PHYSICAL REVIEW A, VOLUME 62, 062510

Electronic-structure kinetic-energy functional based on atomic local-scaling transformations

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(Received 6 July 2000; published 13 November 2000)

Two explicit noninteracting kinetic-energy functionals for electronic-structure calculations of molecules are presented. These functionals are obtained by combining kinetic-energy functionals for isolated atoms—generated by means of local-scaling transformations—so as to produce kinetic-energy functionals applicable to the electronic structure of molecules. The adequacy of these functionals was tested by calculating the kinetic energy of a few diatomic molecules. In spite of the fact that computationally these functionals are not harder to apply than the SGA and the generalized-gradient-approximation kinetic-energy functionals, they lead, nevertheless, to a considerably higher accuracy.

PACS number(s): 31.15.Ew

I. INTRODUCTION

The search for an adequate representation of the kinetic energy functional $T_s[\rho]$ of noninteracting systems is an important, albeit difficult problem in density-functional theory (DFT). The difficulty stems from the fact that the kinetic energy is generally one order of magnitude larger than the exchange energy and two orders of magnitude larger than the correlation energy. This means, accordingly, that the accuracy needed to represent this functional must be one or two orders of magnitude larger than that required to represent exchange and correlation energy functionals, respectively.

Of course, in the Kohn-Sham theory, this problem is circumvented by writing $T_s[\rho]$ exactly in terms of the Kohn-Sham orbitals. The price one must pay, however, is that one must deal with a system of N coupled orbital equations. In this sense, it would be highly desirable to express $T_s[\rho]$ as an explicit (and analytic) functional of the density because it would allow us to develop a version of DFT where energy calculations can be carried out by solving a single equation involving only the density. Moreover, such an orbital-independent approach would present considerable advantages over the usual orbital-based ones for problems such as molecular-dynamics simulations [1]. But, it must be understood that for this type of simulation, highly accurate analytical approximations to the kinetic-energy functional $T_s[\rho]$ are necessary.

In this paper we advance a method, based on local-scaling transformations, for the purpose of constructing such approximations to $T_s[\rho]$ for molecules. We present two such approximations. In the first one, we replace the total molecular kinetic-energy modulating factor by its simpler *atomic* counterpart. In the second, in addition, we introduce a more elaborate approximation for the molecular local-scaling factor. In both cases we have used factors generated for spherically symmetric atoms.

In Sec. II A, we introduce, for completeness, a previously derived expression for the kinetic-energy functional of atoms [2]. In Sec. II B, we advance two approximations leading to the model kinetic-energy functionals employed in this work. In Sec. II C, we extend these models to molecules and clusters. Finally, in Sec. III, we present calculations based on these models both for atoms and diatomic molecules.

II. METHOD

A. LST kinetic-energy atomic functional

Local-scaling transformations (LST) permit us to construct an orthonormal orbital set $\{\phi_{\rho,i}(\vec{r})\}_{i=1}^{N}$, where the orbitals are constrained to yield a fixed density ρ. Moreover, the minimization of the noninteracting kinetic-energy functional constructed from these orbitals under the constraint that ρ is the exact density leads to Kohn-Sham orbitals $\{\phi_{\rho,i}^{\mathrm{KS}}(\vec{r})\}_{i=1}^{N}$ [2–4].

Consider the set $\{\phi_{\rho,i}(\vec{r})\}_{i=1}^{N}$ of locally scaled atomic orbitals which can be written as the product of a radial times a spherical harmonic function:

$$\phi_{\rho,i}(\vec{r})=R_{\rho,n_il_i}(r)Y_{l_i,m_i}(\theta,\phi). \tag{1}$$

For such a set, the kinetic-energy functional is given by (see details in Ref. [2])

$$\begin{aligned}T_s[\rho]&=\frac{1}{2}\sum_{i=1}^{N}\int d^3\vec{r}\,\nabla_{\vec{r}}\phi_{\rho,i}^{*}(\vec{r})\nabla_{\vec{r}}\phi_{\rho,i}(\vec{r})\\&=T_W[\rho]+\frac{1}{2}\int d^3\vec{r}\,\rho^{5/3}(\vec{r})A_N([\rho];\vec{r}),\end{aligned} \tag{2}$$

where $T_W[\rho]$ is the Weiszäcker kinetic-energy functional [5]:

$$T_W[\rho]=\frac{1}{8}\int d^3\vec{r}\,\frac{[\nabla\rho(\vec{r})]^2}{\rho(\vec{r})}. \tag{3}$$

