Nonuniform coordinate scaling requirements in density-functional theory

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For the purpose of improving upon present approximate functionals, *nonuniform* coordinate scaling is introduced into density-functional theory, where $n_\lambda^x(x,y,z)=\lambda n(\lambda x,y,z)$ is an example of a nonuniformly scaled electron density. Inequalities are derived for the exact noninteracting kinetic energy $T_s[n]$. For example, $T_s[n_\lambda^x]\le\lambda^2T_s^x[n]+T_s^y[n]+T_s^z[n]$, where T_s^x,T_s^y, and T_s^z are the x,y, and z components of T_s. Surprisingly, the gradient expansion through fourth order violates the inequalities. We also observe that the Thomas-Fermi approximation for $T_s,T_s^{\rm TF}$, and the local-density approximation for the exchange-correlation energy, $E_{\rm xc}^{\rm LDA}$, *do not distinguish* between nonuniform scaling along different coordinates. That is, $T_s^{\rm TF}[n_\lambda^x]=T_s^{\rm TF}[n_\lambda^y]$ and $E_{\rm xc}^{\rm LDA}[n_\lambda^x]=E_{\rm xc}^{\rm LDA}[n_\lambda^y]$. In contrast, for the true noninteracting kinetic energy it is proved that $T_s[n_\lambda^x]\ne T_s[n_\lambda^y]$ for a general density without special symmetry, and corresponding inequalities are conjectured to apply as well to the exact $E_{\rm xc}$. Moreover, $T_s^{\rm TF}$ incorrectly gives the *same* value for its x, y, and z components.

I. INTRODUCTION

In density-functional theory,[1] the exact ground-state energy for external potential $v(\mathbf{r})$ may be obtained from

$$E=\min_n\left[T_s[n]+\int v(\mathbf{r})n(\mathbf{r})d^3r+\frac{1}{2}\int\int\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3r\,d^3r'+E_{\rm xc}[n]\right], \tag{1}$$

where $E_{\rm xc}[n]$ is the exchange-correlation functional and $T_s[n]$ is the noninteracting kinetic energy. Many techniques have been used to produce approximate forms for $T_s[n]$ and $E_{\rm xc}[n]$, one of which is the uniform scaling technique which has been very useful for determining the general structures of $T_s[n]$ and $E_{\rm xc}[n]$. For the purpose of further improving upon present approximate density functionals, this paper introduces the use of *nonuniform* coordinate scaling.

Let us first briefly review uniform scaling properties used in density-functional theory. The uniformly scaled density $n_\lambda(\mathbf{r})$ is defined by $n_\lambda(\mathbf{r})=\lambda^3n(\lambda x,\lambda y,\lambda z)$ since λ acts equally on all three coordinates. Here the scale factor λ^3 assures that $n_\lambda(\mathbf{r})$ is normalized to N electrons. Even though $E_{\rm xc}$ satisfies uniform scaling inequalities,[2] it has been proven that $T_s[n]$ and the exchange energy $E_x[n]$ satisfy uniform scaling equalities:[2]

$$T_s[n_\lambda]=\lambda^2T_s[n]\ , \tag{2}$$

and

$$E_x[n_\lambda]=\lambda E_x[n]\ . \tag{3}$$

The Thomas-Fermi functional for $T_s[n]$ and the Dirac functional for $E_x[n]$ are the only possible choices in the local-density approximation (LDA) to satisfy Eqs. (2) and (3), respectively. We write

$$T_s^{\rm LDA}[n]=T_s^{\rm TF}[n]=c\int n^{5/3}d^3r\ , \tag{4}$$

$$E_x^{\rm LDA}[n]=E_x^D[n]=d\int n^{4/3}d^3r\ . \tag{5}$$

Equations (2) and (3) are always imposed upon approximations to $T_s[n]$ and $E_x[n]$.

