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Nonlocal kinetic energy functional for nonhomogeneous electron systems

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We present three density-functional models for the kinetic energy of the electron gas. The density functionals are constructed to give the exact energy and linear response of homogeneous systems. We include nonlocal behavior through an "averaged density" evaluated with the aid of a weight function. By a scaling hypothesis we obtain a universal (i.e., density independent) differential equation for the weight functions in k space. We have used these three functionals for jellium surfaces and light atoms to compare the results with the exact results and the calculations of other functional approximations.

I. INTRODUCTION

For any system of electrons, the density-functional (DF) formalism developed by Hohenberg and Kohn, and Kohn and Sham,[1,2] proves the existence of an energy-density functional $E[\rho(\mathbf{r})]$ such that it reaches its minimum value at the density distribution of the ground state, and the value of the functional with this density gives the energy of this state. The functional $E[\rho]$ may be separated into an intrinsic nonelectrostatic term $G[\rho]$ plus the interactions between the electrons and any external potential $v(\mathbf{r})$:

$$E[\rho]=G[\rho]+\tfrac{1}{2}\int\int\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}'+\int\rho(\mathbf{r})v(\mathbf{r})d\mathbf{r}\ . \tag{1.1}$$

$G[\rho]$ itself is usually divided[2] into a "kinetic energy" term $T[\rho]$, which would be the full energy of a noninteracting electron system, plus an exchange and correlation term $E_{\text{xc}}[\rho]$. The latter may be modeled in several ways, like the so-called "local-density approximation" (LDA), in which E_{xc} is supposed to be locally equal to the exchange and correlation energy of a uniform system. The kinetic energy $T[\rho]$ can be exactly evaluated in terms of the one-electron wave functions:

$$T[\rho]=\sum_{i=1}^{N}\int d\mathbf{r}\,\psi_i(\mathbf{r})\nabla^2\psi_i(\mathbf{r})\ , \tag{1.2}$$

with

$$\rho(\mathbf{r})=\sum_{i=1}^{N}|\psi_i(\mathbf{r})|^2\ , \tag{1.3}$$

summing over the N electrons. (We will use the rydberg as our unit of energy.) Equation (1.2) requires the knowledge of the full set of one-electron wave functions, and that means that we need much more information than can be easily extracted from the density distribution (1.3). In the latter case, we are using a three-dimensional functional space instead of the $3N$-dimensional space for the wave functions. This means that it would be quite convenient to have a model for $T[\rho]$ without reference to the wave functions, so that all the contributions in Eq. (1.1) could be treated on the same footing and $E[\rho]$ could be minimized either by a variational procedure over a family of $\rho(\mathbf{r})$ or by using the exact extreme conditions

$$\delta E[\rho]/\delta\rho=0\ . \tag{1.4}$$

In a uniform system, with $\rho(\mathbf{r})=\rho_0$, the kinetic energy may be written as $T[\rho]=Nt(\rho_0)$, where $t(\rho_0)$, the mean kinetic energy per electron, can be exactly evaluated from (1.2) as

$$t(\rho_0)=\tfrac{3}{5}k_F^2(\rho_0)=\tfrac{3}{5}(3\pi^2\rho_0)^{2/3}\ . \tag{1.5}$$

So, the simplest model for $T[\rho]$ is the LDA:

$$T_{\text{LDA}}[\rho]=\int d\mathbf{r}\,\rho(\mathbf{r})t(\rho)\ . \tag{1.6}$$

This corresponds to the Thomas-Fermi approximation.[3] The first attempt[1] at treating nonuniform systems and improving over the LDA was to include the leading term in a density-gradient expansion for $T[\rho]$, given by

$$T[\rho]=T_{\text{LDA}}[\rho]+\tfrac{1}{36}\int\frac{(\nabla\rho)^2}{\rho(\mathbf{r})}d\mathbf{r}\ , \tag{1.7}$$

where the coefficient of the square-gradient term was calculated to give the correct limit of the energy of a uniform and noninteracting system under the action of a long-wavelength perturbation in the density.

Hohenberg and Kohn[1] have shown that the response function of the system is directly related to the second functional derivative of $G[\rho]$, so that for a noninteracting system we get

$$K(r,r')=\frac{\delta^2 T[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}\ , \tag{1.8}$$

where the function $K(\mathbf{r},\mathbf{r}')$ is defined as minus the functional inverse of the electron-gas susceptibility $\chi_0(\mathbf{r},\mathbf{r}')$. In a homogeneous system both $K(\mathbf{r},\mathbf{r}')$ and $\chi_0(\mathbf{r},\mathbf{r}')$ depend only on $|\mathbf{r}-\mathbf{r}'|$, and the connection between them is much easier in Fourier space

$$K(k)=-\frac{1}{\chi_0(k)}\ , \tag{1.9}$$

where $\chi_0(k)$ is the Lindhard[4] susceptibility

$$\chi_0(k)=-\frac{k_F}{4\pi^2}\left[1+\frac{1-\eta^2}{2\eta}\ln\left|\frac{1+\eta}{1-\eta}\right|\right]\ , \tag{1.10}$$

with $\eta\equiv k/2k_F$.

It is straightforward to show that taking $T_{\mathrm{LDA}}[\rho]$ in (1.8) is equivalent to approximating $\chi_0(k)$ by its $k=0$ limit, that is, in the Thomas-Fermi limit. The square-gradient correction to LDA in (1.7) was obtained[1] by taking the next term in the small-k expansion of $\chi_0(k)$

$$-\frac{1}{\chi_0(k)}=\frac{2\pi^2}{k_F}\left[1+\frac{1}{3}\left[\frac{k}{2k_F}\right]^2+\cdots\right]\ . \tag{1.11}$$

The next term, of order k^4, in (1.11) corresponds to the inclusion of the second kinetic energy density-gradient correction in (1.8).[5,6] In atoms, the functional derivative of this correction diverges for $r\rightarrow\infty$, due to the long-range behavior of the response of the electron gas. This divergence will introduce nonphysical properties in the Euler equation (1.4) of the DF formalism. The series expansion of $T[\rho]$ in terms of the gradient of ρ could be extended further but there is no guarantee of convergence and, more importantly, it can never be made to reproduce the logarithmic singularity of $\chi_0(k)$ for $k=2k_F$, which produces some of the most striking features of the inhomogeneous electron gas, like Friedel oscillations, atomic-shell structure, etc.

