

## Kinetic-energy density functional: Atoms and shell structure

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We present a nonlocal kinetic-energy functional which includes an anisotropic average of the density through a symmetrization procedure. This functional allows a better description of the nonlocal effects of the electron system. The main consequence of the symmetrization is the appearance of a clear shell structure in the atomic density profiles, obtained after the minimization of the total energy. Although previous results with some of the nonlocal kinetic functionals have given incipient structures for heavy atoms, only our functional shows a clear shell structure for most of the atoms. The atomic total energies have a good agreement with the exact calculations. Discussion of the chemical potential and the first ionization potential in atoms is included. The functional is also extended to spin-polarized systems. [S1050-2947(96)08208-X]

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### I. INTRODUCTION

The density-functional theory [1–4] proves that, for any electron system under the action of an external potential  $v_{\text{ext}}(\mathbf{r})$ , there is an energy functional of the electron density  $n(\mathbf{r})$ ,

$$E[n] = F[n] + \int v_{\text{ext}}(\mathbf{r})n(\mathbf{r})d\mathbf{r}, \quad (1)$$

which has its minimum for the ground-state density and it is equal to the ground energy of the system. The functional  $F[n]$  is universal [i.e., it depends on neither the external potential  $v_{\text{ext}}(\mathbf{r})$  nor the number  $N$  of electrons]. It is usually divided into three terms (atomic units are used throughout this paper):

$$F[n] = T_S[n] + \frac{1}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{\text{xc}}[n], \quad (2)$$

where  $T_S[n]$  is the kinetic-energy functional of a noninteracting electron system, the second term is the classical electrostatic interaction energy (Hartree energy), and  $E_{\text{xc}}[n]$  is the so-called exchange-correlation (xc) energy.

$T_S[n]$  can be evaluated exactly through a set of one-electron wave functions, the Kohn-Sham (KS) orbitals [5], and the minimization of the functional (1) becomes the resolution of a set of coupled Schrödinger-like equations for the KS orbitals (KS method). However, the construction of functionals depending explicitly on the density  $n(\mathbf{r})$  (without any reference to the wave functions) has an undoubted formal interest, as was pointed out in the original Hohenberg-Kohn theorem. Moreover, in first-principles molecular dynamics [6], the use of an approximate orbital-free kinetic-energy functional, instead of the KS method, makes easier the evaluation of the forces and reduces the computational cost of complex calculations, transforming the  $(3N)$ -dimensional problem into a three-dimensional one [7–9]. Accurate explicit  $T_S[n]$  functionals, which give not only good energies but also correct density profiles for the electron ground state, are clearly needed.

The well known Thomas-Fermi (TF) model [10],

$$T_{\text{TF}}[n] = \int t_0[n(\mathbf{r})]n(\mathbf{r})d\mathbf{r} = \int \frac{3[3\pi^2n(\mathbf{r})]^{2/3}}{10} n(\mathbf{r})d\mathbf{r}, \quad (3)$$

which is the simplest approximation to  $T_S[n]$ , gives poor results when applied to atoms: no accurate total energies, divergent density profiles at the nucleus, no exponential decay when  $r \rightarrow \infty$ , and lack of the characteristic atomic shell structure.

The second order gradient correction to the TF functional, constructed by addition of the Weizsäcker term  $T_W[n]$  [11], constitutes the family of TF( $\lambda$ ) $W$  models:

$$\begin{aligned} T_{\text{TF}(\lambda)W}[n] &= T_{\text{TF}}[n] + \lambda T_W[n] \\ &= T_{\text{TF}}[n] + \lambda \frac{1}{8} \int \frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})} d\mathbf{r}. \end{aligned} \quad (4)$$

$T_W[n]$  is the exact kinetic energy of a system composed of only one electron or by two electrons in the same spatial state. It guarantees the correct exponential decay of the density in atoms and metal surfaces, as well as the Kato cusp condition [12,13]. It is also a lower bound of  $T_S[n]$  and describes the leading term in the linear response of a homogeneous electron gas under short wavelength perturbations [14,15]. These functionals avoid some limitations of the TF model, e.g., the density is finite at the nucleus and the profile has an exponential decay [16], but the resulting ground state densities do not exhibit any shell structure. For  $\lambda = 1$ , there is a large overestimation of the total energies. For  $\lambda = 1/9$ , the functional (4) reproduces the linear response of a homogeneous electron gas under a long wavelength perturbation, getting the conventional second order gradient expansion [17]. In this case, there is a large underestimation of the total energies obtained after minimization of the energy functional. Finally, the interpolation value  $\lambda = 1/5$  proposed by Tomishima and Yonei [18] leads to a sensible improvement in the atomic ground energies but not in the density profiles. The kinetic-energy functionals with density gradients of

higher order [19,20] do not change appreciably the ground energies and the densities' profiles remain without shell structure [21]. Note that the shell structure of atoms can be obtained by introducing into these gradient expansion models some *ad hoc* procedures [22,23].

Different alternatives have been formulated in order to get better descriptions than those given by the gradient expansion models. The Weizsäcker term  $T_w[n]$  introduced in Eq. (4) can be considered as an essential component of  $T_S[n]$  [15]. Therefore the kinetic-energy functional can be written as

$$T_S[n] = T_w[n] + T_{nl}[n], \quad (5)$$

where  $T_{nl}[n]$ , as emphasized by Herring [24], must be of high nonlocal nature.

Several models following this procedure have been proposed. The weighted density approximation (WDA) by Alonso and Girifalco [25], based on the relationship between the exchange hole and the kinetic energy within the Hartree-Fock approximation, gives accurate total atomic energies [26] and an incipient shell structure for closed-shell atoms with  $Z > 30$  [27]. The internal consistency between the exchange and the kinetic terms makes it unclear whether the appearance of oscillations in the density profiles is due to the kinetic functional itself or is because they also use a nonlocal exchange functional. On the other hand, the WDA model using the exact Hartree-Fock exchange hole shows numerical difficulties in jellium surface calculation [28].