The total kinetic-energy modulating factor A_N introduced in [6] is

$$\begin{aligned}A_N([\rho];\vec{r})=2[&L^{4/3}([\rho];\vec{r})\tau_N(\vec{f}(\vec{r}))\\&+L^{-2/3}([\rho];\vec{r})\kappa_N(\vec{f}(\vec{r}))],\end{aligned} \tag{4}$$

where $L([\rho];\vec{r})$ is the local-scaling modulating factor:

$$L([\rho];\vec{r})=1+\vec{r}\cdot\nabla_{\vec{r}}\ln\lambda([\rho];\vec{r}) \tag{5}$$

and τ_N and κ_N are the radial and the angular kinetic-energy modulating factors, respectively, given by

$$\tau_N(\vec{f}(\vec{r}))=\frac{1}{\rho_g^{8/3}(\vec{f})}\frac{1}{2}\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\left[R_{g,n_il_i}(f)\frac{dR_{g,n_jl_j}(f)}{df}-R_{g,n_jl_j}(f)\frac{dR_{g,n_il_i}(f)}{df}\right]^2 \tag{6}$$

and

$$\kappa_N(\vec{f}(\vec{r}))=\frac{1}{\rho_g^{5/3}(\vec{f})}\frac{1}{2}\sum_{i=1}^{N}l_i(l_i+1)\left(\frac{R_{g,n_il_i}(f)}{f}\right)^2. \tag{7}$$

There is the following first-order differential equation involving the one-particle generating (initial) density ρ_g, the final density ρ, and the local-scaling transformation function $\lambda([\rho];\vec{r})=f(\vec{r})/r$ (here $f\equiv f(\vec{r})=|\vec{f}(\vec{r})|=|\lambda([\rho];\vec{r})\vec{r}|$):

$$\lambda([\rho];\vec{r})=\left(\frac{\rho(\vec{r})}{\rho_g(\vec{f})}\frac{1}{L([\rho];\vec{r})}\right)^{1/3}. \tag{8}$$

It is clear that in the formulation of the atomic kinetic-energy functional given by Eq. (2), because we assume that the transformed functions are of the form given by Eq. (1), the local-scaling transformation function is just a function of the radial coordinate, namely, $\lambda(r)$. As a consequence, the first-order differential equation becomes in this particular case

$$\lambda([\rho];r)=\left(\frac{\rho(r)}{\rho_g(f)}\right)^{1/3}\left(1+r\frac{d\ln\lambda([\rho],r)}{dr}\right)^{-1/3}, \tag{9}$$

where the initial density is given by

$$\rho_g(r)=\sum_{i=1}^{N}|R_{g,n_il_i}(r)|^2. \tag{10}$$

After solving Eq. (9), the transformed radial orbitals $R_{\rho,n_il_i}(r)$ can be calculated through the expression

$$R_{\rho,n_i,l_i}(r)=\sqrt{\frac{\rho(r)}{\rho_g(f)}}R_{g,n_il_i}(f), \tag{11}$$

where $f(r)=\lambda(r)r$.

In Eqs. (5) and (8), we emphasize the fact that there is a nonexplicit dependence between the transformation function λ and the final density ρ. It should be noted that the transformed vector $\vec{f}$ and hence the modulating factors $L([\rho];\vec{r})$, τ_N, and κ_N also evince the same nonexplicit dependence on the final density.

B. Approximate functional: Atoms

Let us consider two final densities: a reference one, $\rho(\vec{r})$, which could be nonspherically symmetric, and a spherically symmetric one, $\rho_0(\vec{r})$. The latter is connected to an initial density ρ_g through the known LST transformation function $\lambda([\rho_0];\vec{r})$. If the reference density ρ is close to the final density ρ_0, then the transformation function $\lambda([\rho_0];\vec{r})$ should be close to $\lambda([\rho];\vec{r})$, namely, to the local-scaling transformation function connecting ρ_g to the final density ρ:

$$\lambda([\rho];\vec{r})\approx\lambda([\rho_0];\vec{r}). \tag{12}$$

In general, we see that if the density ρ is nonspherically symmetric and it deviates considerably from the spherically symmetric case, then this approximation would not be adequate at all.

The idea is, hence, to obtain approximate kinetic-energy functionals by introducing in Eqs. (2) and (4) the transformation function $\lambda([\rho_0];\vec{r})$, the transformed vector $\vec{f}_0(\vec{r})$, and the modulating factors $L([\rho_0];\vec{r})$, $\tau_N(\vec{f}_0(\vec{r}))$, and $\kappa_N(\vec{f}_0(\vec{r}))$ calculated for the spherically symmetric density ρ_0, instead of for the reference one. Thus, in this first ansatz the approximate functional becomes

$$T_s^{m0}[\rho]=T_W[\rho]+\frac{1}{2}\int d^3\vec{r}\,\rho^{5/3}(\vec{r})A_N([\rho_0];\vec{r}), \tag{13}$$

where

$$A_N([\rho_0];\vec{r})=2[L^{4/3}([\rho_0];\vec{r})\tau_N(\vec{f}_0(\vec{r}))+L^{-2/3}([\rho_0];\vec{r})\kappa_N(\vec{f}_0(\vec{r}))]. \tag{14}$$

The approximate Eqs. (13) and (14) are based on the closeness of local-scaling transformations [Eq. (12)] for two close densities.

