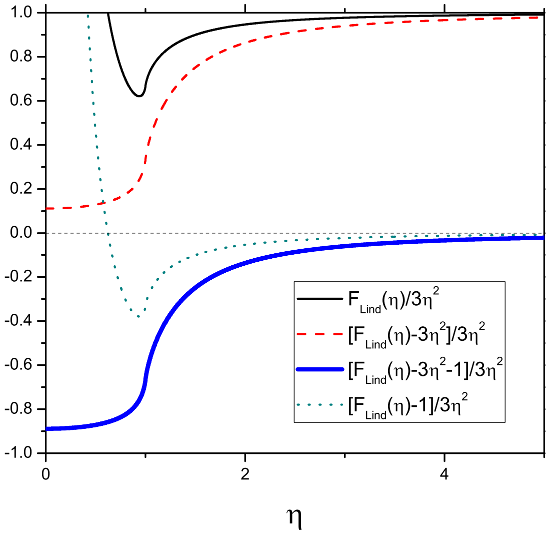

FIG. 1. (Color online) Different kernels for the NLS-vW functionals as functions of the scaled momentum η. They show the role played by the TF and vW terms.

range effects. The functional must include both a TF and a vW term and gives the correct kinetic energy in the homogeneous limit.

These three requirements are satisfied by the functional

$$T_S^{\text{NLS-vW-Iv}}[n] = T_{\text{vW}}[n] + T_{\text{TF}}[n] + T_{\text{nl}}^{\text{NLS-vW-Iv}}[n] \tag{29}$$

with the algebraic kernel given by Eq. (27).

B. Second nonlocal functional

Using the expression given in Eq. (15) we can proceed in the same way to construct a second local functional with a vW-like nonlocal term (NLS-vW-II functional). Equation (15) can be recast as

$$T_{\text{vW}}[n] = -\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\varphi(\mathbf{r})\nabla^2\varphi(\mathbf{r}')\,\delta(\mathbf{r}-\mathbf{r}'), \tag{30}$$

and writing a kernel Ω instead of the Dirac δ function we have

$$T_{\text{nl}}^{\text{NLS-vW-II}}[n] = -\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\varphi(\mathbf{r})\nabla^2\varphi(\mathbf{r}')\,\Omega(n_0,|\mathbf{r}-\mathbf{r}'|). \tag{31}$$

It is convenient to extract again the complete TF and vW functionals, and the KEDF becomes

$$T_S^{\text{NLS-vW-II}}[n] = T_{\text{vW}}[n] + T_{\text{TF}}[n] + T_{\text{nl}}^{\text{NLS-vW-II}}[n]. \tag{32}$$

In the homogeneous limit we have

$$\left.\frac{\delta^2 T_{\text{nl}}^{\text{NLS-vW-II}}[n]}{\delta n(\mathbf{r}_1)\,\delta n(\mathbf{r}_2)}\right|_{n_0} = -\frac{1}{8n_0}\int d\mathbf{r}\int d\mathbf{r}'\,\delta(\mathbf{r}-\mathbf{r}_1)\nabla^2\delta(\mathbf{r}'-\mathbf{r}_2)\Omega(n_0,|\mathbf{r}-\mathbf{r}'|) - \frac{1}{8n_0}\int d\mathbf{r}\int d\mathbf{r}'\,\delta(\mathbf{r}-\mathbf{r}_2)\nabla^2\delta(\mathbf{r}'-\mathbf{r}_1)\Omega(n_0,|\mathbf{r}-\mathbf{r}'|)$$
$$-\frac{1}{8n_0}\int d\mathbf{r}\int d\mathbf{r}'\,\nabla^2[\delta(\mathbf{r}'-\mathbf{r}_1)\,\delta(\mathbf{r}'-\mathbf{r}_2)]\Omega(n_0,|\mathbf{r}-\mathbf{r}'|). \tag{33}$$

As a result of the kernel normalization

$$\int d\mathbf{r}\;\Omega(n_0,|\mathbf{r}-\mathbf{r}'|) = C(\mathbf{r}') = C \tag{34}$$

(it must have the same value for any point of the space; remember we are in the homogeneous limit), the third term of the right-hand side of this equation can be integrated over $\mathbf{r}$, giving a constant value. So this third term now involves a product of Dirac δ functions with a zero result:

$$-\frac{1}{8n_0}C\int d\mathbf{r}'\,\nabla^2[\delta(\mathbf{r}'-\mathbf{r}_1)\,\delta(\mathbf{r}'-\mathbf{r}_2)] = -\frac{1}{8n_0}C2\int d\mathbf{r}'\;\nabla\,\delta(\mathbf{r}'-\mathbf{r}_1)\;\nabla\,\delta(\mathbf{r}'-\mathbf{r}_2) - \frac{1}{8n_0}C\int d\mathbf{r}'\,\nabla^2\delta(\mathbf{r}'-\mathbf{r}_1)\,\delta(\mathbf{r}'-\mathbf{r}_2)$$
$$-\frac{1}{8n_0}C\int d\mathbf{r}'\,\delta(\mathbf{r}'-\mathbf{r}_1)\nabla^2\delta(\mathbf{r}'-\mathbf{r}_2)$$
$$= -\frac{1}{8n_0}C[-2\nabla^2\delta(\mathbf{r}_1-\mathbf{r}_2) + \nabla^2\delta(\mathbf{r}_1-\mathbf{r}_2) + \nabla^2\delta(\mathbf{r}_1-\mathbf{r}_2)] = 0. \tag{35}$$

For the two other terms in Eq. (33) two convolution products are obtained; these products become the same by reordering the subindices

$$\begin{aligned}\left.\frac{\delta^2 T_{\rm nl}^{\text{NLS-vW-II}}[n]}{\delta n(\mathbf{r}_1)\delta n(\mathbf{r}_2)}\right|_{n_0} &= -\frac{1}{8n_0}\{\delta * \{\Omega * \nabla^2 \delta\}\}\\ &\quad -\frac{1}{8n_0}\{\{\delta * \Omega\} * \nabla^2 \delta\}\\ &= -\frac{3\pi^2}{4k_F^3}\{\delta * \{\Omega * \nabla^2\delta\}\}, \qquad (36)\end{aligned}$$

and when Fourier transforming we get an expression for the kernel,

$$\begin{aligned}\mathcal{F}\left(\left.\frac{\delta^2 T_{\rm nl}^{\text{NLS-vW-II}}[n]}{\delta n(\mathbf{r}_1)\delta n(\mathbf{r}_2)}\right|_{n_0}\right) &= \frac{3\pi^2}{k_F}\eta^2\omega(\eta)\\ &= \frac{\pi^2}{k_F}[F_{\rm Lind}(\eta) - 3\eta^2 - 1]. \qquad (37)\end{aligned}$$

We have obtained the same kernel given by Eq. (27), even though the functionals have a different structure. An equivalent result was also obtained for the kernels of the NLS-TF family of functionals [4].