In this paper, it shall be shown that with nonuniform scaling there does not exist an equality like Eq. (2). Instead, there exist two interesting inequalities for the exact $T_s[n]$. These inequalities are neither satisfied by the von Weizsächer term $T_s^W[n]$ nor by the gradient expansion through fourth order $T_s^{\rm GE}[n]$. For some special cases such as one- and two-electron systems and noninteracting systems whose potentials can be separated into x,y, and z component, the inequalities reduce to equalities. Once again, $T_s^{\rm TF}$ does not satisfy these equalities. We shall also derive nonuniform scaling properties for $E_x[n]$ for special cases. With $E_x^{\rm LDA}$, the nonuniform scaling requisites are violated for the special cases and $E_x^{\rm LDA}$ is conjectured to violate nonuniform scaling requisities in general.

II. NONUNIFORM SCALING REQUIREMENTS FOR $T_s[n]$

We first define the nonuniformly scaled density

$$n_\lambda^x(x,y,z)=\lambda n(\lambda x,y,z) \tag{6}$$

with analogous definitions for n_λ^y and n_λ^z. Note that λ multiples only the x coordinate in n_λ^x. The prefactor λ assures that n_λ^x integrates to N electrons. The corresponding scaled kinetic energy functional $T_s[n_\lambda^x]$ is defined by[3]

$$T_s[n_\lambda^x]=\langle\Phi_{n_\lambda^x}^{\min}|\hat{T}|\Phi_{n_\lambda^x}^{\min}\rangle\ , \tag{7}$$

where $\Phi_{n_\lambda^x}^{\min}$ is that single determinant which yields n_λ^x and minimizes $\langle\hat{T}\rangle$. Recall that with uniform scaling[2]

$$\Phi_{n_\lambda}^{\min}(\mathbf{r}_1,\ldots,\mathbf{r}_N)=\lambda^{3N/2}\Phi_n^{\min}(\lambda\mathbf{r}_1,\ldots,\lambda\mathbf{r}_N)\ . \tag{8}$$

One may therefore be tempted to write a similar relation for nonuniform scaling:

$$\Phi^{\min}_{n^x_\lambda}(\mathbf{r}_1,\ldots,\mathbf{r}_N)=\lambda^{N/2}\Phi^{\min}_n(\lambda x_1,y_1,z_1,\ldots,\lambda x_N,y_N,z_N). \tag{9}$$

Unfortunately, Eq. (9) does not hold in general because

$$\lambda^{N/2}\Phi^{\min}_n(\lambda x_1y_1z_1,\ldots,\lambda x_Ny_Nz_N)$$

does not generally minimize $\langle \hat{T}\rangle$. Instead, we shall show below that

$$\lambda^{N/2}\Phi^{\min}_n(\lambda x_1y_1z_1,\ldots,\lambda x_Ny_Nz_N)$$

yields n^x_λ and minimizes

$$\langle \hat{T}_x+\lambda^2\hat{T}_y+\lambda^2\hat{T}_z\rangle \quad \text{where } \hat{T}_x=\sum_{i=1}^{N}-\frac{1}{2}\frac{\partial^2}{\partial x_i^2}\ ,$$

etc.

It is straightforward to work out that $\lambda^{N/2}\Phi^{\min}_n(\lambda x_1y_1z_1,\ldots,\lambda x_Ny_Nz_N)$ gives n^x_λ:

$$\begin{aligned}\int\cdots\int &\lambda^{N/2}\Phi^{\min}_n(\lambda x_1y_1z_1,\ldots,\lambda x_Ny_Nz_N)^*\lambda^{N/2}\Phi^{\min}_n(\lambda x_1y_1z_1,\ldots,\lambda x_Ny_Nz_N)dx_2dy_2dz_2\cdots dx_Ndy_Ndz_N\\ &=\lambda\int\cdots\int\Phi^{\min}_n(\lambda x_1y_1z_1,\ldots,\lambda x_Ny_Nz_N)^*\Phi^{\min}_n(\lambda x_1y_1z_1,\ldots,\lambda x_ny_nz_n)d(\lambda x_2)dy_2dz_2\cdots d(\lambda x_N)dy_Ndz_N\\ &=\lambda n(\lambda x_1,y_1,z_1)=n^x_\lambda(x_1,y_1,z_1)\ .\end{aligned} \tag{10}$$