Chacón *et al.* [29] came to similar conclusions using an averaged density approximation (ADA) functional which reproduces entirely the linear response of the homogeneous electron gas. Total energies for atoms are quite good, but not as good as the WDA ones. A second peak in the radial density  $4\pi r^2 n(r)$  appears for the Kr and the Xe atoms, but does not in lighter atoms. However, this functional exhibits a long-range behavior which implies poor results for jellium surfaces [30] and for the chemical potential of heavy atoms. These convergence problems in extended systems can be avoided by averaging the local Fermi momentum  $k_F(\mathbf{r}) = [3\pi^2 n(\mathbf{r})]^{1/3}$  instead of the density [30], but the atomic density profiles do not show a clear improvement on the previously quoted results.

Another nonlocal functional is the one developed by Wang and Teter [31], which also reproduces the linear response of the homogeneous electron gas. Calculations of atomlike models (composed of noninteracting electrons under a central Coulomb potential) show weak oscillations in the density, but the first functional derivative of this functional diverges when  $r \rightarrow \infty$ , with the correct limit for localized systems being

$$\lim_{r \rightarrow \infty} \frac{\delta T_{nl}[n]}{\delta n(\mathbf{r})} = 0. \quad (6)$$

Using the basic ideas of the ADA functional, the recent kinetic-energy functionals proposed for solids by Perrot [32] and Smargiassi and Madden [33] need as an input the mean density  $N/V$  of the system and hence their implementation for atomic or molecular systems is not possible.

Concluding, several of the mentioned functionals give good agreement with the KS energies for atomic systems, but they get density profiles that cannot be compared favorably with the exact KS ones. Besides, all the functionals which give densities with a weak shell structure have numerical complications either in extended or in atomic systems.

The absence of a clear atomic shell structure using any kinetic-energy functional is probably due to an incomplete description of nonlocal properties. In this work we present a kinetic-energy functional, generalizing the ADA functional via a symmetrization procedure of the scaling used in the evaluation of the averaged density. That will imply a much better description of the nonlocality of the system. In fact, when applied to atoms, it gives not only accurate total energies but also density profiles with a greatly improved shell structure.

## II. THEORY

In order to obtain a better inclusion of the nonlocal effects of an electron system, we propose a generalization of the ADA functional [29], where the nonlocal component of Eq. (5) is given by

$$T_{nl}[n] = \frac{8}{5} \int t_0[\tilde{n}(\mathbf{r})] n(\mathbf{r}) d\mathbf{r} - \frac{3}{5} T_{TF}[n], \quad (7)$$

with  $\tilde{n}(\mathbf{r})$  being an average of the density,

$$\tilde{n}(\mathbf{r}) = \int n(\mathbf{r}') \Omega(\zeta(\mathbf{r}, \mathbf{r}'), |\mathbf{r} - \mathbf{r}'|) d\mathbf{r}'. \quad (8)$$

$\Omega$  is a normalized weight function and  $\zeta(\mathbf{r}, \mathbf{r}')$  is a function of the density at  $\mathbf{r}$  and  $\mathbf{r}'$ . The inclusion of the TF term in Eq. (7), explained in Ref. [29], allows the proper description of the short wavelength limit of the linear response of a homogeneous electron gas.

While in the original ADA functional  $\zeta(\mathbf{r}, \mathbf{r}') = k_F(\mathbf{r})$ , meaning a spherical average around the point  $\mathbf{r}$  in Eq. (8), a general function  $\zeta(\mathbf{r}, \mathbf{r}')$  will yield a nonspherical average when  $\tilde{n}(\mathbf{r})$  is evaluated. A simple choice for the two-point function  $\zeta(\mathbf{r}, \mathbf{r}')$  is the following symmetrized form:

$$\zeta(\mathbf{r}, \mathbf{r}') = 2^{1/\beta} \left[ \frac{1}{k_F(\mathbf{r})^\beta} + \frac{1}{k_F(\mathbf{r}')^\beta} \right]^{-1/\beta}, \quad (9)$$

where the constant factor  $2^{1/\beta}$  is included in order that  $\zeta(\mathbf{r}, \mathbf{r}')$  be equal to the Fermi momentum in the homogeneous limit. The parameter  $\beta$  will be determined afterwards.

The weight function  $\Omega$  is obtained by imposing the functional to reproduce the physical properties of the homogeneous limit; in particular, its energy and its linear response. The first point is merely accomplished by the normalization condition of the weight function and the second is achieved by means of the equation

$$\begin{aligned} \mathcal{F}\left(\frac{\delta^2 T_S[n]}{\delta n(\mathbf{r}_1)\delta n(\mathbf{r}_2)}\Big|_{n_0}\right) \\ = -\hat{\chi}_0(q, n_0)^{-1} \\ = \frac{1}{k_F} \frac{2\pi^2}{1+[(1-\eta^2)/2\eta]\ln|(1+\eta)/(1-\eta)|}, \end{aligned} \quad (10)$$

where  $\hat{\chi}_0(q, n_0)$  is the Fourier form of the homogeneous noninteracting electron gas (Lindhard) susceptibility [34],  $\eta = q/2k_F$  is a dimensionless momentum, and  $\mathcal{F}$  denotes the Fourier transform. Subtraction of the Weizsäcker term transforms Eq. (10) into

$$\begin{aligned} k_F \mathcal{F}\left(\frac{\delta^2 T_{nl}[n]}{\delta n(\mathbf{r}_1)\delta n(\mathbf{r}_2)}\Big|_{n_0}\right) \\ = \frac{2\pi^2}{1+[(1-\eta^2)/2\eta]\ln|(1+\eta)/(1-\eta)|} - 3\pi^2 \eta^2. \end{aligned} \quad (11)$$