On the other hand, one can discuss the opposite limit: systems with only one or two localized electrons. Weizsäcker[7] included a correction to the LDA kinetic energy in terms of the square gradient of the charge density but fitted to the $k\rightarrow\infty$ limit of $\chi_0(k)$ rather than to $k\rightarrow 0$ as in (1.11). This approach gives the same functional form as (1.7) but with an extra factor of 9. This Weizsäcker term happens to be by itself and without the LDA term, the exact kinetic energy functional for one- or two-electron systems treated in the Hartree-Fock approximation.[8] Furthermore, it has been well established[8,9] that the Weizsäcker term is not only a natural component of the density-energy functional but an important term when discussing the ground-state energy of an atom or ion using DF formalism. In these cases it has been pointed out that there is some theoretical evidence supporting the description of $T[\rho]$ with the full Weizsäcker term, incorporating the local-density one as a correction to it.

So, in order to obtain a functional for the kinetic energy of a multielectron system, we are compelled to connect the two extreme limits cited above: the limit of the uniform system on one side, and the case of systems with well-separated electrons, so to speak, the Weizsäcker limit for $T[\rho]$.

The aim of this paper is to construct a functional model for $T[\rho]$ containing the full linear response of a uniform noninteracting system of electrons. That means that the second functional derivative of our $T[\rho]$ will be exact, in the homogeneous free-electron limit. In our treatment, the Weizsäcker term arises in a clear way in the energy functional by using simple physical reasons. For illustration of the procedure for constructing $T[\rho]$, we will develop three different functionals which we will compare in applications to surfaces and atoms.

II. CONSTRUCTION OF $T[\rho(\mathbf{r})]$

We try to construct a functional model for $T[\rho]$ of the type

$$T[\rho(\mathbf{r})]=\int d\mathbf{r}\,\rho(\mathbf{r})t(\bar{\rho}(\mathbf{r}))\ , \tag{2.1}$$

which looks like $T_{\mathrm{LDA}}[\rho]$ in (1.7), but where the function $t(\rho)$ is not evaluated at the local value of the density $\rho(\mathbf{r})$ but at a value $\bar{\rho}(\mathbf{r})$ of a new function which is itself a nonlocal functional of $\rho(\mathbf{r})$. Functionals like (2.1) have been used in describing the free energy of classical fluids[10–13] and the exchange and correlation energy of a system of electrons.[14] The idea behind it is to take advantage of the degrees of freedom not fixed in the prescription of $\bar{\rho}(\mathbf{r})$ for getting the correct linear response of a free-electron gas given by (1.8)–(1.10).

Here we take

$$\bar{\rho}(\mathbf{r})=\int d\mathbf{r}'\rho(\mathbf{r}')w(|\mathbf{r}-\mathbf{r}'|,\rho(\mathbf{r}))\ , \tag{2.2}$$

so that $\bar{\rho}(\mathbf{r})$ may be interpreted as an "averaged" density obtained by convoluting $\rho(\mathbf{r})$ with a weight function $w(\mathbf{r},\rho(\mathbf{r}))$, which should be obviously normalized at fixed ρ as

$$\int d\mathbf{r}\,w(\mathbf{r},\rho)=1\ . \tag{2.3}$$

In early attempts[14] to use this type of density functional in electron systems, the weight function in (2.2) was taken as depending on $\bar{\rho}(\mathbf{r})$ rather than on $\rho(\mathbf{r})$. There is no "*a priori*" reason to prefer one of these forms over the other but, as we will see below, our choice is in the end much better for technical reasons.

By evaluating the second functional derivative of $T[\rho]$ at uniform density $\rho(\mathbf{r})=\rho_0$, we get

$$\left.\frac{\delta^2 T[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}\right|_{\rho_0} = t'(\rho_0)\left[\frac{\delta\bar{\rho}(\mathbf{r})}{\delta\rho(\mathbf{r}')}+\frac{\delta\bar{\rho}(\mathbf{r}')}{\delta\rho(\mathbf{r})}\right]+\rho_0 t''(\rho_0)\int d\mathbf{r}''\frac{\delta\bar{\rho}(\mathbf{r}'')}{\delta\rho(\mathbf{r})}\frac{\delta\bar{\rho}(\mathbf{r}'')}{\delta\rho(\mathbf{r}')}+\rho_0 t'(\rho_0)\int d\mathbf{r}''\frac{\delta^2\rho(\mathbf{r}'')}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}$$

$$=2t'(\rho_0)w(|\mathbf{r}-\mathbf{r}'|,\rho_0)+\rho_0 t''(\rho_0)\int d\mathbf{r}'' w(|\mathbf{r}-\mathbf{r}''|,\rho_0)w(|\mathbf{r}'-\mathbf{r}''|,\rho_0)+2\rho_0 t'(\rho_0)\frac{dw(|\mathbf{r}-\mathbf{r}'|,\rho_0)}{d\rho_0}, \quad (2.4)$$

where $t'(\rho)$ and $t''(\rho)$ are, respectively, the first and second derivatives of $t(\rho)$. By using (1.8), the function $K(k,\rho_0)$ for a free-electron gas is given in Fourier space as

$$K(k,\rho_0)=2t'(\rho_0)w(k,\rho_0)+\rho_0 t''(\rho_0)[w(k,\rho_0)]^2 + 2\rho_0 t'(\rho_0)\frac{dw(k,\rho_0)}{d\rho_0}, \quad (2.5)$$

where $w(k,\rho_0)$ is the Fourier-transformed weight function and $K(k,\rho_0)$ is given by (1.9).