(Note that we are suppressing spin in this paper for simplicity of presentation.) Next, one finds

$$\begin{aligned}\lambda^{-2}\langle &\lambda^{N/2}\Phi^{\min}_n(\lambda x_1y_1z_1,\ldots,\lambda x_Ny_Nz_N)|\hat{T}_x+\lambda^2\hat{T}_y+\lambda^2\hat{T}_z|\lambda^{N/2}\Phi^{\min}_n(\lambda x_1y_1z_1,\ldots,\lambda x_Ny_Nz_N)\rangle\\ &=\lambda^{-2}\langle\Phi^{\min}_n(x_1y_1z_1,\ldots,x_Ny_Nz_N)|\lambda^2(\hat{T}_x+\hat{T}_y+\hat{T}_z)|\Phi^{\min}_n(x_1y_1z_1,\ldots,x_Ny_Nz_N)\rangle\\ &=\langle\Phi^{\min}_n(x_1y_1z_1,\ldots,x_Ny_Nz_N)|\hat{T}|\Phi^{\min}_n(x_1y_1z_1,\ldots,x_Ny_Nz_N)\rangle\ ,\end{aligned} \tag{11}$$

which completes the proof that

$$\lambda^{N/2}\Phi^{\min}_n(\lambda x_1y_1z_1,\ldots,\lambda x_Ny_Nz_N)$$

minimizes $\lambda^{-2}\langle \hat{T}_x+\lambda^2\hat{T}_y+\lambda^2\hat{T}_z\rangle$ or minimizes $\langle \hat{T}_x+\lambda^2\hat{T}_y+\lambda^2\hat{T}_z\rangle$. Hence, although

$$\lambda^{N/2}\Phi^{\min}_n(\lambda x_1y_1z_1,\ldots,\lambda x_Ny_Nz_N)$$

and $\Phi^{\min}_{n^x_\lambda}$ both belong to the same density n^x_λ, it is obvious that in general

$$\Phi^{\min}_{n^x_\lambda}\neq\lambda^{N/2}\Phi^{\min}_n(\lambda x_1y_1z_1,\ldots,\lambda x_Ny_Nz_N)\ . \tag{12}$$

Consequently, from the minimization statement in the definition of $\Phi^{\min}_{n^x_\lambda}$, we obtain

$$\langle\Phi^{\min}_{n^x_\lambda}|\hat{T}|\Phi^{\min}_{n^x_\lambda}\rangle\le\langle\lambda^{N/2}\Phi(\lambda x_1y_1z_1,\ldots,\lambda x_Ny_Nz_N)|\hat{T}|\lambda^{N/2}\Phi(\lambda x_1y_1z_1,\ldots,\lambda x_Ny_Nz_N)\rangle\ , \tag{13}$$

and

$$\begin{aligned}\langle &\lambda^{N/2}\Phi^{\min}_n(\lambda x_1y_1z_1,\ldots,\lambda x_Ny_Nz_N)|\hat{T}_x+\lambda^2\hat{T}_y+\lambda^2\hat{T}_z|\lambda^{N/2}\Phi^{\min}_n(\lambda x_1y_1z_1,\ldots,\lambda x_Ny_Nz_n)\rangle\\ &\le\langle\Phi^{\min}_{n^x_\lambda}|\hat{T}_x+\lambda^2\hat{T}_y+\lambda^2\hat{T}_z|\Phi^{\min}_{n^x_\lambda}\rangle\ .\end{aligned} \tag{14}$$

We shall later show that Eq. (9) holds for some special cases, so that the inequalities become equalities in Eqs. (13) and (14) for these special cases.