Another approximate relation for the unknown transformation function $\lambda([\rho];\vec{r})$ can be obtained by replacing in the right-hand side of Eq. (8) the function $\lambda([\rho];\vec{r})$ by $\lambda([\rho_0];\vec{r})$:

$$\lambda([\rho];\vec{r})\approx\lambda^{(1)}([\rho];\vec{r})\equiv\left(\frac{\rho(\vec{r})}{\rho_g(\vec{f}_0)}\frac{1}{L([\rho_0];\vec{r})}\right)^{1/3}. \tag{15}$$

Clearly, another approximate kinetic-energy functional can be obtained by introducing in Eqs. (2), (4), and (5) the $\lambda^{(1)}([\rho];\vec{r})$ given by Eq. (15) and the transformed vector $\vec{f}_0(\vec{r})$ calculated for the density ρ_0:

$$T_s^{m1}[\rho]=T_W[\rho]+\frac{1}{2}\int d^3\vec{r}\,\rho^{5/3}(\vec{r})A_N^{(1)}([\rho,\rho_0];\vec{r}), \tag{16}$$

where $A_N^{(1)}$ is defined as

$$A_N^{(1)}([\rho,\rho_0];\vec{r})=2[\{L^{(1)}([\rho,\rho_0];\vec{r})\}^{4/3}\tau_N(\vec{f}_0(\vec{r}))+\{L^{(1)}([\rho,\rho_0];\vec{r})\}^{-2/3}\kappa_N(\vec{f}_0(\vec{r}))] \tag{17}$$

and

$$L^{(1)}([\rho,\rho_0];\vec{r}) \equiv 1+\vec{r}\cdot\boldsymbol{\nabla}_{\vec{r}}\ln\lambda^{(1)}([\rho];\vec{r})$$

$$=\frac{1}{3}\,\frac{\vec{r}\cdot\boldsymbol{\nabla}_{\vec{r}}\rho(\vec{r})}{\rho(\vec{r})}-\frac{1}{3}\vec{r}\cdot\boldsymbol{\nabla}_{\vec{r}}\ln[\rho_g(f_0(r))$$

$$\times\{1+\vec{r}\cdot\boldsymbol{\nabla}_{\vec{r}}\ln\lambda([\rho_0];\vec{r})\}]. \qquad (18)$$

For atoms, for example, we may assume that the two densities ρ and ρ_0 are the exact and the Hartree-Fock (HF) ones. These densities are used to test the approximate functionals defined by Eqs. (13) and (16) for atoms.

C. Approximate functional: An extension to molecules and clusters

Let us consider an electronic system (molecule or cluster) which consists of M atoms. For a given atom A, the LST given by Eq. (8) can be solved exactly for some final density ρ_{0A} and, hence, in this way, the transformed functions $\lambda([\rho_{0A}];\vec{r})$, $A=1,\ldots,M$ can be found. Then the whole space can be divided into M subvolumes $\{\Omega_A\}_{A=1,\ldots,M}$, each one of them corresponding to a given atom. For, example, for the system composed by the same atoms the space can be divided in the following way:

$$\vec{r}\in\Omega_A \quad \text{if} \quad \min_{B=1,\ldots,M}|\vec{r}-\vec{R}_B|=|\vec{r}-\vec{R}_A|, \qquad (19)$$

where the vectors $\vec{R}_A$ denote the nuclear positions. In each volume Ω_A we choose a coordinate system whose origin is at the nucleus A. Within a volume Ω_A we assume that $A_N \simeq A_N([\rho_{0A}];\vec{r})$ and $L^{(1)}\simeq L^{(1)}([\rho,\rho_{0A}];\vec{r})$ calculated for atom A, i.e., we define A_N and $L^{(1)}$ in Eqs. (13), (16), and (17) for the whole system in the following way:

$$A_N([\rho_0];\vec{r})\equiv A_N([\rho_{0A}];\vec{r}) \quad \text{if} \quad \vec{r}\in\Omega_A,$$

$$L^{(1)}([\rho,\rho_0];\vec{r})\equiv L^{(1)}([\rho,\rho_{0A}];\vec{r}) \quad \text{if} \quad \vec{r}\in\Omega_A, \qquad (20)$$

where $A_N([\rho_{0A}];\vec{r})$ and $L^{(1)}([\rho,\rho_{0A}];\vec{r})$ are defined by Eqs. (14) and (18) for the atomic density ρ_{0A}. The factors $A_N([\rho_0];\vec{r})$ and $L^{(1)}([\rho,\rho_0];\vec{r})$ are functionals of the nonphysical density ρ_0 which is the composition of the initial atomic densities:

$$\rho_0(\vec{r})=\rho_{0A}(\vec{r}) \quad \text{if} \quad \vec{r}\in\Omega_A. \qquad (21)$$