C. First nonlocal functional (scalar)

We now develop a first scalar nonlocal functional (NLS-vW-Is functional). Rewriting Eq. (14) in the form

$$\begin{aligned}T_{\rm vW}[n] &= \frac{1}{2}\int |\nabla\varphi(\mathbf{r})|^2 d\mathbf{r}\\ &= \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'|\nabla\varphi(\mathbf{r})||\nabla\varphi(\mathbf{r}')|\delta(\mathbf{r}-\mathbf{r}'), \qquad (38)\end{aligned}$$

we obtain a new nonlocal term for $T[n]$ by introducing a kernel Ω instead of the Dirac δ function, i.e.,

$$T_{\rm nl}^{\text{NLS-vW-Is}}[n] = \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'|\nabla\varphi(\mathbf{r})||\nabla\varphi(\mathbf{r}')|\Omega(n_0,|\mathbf{r}-\mathbf{r}'|). \qquad (39)$$

As for the NLS-vW-Iv functional, when evaluating the functional derivative of the functional only those terms with a functional derivative of the absolute value of the gradient will not be zero. Deriving

$$\begin{aligned}\frac{\delta|\nabla\varphi(\mathbf{r})|}{\delta n(\mathbf{r}_1)} &= \frac{\delta}{\delta n(\mathbf{r}_1)}\sqrt{[\nabla\varphi(\mathbf{r})]^2}\\ &= \frac{1}{2}\frac{1}{\sqrt{[\nabla\varphi(\mathbf{r})]^2}}2\,\nabla\varphi(\mathbf{r})\cdot\nabla\left(\frac{1}{2\varphi(\mathbf{r})}\delta(\mathbf{r}-\mathbf{r}_1)\right)\\ &= \mathbf{u}_{\nabla\varphi(\mathbf{r})}\nabla\left(\frac{1}{2\varphi(\mathbf{r})}\delta(\mathbf{r}-\mathbf{r}_1)\right), \qquad (40)\end{aligned}$$

where $\mathbf{u}_{\nabla\varphi(\mathbf{r})}$ is the unit vector along the gradient of the pseudo-orbital. In the homogeneous limit we get

$$\left.\frac{\delta|\nabla\varphi(\mathbf{r})|}{\delta n(\mathbf{r}_1)}\right|_{n_0} = \frac{1}{2n_0^{1/2}}\mathbf{u}_{\nabla\varphi(\mathbf{r})}\nabla\,\delta(\mathbf{r}-\mathbf{r}_1), \qquad (41)$$

and the second functional derivative of the nonlocal term in the homogeneous limit is

$$\begin{aligned}\left.\frac{\delta^2 T_{\rm nl}^{\text{NLS-vW-Is}}[n]}{\delta n(\mathbf{r}_1)\delta n(\mathbf{r}_2)}\right|_{n_0} &= \frac{1}{8n_0}\int d\mathbf{r}\int d\mathbf{r}'[\mathbf{u}_{\nabla\varphi(\mathbf{r})}\nabla\,\delta(\mathbf{r}-\mathbf{r}_1)][\mathbf{u}_{\nabla\varphi(\mathbf{r}')}\nabla\,\delta(\mathbf{r}'-\mathbf{r}_2)]\Omega(\zeta(\mathbf{r},\mathbf{r}'),|\mathbf{r}-\mathbf{r}'|)\\ &\quad + \frac{1}{8n_0}\int d\mathbf{r}\int d\mathbf{r}'[\mathbf{u}_{\nabla\varphi(\mathbf{r})}\nabla\,\delta(\mathbf{r}-\mathbf{r}_2)][\mathbf{u}_{\nabla\varphi(\mathbf{r}')}\nabla\,\delta(\mathbf{r}'-\mathbf{r}_1)]\Omega(\zeta(\mathbf{r},\mathbf{r}'),|\mathbf{r}-\mathbf{r}'|),\end{aligned}$$

which can be arranged as two double convolution products,

$$\begin{aligned}\left.\frac{\delta^2 T_{\rm nl}^{\text{NLS-vW-Is}}[n]}{\delta n(\mathbf{r}_1)\delta n(\mathbf{r}_2)}\right|_{n_0} &= \frac{3\pi^2}{8k_F^3}\{\mathbf{u}_{\nabla\varphi(\mathbf{r})}\nabla\,\delta * \{\Omega * \mathbf{u}_{\nabla\varphi(\mathbf{r}')}\nabla\,\delta\}\}\\ &\quad + \frac{3\pi^2}{8k_F^3}\{\{\mathbf{u}_{\nabla\varphi(\mathbf{r})}\nabla\,\delta * \Omega\} * \mathbf{u}_{\nabla\varphi(\mathbf{r}')}\nabla\,\delta\}. \qquad (42)\end{aligned}$$

We have an indetermination, because the direction of the unit vector is not uniquely defined in the homogeneous limit (and we must multiply it by the gradient of a Dirac δ function). We decide that the unit vectors must have the same direction as in the NLS-vW-Iv functional: parallel to the gradients of the Dirac δ functions. In that case, the Fourier transform is quite similar to that used for obtaining the kernel of the NLS-vW-Iv functional. We have also extracted the contributions that come from the $T_{\rm TF}$ and $T_{\rm vW}$ functionals, and the kernel becomes the same one obtained for the two other types of functional,

$$\begin{aligned}&\left(\frac{\pi^2}{k_F}\right)^{-1}\mathcal{F}\left(\left.\frac{\delta^2 T_{nl}^{\text{NLS-vW-Is}}[n]}{\delta n(\mathbf{r}_1)\delta n(\mathbf{r}_2)}\right|_{n_0}\right)\\ &\quad = 3\eta^2\omega(\eta) = F_{\rm Lind}(\eta) - 3\eta^2 - 1. \qquad (43)\end{aligned}$$

We stress that indeterminations have been solved using an argument based on the similarity with the NLS-vW-Iv functional, which has a similar structure. We propose this functional here because it is much easier to evaluate than the NLS-vW-Iv functional in three-dimensional systems with spherical symmetry. So we must wait for the results we will present below to get confidence in using the functional.

IV. KINETIC ENERGY FUNCTIONALS WITH A NONLOCAL SIMPLIFIED TERM THAT HAVE THE VON WEIZSÄCKER STRUCTURE: DENSITY-DEPENDENT KERNEL

In order to take a step ahead in the description of nonlocal KEDFs, we want to study density-dependent kernels via the use of the two-body Fermi wave vector $\zeta(\mathbf{r},\mathbf{r}')$. As the behavior of the kernel $\omega(\eta)$ for both large and small values of η is the same as in the case of the density-independent kernels, the previous discussion about how the TF and vW terms must be included in $T_S[n]$ is also pertinent. But we now expect to get differential equations for the kernels, as yielded by the functionals with a TF-like nonlocal term (see [4]). In any case, we also expect kernels with a similar behavior to their density-independent counterparts, obtained by means of an algebraic equation.

