Scaling properties and local forms of the correlation-energy functional

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The scaling properties of the exact correlation-energy functional are applied in the study of the general rational, polynomial, and logarithmic local forms (and their combinations) of the correlation-energy functional, which depend on the density. It is concluded that these forms cannot satisfy the uniform and nonuniform scaling properties at the same time; therefore, they would have to be modified to represent exact forms of the correlation-energy density functional, at least in the high- and low-density limits. These results are not affected by the application of the local spin density or the self-interaction correction procedures to the above functionals. [S1050-2947(97)00312-0]

PACS number(s): 31.15.Ew, 31.25.−v

I. INTRODUCTION

There is an increasing interest in density-functional theory [1–3] because it represents a very important simplification of the many-electron problem. In the context of this theory the energy functional takes the form

$$E[\rho] = T_s[\rho] + \frac{1}{2} \int \int d^3\vec{r}_1 d^3\vec{r}_2 \, \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}}$$
$$+ \int d^3\vec{r} \, \rho(\vec{r})v(\vec{r}) + E_{\text{xc}}[\rho], \tag{1}$$

where ρ, T_s, E_{xc}, and v are the electron density, the noninteracting kinetic energy, the exchange–correlation-energy functional, and the external potential, respectively.

The properties of these functionals have been studied through the years and many forms for the above functionals have been proposed, starting from Thomas and Fermi in the early days of quantum mechanics to the most sophisticated forms (see, e.g., [1] and references therein). The uniform and nonuniform scaling properties of the exchange-correlation functionals have been intensively studied by Levy and co-workers (see, e.g., [4] and references therein). It may be possible to decompose the exchange-correlation functional if we can make the separation

$$E_{\text{xc}}[\rho] = E_x[\rho] + E_c[\rho] \tag{2}$$

where the correlation and exchange energy are defined, respectively, by

$$E_c[\rho] = \langle \Psi_\rho^{\min}|\hat{T} + \hat{V}_{ee}|\Psi_\rho^{\min}\rangle - \langle \Phi_\rho^{\min}|\hat{T} + \hat{V}_{ee}|\Phi_\rho^{\min}\rangle, \tag{3}$$

$$E_x[\rho] = \langle \Phi_\rho^{\min}|\hat{V}_{ee}|\Phi_\rho^{\min}\rangle - \frac{1}{2} \int \int d\vec{r}_1 d\vec{r}_2 \, \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}}, \tag{4}$$

with $\hat{V}_{ee} = \Sigma_{i>j} r_{ij}^{-1}$. $\Psi_\rho^{\min}$ yields ρ and minimizes $\langle \hat{T} + \hat{V}_{ee}\rangle$, while $\Phi_\rho^{\min}$ yields ρ and minimizes $\langle \hat{T}\rangle$. We are interested mainly in the scaling properties of the correlation functional.

Levy and Ou-Yang first conjectured [5] and later proved [6] the unreasonability of the local-density approximation correlation functionals (see, e.g., [2]) based on the argument that they scaled in the same way if we apply one-coordinate scaling on x, y, and z. In this Brief Report we apply the scaling properties of the exact correlation-energy functional to the study of some general local forms of this functional depending only on the density. Also, we briefly discuss the case of including some dependence on the gradient of the density. We conclude that these expressions cannot satisfy the uniform and nonuniform scaling properties at the same time. Therefore, they should be modified in order to represent exact forms of the correlation-energy density functional, in the sense of the scaling properties, guaranteeing correct behavior in both the low- and high-density limits. In the local spin density or the self-interaction correction formalisms [1,2], the results remain unaffected.

II. THE SIMPLEST FUNCTIONAL

Let us define the scaled densities we will use:

$$\rho_\lambda(x,y,z) = \lambda^3 \rho(\lambda x, \lambda y, \lambda z), \tag{5}$$

$$\rho_{\lambda\lambda}^{xy}(x,y,z) = \lambda^2 \rho(\lambda x, \lambda y, z), \tag{6}$$

$$\rho_\lambda^x(x,y,z) = \lambda \rho(\lambda x, y, z). \tag{7}$$

The first is called uniform scaling, while the other two correspond to nonuniform scaling. The low- and high-density limits can be obtained by taking the scaling constant λ small and large enough, respectively. Then, the main uniform scaling properties of the correlation-energy functional are [4,5,7,8]