Thus the factors $A_N([\rho_0];\vec{r})$ and $L^{(1)}([\rho,\rho_0];\vec{r})$ for the whole molecular system, defined by Eq. (20) on the basis of the atomic factors $\{A_N([\rho_{0A}];\vec{r})\}_{A=1,\ldots,M}$ and $\{L^{(1)}([\rho,\rho_{0A}];\vec{r})\}_{A=1,\ldots,M}$, may then be used to construct the approximate kinetic-energy functionals T_s^{m0} and T_s^{m1} described by Eqs. (13) and (16). The approximation given by Eqs. (13) and (16) is based on the assumption that the local-scaling transformations described by Eq. (12) are interchangeable provided that the molecular and the isolated-atom densities are quite close within a given atomic region. The plausibility of this assumption is guaranteed by the fact that in most chemical systems the molecular density can be envisioned as being produced by small perturbations of the isolated-atom densities. Let us note that these approximate kinetic-energy functionals may also be used for the description of clusters.

TABLE I. Atomic noninteracting kinetic energies for exact density (in hartrees).

Specie	$T_{\rm TF}+\frac{1}{9}T_W$	$T^{\rm GGA}$	T_s^{m0}	T_s^{m1}	$T_s^{\rm KS}$
Li	7.47733	7.47891	7.43572	7.43842	7.43613
Be^{+}	14.32860	14.33159	14.27928	14.28291	14.27999
B^{+2}	23.41770	23.42254	23.37713	23.38130	23.37796
C^{+3}	34.74270	34.74985	34.72671	34.73102	34.72763
N^{+4}	48.30277	48.31267	48.32716	48.33188	48.32813
O^{+5}	64.09762	64.11072	64.17811	64.18265	64.17911
F^{+6}	82.12709	82.14384	82.27939	82.28427	82.28040
Ne^{+7}	102.39108	102.41193	102.63081	102.63575	102.63185
STD [a]	0.11	0.099	0.0009	0.0034	
Be	14.64270	14.64571	14.58019	14.60272	14.59312
B^{+1}	24.24209	24.24699	24.23846	24.27190	24.26297
C^{+2}	36.29770	36.30496	36.40254	36.44807	36.44323
N^{+3}	50.78956	50.79964	51.05537	51.11391	51.11617
STD [a]	0.18	0.17	0.039	0.007	

[a] STD stands for the standard deviation.

III. RESULTS

A. Atoms

Kinetic-energy functionals Eqs. (13) and (16) were applied to calculate the kinetic-energy values corresponding to the ‘‘exact’’ densities of the Li $Z=3,4,\ldots,10$, and Be $Z=4,5,6,7$ isoelectronic series. The density ρ_0 for which LST were performed was taken to be the HF one. The ‘‘exact’’ densities for the Li isoelectronic series were those given in Ref. [7] (obtained from Hylleras-type wave functions). The ‘‘exact’’ densities for the Be isoelectronic series employed in this work corresponded to highly accurate CI wave functions calculated by means of the program ATMOL [8,9].

In Table I, we compare the results of the present work for T_s^{m0} and T_s^{m1} with those obtained using the second-order gradient expansion in the slowly varying limits (SGA) [10],

$$T^{\rm SGA}=\frac{3}{10}(3\pi^2)^{2/3}\int d^3\vec{r}\rho^{5/3}(\vec{r})(1+0.1234s^2)$$

$$=T_{\rm TF}+\frac{1}{9}T_W, \qquad (22)$$

and the generalized-gradient approximation (GGA) [11],

$$T^{\rm GGA}=\frac{3}{10}(3\pi^2)^{2/3}\int d^3\vec{r}\,\rho^{5/3}(\vec{r})\frac{1+88.3960s^2+16.3683s^4}{1+88.2108s^2}, \qquad (23)$$

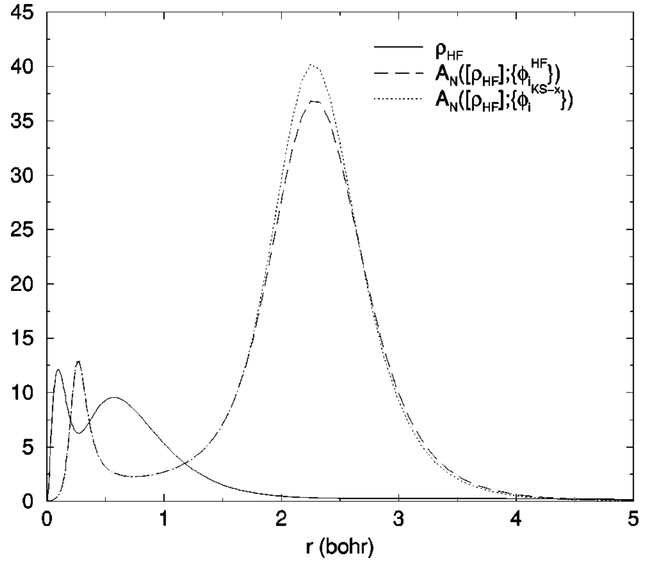

FIG. 1. Comparison of modulating factors calculated through KS-*x*-only orbitals (dashed line) and HF orbitals (dotted line) for Na atom. The solid line is the corresponding HF density.