A. First nonlocal functional (vectorial)

The procedure is the same that we used in Sec. III A for the density-independent kernel, verifying the three properties mentioned, and the nonlocal term is now given by

$$T_{\mathrm{nl}}^{\text{NLS-vW-Iv}}[n]=\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\boldsymbol{\nabla}\varphi(\mathbf{r})\cdot\boldsymbol{\nabla}\varphi(\mathbf{r}')\times\Omega(\zeta(\mathbf{r},\mathbf{r}'),|\mathbf{r}-\mathbf{r}'|),\tag{44}$$

with the new scaling factor $\zeta(\mathbf{r},\mathbf{r}')$.

The evaluation of the Fourier transform of the second functional derivative in the homogeneous limit gives an unusual result. Any term that contains a functional derivative of the kernel and $\zeta(\mathbf{r},\mathbf{r}')$ gives a zero value in the homogeneous limit (see the Appendix), because they always appear multiplied by the gradient of the electron density—which is constant in this limit. As a consequence, the kernel is the same one that we obtained for the density-independent functional. We then get an algebraic equation for the kernel, and not the differential equation usually obtained for density-dependent functionals [4]. Moreover, the kernel does not depend on the way we define the scaling factor $\zeta(\mathbf{r},\mathbf{r}')$.

B. Second nonlocal functional

The nonlocal term is now written as

$$T_{\mathrm{nl}}^{\text{NLS-vW-II}}[n]=-\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\varphi(\mathbf{r})\nabla^2\varphi(\mathbf{r}')\times\Omega(\zeta(\mathbf{r},\mathbf{r}'),|\mathbf{r}-\mathbf{r}'|).\tag{45}$$

For the second functional derivative of $T_{\mathrm{nl}}^{\text{NLS-vW-II}}[n]$ we get two new terms, both with first functional derivatives of the kernel:

$$\begin{aligned}\left.\frac{\delta^2 T_{\mathrm{nl}}^{\text{NLS-vW-II}}[n]}{\delta n(\mathbf{r}_1)\,\delta n(\mathbf{r}_2)}\right|_{n_0}={}&-\frac{1}{8n_0}\int d\mathbf{r}\int d\mathbf{r}'\,\delta(\mathbf{r}-\mathbf{r}_1)\nabla^2\delta(\mathbf{r}'-\mathbf{r}_2)\Omega(n_0,|\mathbf{r}-\mathbf{r}'|)-\frac{1}{8n_0}\int d\mathbf{r}\int d\mathbf{r}'\,\delta(\mathbf{r}-\mathbf{r}_2)\nabla^2\delta(\mathbf{r}'-\mathbf{r}_1)\Omega[n_0,|\mathbf{r}-\mathbf{r}'|]\\&-\frac{1}{4}\int d\mathbf{r}\int d\mathbf{r}'\nabla^2\delta(\mathbf{r}'-\mathbf{r}_2)\frac{d\Omega(n_0,|\mathbf{r}-\mathbf{r}'|)}{dk_F}\left.\frac{\delta\zeta(\mathbf{r},\mathbf{r}')}{\delta n(\mathbf{r}_1)}\right|_{n_0}\\&-\frac{1}{4}\int d\mathbf{r}\int d\mathbf{r}'\nabla^2\delta(\mathbf{r}'-\mathbf{r}_1)\frac{d\Omega(n_0,|\mathbf{r}-\mathbf{r}'|)}{dk_F}\left.\frac{\delta\zeta(\mathbf{r},\mathbf{r}')}{\delta n(\mathbf{r}_2)}\right|_{n_0}.\end{aligned}\tag{46}$$

These last two terms (which did not appear for the NLS-vW-II density-independent functional) equal each other and include a first functional derivative of $\zeta(\mathbf{r},\mathbf{r}')$. But we have

$$\left.\frac{\delta\zeta(\mathbf{r},\mathbf{r}')}{\delta n(\mathbf{r}_1)}\right|_{n_0}=\frac{(3\pi^2)^{1/3}}{6n_0^{2/3}}[\delta(\mathbf{r}-\mathbf{r}_1)+\delta(\mathbf{r}'-\mathbf{r}_1)],\tag{47}$$

and these terms are evaluated as

$$\begin{aligned}
&-\frac{1}{4}\int d\mathbf{r}\int d\mathbf{r}'\nabla^2\delta(\mathbf{r}'-\mathbf{r}_2)\frac{d\Omega[n_0,|\mathbf{r}-\mathbf{r}'|]}{dk_F}\left.\frac{\delta\zeta(\mathbf{r},\mathbf{r}')}{\delta n(\mathbf{r}_1)}\right|_{n_0}\\
&=-\frac{1}{4}\int d\mathbf{r}\int d\mathbf{r}'\nabla^2\delta(\mathbf{r}'-\mathbf{r}_2)\frac{d\Omega(n_0,|\mathbf{r}-\mathbf{r}'|)}{dk_F}\frac{(3\pi^2)^{1/3}}{6n_0^{2/3}}[\delta(\mathbf{r}-\mathbf{r}_1)+\delta(\mathbf{r}'-\mathbf{r}_1)]\\
&=-\frac{1}{4}\frac{(3\pi^2)^{1/3}}{6n_0^{2/3}}\int d\mathbf{r}\int d\mathbf{r}'\nabla^2\delta(\mathbf{r}'-\mathbf{r}_2)\frac{d\Omega(n_0,|\mathbf{r}-\mathbf{r}'|)}{dk_F}\delta(\mathbf{r}-\mathbf{r}_1)\\
&\quad-\frac{1}{4}\frac{(3\pi^2)^{1/3}}{6n_0^{2/3}}\int d\mathbf{r}'\,\delta(\mathbf{r}'-\mathbf{r}_1)\nabla^2\delta(\mathbf{r}'-\mathbf{r}_2)\int d\mathbf{r}\frac{d\Omega(n_0,|\mathbf{r}-\mathbf{r}'|)}{dk_F}\\
&=-\frac{1}{2}\frac{\pi^2}{4k_F^2}\left\{\left\{\delta*\frac{d\Omega}{dk_F}\right\}*\nabla^2\delta\right\},
\end{aligned}\tag{48}$$

where we have used that the kernel is normalized and that

$$\int d\mathbf{r}\frac{d\Omega(n_0,|\mathbf{r}-\mathbf{r}'|)}{dk_F}=\frac{d}{dk_F}\int d\mathbf{r}\ \Omega(n_0,|\mathbf{r}-\mathbf{r}'|)=\frac{d}{dk_F}C=0.\tag{49}$$