The normalization (2.3) implies $w(k=0,\rho_0)=1$, so that for $k=0$,

$$K(0,\rho_0)=2t'(\rho_0)+\rho_0 t''(\rho_0)=[\rho_0 t(\rho_0)]''. \quad (2.6)$$

This result is consistent with the compressibility sum rule[15] and, of course, with the value obtained for $\chi_0(\rho_0)$ using (1.10). Lindhard susceptibility has the dependence on k through the scaled variable $\eta=k/2k_F(\rho_0)$, so that $K(k,\rho_0)$ in (2.5) can be written as

$$K(k,\rho_0)=\frac{-1}{\chi_0(k,\rho_0)}=\frac{2\pi^2}{k_F(\rho_0)}F(\eta) = [\rho_0 t(\rho_0)]''F(\eta), \quad (2.7)$$

with

$$F(\eta)=\frac{2}{1+\frac{1-\eta^2}{2\eta}\ln\left|\frac{1+\eta}{1-\eta}\right|}. \quad (2.8)$$

We try the same scaling of k for the weight function, i.e.,

$$w(k,\rho)=w(k/2k_F(\rho))=w(\eta), \quad (2.9)$$

which gives [note that $k_F^3(\rho)=3\pi^2\rho$]

$$\frac{d}{d\rho_0}w(k,\rho_0)=-\frac{1}{3}\frac{\eta}{\rho_0}w'(\eta), \quad (2.10)$$

where $w'(\eta)$ is the first derivative of $w(\eta)$. With this scaling, Eq. (2.5) becomes

$$2t'(\rho_0)w(\eta)+\rho_0 t''(\rho_0)w^2(\eta)-\tfrac{2}{3}\eta w'(\eta)=[\rho_0 t(\rho_0)]''F(\eta). \quad (2.11)$$

We can see that all the explicit dependence on ρ_0 can be eliminated so that we get an universal (i.e., density-independent) differential equation for $w(\eta)$:

$$2w(\eta)-\tfrac{1}{3}w^2(\eta)-\tfrac{2}{3}\eta w'(\eta)=\tfrac{5}{3}F(\eta). \quad (2.12)$$

This equation will play a major role in all the discussion below.

We must point out that the right-hand side of (2.12) is fixed by the "input" response function we want to reproduce, while the left-hand side is given by the structure of the functional we are going to construct, expressed in this case by Eqs. (2.1) and (2.2). Thus, had we taken $w(\mathbf{r},\rho_0)=w(\mathbf{r})$, with no dependence on ρ_0, we would get instead of (2.12) an algebraic equation for $w(k)$,

$$2w(k)+\tfrac{1}{3}w^2(k)=\tfrac{5}{3}F(k/2k_F),$$

which requires a special choice of k_F (or the density) at which the Lindhard response function will be achieved for each k; that is, the weight function would not be able to reproduce the response of a system with a given density for all k. Moreover, if we take the weight function as depending on $\bar{\rho}(\mathbf{r})$ rather than on $\rho(\mathbf{r})$, as was tried[14] for $E_{\mathrm{xc}}[\rho]$, we get a term $\eta w(\eta)w'(\eta)$ instead of $\eta w'(\rho)$ in (2.12). This change produces a very nasty divergence of the derivative $w'(\eta)$ whenever $w(\eta)$ goes to zero, making it difficult to integrate the differential equation for a sensible function $w(\eta)$.

In the rest of this section we keep the left-hand side of (2.12) as it stands, but we will play with the right-hand side by taking some parts of the Lindhard response function out of $F(\eta)$, for reasons we will explain below. In this way, we will explore three different models for $T[\rho]$, which in the next sections we will test for surfaces and atoms.

A. First functional model $T_1[\rho]$

If we solve Eq. (2.11) as it stands, with $F(\eta)$ given in (2.8), that is, trying to get the full Lindhard response function out of the functional (2.1), we get that $F(\eta)$ diverges for large η:

$$F(\eta)=3\eta^2-\tfrac{3}{5}+O(1/\eta^2) \quad (2.13)$$

when $\eta\to\infty$, and this divergence propagates to $w(\eta)$ through (2.11). $w(r,\rho_0)$ must have an extremely strong diverging structure, much worse than a δ function, to get this behavior in $w(\eta)$ when k is large. We must track the problem back to a physical reason and try to take it out of the differential equation. In fact, for getting a density fluctuation with wave vector k in a free-electron system, it is necessary to excite electrons with this wave vector. This means a kinetic energy k^2 per excited electron, which must be reflected in the susceptibility $\chi_0(k)$. The functional $\bar{\rho}(\mathbf{r})$ may include this effect, stronger for larger k, which is opposite to any intuitive idea behind (2.3), where we suppose $\bar{\rho}(\mathbf{r})$ to be some sort of "averaged" $\rho(\mathbf{r})$.

Thus, it is clear that if we want to keep this naïve idea of $\bar{\rho}(\mathbf{r})$ and, more importantly, to make feasible any numerical solution for $w(\eta)$, we have to take the leading term in (2.13) out of the right-hand side of the differential equation (2.12). One possible way to do that is by including explicitly in our functional model for $T[\rho]$ a term in square gradients which will give exactly the large-k limit of $-1/\chi_0(k,\rho_0)$.

Thus, we get our first functional model

$$T_1[\rho]=\int d\mathbf{r}\rho(\mathbf{r})t(\bar{\rho}(\mathbf{r}))+\tfrac{1}{4}\int d\mathbf{r}\frac{|\nabla\rho|^2}{\rho(\mathbf{r})}\ , \qquad (2.14)$$

with $\bar{\rho}(\mathbf{r})$ given by (2.2) where the weight function is fixed by the new differential equation

$$2w(\eta)-\tfrac{1}{3}w^2(\eta)-\tfrac{2}{3}\eta w'(\eta)=\tfrac{5}{3}[F(\eta)-3\eta^2]\ . \qquad (2.15)$$

The density-gradient term in (2.14) is precisely Weizsäcker's correction to the local-density approximation, as commented on in the Introduction. As is well known, this term gives by itself the exact kinetic energy of any one-electron density distribution, and we have obtained it by treating exactly the single-electron part of the Lindhard response function.