Eqs. (13) and (14) give, respectively,

$$T_s[n^x_\lambda]\le\lambda^2T^x_s[n]+T^y_s[n]+T^z_s[n] \tag{15}$$

and

$$\lambda^2T_s[n]\le T^x_s[n^x_\lambda]+\lambda^2T^y_s[n^x_\lambda]+\lambda^2T^z_s[n^x_\lambda] \tag{16}$$

for any n and any non-negative λ. In general, the strict inequalities in Eqs. (15) and (16) hold for $\lambda\neq1$ because, except for the special situations to be discussed later, the inequality in Eq. (12) holds. In Eqs. (15) and (16), we have defined

$$T^q_s[n]=\langle\Phi^{\min}_n|\hat{T}_q|\Phi^{\min}_n\rangle,\quad q=x,\ y,\ \text{or}\ z \tag{17}$$

so that

$$T_s[n]=T^x_s[n]+T^y_s[n]+T^z_s[n]\ . \tag{18}$$

The components T^q_s may be obtained from T_s by employment of Eq. (15). By rearranging Eq. (15) one finds

$$\lambda^2T^x_s[n]+T^y_s[n]+T^z_s[n]-T_s[n^x_\lambda]\ge0\ . \tag{19}$$

Since the left-hand side has its minimum at $\lambda=1$, it follows that

$$T^x_s[n]=\tfrac{1}{2}(\partial T_s[n^x_\lambda]/\partial\lambda)_{\lambda=1}\ . \tag{20}$$

Thus

$$T_s^q[n]=\tfrac{1}{2}(\partial T_s[n_\lambda^q]/\partial\lambda)_{\lambda=1} . \tag{21}$$

III. UNREASONABLE NONUNIFORM SCALING EQUALITIES FOR T_s^{TF} AND $E_{\mathrm{xc}}^{\mathrm{LDA}}$

By means of Eq. (21) we now assert that the Thomas-Fermi kinetic energy gives the incorrect result that *always*

$$T_s^{X,\mathrm{TF}}[n]=T_s^{Y,\mathrm{TF}}[n]=T_s^{Z,\mathrm{TF}}[n]=\tfrac{1}{3}T_s^{\mathrm{TF}}[n] . \tag{22}$$

In contrast, unless there is special symmetry for n, the true T_s of course satisfies

$$T_s^x[n]\neq T_s^y[n]\neq T_s^z[n] . \tag{23}$$

To see how Eq. (22) arises observe that

$$T_s^{\mathrm{TF}}[n_\lambda^x]=\lambda^{2/3}c\int n(\lambda x,y,z)^{5/3}d(\lambda x)dy\,dz , \tag{24}$$

which dictates

$$T_s^{\mathrm{TF}}[n_\lambda^q]=\lambda^{2/3}T_s^{\mathrm{TF}}[n], \quad q=x,\ y, \text{ or } z . \tag{25}$$

Equation (22), in turn, stems from combination of Eqs. (25) and (21).

It is important to observe that *all* local-density functionals, such as T_s^{TF} and $E_{\mathrm{xc}}^{\mathrm{LDA}}$, etc, are *unreasonable* from the viewpoint of proper nonuniform scaling because they *do not distinguish* between nonuniform scaling along the different coordinates. Instead, Eq. (25) shows that $T_s^{\mathrm{TF}}[n_\lambda^q]$ is *always independent* of q and, as shall be shown below,

$$E_{\mathrm{xc}}^{\mathrm{LDA}}[n_\lambda^x]=E_{\mathrm{xc}}^{\mathrm{LDA}}[n_\lambda^y]=E_{\mathrm{xc}}^{\mathrm{LDA}}[n_\lambda^z] , \tag{26}$$

even when n possesses no special symmetry. Equation (26) follows from the fact that

$$E_{\mathrm{xc}}^{\mathrm{LDA}}[n]=\int n\varepsilon_{\mathrm{xc}}[n]d^3r \tag{27}$$

implies

$$\begin{aligned}E_{\mathrm{xc}}^{\mathrm{LDA}}[n_\lambda^x]&=\int n(\lambda x,y,z)\varepsilon_{\mathrm{xc}}[\lambda n(\lambda x,y,z)]d(\lambda x)dy\,dz\\&=\int n(\mathbf{r})\varepsilon_{\mathrm{xc}}[\lambda n(\mathbf{r})]d^3r .\end{aligned} \tag{28}$$

We confirm Eq. (26) by noting that the right-hand side of Eq. (28) is independent of q.