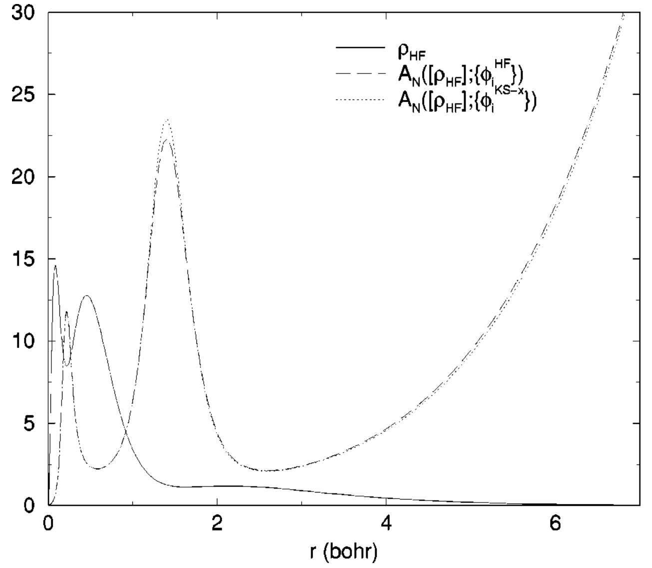

FIG. 2. Comparison of modulating factors calculated through KS-*x*-only orbitals (dashed line) and HF orbitals (dotted line) for Al atom. The solid line is the corresponding HF density.

where $s=|\nabla\rho(\vec r)|/2(3\pi^2)^{1/3}\rho^{4/3}(\vec r)$ and the ''exact'' KS values. KS noninteracting kinetic energies for ''exact'' density were calculated by means of the local-scaling transformation version of DFT (LS-DFT) [12,13]. The SGA and the GGA functionals overestimate the T_s values for the first three terms of the Li isoelectronic series and for the first two terms of the Be series and underestimate the T_s values for other terms of the series. The standard deviations (STD) for the T_s^{m0} and T_s^{m1} functionals are one or two orders of magnitude smaller than those for the SGA and the GGA functionals.

The modulating factor $A_N([\rho_{\mathrm{HF}}];\vec r)$ can be calculated through Eq. (14). However, for comparison purposes, it is also convenient to write its exact expression in terms of KS-*x-only* orbitals:

$$\frac{1}{2}A_N([\rho_{\mathrm{HF}},\{\psi_i^{\mathrm{KS}-x}\}];\vec r) = \frac{\dfrac{1}{2}\sum_{i=1}^{N}\nabla\psi_i^{*\mathrm{KS}-x}(\vec r)\nabla\psi_i^{\mathrm{KS}-x}(\vec r)-\dfrac{1}{8}\dfrac{\nabla\rho_{\mathrm{HF}}(\vec r)^2}{\rho_{\mathrm{HF}}(\vec r)}}{\rho_{\mathrm{HF}}(\vec r)^{5/3}}. \tag{24}$$

The last equation is evident from Eqs. (2), (3), (13), and (14) with $\rho=\rho_0=\rho_{\mathrm{HF}}$ and $\phi_{\rho,i}=\psi_i^{\mathrm{KS}-x}$. Equation (24) with HF orbitals instead of KS-*x-only* ones can be applied to calculate approximations to A_N. The behavior of the total modulating factor A_N calculated through the KS-*x-only* and the HF orbitals as a function of *r* are presented in Figs. 1 and 2, respectively, for the ground states of the Na and Al atoms. It is evident from these curves that the error arising from the use of HF orbitals instead of KS-*x-only* ones in the total modulating factor calculation appears near the second maximum of A_N at $r\approx 2.0-2.7$ bohr for the Na atom and at $r\approx 1.3-1.7$ bohr for the Al atom. The error in kinetic-energy value $T_s^{\mathrm{KS}-x}$ stemming from the use of $A_N([\rho_{\mathrm{HF}},\{\psi_i^{\mathrm{HF}}\}];\vec r)$ instead of $A_N([\rho_{\mathrm{HF}},\{\psi_i^{\mathrm{KS}-x}\}];\vec r)$ is exactly equivalent to the difference between HF and KS-*x-only* kinetic-energy values. This amounts to 0.0024 hartree for the Na atom and to 0.0031 hartree for Al.