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$$\begin{aligned} 6\hat{\omega}(\eta) - \hat{\omega}(\eta)^2 - \frac{11+\beta}{6}\eta\hat{\omega}'(\eta) - \frac{1}{36}[\eta\hat{\omega}'(\eta)]^2 + \frac{1}{3}\hat{\omega}(\eta)\eta\hat{\omega}'(\eta) + \frac{1}{6}\eta^2\hat{\omega}''(\eta) \\ = \frac{5}{8}\left(3 + \frac{10}{1+[(1-\eta^2)/2\eta]\ln|(1+\eta)/(1-\eta)|} - 15\eta^2\right), \end{aligned} \quad (14)$$

with no explicit dependence on the density. Solving this equation numerically, imposing the conditions  $\hat{\omega}(0)=1$  and  $\lim_{\eta\rightarrow\infty}\hat{\omega}(\eta)=0$ , we get the function  $\hat{\omega}(\eta)$ . The shape of the weight function  $\omega(x)$  is given in the Appendix.

In order to finish the construction of our  $T_S[n]$  we must fix  $\beta$ . For  $|\beta| > 1$ , the first functional derivative of  $T_S[n]$  has a very slow decay for atomic density profiles. The final value  $\beta = 1/2$  was chosen after the minimization of the total energy of atoms for several values of  $\beta$  within  $(-1, 1)$  and comparing both the ground energies and the density profiles with those obtained with the KS method. When  $\beta = 3/4$  is used in the calculations, the results are quite similar to those presented in this paper, giving better energies for heavy atoms but, in general, poorer energies and ionization potentials for light atoms. For other values of  $\beta$  within  $(-1, 1)$  the density profiles also show shell structure, but the energies worsen by about 10%.

Finally, we have to comment that it is possible to develop a model similar to Eqs. (7) and (8) by averaging a certain power  $\gamma$  of the density, instead of the density itself. However, the first functional derivative is not divergent only if  $\gamma \geq 1$ . Prospective calculations with  $\gamma = 4/3$  give much poorer results than those obtained with  $\gamma = 1$ .

### III. RESULTS

In this section we present the results obtained with our functional for the ground-state energies and densities of atoms. We have minimized the total energy (1) solving the Euler-Lagrange equation

The left member in (11) includes the Fourier form  $\hat{\Omega}(q, n_0)$  of the weight function and its derivatives with respect to  $q$ . The right member is dimensionless and it only depends on  $\eta$ , so  $\hat{\Omega}(q, n_0)$  is also scaled in the same way,

$$\hat{\Omega}(q, n_0) = \hat{\omega}(\eta), \quad (12)$$

implying the following form for the real space weight function  $\Omega$ :

$$\Omega(\zeta(\mathbf{r}, \mathbf{r}'), |\mathbf{r} - \mathbf{r}'|) = [2\zeta(\mathbf{r}, \mathbf{r}')]^3 \omega(2\zeta(\mathbf{r}, \mathbf{r}')|\mathbf{r} - \mathbf{r}'|), \quad (13)$$

where  $\omega(x)$  is the inverse Fourier transform of  $\hat{\omega}(\eta)$ . This equation shows that the function  $\zeta(\mathbf{r}, \mathbf{r}')$  is a scaling factor which depends on the density at both points  $\mathbf{r}$  and  $\mathbf{r}'$ . We expect that the nonspherical average in Eq. (8) will improve the treatment of the nonlocal effects.

Using these considerations, Eq. (11) becomes

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$$\frac{\delta E[n]}{\delta n(\mathbf{r})} = \mu, \quad (15)$$

where  $\mu$  is a Lagrange multiplier related to the conservation of the number of electrons; it can be identified with the chemical potential of the system [3]. We have chosen for  $E_{xc}[n]$  the local density approximation (LDA) proposed by Perdew and Wang [35], adjusted to the Monte Carlo calculations by Ceperley and Alder [36], which is easy to extend to spin polarized densities. All calculations in this paper, including those performed with the KS method, have been carried out using this xc functional in order to allow a proper comparison between the different kinetic-energy functionals and the exact KS method.

To solve Eq. (15) we have made the well known transformation into a Schrödinger-like equation by means of the substitution  $\Psi(\mathbf{r}) = \sqrt{n(\mathbf{r})}$  [37], resulting in the equation

$$\left[-\frac{1}{2}\nabla^2 + V_e(\mathbf{r})\right]\Psi(\mathbf{r}) = \mu\Psi(\mathbf{r}), \quad (16)$$

with the effective potential

$$V_e(\mathbf{r}) = \frac{\delta T_{nl}[n]}{\delta n(\mathbf{r})} + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} - \frac{Z}{r} + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \quad (17)$$

In Table I we compare the exact KS total energies for several closed-shell atoms with those obtained, after their minimization, with our new functional and with the original nonsymmetric ADA functional [29] (which we will refer to

TABLE I. Total energies for several closed-shell atoms (in atomic units) obtained through the Kohn-Sham method and the kinetic-energy functionals quoted in the text.

	KS	This work	nsADA	TF(1/5)W	TF(1/9)W
He	-2.834	-2.848	-2.839	-2.917	-3.324
Ne	-128.23	-128.70	-140.42	-129.53	-140.62
Ar	-525.93	-521.62	-554.03	-526.31	-563.42
Kr	-2750.1	-2742.7	-2760.8	-2748.6	-2902.0
Xe	-7228.8	-7205.3	-7159.4	-7218.1	-7569.0
Be	-14.446	-14.786	-15.666	-14.717	-16.399
Mg	-199.13	-198.43	-215.47	-200.05	-216.20
Ca	-675.73	-671.15	-707.17	-676.73	-722.78
Sr	-3129.4	-3120.8	-3132.5	-3126.5	-3297.6

as nsADA). We also include the results for the TF(1/9)W and TF(1/5)W functionals. Our functional and the TF(1/5)W functional give a clear improvement upon the nsADA and TF(1/9)W functionals, with a very good agreement with the KS results. Note that the differences between our TF( $\lambda$ )W results and those found in the paper by Stich *et al.* [38] are due to the absence of correlation in their calculations. On the other hand, our KS results are in agreement with previous calculations [4] performed with another LDA parametrization of the xc functional done by Perdew and Zunger [39].