We get the final expression

$$\left.\frac{\delta^2T_{\text{nl}}^{\text{NLS-vW-II}}[n]}{\delta n(\mathbf{r}_1)\delta n(\mathbf{r}_2)}\right|_{n_0}=-\frac{3\pi^2}{4k_F^3}\{\delta*\{\Omega*\nabla^2\delta\}\}-\frac{\pi^2}{4k_F^2}\left\{\left\{\delta*\frac{d\Omega}{dk_F}\right\}*\nabla^2\delta\right\},\tag{50}$$

which gives the relation with the Lindhard function,

$$\mathcal{F}\left(\left.\frac{\delta^2T_{\text{nl}}^{\text{NLS-vW-II}}[n]}{\delta n(\mathbf{r}_1)\delta n(\mathbf{r}_2)}\right|_{n_0}\right)=\frac{\pi^2}{k_F}[3\eta^2\omega(\eta)-\eta^3\omega'(\eta)]\tag{51}$$

$$\begin{aligned}
&=\frac{\pi^2}{k_F}3\eta^2\left(\omega(\eta)-\frac{1}{3}\eta\omega'(\eta)\right)\\
&=\frac{\pi^2}{k_F}[F_{\text{Lind}}(\eta)-3\eta^2-1],
\end{aligned}\tag{52}$$

and the first-order differential equation for the kernel of this functional is

$$\omega(\eta)-\frac{1}{3}\eta\omega'(\eta)=\frac{F_{\text{Lind}}(\eta)-3\eta^2-1}{3\eta^2}.\tag{53}$$

Note that we have obtained a first-order differential equation, much simpler than the second-order ones that are usually obtained for functionals with a TF-like nonlocal term [4,11,15]. For the numerical solution of Eq. (53) we have chosen a Runge-Kutta method, starting the integration at infinity to avoid numerical problems.

C. First nonlocal functional (scalar)

In the way as for the other two functionals, the density-dependent kernel is introduced through the two-body Fermi wave vector $\zeta(\mathbf{r},\mathbf{r}')$. Using the same procedure explained for the density-independent case, the nonlocal term is now given by

$$T_{\text{nl}}^{\text{NLS-vW-Is}}[n]=\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'|\nabla\varphi(\mathbf{r})||\nabla\varphi(\mathbf{r}')|\times\Omega(\zeta(\mathbf{r},\mathbf{r}'),|\mathbf{r}-\mathbf{r}'|).\tag{54}$$

As obtained for the NLS-vW-Iv functional, the evaluation of the Fourier transform of the second functional derivative in the homogeneous limit gives again the result that the kernel coincides with that obtained for the density-independent functional. As a consequence, we get an algebraic equation instead of the differential equation usually found for density-dependent functionals.

So for the three NLS-vW functionals (in both the density-dependent and density-independent cases) we have obtained the same kernel, except for the density-dependent kernel of the NLS-vW-II functional. Figure 2 shows the kernels for all the functionals. All density-independent functionals share the kernel with the density-dependent type I functionals (NLS-vW-I). Note that type-II density-dependent functional (NLS-vW-II) has a softer structure.

D. Evaluation in momentum space

The NLS-vW functionals have another important advantage that must be pointed out. By construction, these nonlocal functionals can be evaluated as a single integral in momentum space if an adequate reference density is defined, following the method developed by Wang, Govind, and Carter for their functional [15]. The expression that evaluates the nonlocal term with the vW-like structure can be easily obtained through

$$T_{\text{nl}}^{\text{NLS-vW}}[n]=\frac{1}{2}\int d\mathbf{q}[q\varphi(\mathbf{q})]^2\omega(\eta),\tag{55}$$

where $\varphi(\mathbf{q})$ is the Fourier transform of the pseudo-orbital $\varphi(\mathbf{q})=\mathcal{F}[\varphi(\mathbf{r})]$. Using this numerical approach, quasilinear scaling for the computational cost can be achieved and large

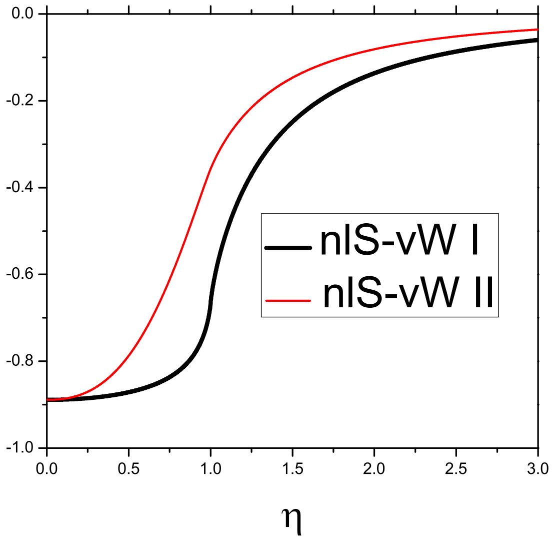

FIG. 2. (Color online) Kernels for the NLS-vW functionals as functions of the scaled momentum η. Label I indicates all density-dependent and density-independent kernels, except the density-dependent NLS-vW-II.

extended systems may be calculated. Note that all the functional forms previously presented in the paper yield the same expression in momentum space, namely, Eq. (55).

V. CLOSED-SHELL ATOMS: TOTAL KINETIC ENERGIES

We must point out that all calculations presented in this paper have been done with double density-dependent kernel functionals, i.e.,

$$T_S^{\text{NLS-vW}}[n] = T_{\text{vW}}[n] + T_{\text{TF}}[n] + T_{\text{nl}}^{\text{NLS-vW}}[n],$$

where the kernel of the nonlocal term $T_{\text{nl}}^{\text{NLS-vW}}[n]$ uses a two-body Fermi wave vector $\zeta(\mathbf{r},\mathbf{r}')$ as the scaling factor. We will not present any test of the simpler density-independent functionals.

We first check the quality of our proposal for the development of KEDFs by making an evaluation of the total kinetic energy of atoms using good electron densities. The NLS-vW functionals depend only on the parameter γ, which defines the power in the scaling factor $\zeta(\mathbf{r},\mathbf{r}')$ of the double density-dependent kernel. So the comparison of the total kinetic energy with the exact one (i.e., the solution of the KS method) can be used as a first step to fix the best value of γ. With this aim, we have evaluated the kinetic energy with the NLS-vW functionals using the output densities obtained by the solution of the KS scheme through the GAUSSIAN package [36]. We have performed total energy calculations for some closed-shell atoms, from He to Xe, with the basis set 6-311++$G(d,p)$ for all atoms (for Sr and Xe the basis 3-21G^{**} was used instead). These basis sets are big enough to yield quality electronic densities and energies within the local density approximation for the XC. Note that all the calculations were performed for the most sophisticated functionals with the double density-dependent kernels.

In Table I we present the relative errors of the total kinetic energies obtained with the NLS-vW-Iv functional, as compared with the KS *exact* results, as well as the average of the absolute values of the errors. We get relative errors close to 4%, and these large errors slightly depend on γ. In any case, the improvement saturates for $\gamma \leq -0.6$. The results show that this functional yields accurate energies for some atoms of intermediate size (Ne to Ca), but gives large errors for the other cases. We think this functional is not useful for evaluating the kinetic energies because the average errors for any value of γ are too large (the results for the best semilocal functionals [35] and for the CAT and NLS-TF families [4] are less than 1%).

In Table II the relative errors of the total kinetic energies obtained with the NLS-vW-II functional are shown. Again, the errors vary slightly with γ. In this case we get small values of relative errors, with an accuracy close to that of the semilocal [35] and fully nonlocal functionals [4] studied before. The best results are found for $\gamma \in (-0.2, -0.3)$, where the mean of relative errors is 0.5%, smaller than for any functional of the CAT and NLS-TF families [4].