The behavior of A_N in the region of large-*r* values is very different for the Na and Al atoms. A_N for the Na atom decays rapidly whereas it grows exponentially for Al. The reason is that the Na atom has only one valence electron and thus the Weiszäker term reproduces exactly the kinetic-energy density in this region, i.e., the numerator in Eq. (24) tends to zero for large-*r* values. For the Al atom the situation is different as there are two valence electrons, $3s$ and $3p$. The cancellation in the numerator of Eq. (24) no longer occurs and in this case A_N grows exponentially due to the presence of the term $\rho^{5/3}$ in the denominator.

B. Diatomic molecules

Numerical calculations of the kinetic energy, employing the approximate functionals described by Eqs. (13) and (16) at the HF density, were performed for the diatomic molecules $\mathrm{Na}_2(^1\Sigma_g^+)$ and $\mathrm{Al}_2(^3\Sigma_g^-)$ at different internuclear separations. The full numerical program developed by Laaksonen and co-workers [14,15] was used to calculated HF densities. The kinetic-energy functionals given by Eqs. (13) and (16), where the ρ_{0A} densities appearing in Eq. (20) for the definition of A_N and $L^{(1)}$ are the *atomic* HF densities for the Ne and Al atoms, were incorporated into this program.

Results for the $\mathrm{Na}_2(^1\Sigma_g^+)$ molecule at different internuclear distances are presented in Table II and are compared with the values obtained using the SGA and the GGA functionals and with the KS-*x-only* values for atoms. The difference between KS-*x-only* and HF kinetic-energy values for atoms is quite small (for example, for the F atom, T_s^{HF}

TABLE II. Noninteracting kinetic energies for different internuclear distances of the $Na_2(^1\Sigma_g^+)$ molecule for Hartree-Fock density (in hartrees).

R (bohr)	$T_{TF}+\frac{1}{9}T_W$	T^{GGA}	T_s^{m0}	T_s^{m1}	T_{HF}
3.0	322.5924	322.6407	323.7984	324.0635	324.1806
4.0	322.2906	322.3390	323.7972	324.0295	323.8779
5.82	322.1656	322.2140	323.7562	323.8798	323.7321
15.0	322.0315	322.0799	323.6486	323.6021	323.5986
30.0	322.0460	322.0944	323.6576	323.6158	323.6204
STD	1.58	1.53	0.18	0.11	

$-T_s^{KS-x}=0.0015$ hartree). Moreover, the atomic modulating factors A_N calculated by Eq. (24) using KS-*x-only* turn out to be very close to those obtained using HF orbitals.

The same result, namely that the HF and the KS-*x-only* kinetic energies lie close together, also holds for molecules. For example, for $F_2(R=2.0668$ bohr) $T_s^{HF}-T_s^{KS-x}=0.0068$ hartree [2].

It is seen from Table II that the approximate kinetic-energy functionals employed in the present work reproduce the HF kinetic energy much better than the SGA and the GGA functionals for all internuclear distances. For example, for the T_s^{m0} functional, the standard deviation is of 0.18 hartree. The corresponding deviations for the SGA and GGA functionals are 1.58 and 1.53 hartree, respectively.

We observe that the error in our model functionals grows as the internuclear distance decreases. This could be explained by the fact that the model functionals when applied to separated atoms reproduce exactly the KS-*x-only* kinetic energy of the system, which in this case is the sum of KS-*x-only* kinetic energies of the individual atoms. Clearly, when the atoms are brought together, the deviation of the real density of the system from that arising from the superposition of separated atoms becomes larger.

In Table III, the results for the $Al_2(^3\Sigma_g^-)$ molecule are presented. We see here that the same trend is observed in the case of the Na_2 molecule when we compare the results obtained from the SGA, GGA, and present work model functionals. The standard deviations for the gradient expansion functional are approximately one order of magnitude larger than those for the model functionals.

TABLE III. Noninteracting kinetic energies for different internuclear distances of the $Al_2(^3\Sigma_g^-)$ molecule for Hartree-Fock density (in hartrees).

R (bohr)	$T_{TF}+\frac{1}{9}T_W$	T^{GGA}	T_s^{m0}	T_s^{m1}	T_{HF}
3.0	482.7933	482.8617	484.7545	485.8669	485.0745
4.66	481.6946	481.7631	483.6755	483.7596	483.8103
10.0	481.4979	481.5665	483.6514	483.5958	483.6169
15.0	481.5098	481.5784	483.6752	483.6246	483.6363
30.0	481.5113	481.5799	483.6796	483.6304	483.6428
STD	2.16	2.09	0.16	0.36	