$$E_c[\rho_\lambda] < \lambda E_c[\rho], \quad \lambda < 1 \tag{8}$$

$$E_c[\rho_\lambda] > \lambda E_c[\rho], \quad \lambda > 1 \tag{9}$$

$$\lim_{\lambda \to \infty} E_c[\rho_\lambda] = \text{const} > -\infty, \tag{10}$$

and

$$\lim_{\lambda \to 0} E_c[\rho_\lambda] = 0 \tag{11}$$

because the correlation energy should be zero in the null density limit. For nonuniform scaling the following relations will apply [9]:

$$\lim_{\lambda \to \infty} E_c[\rho_\lambda^x] = 0, \tag{12}$$

$$\lim_{\lambda \to \infty} \lambda E_c[\rho_\lambda^x] = \text{const}, \tag{13}$$

$$\lim_{\lambda \to \infty} E_c[\rho_{\lambda\lambda}^{xy}] = 0, \tag{14}$$

$$\lim_{\lambda \to 0} \lambda^{-1} E_c[\rho_\lambda^x] = 0, \tag{15}$$

$$\lim_{\lambda \to 0} \lambda^{-1} E_c[\rho_{\lambda\lambda}^{xy}] = 0, \tag{16}$$

$$\lim_{\lambda \to 0} \lambda^{-2} E_c[\rho_{\lambda\lambda}^{xy}] = \text{const}. \tag{17}$$

Let us consider the following form of the correlation-energy functional:

$$E_c[\rho] = C \int d^3\vec{r} \; \rho^s, \tag{18}$$

where C is some constant. Now, applying Eqs. (5)–(7) and considering that the volume scales as λ^{-D}, we obtain

$$E_c[\rho_\lambda] = C \int \frac{d^3\vec{r}}{\lambda^D} (\lambda^D \rho)^s = \lambda^{D(s-1)} E_c[\rho], \tag{19}$$

where D is the order of the scaling: 3 for the uniform case and 1 and 2 for the nonuniform case, when we scale one or two coordinates. Using Eqs. (12) and (14) and Eqs. (15) and (16) we obtain

$$\lim_{\lambda \to \infty} \lambda^{D(s-1)} E_c[\rho] = 0 \tag{20}$$

and

$$\lim_{\lambda \to 0} \lambda^{D(s-1)-1} E_c[\rho] = 0 \tag{21}$$

for $D = 1$ and 2. Excluding the trivial case of $E_c[\rho] = 0$, Eqs. (20) and (21) respectively imply that

$$D(s-1) < 0, \tag{22}$$

$$D(s-1) > 1. \tag{23}$$

This is, of course, contradictory.

Another way of getting a contradiction is by using Eq. (10),

$$\lim_{\lambda \to \infty} \lambda^{3(s-1)} E_c[\rho] = \text{const} > -\infty, \tag{24}$$

with $s = 1$, and Eq. (13),

$$\lim_{\lambda \to \infty} \lambda^s E_c[\rho] = \text{const}, \tag{25}$$

with $s = 0$, in contradiction with Eq. (24). This kind of functional has been used by Boada, Maldonado, and Karasiov [10], with $s = \frac{5}{3}$, where C is a function of the nuclear charge and the number of electrons.

III. GENERALIZED POLYNOMIAL AND RATIONAL FORMS

Let us define generalized polynomial and rational forms. We do not expect to have integer exponents, just real nonnegative ones. We require that the forms have a finite number of terms

$$P(\rho) = \sum_{i=1}^{N} c_i \rho^{\alpha_i}, \quad \alpha_N > \alpha_{N-1} > \cdots > \alpha_1 > 0, \quad N < \infty \tag{26}$$

and

$$Q(\rho) = P_n(\rho) / P_d(\rho), \tag{27}$$

where the subscript n stands for the numerator, d for the denominator, and the variable ρ is the electronic density. The coefficients c_i can depend on quantities such as charge, number of electrons, or anything that always scales with the zeroth power of λ. Without any loss of generality, we have ordered the powers in Eq. (26).

