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Brief Reports

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Variational test on the relationship between gradient expansion terms in the kinetic energy density functional

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By using an approximate analytical trial density and the consideration of an energy density functional which includes a modified gradient correction, the relationship between the zeroth-order and the first gradient correction is tested and the results compared with those obtained through the use of Hartree-Fock-Roothaan-Clementi densities.

I. INTRODUCTION

Single-particle density is a physical observable which plays a basic role in the quantum description of many-electron systems. There are many physical properties of atomic, molecular, and nuclear systems which can be interpreted in terms of the electron density of the system.[1]

Some years ago, Pathak and Gadre[2] obtained lower bounds for the first gradient-expansion correction to the kinetic and exchange-energy terms of the atom. The spirit of this work was to establish a relationship between the zeroth-order and the first gradient corrections for all well-behaved densities. This is important because it would be possible to make variational calculations employing the bounds as gradient-free expansions of the corrections.[3]

One way of testing these relationships is to use known well-behaved densities for the calculation of the bounds. Pathak and Gadre have carried out a numerical investigation of these lower bounds using electron densities constructed from Hartree-Fock wave functions.[4] Notwithstanding, in a fully variational calculation, it is necessary to resort to approximate trial electron densities. So, it would be interesting to verify whether these bounds are still valid for variational densities. A similar calculation has been done recently by Csavinszky[5] using a trial electron density constructed from hydrogenlike one-electron wave functions in order to make a comparison of the Perdew-Wang[6] expression for the exchange energy of a many-electron system with the corresponding expression given by Dirac.[7]

Recently, Glossman and Castro[8] have presented an analytical approximation to the solution of the Thomas-Fermi-Dirac-Weizsäcker (TFDW) model[9,10] in the form of a superposition of exponentials. This analytical ansatz has given remarkably accurate atomic energies. Some physical quantities and related properties calculated through this model show an improvement over previous investigations.[11-18]

The purpose of this paper is to test the kinetic energy bound obtained by Pathak and Gadre[2] by means of the analytical approximation of Glossman and Castro.[8]

II. DISCUSSION

The lowest energy of an atomic system in the TFDW model is given by the functional

$$E(\rho)=E_k(\rho)+E_{ne}(\rho)+E_{ee}(\rho)+E_{\mathrm{ex}}(\rho)\ , \tag{1}$$

where ρ is the electron number density, E_k is the kinetic energy of the electrons, E_{ne} is the attractive interaction energy between the nucleus of atomic number Z and the N electrons, E_{ee} is the repulsive interaction energy among the N electrons, and E_{xc} is the homogeneous electron gas approximation of Dirac for the exchange energy. The quantities E_{ne}, E_{ee}, and E_{xc} have been defined before.[8,11-18]

TABLE I. Values of T_0, T_{2c}, and the ratio $R_1 = T_{2c}N^{2/3}/T_0$ for several atoms (in a.u.).

Z	Atom	$T_0(\rho)$	$T_{2c}(\rho)$	R_1
2	He	2.0718	0.7463	0.572
3	Li	5.5958	1.7245	0.641
4	Be	11.3526	3.1277	0.694
5	B	19.6645	4.9641	0.738
6	C	30.7798	7.2347	0.776
7	N	44.9656	9.9754	0.812
8	O	62.4372	13.2835	0.851
9	F	83.4305	17.6047	0.913
10	Ne	108.2540	22.1530	0.950
11	Na	137.0282	26.9676	0.973
12	Mg	169.9008	32.1786	0.993
13	Al	207.0242	37.8057	1.010
14	Si	248.5453	43.8537	1.025
15	P	294.6039	50.3227	1.039
16	S	345.3344	57.2116	1.052
17	Cl	400.8648	64.5180	1.064
18	Ar	461.3184	72.2396	1.076
36	Kr	2509.6138	278.9105	1.212
54	Xe	6703.7726	602.2390	1.283
86	Rn	20 547.2195	1419.4496	1.346