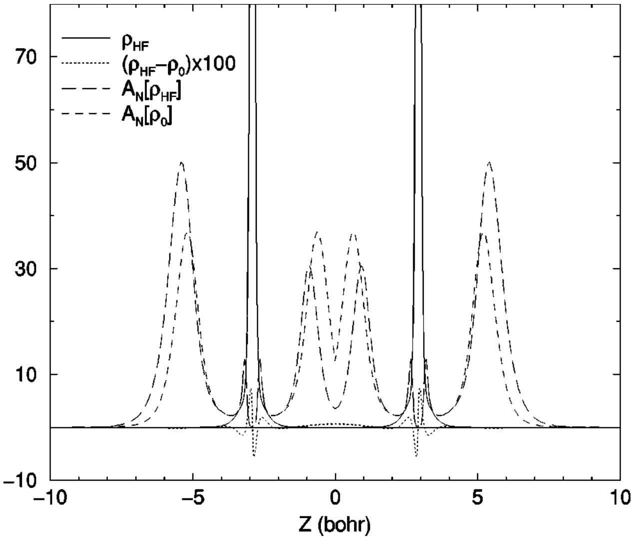

FIG. 3. Comparison of densities ρ_{HF} and ρ_0 and modulating factors $A_N[\rho_{HF}]$ and $A_N[\rho_0]$ for $Na_2(^1\Sigma_g^+)$ molecule, $R=5.82$ bohr.

In Figs. 3 and 4, the $A_N[\rho_0]$ modulating factors Eq. (20) and the modulating factors calculated by Eq. (24) for the HF density and for the HF molecular orbitals are presented for the Na_2 and Al_2 molecules. The HF molecular density and the difference of this density with the density ρ_0 calculated according to Eq. (21) are also graphed. From these figures we can see that the difference between the molecular HF density and ρ_0 is noticeable in the bond region between the atoms. Their asymptotic behavior is, however, alike. The modulating factor A_N calculated from the superposition of atomic modulating factors Eq. (20) reproduces well the structure of the modulating factor calculated via Eq. (24) employing HF molecular orbitals. There is a small shift of about 0.5 bohr in the positions of the maxima in A_N for the Na_2 molecule. This shift is negligible for Al_2. From Fig. 3 we may conclude that there is a compensation of errors in the calculation of the last integral of Eq. (13). This compensation

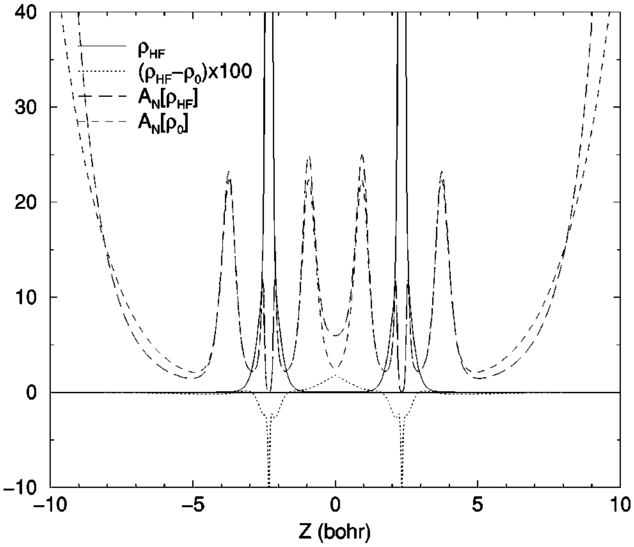

FIG. 4. Comparison of densities ρ_{HF} and ρ_0 and modulating factors $A_N[\rho_{HF}]$ and $A_N[\rho_0]$ for $Al_2(^3\Sigma_g^-)$ molecule, $R=4.66$ bohr.

TABLE IV. Optimized exponents and coefficients for the analytical form of $\frac{1}{2}A_N$ factor for the Na atom.

Coefficient	$k=1$	$k=2$	$k=3$
ζ_s	11.054028	5.321785	2.275963
ζ_p	5.497534	4.599246	4.886950
C_k^{1s}	0.943237	-0.004627	0.002578
C_k^{2s}	0.015037	0.801684	0.362281
C_k^{3s}	-0.003422	-0.020584	0.007383
C_k^{2p}	0.447312	0.278228	0.237544

comes about from the fact that $A_N[\rho_0]$ overestimates $A_N[\rho_{\mathrm{HF}}]$ in the internuclear region and underestimates it in the tail region. A similar error compensation also takes place for the Al$_2$ molecule.

C. Analytical representation of the A_N modulating factor for the Na and Al atoms

The total modulating factor A_N can be calculated by the prescription given by Eq. (14) involving the determination of the LST function λ and the radial and angular kinetic-energy modulating factors. However, a more direct way to calculate A_N is provided by Eq. (24). In this case, the KS orbitals are needed either in numerical or analytical form. In the present work, A_N was calculated numerically by means of Eq. (14), where the LST function $\lambda([\rho_{\mathrm{HF}}];r)$ and the angular and the radial modulating factors corresponding to KS-*x-only* orbitals were used. Of course, Eq. (24) with KS-*x-only* orbitals yields exactly the same result.