Going back to (2.15), we can rearrange the differential equation for $w(\eta)$ as

$$w'(\eta)=\frac{1}{\eta}\left[3w(\eta)-\tfrac{1}{2}w^2(\eta)-\left[\frac{5}{1+\dfrac{(1-\eta^2)}{2\eta}\ln\left|\dfrac{1+\eta}{1-\eta}\right|}-\frac{15}{2}\eta^2\right]\right]\ , \qquad (2.16)$$

which, in principle, would be solved with the initial value $w(0)=1$. In fact, that is not feasible because (2.16) presents an unstable solution when integrated from $\eta=0$, so that any small deviation, e.g., inaccuracy in the numerical integration, will drive $w(\eta)$ to extremely different values of $w(\eta)$ for large η. To avoid this problem, we analyzed the large-η behavior of (2.16) and found that $w(\eta)$ will go flat as $\eta\rightarrow\infty$ [i.e., $w'(\infty)=0$] with only two values, which are the roots of the equation

$$3w_\infty-\tfrac{1}{2}w_\infty^2+\tfrac{3}{2}=0\ ,$$

w_∞ being equal to $\lim_{\eta\rightarrow\infty}w(\eta)$. Thus, we have $w_\infty=3\pm\sqrt{12}$. Now, if we integrate (2.16) backwards from large η with any of these values, the solution is quite stable. Nevertheless, in the limit $\eta\rightarrow 0$, only the solution with $w_\infty=3-\sqrt{12}$ goes to the prescribed value $w(0)=1$, so that this is the solution with physical meaning.

Now we can make the inverse Fourier transform of $w(\eta)$ get the weight function in real space as

$$w(r,\rho)=8k_F^3(\rho)w(2k_F(\rho)r)\ , \qquad (2.17)$$

where the $2k_F$ enters not only as a scaling factor in the universal function $w(x)$, but also as the prefactor necessary to keep the normalization (2.3). The fact that $w(\rho)$ goes to a nonzero constant when $\eta\rightarrow\infty$ means that there is a δ-function component in $w(x)$, with a factor given by the value of w. So $\bar{\rho}(\mathbf{r})$ has a term proportional to the local density $\rho(\mathbf{r})$, with a coefficient $c=3-\sqrt{12}=-0.464\,101\,6$. It is somehow unnerving to find a negative local direct contribution to $\bar{\rho}(\mathbf{r})$ which may be compensated for by the nonlocal part, though in some cases it can lead to negative values for $\bar{\rho}(\mathbf{r})$ itself. In fact, this is the case when the functional model $T_1[\rho]$ is used to describe the hydrogen atom, which should be considered as an extremely hard test for any functional model which has been constructed with ingredients, say $t(\rho)$ and $\chi_0(k,\rho)$, taken from the homogeneous limit. Getting negative values of $\bar{\rho}(\mathbf{r})$ is discouraging from the point of view of the "physical interpretation" of this object, but if we condescend to any interpretation and consider it as a mere tool to construct a function $T_1[\rho]$ with some well-defined specifications, we can go ahead with a straightforward extension of $t(\rho)$ to negative arguments. In this case the values obtained for the ground-state energy and the density must be compared with the exact results for deciding the accuracy of the functional model.

B. Second functional model $T_2[\rho]$

Despite the arguments just given about the viability of the functional $T_1[\rho]$, even when $\bar{\rho}(\mathbf{r})$ reaches negative values somewhere, it may be useful to look for the origin of this behavior. In the large-η limit we have removed from the right-hand side of (2.15) the diverging term $3\eta^2$ but the constant term $-\frac{3}{5}$ is left. So we have at large k an inverse response function

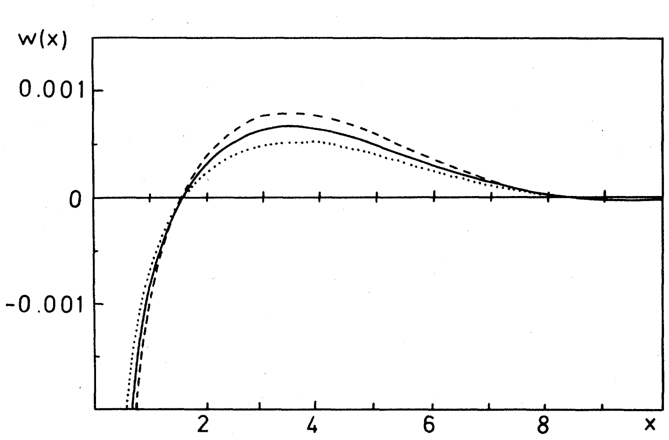

FIG. 1. Weight functions for the three kinetic functionals. Dashed line: T_1. Dotted line: T_2. Solid line: T_3. Local contributions are taken out.

$$\Delta K(k) \equiv \left[-\frac{1}{\chi_0(k,\rho_0)} - \frac{6\pi^2}{k_F}\eta^2 \right] = -\frac{6\pi^2}{5k_F} + O(1/k^2) \, .$$

It is easy to see the physical origin of this constant term; it is the same as for the quadratic term in (2.13), coming from the energy of one-electron states, with wave vector k being excited to generate a density fluctuation with the same value of k. In fact, the excitation of this electron implies the creation of a hole in the Fermi sphere, which has a negative energy. For $k \gg k_F$, the energy of the hole can be calculated by averaging over the Fermi sphere, giving the $-\frac{3}{5}$ term in (2.13).

Now, in the formulation of a new functional, we can try to extract from the construction of $\bar{\rho}(\mathbf{r})$, not only the excited electrons, but also the hole being left in the Fermi sphere in the large-k limit. So we let all other possible excitations be described by a functional of the type (2.1).

To get a constant response function (in k), we need a local-density functional or a δ-function response in real space. Thus, we include explicitly in $T_2[\rho]$ a LDA term with a $-\frac{3}{5}$ prefactor and write

$$T_2[\rho] = \tfrac{8}{5} \int d\mathbf{r}\, \rho(\mathbf{r}) t(\bar{\rho}(\mathbf{r})) - \tfrac{3}{5} \int d\mathbf{r}\, \rho(\mathbf{r}) t(\rho(\mathbf{r}')) + \tfrac{1}{4} \int d\mathbf{r} \frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})} \, , \tag{2.18}$$

as our second functional model for $T[\rho]$. In this case, $\bar{\rho}(\mathbf{r})$ is defined by (2.2), while the weight function is the solution of

$$w'(\eta) = \frac{1}{\eta} \left[3w(\eta) - \tfrac{1}{2} w^2(\eta) - \frac{25}{8} \left[\frac{2}{1 + \dfrac{(1-\eta^2)}{2\eta} \ln \left| \dfrac{1+\eta}{1-\eta} \right|} - 3\eta^2 + \frac{3}{5} \right] \right] , \tag{2.19}$$

where we have extracted from $F(\eta)$ the two trouble-making terms. Again, as for (2.16), the solutions to this equation are unstable if we start integration from $\eta = 0$. However, we get the limit $w(\eta) \to 0$ when $\eta \to \infty$ and the backwards integration from this value leads to the correct $w(0) = 1$.