We have not included the Hartree-Fock [40] and WDA [26] energies because of the different treatment of the xc energy in each case. Anyway, the differences between our energies and the KS ones, using any LDA for the xc, are lower than 1%; they are of the same order of magnitude as the differences between the KS values and the Hartree-Fock or WDA energies (see also [41]).

In Fig. 1 we plot the electronic density profiles of the Ne, Ar, and Kr atoms. KS densities are compared with those obtained with the mentioned models. The TF(1/5)W functional smooths out the shell structure and the densities are very similar to those obtained with any other TF( $\lambda$ )W functional. The profiles obtained with the nsADA functional show a clear improvement in the position and height of the first maximum ( $K$  shell) but there is no structure associated to the second ( $L$ ) shell for lighter atoms. However, for heavier atoms like Kr, the nsADA functional gives a density with a second peak, showing a trend similar to that observed with the WDA functional (see Fig. 2). Finally, our symmetrized model gives an excellent description of the  $K$  shell for every atom and, besides, there is a second oscillation in the Ne atom profile that represents the  $L$  shell, although the height and position of this second maximum are displaced with respect to the KS one. The density of the Ar and Kr atoms also exhibits a second peak between the  $L$  and third ( $M$ ) shells. Moreover, as presented in the inset, Kr and heavier atoms' profiles show some additional weak structure in the outer region of the atom.

In Fig. 2 we compare the density profiles obtained with our functional and the WDA results [25,27] for the Ar and Kr atoms. We have to remark again the different treatment of the xc term in the WDA model. But we want to include a comparison between density profiles obtained by accurate nonlocal functionals, which make no reference to the KS

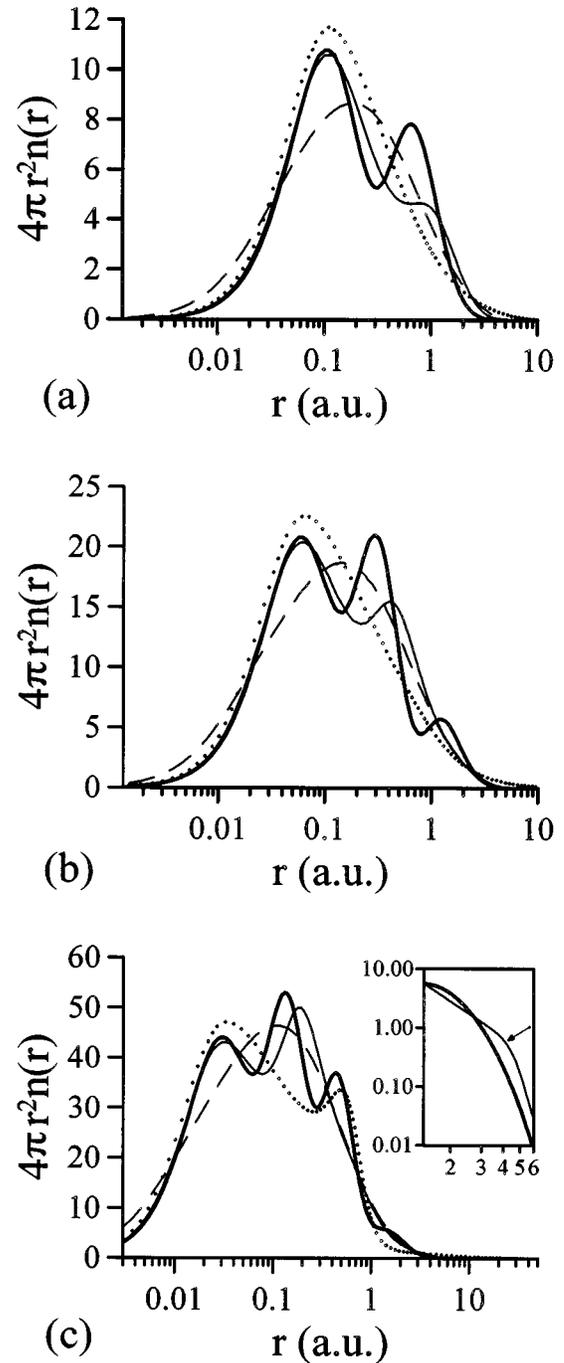


FIG. 1. Radial density  $4\pi r^2 n(r)$  for the Ne atom (a), the Ar atom (b), and the Kr atom (c). Thick solid line, Kohn-Sham; solid line, present work; dotted line, nsADA functional; dashed line, TF(1/5)W.

orbitals. As was mentioned in the Introduction, the WDA profiles show a weak structure with two local maxima. However, the description of the  $K$  shell is worse than that performed with our functional, although the positions of the second maximum are very similar in both cases. Additional structure for heavy atoms is not observed in the WDA profiles.