Now let us consider a correlation-energy functional, which has a generalized rational form and depends on the density,

$$E_c[\rho] = \int d^3\vec{r} \; Q(\rho). \tag{28}$$

All the coefficients of P_n and P_d should be real and finite and $Q(\rho)$ should be such that the above integral exists. If we scale expression (28), then we obtain a generalized rational form in terms of the scaling constant (λ), i.e.,

$$E_c[\rho_\lambda^{(D)}] = \int \frac{d^3\vec{r}'}{\lambda^D} \frac{\displaystyle\sum_{i=1}^{N_n} c_i [\lambda^D \rho(\vec{r}')]^{\alpha_i}}{\displaystyle\sum_{j=1}^{N_d} b_j [\lambda^D \rho(\vec{r}')]^{\beta_j}}$$

$$= \int d^3\vec{r}' \frac{\displaystyle\sum_{i=1}^{N_n} c_i \rho(\vec{r}')^{\alpha_i} \lambda^{D(\alpha_i-1)}}{\displaystyle\sum_{j=1}^{N_d} b_j \rho(\vec{r}')^{\beta_j} \lambda^{D\beta_j}}, \tag{29}$$

where $\vec{r}'$ is the scaled position variable and $D = 1$, 2, or 3 for nonuniform on one coordinate, on two coordinates, or uniform scaling, respectively. In the limit $\lambda \to \infty$, the dominant power of λ will be $D(\alpha_{N_n} - \beta_{N_d} - 1) \equiv D\Delta_N$, in the limit $\lambda \to 0$, $D(\alpha_1 - \beta_1 - 1) \equiv D\Delta_1$ will dominate. From Eqs. (13) and (10),

$$\Delta_N + 1 = 0 \quad (D=1), \tag{30}$$

$$3\Delta_N = 0 \quad (D=3). \tag{31}$$

These equations are in obvious contradiction. From Eqs. (17) and (11),

$$2\Delta_1 - 2 = 0 \quad (D=2), \tag{32}$$

$$3\Delta_1 < 0 \quad (D=3), \tag{33}$$

also in contradiction. It should be remarked that there are contradictions in both low- and high-density limits. So no generalized polynomial or rational form depending on the density can represent an exact form of the correlation-energy functional *either for the low- or for the high-density limit*. The polynomial case is just a special case of the rational form described above.

There are many functionals in the literature that have polynomial or rational forms, from Wigner's functional [11] to the fitting [12] of Monte Carlo results and to the recently proposed form of [13]. In all these cases, the results obtained above are valid. Fuentealba [14] proposed some functionals obtained from a Gaussian correlation-factor model (one of them is Wigner-like) and discussed the fulfillment of the scaling conditions, checking that they violate at least two of the nonuniform conditions, which is in agreement with our findings.

IV. LOGARITHMIC DEPENDENCE

Let us consider now a logarithmic form that contains a rational or polynomial form of the coordinates and the density

$$E_c[\rho] = \int d^3\vec{r}\, \ln[Q(\rho)]. \tag{34}$$

After applying a scaling procedure of order D and some elementary algebra, we get for the high- and low-density limits

$$E_c^\lambda[\rho] = \lambda^{-D}\left(\int d^3\vec{r}'\, \ln[\widetilde{Q}(\vec{r}',\rho;\lambda)] \right.$$
$$\left. + D(\alpha-\beta)\ln\lambda \int d^3\vec{r}' \right), \tag{35}$$

where $\vec{r}'$ is the scaled position variable, $\alpha = \alpha_{N_n}$, and $\beta = \beta_{N_d}$ for the high-density limit and $\alpha = \alpha_1$ and $\beta = \beta_1$ for the low-density limit.

Any nonzero power of λ goes to zero or infinity faster than the logarithm; therefore, in the null density limit it would give infinity. This in contradiction with the fact that in the null limit, the correlation energy should be zero. It is remarkable that in the case of using the whole space as the integration volume (e.g., in atoms or molecules) we should require that $\alpha = \beta$ because otherwise an untractable infinity appears. Even in this case, when $\lambda \to \infty$, Eq. (10) gives zero, which is unphysical.

No logarithmic form can represent an exact correlation-energy functional (either in the low- or in the high-density limit). For the low-density limit, this result was known (see, e.g., [8,15]) for the case of simple logarithmic functionals

using uniform scaling. In the limit of high density it is common to use logarithm of a polynomial, as in [16–18].

V. DISCUSSION

If we consider a wider class of generalized rational forms

$$E_c[\rho] = \int d^3\vec{r}\sum_{k=1}^{M} [P_k^n(\rho)]^{\epsilon_k} \left/ \sum_{k=1}^{N} [P_k^d(\rho)]^{\nu_k} \right. \tag{36}$$

for this case, all the results obtained in Sec. IV are trivially valid. Boada, Maldonado, and Karasiov [10] also derived several expressions of the form

$$E_c[\rho] = \sum_k \left[\int d^3\vec{r}\, Q_k(\rho) \right]^{\epsilon_k}, \tag{37}$$

which is a special case of Eq. (36).