The weight function in real space, scaled with k_F in the same way as (2.17), is represented in Fig. 1 together with the nonlocal part of the weight function in the first functional model, both of which have an integrable divergence ($\sim 1/r$) at the origin.

C. Third functional model $T_3[\rho]$

At this point, it should be quite clear that there is a lot of freedom in the construction of a kinetic-energy functional, even with the requirement of reproducing both the energy and the full linear response function of a free-electron gas. On the other hand, we want to get a functional that adequately describes strongly inhomogeneous situations in electron systems. In the Introduction, we have recalled Weizsäcker's correction itself as the exact functional for the kinetic energy of a single electron system. $T_1[\rho]$ and $T_2[\rho]$ include this term but they do not reproduce the energy of such an electronic state. All the ingredients used in $T_1[\rho]$ and $T_2[\rho]$ come from the homogeneous limit, and our aim being to construct a $T[\rho]$ for inhomogeneous systems, we could ask ourselves for a functional model tailored to some specific situations. In particular, it would be especially rewarding to have a functional which, besides giving the correct limit for homogeneous density distributions, would give the exact energy in the Weizsäcker limit. In this way we could tie up the two extreme cases we discussed in the Introduction, in the hope that the functional would describe better than T_1 and T_2 any intermediate case.

Let us discuss the localized density of an s state in the hydrogen atom. In this case the Weizsäcker term given, by itself the exact result, so that it would be desirable to get rid of the remaining terms of the kinetic energy functional which, on the other hand, are the important ones for the homogeneous limit. However, these extra terms give a positive contribution of about 24% of the exact value when using $T_1[\rho]$ and a negative contribution of about 11% for $T_2[\rho]$. This suggests a functional model somewhere in between both functionals, so that the terms, apart from the density-gradient one, will strictly vanish when evaluated for an s-orbital density distribution. Because of the scaling of k to k_F in (2.8), this property will hold for any one-electron s state, whichever arbitrary parameter is used in the wave function.

We assume our third functional to read as

$$T_3[\rho] = (1+d) \int d\mathbf{r}\, \rho(\mathbf{r}) t(\bar{\rho}(\mathbf{r})) - d \int d\mathbf{r}\, \rho(\mathbf{r}) t(\rho(\mathbf{r})) + \tfrac{1}{4} \int d\mathbf{r} \frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})} , \tag{2.20}$$

where d is a fitting constant to give the vanishing result cited above. The functional $\bar{\rho}$ is evaluated by (2.2) with the weight function obtained from the differential equation

$$w'(\eta) = \frac{1}{\eta} \left[3w(\eta) - \tfrac{1}{2} w^2(\eta) - \frac{5}{2(1+d)} \left[\frac{2}{1 + \dfrac{1-\eta^2}{2\eta} \ln \left| \dfrac{1+\eta}{1-\eta} \right|} - 3\eta^2 + d \right] \right] . \tag{2.21}$$

Clearly, Eqs. (2.20) and (2.21) reduce to (2.14) and (2.16), and (2.18) and (2.19), respectively, if we make $d=0$ and $d=\frac{3}{5}$. The weight function can be integrated backwards from the constant asymptotic value of

$$w_\infty = 3 - \left[9 + \frac{3-5d}{1+d} \right]^{1/2} . \tag{2.22}$$

For each value of d we get a different $w(x)$ and a different result for the kinetic energy of the s orbital in the hydrogen atom. Varying d, we can solve the implicit equation for d and get the correct value of the energy. The resulting value is $d=0.22 \simeq \frac{2}{9}$ (within the numerical precision). The weight in real space has a δ-function contribution with a factor $w_\infty = -0.247$; we represent the nonlocal part in Fig. 1.

That completes our search for different descriptions of the kinetic energy functional $T[\rho]$ in terms of functional models like (2.1). The three models give the same results for weak deviation from a homogeneous density distribution but will lead us to different results when treating strong inhomogeneous systems. We can decide which of these functionals is better in any given situation based only on the results we obtain.

In order to simplify the numerical evaluation of $\bar{\rho}(\mathbf{r})$ and $T|\rho|$, we have developed an analytical fit of the weight functions (see Appendix) and we should note that all the calculations we present in this paper were done with these parametrized weight functions.

III. APPLICATION TO SURFACES

In this section we will use our three functional models for $T[\rho]$ to determine the surface electronic structure of a metal within the jellium model, i.e., when the positive charges are replaced by a steplike background with uniform density ρ_0 in the solid and zero outside. This model was studied by Lang and Kohn[16] (LK) using the LDA for the exchange and correlation energy $E_{xc}[\rho]$, and the formalism of Kohn and Sham[2] to evaluate exactly the kinetic energy $T[\rho]$ from the wave-function solution of the effective one-electron Schrödinger equation. The same system was also studied by Smith[17] using a first-gradient correction to the LDA for $T[\rho]$, and later by Ma and Sahni[18] (MS) with a functional model for $T[\rho]$ which includes the next-order gradient corrections to $T_{\mathrm{LDA}}[\rho]$. Here, we will use the same approximations for the exchange and correlation energy and compare the predictions of our models $T_1[\rho]$, $T_2[\rho]$, and $T_3[\rho]$ with the results for the exact $T[\rho]$ (LK) and the gradient expansion (GE).