Numerical values of $A_N([\rho_{\mathrm{HF}}];r)$ as a function of r for Na and Al atoms were fitted to the analytical form given by Eq. (24), where the atomic orbitals ψ_i were assumed to have the following three-term STO expansion:

$$\psi_{nl}(\vec{r})=\sum_{k=1}^{3} C_k^{nl}\left(\frac{(2\zeta_l)^{2n+1}}{(2n)!}\right)^{1/2} r^{n-1}\exp(-\zeta_l r)Y_{lm_k}(\theta,\phi) \tag{25}$$

and where the density appearing in Eq. (24) was assumed to have the form $\rho=\Sigma_{i=1}^{N}|\psi_i|^2$.

Subsequently, all orbital coefficients and exponents were optimized in order to minimize the integral

$$\frac{1}{2}\int d^3\vec{r}\,\rho_{\mathrm{HF}}^{5/3}(\vec{r})A_N([\rho_{\mathrm{HF}}];\vec{r}), \tag{26}$$

which is the second contribution to the kinetic energy in Eq. (13). The orthonormalization of three-term STO atomic orbitals was not conserved during this minimization.

In Tables IV and V the optimized coefficients and exponents for Na and Al atoms are presented. The numerical value of the integral in Eq. (26) is 51.3480 hartree and the fitted value is 51.3688 hartree for the Na atom. The corresponding values for the Al atom are 85.1140 and 85.1485 hartree, respectively.

TABLE V. Optimized exponents and coefficients for the analytical form of $\frac{1}{2}A_N$ factor for the Al atom.

Coefficient	$k=1$	$k=2$	$k=3$
ζ_s	13.120602	6.267531	4.761970
ζ_p	6.513458	5.441190	1.814707
C_k^{1s}	0.967128	0.004739	-0.001795
C_k^{2s}	-0.013206	0.761518	0.078400
C_k^{3s}	0.096673	-0.339863	-0.064508
C_k^{2p}	0.529595	0.677989	0.002495
C_k^{3p}	0.021212	0.065571	2.266528

Let us notice that in order to calculate the modulating factor $A_N^{(1)}$ of Eq. (16) coming from the approximate treatment of Eq. (15), the transformation function for atomic densities $\lambda([\rho_{0A}];\vec{r})$ and the density of the whole system ρ are needed.

IV. CONCLUSIONS

In the present work we advance two approximate molecular kinetic-energy functionals developed in the context of local-scaling transformations. For the construction of these approximate functionals we make use of the fact that a true molecular density differs only slightly from the model molecular density arising from the superposition of isolated atom densities. This fact reflects itself in the constancy of the inner shell structure of the interacting atoms, which in turn is closely connected with the structure of the total kinetic-energy modulating factors $A_N([\rho];\vec{r})$. Thus, in these approximations, we construct the molecular modulating factors using densities, local-scaling transformations functions, etc. for isolated atoms.

Applications of these functionals to the diatomic molecules Na$_2$ and F$_2$ (at the HF density level) lead to values of the kinetic energy which are in excellent agreement with the HF kinetic-energy values. In fact, the accuracy obtained with the present functionals is about one order of magnitude better than that obtained from SGA and GGA kinetic-energy functionals.

This preliminary test clearly indicates that the constructive approach to the generation of a molecular kinetic-energy functional in the context of local-scaling transformations leads to reasonable results even when we use isolated-atom parameters in order to represent the molecular functional. But more important, the present method provides the possibility for introducing systematic improvements in the construction of increasingly accurate functionals. Moreover, through the analytic representation of atomic modulating factors, we can obtain fully analytic approximate functionals for molecules and clusters.

As a final word, we would like to stress that the present approach is orbital-free, as neither for isolated atoms nor for molecules do we ever have to solve orbital equations in order to obtain an orbital set. In fact, we can select any set of orthogonal orbitals for the initial atomic orbital set $\{\phi_i\}_{i=1}^{N}$

from which we obtain the atomic locally scaled orbitals $\{\phi_{\rho,i}\}_{i=1}^{N}$. For atoms, our most convenient choice has turned out to be that of generalized Slater-type orbitals [16], because they retain the simplicity of single-ζ orbitals and, moreover, each atomic orbital is described by a single function so that we never have a linear combination of atomic orbitals whose coefficients must be calculated. Using these very simple functions in the context of the local-scaling transformation version of DFT, we have been able to obtain, nevertheless, atomic energies that differ in the millihartrees from the Hartree-Fock ones [16]. Clearly, therefore, the present extension to molecules, being based on our previous work on atoms, is also orbital-free.

ACKNOWLEDGMENT

The authors would like to gratefully acknowledge support of this work by CONICIT of Venezuela through Group Project No. G-97000741.

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