In the case of mixed rational-logarithmic dependences (i.e., combinations of rational and logarithmic forms)

$$E_c[\rho] = \int d^3\vec{r}\, Q_1(\rho)\ln[Q_2(\rho)]. \tag{38}$$

It is clear that if we scale Eq. (38) by any of the former procedures, the leading behavior in terms of λ will correspond to the multiplying rational form (Q_1), so the results of Sec. IV will hold. In the case of zero power leading behavior in both limits for Q_1, the results of Sec. V will be valid.

These combinations are very frequently used (see, e.g., [16,19–24]), obtained mainly from fitting data or interpolating from expressions for low and high densities. In the case of the Carr-Gordon-Kim (see, e.g., [19,25]) approximation the functional is polynomial for low densities and logarithmic-polynomial for high ones.

In some cases it is useful to expand the correlation energy density in terms of the electronic density, as in the case of the Vosko-Wilk-Nussair functional [26], for assessing the behavior at low and high densities. It is enough to expand the term of an unknown behavior, in this case $\tan^{-1}[a/(2x+b)]$, with a and b constants, $x = r_s^{-1/2}$, and r_s having the usual meaning. For x small

$$\tan^{-1}\left(\frac{a}{2x+b} \right) = \tan^{-1}\left(\frac{a}{b} \right) - 2\frac{a}{b^2+a^2}\, x + O(x^2) \tag{39}$$

and for x large

$$\tan^{-1}\left(\frac{a}{2x+b} \right) = \frac{1}{2}\frac{a}{x} + O(x^{-2}). \tag{40}$$

We see that we can apply the previously obtained results in the cases discussed above.

The gradient-corrected functionals are of great use in atomic, molecular, and solid-state calculations (see, e.g., [27] and references therein). For that reason, we will discuss briefly the application of the scaling properties to some forms of such functionals.

Let us consider the correlation energy functional in the form

$$E_c = \int d^3\vec{r}\ Q_1(\rho)F(s) = \int d^3\vec{r}\ Q_1(\rho)(1 + a_1 s + a_2 s^2), \tag{41}$$

where $Q_1(\rho)$ is a local rational form [see Eqs. (26) and (27)] and $s = |\nabla\rho|/\rho^{4/3}$. We retain terms up to second order, in the spirit of a gradient expansion [28,29].

We take into account that, for $D=3$, s does not scale, for $\lambda \to 0$, $s \propto \lambda^{-1/3}$ and $s \propto \lambda^{-2/3}$; and for $\lambda \to \infty$, $s \propto \lambda^{2/3}$ and $s \propto \lambda^{1/3}$ for $D=1$ and $D=2$, respectively. Then the behavior of $F(s)$ will be dominated by the scaling of s^2. Scaling Eq. (41), we will see that Eq. (31) remains unaffected (leading to $\Delta_N=0$), but instead of Eq. (30) we will have

$$\Delta_N + \tfrac{4}{3} + 1 = 0, \tag{42}$$

in obvious contradiction with $\Delta_N=0$.

On the other hand, Eq. (33) remains unaffected ($\Delta_N < 0$), but instead of Eq. (32), we find that

$$2\Delta_1 - \tfrac{2}{3} - 2 = 0, \tag{43}$$

giving $\Delta_1 = \tfrac{4}{3}$, in contradiction with $\Delta_N < 0$. So, for this kind of correction, using the gradient of the density, we can satisfy neither the low-density scaling properties nor the high-density ones. Other forms of gradient corrections could be treated using similar arguments.

For the case of spin-dependent forms (e.g., in the local spin density formalism) (see, e.g., [1,2,26]), i.e.,

$$E_c = E_c[\rho_\alpha, \rho_\beta], \tag{44}$$

where ρ_α and ρ_β stand for the spin-up and -down electron densities, we have that the spin densities scale in the same form as the total density and that the above described results are also valid. If we consider a self-interaction correction procedure [1,2,12,30],

$$E_c = E_c[\rho_\alpha + \rho_\beta] - E_c[\rho_\alpha] - E_c[\rho_\beta], \tag{45}$$

then using the same arguments as above, we find that our conclusions are unaffected.

It is worth remarking that the present results apply only to local (or local gradient) functionals that can be expanded in terms of polynomial, rational, logarithmic forms, or their combinations in the low- or high-density limits (or both). The problem of whether nonlocal functionals satisfy uniform and nonuniform scaling conditions remains an open question.

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