To get the minimum of $E[\rho]$, we have used parametrized trial density distributions $\rho(\mathbf{r})$ in a variational calculation. The result of such a minimization gives a rigorous upper bound to the ground-state energy of the system. We have used a variety of trial functions to get a better estimation of the minimum for $E[\rho]$. It is very important to get a good description of the first peak in the electronic density near the surface. Any monotonic profile gives bad estimations of the real minimum of $E[\rho]$, so we describe this first peak by a Gaussian with its amplitude, center, and decay considered as free parameters. For the decay of $\rho(z)$ in the tail outside the positive background, we assume an exponential form, and as we are also interested in including Friedel-like oscillations, we use the profile suggested by Bosio and Dumezine[19] with seven parameters,

$$\frac{\rho(z)}{\rho_0} = \left[1 + \frac{A_1 \sin(-2\pi z/A_2)}{1+(z/A_3)^2} \right] [1+\exp(z/A_4)]^{-1} + A_5 \exp[-(z-A_6)^2/A_7^2] . \tag{3.1}$$

In Table I we present the results for the surface energy with our three functional models for $T[\rho]$ after minimizing the total energy with respect to the seven parameters in the trial profile (3.1). We also present the results obtained within the same parametrization but using the gradient expansion $T_{\mathrm{GE}}[\rho]$ and the exact (for $T[\rho]$) fully self-consistent calculations of LK, which do not require any trial parametrized density. It is clear that our second and third functional models give better results than the gradient expansion. It has to be pointed out that in the original MS paper, the trial function used in the variational approach was a much simpler exponential-type profile, which gives surface energies quite close to the exact LK values. When the more sophisticated trial function (3.1) is used, the results of MS are driven down so that the previous agreement has to be considered as fortuitous.

In Fig. 2 we present the density profile for three cases: the LK calculation, when the total surface energy of the system is minimized by using our $T_2[\rho]$, and when the T_{GE} functionals are used with the parametrization (3.1). We remark that the density profiles calculated when using $T_3[\rho]$ are quite similar to the ones obtained with $T[\rho]$. Our profile is closer to the LK one than the GE result. Both $T_2[\rho]$ and $T_{\mathrm{GE}}[\rho]$ find a peak near the surface but do not reproduce the oscillations below. We have looked for the reasons of this behavior and have found that it is due to the lack of flexibility of the parametrization, even with the sophisticated Eq. (3.1). In fact, if one tries to fit the LK result for $\rho(z)$ to our form (3.1) by least squares,

TABLE I. Results for the surface energy E_s, as calculated by variational minimization of the surface-energy functionals in the range of metallic densities. Units are ergs/cm^2.

r_s	T_{GE}	T_1	T_2	T_3	Lang-Kohn
2.0	−1082.2	−673.8	−924.5	−768.5	−1008
3.0	155.3	249.6	185.7	223.75	199
4.0	133.46	174.12	149.5	163.39	158
5.0	81.82	103.54	93.51	99.67	98
6.0	50.16	63.62	57.88	60.91	60

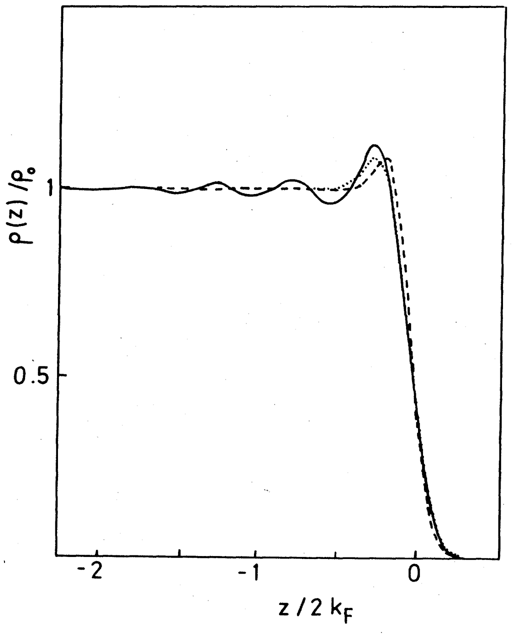

FIG. 2. Electronic density profile after minimization of the surface energy of a jellium with $r_s=5$. Solid line: exact result of LK. Dashed line: GE. Dotted line: T_2.

the resulting profile does not present oscillations beyond the first peak. On the other hand, we have calculated the surface energy using the LK values of the density profile in the different functionals. The results are shown in Table II and we can see that our T_1 and T_2 functionals, except for $r_s=2$, have a surface energy lower than that obtained with (3.1), and so we expect that the real minima $\rho(z)$ of these two functionals are closer to the LK profile than to the $\rho(z)$ obtained with the parametrization (3.1). Furthermore, the results for $T_{\rm GE}$ take the opposite direction, and the profile that minimizes $T_{\rm GE}$ will show a shape closer to the one represented in Fig. 2 than to the LK type.

The results obtained for the surface dipole barrier and the work function with our $T_2[\rho]$ functional, are shown in Table III. The results of LK and of MS with an exponential trial density are also included. As can be seen, our second functional improves the results of MS. However, these values depend delicately on the parametrization of the density profile we have used, and we hope that the results will be better for a profile closer to real minima. To obtain the exact profile within our theory it is necessary to solve self-consistently the Euler equation for the density

$$\frac{\delta T[\rho]}{\delta\rho\,|\mathbf{r}|}+v_{\rm eff}(\rho(\mathbf{r}))=\mu\ ,$$

where

$$v_{\rm eff}(\rho(\mathbf{r}))=v_{\rm ext}(\mathbf{r})+\int\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'+\frac{\delta E_{\rm xc}[\rho]}{\delta\rho}\ .$$

Work towards a solution of these equations is in progress.

IV. ATOMS

In this section we will give some results obtained with our functionals when applied to the calculation of the kinetic energy of light atoms (from H to Ne). So we want to study the feasibility of our functionals, constructed for reproducing the free-electron case, in the description of small localized electronic systems.

In order to simplify the treatment, we have studied only atoms with closed subshells or filled shells, so the electron density has spherical symmetry. We will use Slater orbitals for the one-electron wave functions, orthogonalized to the orbitals with lower energy, and construct the electronic density of the atom using (1.3). This treatment, quite similar to the single-zeta approximation of Clementi and Roetti,[20] is simple but our aim is to compare the results obtained with the three kinetic functionals with the exact values of the kinetic energy. Another approximation, the so-called second-gradient expansion which has been used by Murphy and Wang[21] with the Hartree-Fock electron densities of Clementi and Roetti,[20] is also compared with these results.