Table III summarizes the relative errors of the total kinetic energies as obtained with the NLS-vW-Is functional. We get small relative errors, the smallest of any functionals we have studied, in this paper and in Refs. [35,4]. But we must re-

TABLE I. Relative errors for the functional NLS-vW-Iv.

γ	He	Be	Ne	Mg	Ar	Ca	Kr	Sr	Xe	Av.
0.5	−0.058	−0.050	−0.011	−0.012	0.001	0.006	0.075	0.045	0.123	0.042
0.3	−0.052	−0.046	−0.009	−0.010	0.002	0.007	0.076	0.046	0.124	0.041
0.1	−0.047	−0.042	−0.007	−0.008	0.003	0.008	0.076	0.046	0.125	0.040
−0.2	−0.043	−0.037	−0.003	−0.006	0.004	0.009	0.077	0.047	0.125	0.039
−0.3	−0.043	−0.036	−0.003	−0.006	0.004	0.009	0.077	0.047	0.126	0.039
−0.4	−0.043	−0.035	−0.002	−0.005	0.004	0.008	0.078	0.047	0.126	0.039
−0.5	−0.043	−0.034	−0.001	−0.005	0.003	0.008	0.078	0.047	0.126	0.038
−0.6	−0.044	−0.032	−0.001	−0.005	0.003	0.008	0.078	0.047	0.126	0.038
−0.7	−0.045	−0.031	0.000	−0.004	0.003	0.007	0.078	0.047	0.127	0.038
−0.8	−0.045	−0.031	0.001	−0.003	0.003	0.007	0.077	0.047	0.127	0.038
KS	2.761	14.350	128.155	198.885	524.829	675.535	2749.055	3123.615	7174.034	

TABLE II. Relative errors for the functional NLS-vW-II.

γ	He	Be	Ne	Mg	Ar	Ca	Kr	Sr	Xe	Av.
0.5	0.032	0.042	0.019	0.019	0.016	0.015	0.010	0.007	0.005	0.018
0.3	0.024	0.036	0.016	0.017	0.014	0.013	0.009	0.006	0.004	0.015
0.1	0.011	0.029	0.011	0.013	0.011	0.010	0.007	0.004	0.003	0.011
−0.1	−0.005	0.021	0.006	0.009	0.007	0.006	0.005	0.002	0.001	0.007
−0.3	−0.019	0.015	−0.003	0.001	0.001	0.001	0.002	−0.001	−0.002	0.005
−0.5	−0.032	0.008	−0.007	−0.003	0.000	0.000	−0.001	−0.004	−0.003	0.006
−0.7	−0.042	−0.005	−0.006	0.001	0.001	0.000	0.000	−0.003	−0.002	0.007
−0.9	−0.050	−0.020	−0.004	0.003	0.004	0.003	−0.001	−0.004	−0.002	0.010
−1.1	−0.057	−0.034	−0.006	0.002	0.007	0.007	−0.002	−0.005	−0.005	0.014
−1.3	−0.062	−0.045	−0.010	−0.001	0.008	0.008	−0.002	−0.005	−0.007	0.016
KS	2.761	14.350	128.155	198.885	524.829	675.535	2749.055	3123.615	7174.034	

member that this functional is not completely justified, because we found an indeterminancy when evaluating its kernel, but it yields really good values for the total kinetic energies. For $\gamma=1$ (relative error 0.4%) the two-body scaling factor $\zeta(\mathbf{r},\mathbf{r}')$ is the arithmetic average of the Fermi momenta at $\mathbf{r}$ and $\mathbf{r}'$.

Summing up, of all the functionals we have tested, the NLS-vW-II and NLS-vW-Is functionals appear to be the nonlocal functionals that yield the best total kinetic energies (about 0.5%). Slighter larger errors (0.8%) are found for the CAT and NLS-TF functionals [4] and the best semilocal functionals also achieve mean errors smaller than 1%. The NLS-vW-Iv functional shows bigger errors when evaluating the total kinetic energies and we think it is not a reliable KEDF.

But these results must be corroborated by some other criterion in order to ensure the general quality of the KEDFs and to propose a value for γ. We are now going to put our attention on the local behavior of the functionals, by studying their kinetic energy density (KED), following the ideas presented in [35].

VI. LIGHT ATOMS: TOTAL KINETIC ENERGIES AND THE QUALITY OF THE FUNCTIONALS' LOCAL BEHAVIOR

Section V showed that the nonlocal functionals NLS-vW-II and NLS-vW-Is give very good results for the total kinetic energies in closed-shell atoms. In order to assess the local performance of the KEDFs, in two previous papers we have presented a comparative study of the KED for a number of semilocal functionals [35] and for the CAT and NLS-TF functional families [4]. We concluded that all the semilocal functionals but those with a full vW term place the KED not included in the TF functional in wrong regions of space [35], whereas the functionals with a TF-like nonlocal term (the CAT and NLS-TF families) give better KEDs than the TF and semilocal functionals. Since this result is a positive outcome of adding fully nonlocal terms into the KEDF, we now present the results for the quality of the KED for the functionals we are studying in this paper.

Following Ref. [35], an infinite set of valid KEDs $t_S^L(\mathbf{r})$ can be used (see, e.g., Ref. [37])

TABLE III. Relative errors for the functional NLS-vW-Is.

γ	He	Be	Ne	Mg	Ar	Ca	Kr	Sr	Xe	Av.
1.6	0.012	0.028	0.007	0.008	0.004	0.002	−0.001	−0.001	−0.003	0.007
1.4	0.008	0.024	0.006	0.006	0.003	0.001	−0.002	−0.002	−0.003	0.006
1.2	0.004	0.021	0.004	0.004	0.002	0.000	−0.003	−0.003	−0.004	0.005
1.0	−0.001	0.017	0.002	0.003	0.000	−0.001	−0.004	−0.003	−0.004	0.004
0.8	−0.008	0.012	−0.001	0.001	−0.001	−0.003	−0.005	−0.004	−0.005	0.004
0.6	−0.015	0.006	−0.003	−0.001	−0.003	−0.004	−0.006	−0.005	−0.005	0.005
0.4	−0.025	−0.002	−0.006	−0.004	−0.005	−0.006	−0.007	−0.006	−0.006	0.007
0.2	−0.039	−0.011	−0.009	−0.006	−0.007	−0.008	−0.008	−0.007	−0.007	0.011
−0.2	−0.080	−0.033	−0.017	−0.014	−0.013	−0.014	−0.011	−0.010	−0.009	0.022
−0.4	−0.099	−0.043	−0.023	−0.018	−0.017	−0.017	−0.014	−0.012	−0.010	0.028
KS	2.761	14.350	128.155	198.885	524.829	675.535	2749.055	3123.615	7174.034	

TABLE IV. Values of the Slater orbital exponents.