Intuitively, Eqs. (25) and (26), which apply to T_s^{TF} and $E_{\mathrm{xc}}^{\mathrm{LDA}}$, respectively, can not be valid for a general density. One can always make the nonuniformly scaled densities n_λ^q quite different from one another for different q so that the exact functionals $T_s[n_\lambda^q]$ and $E_{\mathrm{xc}}[n_\lambda^q]$ are expected to be heavily dependent upon q. To clarify our argument, at least for $T_s[n]$, we reveal here a lemma which can be used to test whether $T_s[n_\lambda^q]$ varies with q. With this in mind, we have already proven that T_s^x, T_s^y, and T_s^z are given by Eq. (21). This equation leads to the following lemma: If

$$T_s[n_\lambda^x]=T_s[n_\lambda^y]=T_s[n_\lambda^z] \tag{29}$$

then

$$T_s^x[n]=T_s^y[n]=T_s^z[n] . \tag{30}$$

Conversely, if

$$T_s^x[n]\neq T_s^y[n]\neq T_s^z[n] , \tag{31}$$

then

$$T_s[n_\lambda^x]\neq T_s[n_\lambda^y]\neq T_s[n_\lambda^z] , \tag{32}$$

which means that $T_s[n_\lambda^q]$ *must vary* with q is $T_s^x[n]$, $T_s^y[n]$, and $T_s^z[n]$ are not equal. This latter requisite is violated by T_s^{TF} as exhibited in Eq. (25). To reiterate the development above, the local-density approximation for T_s, and probably for E_{xc}, does not generally meet nonuniform scaling requirements.

IV. NONUNIFORM SCALING INADEQUACIES OF FOURTH-ORDER GRADIENT EXPANSION FOR T_s

The von Weizsäcker kinetic energy term T_s^W, does *not* generally satisfy Eqs. (15) and (16) when the strict inequalities apply with the exact T_s. To see this note that T_s^W is defined by

$$T_s^W[n]=\int n^{1/2}(-\tfrac{1}{2}\nabla^2)n^{1/2}d^3r . \tag{33}$$

This means that by Eq. (21) we have

$$T_s^{q,W}[n]=\int n^{1/2}\left[-\frac{1}{2}\frac{\partial^2}{\partial q^2}\right]n^{1/2}d^3r , \tag{34}$$

which gives, in contrast to Eqs. (15) and (16), the equalities

$$T_s^W[n_\lambda^x]=\lambda^2T_s^{x,W}[n]+T_s^{y,W}[n]+T_s^{z,W}[n] \tag{35}$$

and

$$\lambda^2T_s^W[n]=T_s^{x,W}[n_\lambda^x]+\lambda^2T_s^{y,W}[n_\lambda^x]+\lambda^2T_s^{z,W}[n_\lambda^x] . \tag{36}$$

The Hodges gradient expansion[4] through fourth order is $T_s^{\mathrm{GE}}[n]=T_s^{\mathrm{TF}}[n]+\frac{1}{9}T_s^W[n]+T_4[n]$, where $T_4[n]$ is given by

$$T_4[n]=C_4\int\left[\frac{(\nabla^2n)^2}{n^{5/3}}-\frac{9}{8}\frac{\nabla^2n|\nabla n|^2}{n^{8/3}}+\frac{1}{3}\frac{|\nabla n|^4}{n^{11/3}}\right]d^3r , \tag{37}$$

and where C_4 is a constant. Consider the fourth-order term $T_4[n]$. With some algebra, it can be shown that