In Table IV we show the kinetic energy of some atoms, using the electron density obtained with the Slater coefficients of the single-zeta functions of Clementi and Roetti.[20] In the parentheses we present the percent error of each value when compared with the exact kinetic energy of the atom, obtained directly by means of the Slater coefficients. Obviously, $T_3[\rho]$ given by construction gives the exact results for H and He, but $T_2[\rho]$ gives better results for the other atoms. This means that the physical reasons for the construction of $T_3[\rho]$ stand for one- or two-electron atoms, but they fail for other atoms. On the other hand, $T_1[\rho]$ always gives the worst results, just like with the surface problems.

We also note that the values obtained with $T_2[\rho]$ can be positively compared with those of Murphy and Wang[21] which are, to the best of our knowledge, the more accurate results evaluated with kinetic energy functionals. We

TABLE II. Results obtained for surface energy E_s in the range of metallic densities, calculated with the density profile of LK and the kinetic energy functionals. Units are ergs/cm^2.

r_s	$T_{\rm GE}$	T_1	T_2	T_3	Lang-Kohn
2.0	−1065.3	−632.8	−887.2	−746.8	−1008
3.0	167.8	250.8	185.	221.6	199
4.0	142.03	171.73	147.9	161.22	158
5.0	86.91	101.25	90.6	96.58	98
6.0	53.55	61.73	56.27	59.35	60

TABLE III. Surface dipole and work function (in eV). I: Ma and Sahmi with exponential profile. II: our second functional. III: exact treatment of Lang-Kohn.

	I		II		III	
r_s	$\Delta\phi$	ϕ	$\Delta\phi$	ϕ	$\Delta\phi$	ϕ
2	7.31	4.4	6.097	3.183	6.80	3.89
3	2.82	4.00	2.053	3.235	2.32	3.50
4	1.49	3.64	0.915	3.006	0.91	3.06
5	0.94	3.32	0.103	2.479	0.35	2.73
6	0.66	3.03	0.004	2.373	0.04	2.41

must comment also on the results of Alonso and Girifalco,[22] who have calculated the kinetic energy of some of these atoms by using a nonlocal weighted-density approximation in which the kinetic energy functional depends explicitly on the exchange-correlation factor. Their results are comparable with the values shown in Table IV, but we do not include them because they have calculated the kinetic energy using a Hartree-Fock density. Although we present results for simpler densities, we expect that the general trends shown in Table IV would be satisfied if more accurate electron densities were used.

On the other hand, the scaling of the weight functions for the local density $k_F(\rho(\mathbf{r}))$ guarantees that the minimum value of our three functionals for electrons, in the presence of a point-charge Coulomb potential, will satisfy the virial theorem (i.e., the value of $T[\rho]$ is minus the total energy $E[\rho]$). But if we use the aforementioned density profiles with the functionals included in Table IV, we will not obtain the exact virial coefficient. It is clear that we are not at the minimum functional value of the total energy because all these functionals verify the virial theorem in their minima. We must numerically integrate the Euler equation associated with each of the functionals to obtain the actual electron density of the atoms. By now, we will content ourselves with showing in Table V results of the total-energy minimization using orthogonalized single-zeta orbitals to describe the electron density of the atoms. The percent errors presented in the table refer to the difference between the kinetic energy obtained by minimization of the exact total energy and of the total energy evaluated with the kinetic functionals (all calculations were done with the $X\alpha$ method for the exchange-correlation energy α taken from Slater;[23] after minimization the virial theorem is satisfied). As can be seen, these results show differences with respect to Table IV, but the error ranges of the values of the kinetic energy are similar in both tables. Even though the GE approximation gives excellent results for the total kinetic energy, it is known[24] that its local behavior is less accurate than other nonlocal kinetic functionals. In any case, it is clear that we must free all the restrictions on $\rho(r)$ to obtain the actual density profile that will give the minimum functional value of $E[\rho]$. This freedom is not compatible with single-zeta orbitals and so the minimization results of Table V are merely indicative (note that we have proven that it is possible to obtain the same values for the total energy with quite different electron densities). On the other hand, it is well known[25] that to describe the shell structure of the electron density the inclusion of nonlocal terms in the kinetic energy functionals (in addition to the Weizsäcker term) is of fundamental importance. Moreover, if one wishes to obtain a good density, it is necessary to construct a kinetic functional with a good local-energy-density behavior.[25,26] So it is important to discuss the results of the numerical solution of the Euler equation for the density profiles and for the local behavior of the kinetic functionals presented here. Work on this question is in progress and we will report the results elsewhere.

TABLE IV. Kinetic energy of some atoms (in Hartrees) using single-zeta orbitals with distinct functionals. In parentheses, the percent error of each value with respect to the exact kinetic energy.

Atom	$T_1[\rho]$	$T_2[\rho]$	$T_3[\rho]$	T_{GE}
H	0.6179	0.446	0.5	0.3806
	(23.6)	(−10.7)	(0.0)	(−23.9)
He	3.353	2.969	2.845	3.059
	(17.7)	(4.27)	(0.0)	(7.42)
Li	8.535	7.561	7.247	7.795
	(14.6)	(1.6)	(−2.6)	(4.7)
Be	16.408	14.578	13.99	15.110
	(12.7)	(0.15)	(−3.8)	(3.8)
N	58.420	52.646	50.957	54.664
	(7.66)	(−2.99)	(−6.1)	(0.73)
Ne	139.17	127.58	124.40	130.45
	(8.8)	(−0.18)	(−2.66)	(2.06)

TABLE V. Percent errors of the kinetic energy after minimization of the total energy using single-zeta orbitals.

	T_1	T_2	T_3	GE
He	−15.1	−4.1	0.0	−6.9
Be	−4.4	5.2	9.8	−1.1
Ne	−1.0	5.0	7.1	0.7

V. DISCUSSION

We have constructed three functional models for the kinetic energy of a noninteracting system of electrons. The idea was to take functional forms like (2.1) which give the exact energy for a homogeneous system, by taking the exact $t(\rho)$, and to use the prescription for $\bar{\rho}(\mathbf{r})$ in terms of $\rho(\mathbf{r})$ to achieve the correct linear response. This process leads to a density-independent weight function $w(x)$ given by a differential equation like (2.12). We have seen also that in order to avoid strong pathologies in $w(x)$ one has to take out the leading term in the inverse response function for $k \rightarrow \infty$. This term comes from the one-electron excitations in the Lindhard susceptibility $\chi_0(k)$, and so it is not surprising that it is exactly obtained from the Weizsäcker term. That gives our first functional model $T_1[\rho]$. The next step was to take out of the description, through a functional like (2.1), not only the leading but also the next-to-leading term in $\chi_0(k)$ for large k. The new contribution arises from the averaged hole being left in the Fermi sphere by any one-electron excitations. Thus, in our second functional model $T_2[\rho]$ we describe through an "averaged density" $\bar{\rho}(\mathbf{r})$ all the contributions arising from many-electron excitations, keeping out all the one-electron plus averaged hole processes.