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

$$t_S^L(\mathbf{r}) = \frac{1}{2}\sum_{i=1}^{N} |\nabla \phi_i(\mathbf{r})|^2 + a\nabla^2 n(\mathbf{r}), \tag{56}$$

where $t_S^L(\mathbf{r})$ is 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 define a *quality factor*

$$\sigma = \frac{\int d\mathbf{r}|t_S^L(\mathbf{r}) - t_S^{\text{func}}(\mathbf{r})|}{T_S[n]}, \tag{57}$$

where $t_S^{\text{func}}(\mathbf{r})$ is the approximate KED for a given functional. The value of σ can be interpreted as the amount of the approximated KED that is misplaced when compared to the distribution $t_S^L(\mathbf{r})$. To test every functional in the best conditions for itself, we have compared its approximate KED with its closest $t_S^L(\mathbf{r})$, minimizing the value of σ when varying the parameter a, using a *golden search* algorithm [38]. After the minimization process, each functional has a given value of a that yields the lowest value of σ. The closest $t_S^L(\mathbf{r})$ is then constructed by substituting this value of the parameter a in Eq. (56).

As commented in Refs. [4,35], we will represent the approximate orbitals of an atom by orthogonalized Slater orbitals as we need correct evaluation of the atomic electron densities and KEDs, and these Slater orbitals do not add any spurious behavior when the Laplacian of the density is evaluated, and the correct cusp conditions and density decay for $r\to\infty$ can be achieved. The values of the exponents for the Slater orbitals we have used in this paper are presented in Table IV [39,40].

For a simpler presentation we will discuss only atoms with complete shells and complete half shells, from He to Ar, and we discuss results corresponding to the functionals that gave the best total kinetic energies in Sec. V. For that reason, we do not present any result obtained with the NLS-vW-Iv functional.

Table V shows the percent relative errors for the total kinetic energies when evaluated with the NLS-vW-II functional using the density corresponding to the orthogonalized Slater orbitals. The best errors are smaller than 1% (as found in Sec. V), close to the best semilocal [35] and also to the CAT and NLS-TF results [4]. We present the optimized values for the quality factor σ in Table VI. They are smaller than, but close to, those obtained with the TF functional, meaning a better description of the KED than any semilocal functional. The best values for σ are for $\gamma\approx-1/4$, a value that also corresponds to the best values of the energy obtained for the closed-shell atoms (Sec. V), whereas the best results obtained with the orthogonalized Slater orbitals are closer to $\gamma\approx-1/2$.

The NLS-vW-Is functional presents its larger errors for the lightest atoms, but for a range of values of γ the functional yields errors smaller than 1% (see Table VII), i.e., has the same level of accuracy as the best semilocal and CAT and NLS-TF families [4,35]. When γ is about 0.2 we obtain a mean error of about 0.4%, the best result we have found up

TABLE V. Relative errors in the kinetic energies obtained with the functional NLS-vW-II.

γ	He	Be	N	Ne	Mg	P	Ar	Av.
0.5	0.046	0.047	0.018	0.031	0.027	0.021	0.019	0.030
0.3	0.036	0.042	0.013	0.027	0.024	0.019	0.017	0.025
0.1	0.024	0.035	0.008	0.022	0.020	0.015	0.014	0.020
−0.1	0.011	0.026	0.001	0.017	0.015	0.010	0.009	0.013
−0.3	−0.001	0.020	−0.006	0.008	0.007	0.004	0.003	0.007
−0.5	−0.011	0.013	−0.008	0.003	0.004	0.002	0.003	0.006
−0.7	−0.019	0.001	−0.009	0.002	0.006	0.004	0.004	0.006
−0.9	−0.026	−0.013	−0.012	0.002	0.008	0.008	0.007	0.011
−1.1	−0.031	−0.027	−0.018	0.002	0.007	0.010	0.010	0.015
−1.3	−0.036	−0.038	−0.026	0.000	0.005	0.010	0.011	0.018
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 σ obtained with the functional NLS-vW-II.

γ	He	Be	N	Ne	Mg	P	Ar	Av.
0.5	0.160	0.161	0.161	0.164	0.161	0.153	0.147	0.158
0.3	0.156	0.159	0.159	0.163	0.160	0.153	0.147	0.157
0.1	0.154	0.157	0.157	0.163	0.160	0.152	0.146	0.156
−0.1	0.154	0.157	0.153	0.160	0.157	0.150	0.145	0.154
−0.3	0.155	0.160	0.154	0.158	0.158	0.151	0.146	0.155
−0.5	0.157	0.160	0.156	0.161	0.162	0.155	0.149	0.157
−0.7	0.159	0.159	0.156	0.163	0.165	0.158	0.151	0.159
−0.9	0.160	0.157	0.155	0.163	0.165	0.160	0.152	0.159
−1.1	0.162	0.157	0.154	0.163	0.164	0.161	0.154	0.159
−1.3	0.164	0.157	0.153	0.163	0.162	0.161	0.154	0.159
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

to now in our studies. The results for the KED are presented in Table VIII, where the minimized values of σ after varying the parameter a are given. We get better results than with the NLS-vW-II functional, with $\sigma \approx 0.151$ for $\gamma \approx -0.35$. This best value of γ is different from that obtained from the results of the total kinetic energy in Sec. V ($\gamma \approx 0.9$) or with the density coming from the orthogonalized Slater orbital in this section ($\gamma \approx 0.2$).

The NLS-vW functionals we have studied in this section yield in general better results than the best semilocal functionals [35], improving also the results of the fully nonlocal CAT and NLS-TF functionals [4]. Specifically, they present a better description of the global behavior of the KED than any semilocal functional. In relation to the value of the parameter γ to be used, the NLS-vW-II functional is more stable in its results, and the value $\gamma = -1/2$ can be considered as the best choice: it gives very good results for the energies (with mean errors about 0.6%) and a not so good result for the mean value of σ (quite close to the TF one). For the NLS-vW-Is functional the best results in each case correspond to different values of γ, and the γ to be recommended is $-1/4$, with errors in the energies of about 2.5% and a smaller value of σ. These values of γ are used in Figs. 3 and 4.

When the approximated KED of the CAT and NLS-TF functionals were tested they improved the description of those atomic regions close to the neighborhood of the nuclei, as explained in [4]. But the NLS-vW functionals behave differently: when the Laplacian contribution is introduced, we have a quite different KED due to the effects of the differential operators in the nonlocal terms that correct the full vW functional (no such operators appear in any nonlocal term constructed with a TF-like functional). So, KEDs coming from the NLS-vW functionals are not so closely related to the first term in Eq. (56); for that reason, whereas the CAT and NLS-TF functionals correctly describe regions in the neighborhood of the atomic nuclei, Fig. 3 shows that the NLS-vW functionals seem to better describe the decay of the main peak of the KED. This can also be seen in Fig. 4, where we present the differences among the approximate KEDs and the orbital-based one. We see that the NLS-vW functionals make a good description of the intermediate region between s and p shells, $r \in (0.2, 0.4)$, whereas the CAT and NLS-TF functionals give a better description of regions close to the "core" electrons ($r \leq 0.1$).