In Fig. 3 we plot the chemical potentials, obtained after resolution of the Euler-Lagrange equation for different  $Z$  values. They are compared with the highest KS orbital energy,

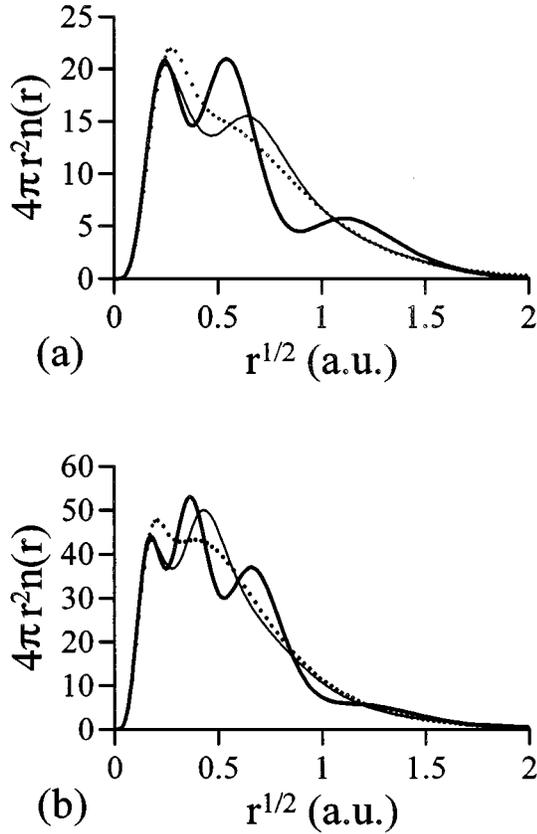


FIG. 2. Radial densities obtained with the symmetrized ADA functional (solid line), with the WDA functional (dotted line), and with the Kohn-Sham method (thick solid line). (a) Ar atom; (b) Kr atom.

which equals the chemical potential in the KS method [42]. We can observe that the TF(1/5)W chemical potential is practically constant for all atoms and that the nsADA values increase monotonously, an indication of stability problems. In contrast, the values obtained with our functional are not monotonic, according to the exact behavior, although for light atoms these values are overestimated. For atoms with  $Z > 20$  our results are better than the TF(1/5)W ones.

In Table II we present the results of the chemical potential

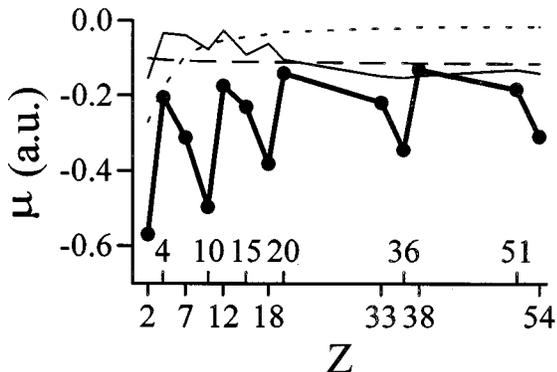


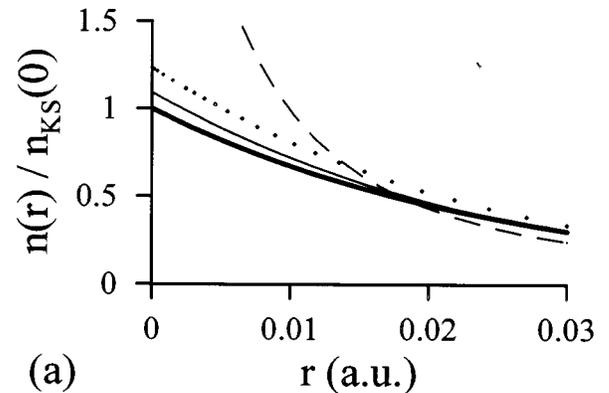
FIG. 3. Chemical potential for several atoms with spherical symmetry. Solid line with points, Kohn-Sham; solid line, present work; dotted line, nsADA functional; dashed line, TF(1/5)W.

TABLE II. Chemical potentials and (in brackets) first ionization energies  $E(N-1) - E(N)$  in a.u. for noble gas atoms, obtained with the Kohn-Sham method and the kinetic-energy functionals quoted in the text.

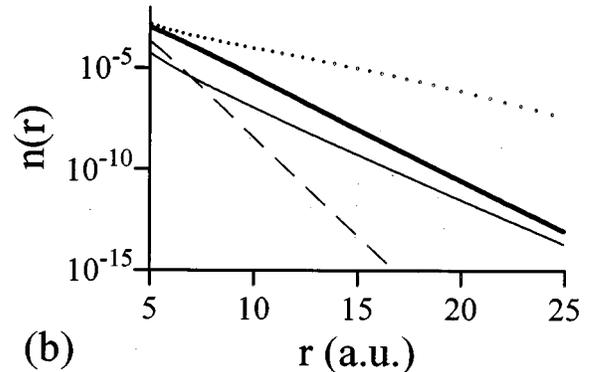
	KS	This work	nsADA	TF(1/5)W	TF(1/9)W
He	-0.570 [0.83]	-0.155 [0.50]	-0.271 [0.60]	-0.101 [0.22]	-0.092 [0.20]
Ne	-0.497 [0.82]	-0.087 [0.29]	-0.063 [0.18]	-0.109 [0.30]	-0.096 [0.28]
Ar	-0.382 [0.59]	-0.072 [0.22]	-0.037 [0.17]	-0.111 [0.28]	-0.097 [0.25]
Kr	-0.345 [0.53]	-0.153 [0.30]	-0.020 [0.06]	-0.113 [0.27]	-0.098 [0.25]
Xe	-0.309 [0.47]	-0.140 [0.28]	-0.017 [0.05]	-0.114 [0.26]	-0.099 [0.24]

of noble gas atoms and their relaxed ionization energies  $I = E(N-1) - E(N)$ , with  $E(N)$  and  $E(N-1)$  being the total energies of the neutral atom and the first positive ion, respectively. Except for He, we get better results than with the nsADA functional.

Figure 4 shows the behavior of the Ca atom ( $Z=20$ ) density near the nucleus. The inclusion of the Weizsäcker term provides a good description of the density when  $r \rightarrow 0$  for both symmetrized and nonsymmetrized ADA func-



(a)



(b)

FIG. 4. Behavior of the density  $n(r)$  for the Ca atom, near the nucleus (a) and for large values of  $r$  (b). Notation is the same as in Fig. 1.