The results, both for the jellium surface and for the atoms, show that this second model is the best, supporting the physical considerations which led us to it.

Both $T_1[\rho]$ and $T_2[\rho]$ were constructed only with the information from the homogeneous density system. Our third model $T_3[\rho]$ is an attempt to include also some information on the one-electron system so that we could bridge the two opposite limits. To do that we used an interpolation between $T_1[\rho]$ and $T_2[\rho]$ to achieve the correct limit for the one electron in a $1s$ orbital, partially sacrificing the separation between one-electron and many-electron processes, followed for $T_2[\rho]$. Unfortunately the results for this third model are not rewarding because, although for the jellium surface they are only a little worse than the results with $T_2[\rho]$, for atoms (other than H and He, which are exact by construction of $T_3[\rho]$), the agreement with the exact $T[\rho]$ is much poorer. This indicates that the interpolation scheme used to get $T_3[\rho]$ is deficient and we have to propose $T_2[\rho]$ as our best model for the whole range of possible systems: from a few electrons to infinite systems. This functional compares very favorably with any existing density functional for $T[\rho]$, making a clear improvement over the gradient expansions.

We also have to point out that our model is perfectly self-consistent and does not require any extra information before applying it to any system. The parametrization for the weight function $w(x)$ corresponding to $T_2[\rho]$ makes it very easy to use in numerical calculations.

APPENDIX: ANALYTICAL PARAMETRIZATION OF THE WEIGHT FUNCTIONS

Due to the differential equation (2.12) that relates the weight function to the response functions of the electron system, two points of nonanalytical behavior of $w(\eta)$ are found. The response function $F(\eta)$ introduces a nonanalyticity for $\eta=1$ ($\eta=k/2k_F$) and the structure of the differential equation introduces a new one for $\eta=0$. That means that the asymptotic decay of $w(r)$ for $r \rightarrow \infty$ is slower than exponential and the numerical evaluation of $\bar{\rho}(\mathbf{r})$ may be delicate. In addition, the calculation of $T[\rho]$ becomes difficult in some cases.

In order to avoid these numerical subtleties, we sought an analytical fitting of the weight function. The behavior of $w(\eta)$ when $\eta \rightarrow \infty$ (up to terms in η^{-4}) is known from (2.12) and we can write

$$w_f(\eta)=e^{-\alpha\eta^2}(A+B\eta^2)+\frac{C}{\eta^2+H^2}+\frac{D+CH^2}{(\eta^2+H^2)^2}+w_\infty , \tag{A1}$$

where

$$C=-\frac{12}{35(1+d)(5+w_\infty)} ,$$

$$D=\left|\frac{C^2}{2}-\frac{28}{175(1+d)}\right|\frac{1}{7-w_\infty} ,$$

A is determined by the normalization condition, and w_∞ and d are given in Sec. II. In Table VI we present the values of the best-fitting constants of the analytical weight functions for our three functionals. The values of

$$\Delta=\left|\int_0^\infty dq[w(q)-w_f(q)]^2\right|^{1/2}$$

are also shown in the table.

The weight function (A1) can be Fourier transformed to obtain

$$w(r)=C\delta(r)+e^{-(r^2/4\alpha)}(a+br^2)+e^{-HR}(f/r+g) , \tag{A2}$$

where

$$a=\frac{(\pi\alpha)^{-3/2}}{8}\left[A+\frac{3D}{2\alpha}\right],\quad b=\frac{(\pi\alpha)^{-3/2}}{8}\frac{B}{4\alpha^2} ,$$
$$f=\frac{C}{4\pi},\quad g=\frac{D+CH^2}{8\pi H} . \tag{A3}$$

TABLE VI. Values of the parameters for the best-fitting analytical weight functions.

	D	α	B	H	Δ
T_1	0.0	2.9088	−3.008	1.3794	0.039
T_2	3/5	3.012	−2.083	1.2256	0.025
T_3	2/9	2.9534	−2.5802	1.3126	0.032

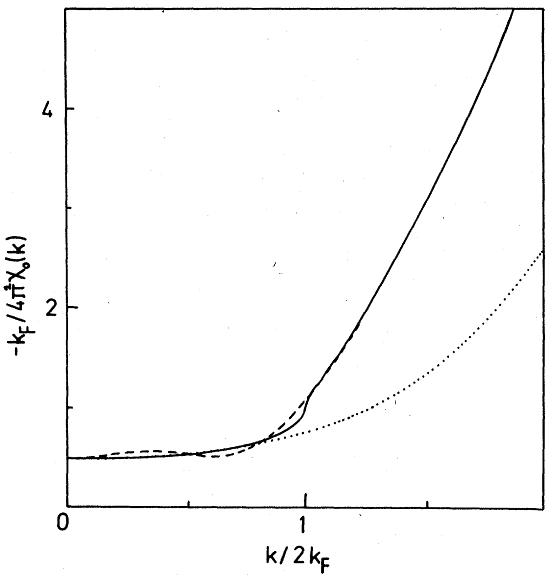

FIG. 3. Response function of the free-electron gas (solid line), compared with the functional derivatives of our parametrized functional (dotted line) and the GE functional (dashed line).

We must stress that the important point in the fitting is to describe the values of $w(\eta)$ when $w \lesssim 1$ as suitably as possible.

On the other hand, we have found it more accurate to fit the values of $w(\eta)$ instead of fitting the response function $F(\eta)$ and then integrating the differential equation (2.12) for $w(\eta)$. But if we differentiate the parametrized weight function (A1), we get the function represented in Fig. 3, quite close to $F(\eta)$. Note that the singularity for $k=2k_F$ has disappeared in the parametrization process. In this figure we depict also the right-hand side of (2.12) as obtained in the second-order gradient approximation (GE).

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