VII. CONCLUSIONS

Our proposal for the construction of fully nonlocal kinetic energy functionals suggests a structure for the nonlocal term that follows that of the vW functional by modifying it through a universal kernel tailored to reproduce the linear response function of the free electron gas. In the nonlocal terms we have allowed nonspherical averaging by introducing the two-body Fermi wave vector $\zeta_\gamma(\mathbf{r},\mathbf{r}')$, a mean of the Fermi wave vectors raised to the power γ at $\mathbf{r}$ and $\mathbf{r}'$. We must point out that the equations for the kernel are much simpler than the differential equations obtained for the fully nonlocal functionals like CAT [5], NLS-TF [4], and those

TABLE VII. Relative errors for the kinetic energy for the functional NLS-vW-Is.

γ	He	Be	N	Ne	Mg	P	Ar	Av.
1.0	0.042	0.030	0.004	0.014	0.010	0.005	0.003	0.015
0.8	0.035	0.025	0.000	0.012	0.008	0.003	0.001	0.012
0.6	0.027	0.019	−0.004	0.008	0.005	0.001	−0.001	0.009
0.4	0.015	0.011	−0.008	0.005	0.003	−0.002	−0.003	0.006
0.2	−0.003	0.001	−0.014	0.001	−0.001	−0.004	−0.005	0.004
−0.2	−0.044	−0.022	−0.029	−0.010	−0.009	−0.011	−0.012	0.020
−0.4	−0.060	−0.032	−0.036	−0.018	−0.014	−0.016	−0.015	0.027
−0.6	−0.074	−0.043	−0.041	−0.023	−0.017	−0.017	−0.017	0.033
−0.8	−0.086	−0.056	−0.044	−0.026	−0.017	−0.016	−0.016	0.037
−1.0	−0.096	−0.069	−0.048	−0.028	−0.016	−0.013	−0.013	0.041
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 VIII. Values of σ obtained with the functional NLS-vW-Is.

γ	He	Be	N	Ne	Mg	P	Ar	Av.
1.0	0.158	0.162	0.172	0.175	0.170	0.164	0.158	0.166
0.8	0.157	0.159	0.170	0.173	0.169	0.162	0.156	0.164
0.6	0.156	0.156	0.167	0.172	0.167	0.161	0.155	0.162
0.4	0.152	0.153	0.165	0.170	0.166	0.159	0.154	0.160
0.2	0.147	0.151	0.162	0.168	0.164	0.158	0.152	0.157
−0.2	0.146	0.148	0.156	0.161	0.157	0.151	0.146	0.152
−0.4	0.147	0.153	0.155	0.158	0.154	0.149	0.144	0.151
−0.6	0.149	0.157	0.156	0.158	0.154	0.148	0.144	0.152
−0.8	0.151	0.160	0.158	0.158	0.155	0.149	0.145	0.154
−1.0	0.152	0.162	0.161	0.160	0.158	0.152	0.146	0.156
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

discussed in [14], being in all cases independent of the value of the parameter γ. Even more, we have found that a density-dependent kernel can be obtained through an algebraic equation.

The kernels we have obtained for all the functionals are adequate for calculations in position space (for both localized and extended systems), with no undesirable long-range effects. The functionals explicitly include the TF and the vW terms. We must remark that all the proposed NLS-vW functionals verify that $\lim_{\eta\to 0}\omega(\eta)=-8/9$ (see Fig. 1); this means that these approximations not only give the TF functional in the homogeneous limit, but naturally include the second-order gradient correction for slowly varying density regions. Note also that the kernels are negative for all values of η, but with $\omega(\eta)>-8/9$. For that reason, all the proposed functionals $T[n]$ are bounded between the TF+$\frac{1}{9}$vW and the TF+vW functionals.

Moreover, these nonlocal NLS-vW functionals can be evaluated as a single integral in momentum space if an adequate reference density is defined. That means a quasilinear scaling for the computational cost, and may allow the calculation of large systems.

We have checked these functionals using good atomic densities, obtaining for the functionals NLS-vW-II and NLS-vW-Is the most accurate total kinetic energies (about 0.5%) in the literature. We have also studied the KEDs by means of the quality factor σ, which allows us to make a quantitative test of the local behavior of the functionals [4,35]. With the same trend as in the CAT and NLS-TF families, the NLS-vW functionals clearly improve the values of σ, giving better KEDs than any semilocal or the TF functional. The behavior of the KEDs shows that they better describe the decay of the main peak and make a good description of the intermediate region between the s and p shells, whereas the CAT and

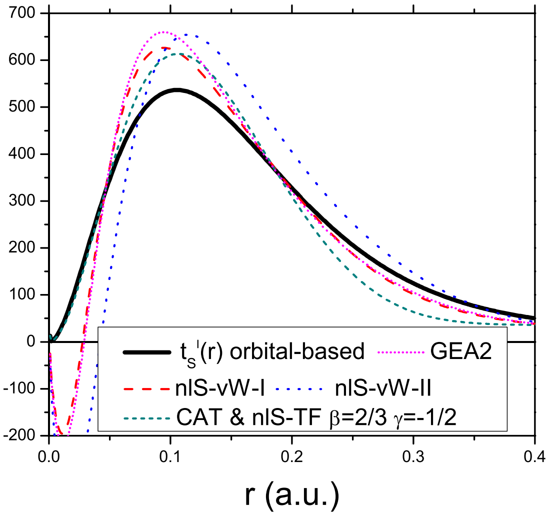

FIG. 3. (Color online) Kinetic energy density of the Ne atom (multiplied by $4\pi r^2$) for some selected functionals.

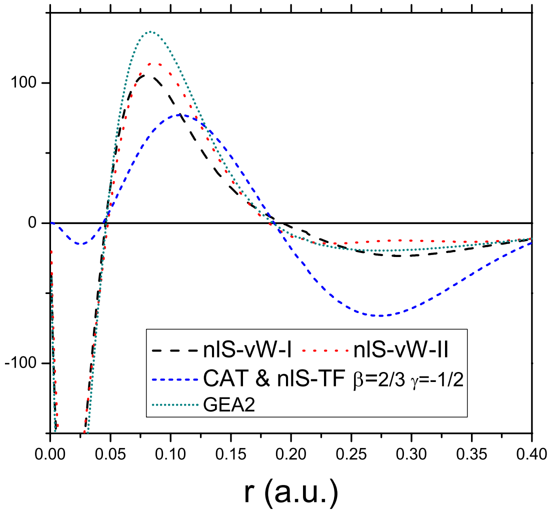

FIG. 4. (Color online) Differences of the kinetic energy density of the Ne atom (multiplied by $4\pi r^2$) for some selected functionals, when compared with the orbital-based kinetic energy density t_S^{I}.

NLS-TF functionals correctly describe regions closer to the core electrons.

We can conclude that these functionals with a vW-like nonlocal term give excellent results for the total kinetic energies of atoms and a much better description of the KED than the semilocal functionals. These results allow strengthening of the concept that with highly nonlocal models for the kinetic energy functionals good results for both the energies and the KEDs can be obtained.