In Eq. (1), E_k is the kinetic energy term, and this quantity can be written as

$$E_k(\rho) = T_0(\rho) + T_{2c}(\rho) \ , \tag{2}$$

where $T_0(\rho)$ is the zeroth-order kinetic energy term, usually called the "Thomas-Fermi kinetic energy term,"[19] and $T_{2c}(\rho)$ is the first gradient expansion correction to $T_0(\rho)$, usually known as Weizsäcker correction term,[20] multiplied by the Yonei and Tomishima[21] correction factor $c = \frac{1}{5}$. Thus

$$T_0(\rho) = \tfrac{3}{10}(3\pi^2)^{2/3} \int \rho^{5/3} d\mathbf{r} \tag{3}$$

and

$$T_{2c}(\rho) = \frac{c}{8} \int \frac{(\nabla\rho)^2}{\rho} d\mathbf{r} \ . \tag{4}$$

Pathak and Gadre[2] have derived the following lower bound for the first gradient-expansion correction to the kinetic energy functional

$$T_{2c}(\rho) \geq \tfrac{10}{40}(2/3)^{2/3}\frac{T_0(\rho)}{N^{2/3}} = \frac{0.190\,79\,T_0(\rho)}{N^{2/3}} \ , \tag{5}$$

where N denotes the number of electrons.

It should be noted that in the original derivation of Eq. (5), Pathak and Gadre[2] considered a correction factor $c = \frac{1}{9}$ and the numerical factor in Eq. (5) is 0.105 99. This correction factor was first proposed in two related papers by Kompaneets and Pavlovskii[22] and by Kirzhnits[23] and there are several other correction factors already published,[24-26] and some of them have been tested in the mentioned article by Csavinszky.[5] We have adapted the bound in order to be able to use our proposed functional.[8] Of course, the validity of the bound does not depend on the value of the constant c, but it has been found by several authors[21,27] that the TFD-cW, with $c = \frac{1}{5}$, is the method that best reproduces the total energy and binding energy of N_2 molecule by solving the Euler equation and the same is true for all atoms in the whole Periodic Table. It has been also found that the Scott conjecture[9] can be derived using a value quite close to $c = \frac{1}{5}$.

As have Pathak and Gadre,[2] we have calculated the ratio

$$R_1 = \frac{T_{2c}(\rho)N^{2/3}}{T_0(\rho)} \tag{6}$$

for several atoms, using our analytical ansatz.[8] For systems with spherical symmetry the relation between the density and the so-called screening function is

$$\rho(r) = \frac{Z}{4\pi r}\phi''(r) \ , \tag{7}$$

where $\phi(r)$ is defined by

$$v(r) = -\frac{Z}{r}\phi(r) \tag{8}$$

and

$$v(r) = -\frac{Z}{r} + \int \frac{\rho(r')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \ . \tag{9}$$

We have constructed the screening function ϕ as a superposition of exponential functions

$$\phi(r) = \frac{1}{K}\sum_i \alpha_i e^{-\beta_i r} \tag{10}$$

where α_i and β_i are variational parameters whose values have been given elsewhere[8] and K is a normalization constant.

Table I shows the R_1 values for elements from $Z = 2-18$ and for $Z = 36$, 54, and 86, together with corresponding $T_0(\rho)$ and $T_{2c}(\rho)$ values. For the sake of comparison, we have recalculated the ratio R_1 for some atoms, but using Hartree-Fock-Roothaan-Clementi (HFRC) densities[4] and considering the same functional, that is, TFDW with $c = \frac{1}{5}$. Table II shows these values together with those calculated with our analytical ansatz.

A glance at Table I shows that the bound is not very tight, and that the ratio $T_{2c}N^{2/3}/T_0$ gradually increases as one goes from He to Ar and then Kr, Xe, and Rn, but

TABLE II. Values of the bound R_1 calculated with the approximate analytical electron density (Ref. 5) and with HFRC densities.

Z	Atom	R_1^{Present}	R_1^{HFRC}
2	He	0.572	0.318
10	Ne	0.950	0.654
18	Ar	1.076	0.804
36	Kr	1.212	1.012
54	Xe	1.283	1.158

in considering the dependence of the bound on the atomic number Z, we can see that the differences in the bound between an atom and the subsequent one are greater for atoms of low atomic number and decreases at the same time that the atomic number grows. Inspection of Table II shows that the bound obtained through the HFRC densities by using the TFDW model with $c=\frac{1}{5}$ are lower than those obtained by means of the analytical ansatz. In the light of the above results, it would be worthwhile to investigate the use of this bound in a variational context.

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