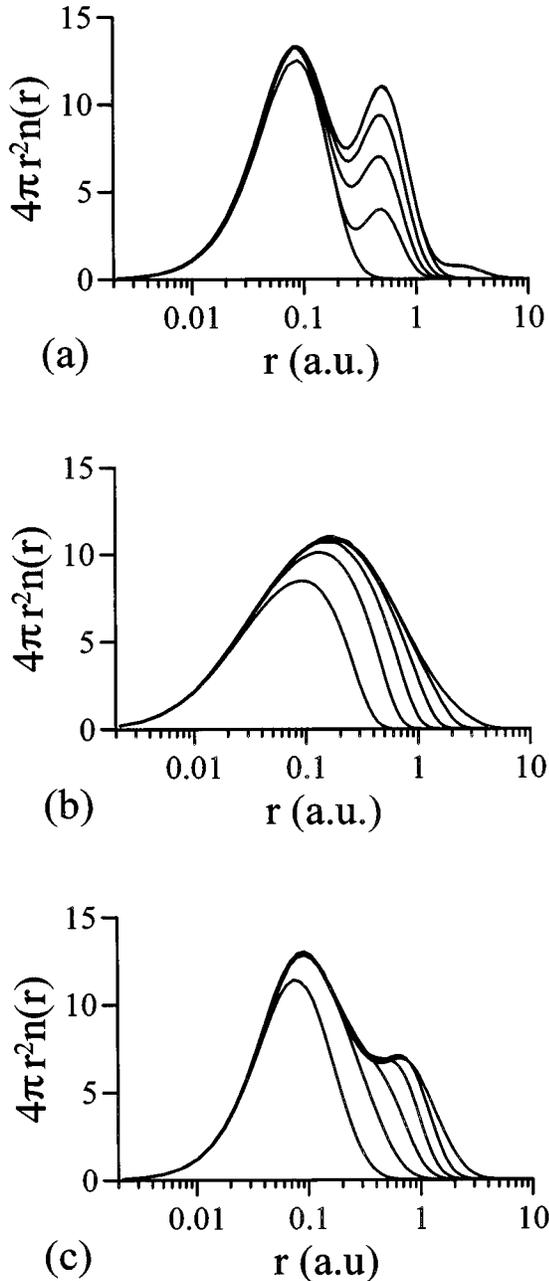


FIG. 5. Radial density for the neutral Mg ( $Z=12$ ) atom and for several of its ions ( $N=10, 8, 6, 4, 2$ ) obtained with (a) the KS method, (b) the TF(1/5)W approximation, (c) our functional.

tionals. In contrast, the TF(1/5)W density is clearly overestimated.

The asymptotic behavior of the density is related to the chemical potential of the atom through the equation

$$n(\mathbf{r}) \sim \exp[-2\sqrt{-2\mu}r] \quad \text{for } r \rightarrow \infty \quad (18)$$

when the exact kinetic functional is used [4]. The relation (18) is verified by those kinetic-energy functionals constructed using Eq. (5) and verifying the additional condition (6). For the TF( $\lambda$ )W model, the correct law (18) is substituted by

TABLE III. Total energies in a.u. for group Vb atoms. Between brackets, total energies when the polarizability is forced to be equal to  $\xi_{\text{KS}}$  in the minimization.

	KS	This work	nsADA	TF(1/5)W	TF(1/9)W
N	-54.134	-55.326	-60.307	-55.407	-60.773
		[-55.261]	[-59.532]	[-55.001]	[-60.349]
P	-340.00	-337.53	-362.87	-340.67	-366.27
		[-337.41]	[362.58]	[-340.42]	[365.97]
As	-2232.6	-2227.1	-2254.1	-2233.9	-2362.3
		[-2227.1]	[-2254.0]	[-2233.7]	[-2362.1]
Sb	-6310.3	-6295.0	-6256.1	-6300.1	-6612.8
		[-6295.0]	[-6256.1]	[-6300.0]	[-6612.3]

$$n(\mathbf{r})_{\text{TF}(\lambda)W} \sim \exp\left[-2\sqrt{-\frac{2\mu}{\lambda}}r\right] \quad \text{for } r \rightarrow \infty. \quad (19)$$

This expression shows that, for the TF( $\lambda$ )W functional and  $\lambda \neq 1$ , the better the chemical potential, the worse the decay of the density, as can be clearly seen in Fig. 4. For the Ca atom the KS chemical potential almost coincides both with that obtained with the TF(1/5)W functional and with our functional, but the decay of our density is much closer to the KS one; the bad behavior of the TF(1/5)W decay reflects the value of  $\lambda$ . On the other hand, the slow decay of the nsADA profile is related to the small absolute value of its chemical potential.

Finally, in Fig. 5 we plot the density profile for the neutral Mg atom ( $Z=12$ ) and several of its ions, as obtained with our functional and with the TF(1/5)W approximation. We see the progressive smearing off of the shells as we remove the electrons of the ions. For our functional, and according to the exact KS behavior, the position of the second peak does not change substantially when the number of electrons is greater than ten and the inner shell remains invariant until the number of electrons is less than four. This trend is not described at all by the TF(1/5)W model.

#### IV. EXTENSION TO SPIN-POLARIZED SYSTEMS

The kinetic-energy functional presented in the previous sections can be generalized in order to include the spin polarization in systems where, in the ground state,

$$n_+(\mathbf{r}) \neq n_-(\mathbf{r}), \quad (20)$$

$n_\sigma(\mathbf{r})$  being the electron density with spin orientation  $\sigma$ . We must remark that only the inclusion of a suitable xc functional can describe spin-polarized systems, but the corresponding extension for the kinetic functional must be done in order to describe any electronic system within a functional theory for the spin density.