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APPENDIX

We will use in this appendix the general expression for the nonlocal term of the NLS-vW-Iv density functional:

$$T_S^{\text{NLS-vW}}[n] = \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\, \nabla\varphi(\mathbf{r})\cdot\nabla\varphi(\mathbf{r}') \times\Omega(\zeta(\mathbf{r},\mathbf{r}'),|\mathbf{r}-\mathbf{r}'|).$$

The second functional derivative yields

$$\begin{aligned}\frac{\delta^2 T_S^{\mathrm{vWnl}}[n]}{\delta n(\mathbf{r}_1)\,\delta n(\mathbf{r}_2)} &= \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\frac{\delta\nabla\varphi(\mathbf{r})}{\delta n(\mathbf{r}_1)}\cdot\frac{\delta\nabla\varphi(\mathbf{r}')}{\delta n(\mathbf{r}_2)}\Omega(\zeta(\mathbf{r},\mathbf{r}'),|\mathbf{r}-\mathbf{r}'|) + \text{c.i.} + \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\frac{\delta^2\nabla\varphi(\mathbf{r})}{\delta n(\mathbf{r}_1)\,\delta n(\mathbf{r}_2)}\nabla\varphi(\mathbf{r}')\Omega(\zeta(\mathbf{r},\mathbf{r}'),|\mathbf{r}\\ &\quad -\mathbf{r}'|) + \text{c.i.} + \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\frac{\delta\nabla\varphi(\mathbf{r})}{\delta n(\mathbf{r}_1)}\cdot\nabla\varphi(\mathbf{r}')\frac{\delta\Omega(\zeta(\mathbf{r},\mathbf{r}'),|\mathbf{r}-\mathbf{r}'|)}{\delta n(\mathbf{r}_2)} + \text{c.i.}\\ &\quad + \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\nabla\varphi(\mathbf{r})\cdot\delta\nabla\varphi(\mathbf{r}')\frac{\delta^2\Omega(\zeta(\mathbf{r},\mathbf{r}'),|\mathbf{r}-\mathbf{r}'|)}{\delta n(\mathbf{r}_1)\,\delta n(\mathbf{r}_2)}.\end{aligned} \tag{A1}$$

After each term, c.i. means all the equivalent terms, with the same structure as the term explicitly written, that come about by changing the corresponding indices $\mathbf{r}_1$ and $\mathbf{r}_2$ of the derivatives and the points $\mathbf{r}$ and $\mathbf{r}'$ used in the evaluations of the integrals.

In the homogeneous limit we have

$$\begin{aligned}\left.\frac{\delta^2 T_S^{\mathrm{vWnl}}[n]}{\delta n(\mathbf{r}_1)\,\delta n(\mathbf{r}_2)}\right|_{n_0} &= \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\left.\frac{\delta\nabla\varphi(\mathbf{r})}{\delta n(\mathbf{r}_1)}\right|_{n_0}\cdot\left.\frac{\delta\nabla\varphi(\mathbf{r}')}{\delta n(\mathbf{r}_2)}\right|_{n_0}\Omega(n_0,|\mathbf{r}-\mathbf{r}'|) + \text{c.i.}\\ &\quad + \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\left.\frac{\delta^2\nabla\varphi(\mathbf{r})}{\delta n(\mathbf{r}_1)\,\delta n(\mathbf{r}_2)}\right|_{n_0}\nabla n_0^{1/2}\Omega(n_0,|\mathbf{r}-\mathbf{r}'|) + \text{c.i.}\\ &\quad + \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\left.\frac{\delta\nabla\varphi(\mathbf{r})}{\delta n(\mathbf{r}_1)}\right|_{n_0}\cdot\nabla n_0^{1/2}\left.\frac{\delta\Omega(\zeta(\mathbf{r},\mathbf{r}'),|\mathbf{r}-\mathbf{r}'|)}{\delta n(\mathbf{r}_2)}\right|_{n_0} + \text{c.i}\,.\\ &\quad + \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\nabla n_0^{1/2}\,\nabla n_0^{1/2}\left.\frac{\delta^2\Omega(\zeta(\mathbf{r},\mathbf{r}'),|\mathbf{r}-\mathbf{r}'|)}{\delta n(\mathbf{r}_1)\,\delta n(\mathbf{r}_2)}\right|_{n_0} + \text{c.i.}\end{aligned}$$

But $\nabla(n_0^{1/2})=0$ and only two terms are nonzero:

$$\begin{aligned}\left.\frac{\delta^2 T_S^{\mathrm{vWnl}}[n]}{\delta n(\mathbf{r}_1)\,\delta n(\mathbf{r}_2)}\right|_{n_0} &= \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\left.\frac{\delta\nabla\varphi(\mathbf{r})}{\delta n(\mathbf{r}_1)}\right|_{n_0}\cdot\left.\frac{\delta\nabla\varphi(\mathbf{r}')}{\delta n(\mathbf{r}_2)}\right|_{n_0}\Omega(n_0,|\mathbf{r}-\mathbf{r}'|)\\ &\quad + \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\left.\frac{\delta\nabla\varphi(\mathbf{r})}{\delta n(\mathbf{r}_2)}\right|_{n_0}\cdot\left.\frac{\delta\nabla\varphi(\mathbf{r}')}{\delta n(\mathbf{r}_1)}\right|_{n_0}\Omega(n_0,|\mathbf{r}-\mathbf{r}'|).\end{aligned} \tag{A2}$$

On the other hand,

$$\left.\frac{\delta\nabla\varphi(\mathbf{r})}{\delta n(\mathbf{r}_1)}\right|_{n_0} = \left.\frac{\delta\nabla n^{1/2}(\mathbf{r})}{\delta n(\mathbf{r}_1)}\right|_{n_0}$$

and using the properties of the functional derivatives (see, e.g., Ref. [41]) we get a result with only two terms. Each of these terms involves two coupled integrals, a double convolution product of gradients of Dirac δ functions and the kernel of the functional:

$$\begin{aligned}\left.\frac{\delta^2 T_S^{\mathrm{vWnl}}[n]}{\delta n(\mathbf{r}_1)\,\delta n(\mathbf{r}_2)}\right|_{n_0} &= \frac{1}{8n_0}\int d\mathbf{r}\int d\mathbf{r}'\,\nabla\,\delta(\mathbf{r}-\mathbf{r}_1)\cdot\nabla\delta(\mathbf{r}'-\mathbf{r}_2)\Omega(n_0,|\mathbf{r}-\mathbf{r}'|)\\ &\quad+\frac{1}{8n_0}\int d\mathbf{r}\int d\mathbf{r}'\,\nabla\,\delta(\mathbf{r}-\mathbf{r}_2)\cdot\nabla\delta(\mathbf{r}'-\mathbf{r}_1)\Omega(n_0,|\mathbf{r}-\mathbf{r}'|)\\ &= \frac{1}{4n_0}\{\nabla\delta*\{\Omega*\nabla\delta\}\}.\end{aligned}\tag{A3}$$

An equivalent treatment, but involving more terms, is needed in the calculation of the second functional derivative of the nonlocal part of the functional $T^{\text{NLS-vW-II}}[n]$, which includes the Laplacian ∇^2 operator.

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