Because of the *noninteracting* character of the system represented by  $T_S[n]$ , the mentioned extension is made directly by means of the definition [43]

$$T_S[n_+, n_-] = \frac{1}{2}T_S[2n_+] + \frac{1}{2}T_S[2n_-], \quad (21)$$

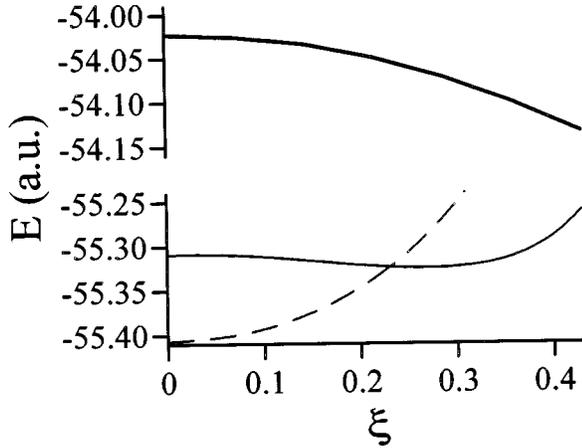


FIG. 6. Total energy vs polarizability for the N atom. Dashed line, TF(1/5)W; solid line, this work; thick solid line, KS.

where  $T_S[n]$  is the non-spin-polarized kinetic-energy functional. (This easy extension cannot be made for the correlation energy functional, which describes properties of the *interacting* electron gas.) Inserting our functional (7) into Eq. (21) we get the definitive expression of the nonlocal kinetic-energy functional. Of course, for non-spin-polarized systems like those described in the preceding section, both formulations are completely equivalent.

To minimize the new functional we solve the two coupled Euler-Lagrange equations for both spin densities,

$$\frac{\delta E[n_+, n_-]}{\delta n_\sigma(\mathbf{r})} = \frac{\delta T_S[n_+, n_-]}{\delta n_\sigma(\mathbf{r})} - \frac{Z}{r} + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}[n_+, n_-]}{\delta n_\sigma(\mathbf{r})} = \mu_\sigma, \quad (22)$$

where the  $E_{xc}[n]$  is, in our calculations, the extension to spin-polarized systems of the functional [35] we have used previously. Conserving the number of electrons with each spin orientation we obtain the energy minimum for a given polarization  $\xi = (N_+ - N_-)/(N_+ + N_-)$ , where  $N_\sigma$  is the number of electrons with spin orientation  $\sigma$ . By varying the distribution of particles between the two possible spin states, we get the final energy of the ground state of the system, its density profile, and its spin polarization. At this point, we must have chemical equilibrium between both spin oriented electron gases, i.e.,  $\mu_+ = \mu_-$ .

Group Vb of the periodic table is a good test for the spin-polarized functionals. The nsADA and all the square gradient based functionals give a non-spin-polarized ground state, i.e.,  $\xi=0$ , for every atom of the group. However, the symmetrized ADA functional gives a spin-polarized ground state with  $\xi=0.272$  for the N atom and  $\xi=0.077$  for the P

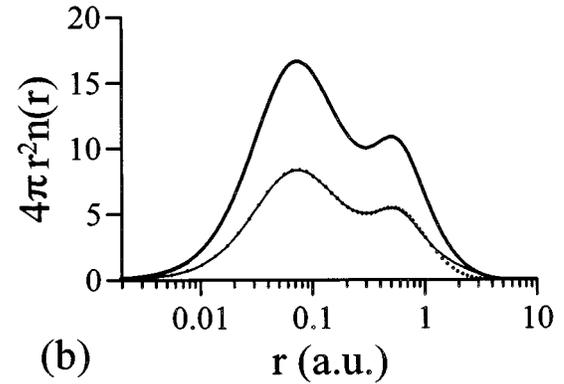
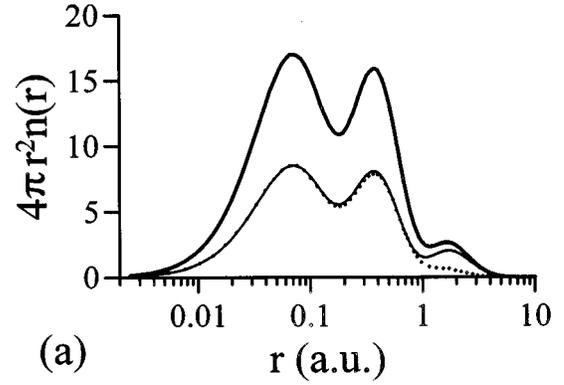


FIG. 7. Radial total density (thick solid line) and spin densities (solid and dotted lines) for the P atom obtained with the KS method (a) and with our spin-polarized functional (b).

(the KS values are, respectively,  $\zeta_{KS}=0.429$  and  $\zeta_{KS}=0.200$ ). In Fig. 6 we plot the functions  $E(\xi)$  obtained with our functional, with the TF(1/5)W functional, and with the KS method for the N atom. On the other hand, for the heavier atoms of group Vb (with a weaker KS polarizability;  $\xi_{KS}=0.091$  for the As and  $\xi_{KS}=0.059$  for the Sb), our functional yields unpolarized ground states.

Note that if we calculate the differences between the atomic energy *with the KS polarization* and the final ground state energy obtained with each functional, the results for our functional are much lower than the ones obtained with any of the other functionals (see Fig. 6 and also Table III, where the total energies of several group Vb atoms are presented). That means the energy versus polarization curve in our symmetrized functional is much flatter than for the other ones.

The total and spin densities for the P atom using the new functional are plotted in Fig. 7. We can see that the total density profile exhibits two inner shells with a practically equal contribution from both spin densities, in complete

TABLE IV. Values of the parameters for the fitting of the weight function  $\omega(x)$ .

$B$	$\delta$	$A$	$a_1$	$a_2$	$a_3$
5.22594	4.23212	-0.0303061	0.276801	1.47097	0.458380
$a_4$	$a_5$	$a_6$	$a_7$	$a_8$	
0.375101	-0.0372670	0.0100745	0.765885	0.405737	

agreement with the exact behavior. On the other hand, the  $M$  shell, mainly due to the  $3p$  electrons, is clearly polarized and our result shows a major presence of electrons of one of the spin orientations in a region around  $r=3$  a.u.

## V. CONCLUSIONS

In this paper we have presented a nonlocal ADA kinetic-energy functional which includes the Weizsäcker term (4) and a nonlocal term (7) with an averaged density calculated through a universal weight function. We have symmetrized via Eq. (9) the evaluation of the averaged density and this symmetrization has clearly increased the nonlocal character of the functional by the inclusion of a nonspherical averaging procedure.

The functional has given very accurate total and kinetic atomic energies, when compared to those obtained with the exact KS method, as well as acceptable first ionization energies and polarized ground states for the lighter atoms of group Vb .

The present kinetic-energy functional gives a clear shell structure in all the atoms, except for Li and Be. Although some of the previous nonlocal kinetic functionals have shown incipient structures for heavy atoms, only when using the present nonspherical average procedure is a clear structure for most of the atoms obtained. Moreover, the polarized version of the functional has been able not only to show the outer shell of polarized atoms but even to distinguish unambiguously the spin density of that shell. So, we confirm the idea that only when using highly nonlocal models for the kinetic-energy functional is it possible to obtain results close to the exact ones, both for energies and for density profiles.

We have constructed our functional with no reference to the specific properties of atomic systems, except in the final choice of the parameter  $\beta$  which appears in Eq. (9). However, when discussing the appearance or not of the shell structure, the important point is the inclusion of the two-point symmetrized function  $\zeta(\mathbf{r}, \mathbf{r}')$  and the specific value of  $\beta$  would be of minor importance.

The main limitations of our functional are the absence of polarization in some heavy atoms of group Vb and that the values of the first ionization energy for light atoms do not clearly improve upon the results obtained with the nsADA and TF(1/5)W functionals. The use of the linear response of the homogeneous electron gas to construct our functional could affect the correct description of electronic systems in regions where either the collective effects or the inhomogeneity of the density are extremely high.

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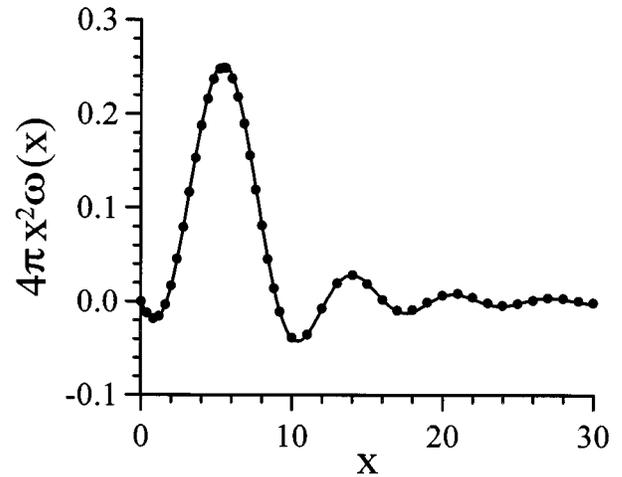


FIG. 8. Weight function  $\omega(x)$  for  $\beta=1/2$ . Dots: numerical values; solid line: parametrized function.

## APPENDIX: PARAMETRIZATION OF THE WEIGHT FUNCTION

Due to the spherical symmetry of the function  $\hat{\omega}(\eta)$  [see Eq. (14)], the function  $\omega(x)$  introduced in Eq. (13) is given by

$$\omega(x) = \frac{1}{2\pi^2 x} \int_0^\infty \eta \sin(\eta x) \hat{\omega}(\eta) d\eta. \quad (\text{A1})$$

It is easy to see that the asymptotic decay of  $\hat{\omega}(\eta)$  for  $\eta \rightarrow \infty$  is proportional to  $\eta^{-2}$ . That implies an integrable singularity in  $\omega(x)$  of the type  $a/x$  when  $x \rightarrow 0$ . On the other hand, the nonanalytical behavior of the Lindhard function at  $\eta=1$  induces a nonanalyticity in  $\hat{\omega}(\eta)$  at  $\eta=1$ . Consequently, the decay of  $\omega(x)$  is not exponential but of the type

$$\omega(x) = \frac{B \cos(x + \delta)}{x^5} + o(x^{-6}), \quad x \gg 0. \quad (\text{A2})$$

This behavior has a minor contribution when using the functional in localized systems as atoms, however, it is important when calculating properties of extended systems like metal surfaces [30].

In order to simplify the use of the functional we present a parametrization of the weight function for  $\beta=1/2$ . Any analytical parametrization of  $\hat{\omega}(\eta)$  will not include the above mentioned nonanalyticity for  $\eta=1$ . For that reason, it is preferable to parametrize  $\omega(x)$  instead of  $\hat{\omega}(\eta)$ . We propose the following fitting for  $x$  in the interval  $[0,16]$ :

$$\omega(x) = \frac{A}{x} \left[ \frac{\cos(a_1 x + a_2)}{\exp(a_3 x)} + \frac{(a_4 + a_5 x + a_6 x^2) \sin(a_7 x)}{\exp(a_8 x)} \right] \quad (\text{A3})$$

and the expression (A2) for  $x \geq 16$ , taking into account the

normalization of  $\omega(x)$  and the continuity of  $\omega(x)$  and its derivative at  $x=16$ . The parameters of the fitting are shown in Table IV. Differences between the parametrized form given in Eqs. (A2) and (A3) and the numerical values of

$\omega(x)$  are negligible (see Fig. 8). Although we have used the numerical weight function in the present paper, we have not found any difference in the results when the parametrized  $\omega(x)$  is used in the calculations.

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