$$T_4[n_\lambda^x]=C_4\lambda^{-2/3}\int\left\{\frac{\left[\left(\lambda^2\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)n(\mathbf{r})\right]^2}{n^{5/3}}\right.$$

$$-\frac{9}{8}\frac{\left(\lambda\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial^2 z}\right)n(\mathbf{r})\left[\lambda^2\left(\frac{\partial}{\partial x}n\right)^2+\left(\frac{\partial}{\partial y}n\right)^2+\left(\frac{\partial}{\partial z}n\right)^2\right]}{n^{8/3}}$$

$$\left.+\frac{1}{3}\frac{\left[\lambda^2\left(\frac{\partial}{\partial x}n\right)^2+\left(\frac{\partial}{\partial y}n\right)^2+\left(\frac{\partial}{\partial z}n\right)^2\right]^2}{n^{11/3}}\right\}d^3r\,. \tag{38}$$

Surprisingly,

$$\lim_{\lambda\to 0}T_4[n_\lambda^x]\to\infty\ , \tag{39}$$

so that

$$\lim_{\lambda\to 0}T_s^{\mathrm{GE}}[n_\lambda^x]\to\infty\ , \tag{40}$$

which violates Eq. (15). It appears that nonuniform scaling requirements are very difficult to satisfy and will thus help construct the very best approximation to $T_s[n]$.

V. EXAMPLES IN WHICH EQUALITIES APPLY IN EQS. (15) AND (16), AND NONUNIFORM SCALING REQUIREMENTS FOR $E_x[n]$

In Sec. II, we have proven that the nonuniformly scaled wave function

$$\lambda^{n/2}\Phi_n^{\min}(\lambda x_1y_1z_1,\ldots,\lambda x_Ny_Nz_N)$$

gives the scaled density n_λ^x but does not necessarily minimize $\langle\hat{T}\rangle$, from which Eq. (12) arises in general. Consequently, the inequalities in Eqs. (15) and (16) take place. However, we have found some special cases in which

$$\lambda^{N/2}\Phi_n^{\min}(\lambda x_1y_1z_1,\ldots,\lambda x_Ny_Nz_N)$$

not only yields n_λ^x, but simultaneously minimizes $\langle\hat{T}\rangle$, so that Eq. (9) holds for these special cases and the inequalities in Eqs. (15) and (16) become equalities:

$$T_s[n_\lambda^x]=\lambda^2T_s^x[n]+T_s^y[n]+T_s^z[n]\ , \tag{41}$$

and

$$\lambda^2T_s[n]=T_s^x[n_\lambda^x]+\lambda^2T_s^y[n_\lambda^x]+\lambda^2T_s^z[n_\lambda^x]\ . \tag{42}$$

Compared to Eqs. (15) and (16), Eqs. (41) and (42) are even more stringent to be satisfied. For instance, $T_s^{\mathrm{TF}}[n]$ does not satisfy Eqs. (41) and (42) when Eq. (30) holds, while $T_s^{\mathrm{TF}}[n]$ satisfies Eqs. (15) and (16) when Eq. (30) holds. In addition, two limiting relations can be deduced from Eqs. (41) and (42):

$$\lim_{\lambda\to 0}T_s[n_\lambda^x]=T_s^y[n]+T_s^z[n]>0\ , \tag{43}$$

$$\lim_{\lambda\to\infty}\frac{1}{\lambda^2}T_s[n_\lambda x]=T_s^x[n]>0\ , \tag{44}$$

which are violated by $T_s^{\mathrm{TF}}[n]$ when Eq. (30) holds.

When Eq. (9) applies, we are able to deduce the exact nonuniform scaling properties of $E_x[n]$ which is given by

$$E_x[n]=-\frac{1}{4}\int\int\frac{|\gamma(\mathbf{r},\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}d^3r\,d^3r'\ , \tag{45}$$

where

$$\gamma(\mathbf{r},\mathbf{r}')=\gamma(x,y,z;x',y',z')=\sum_{i=1}\phi_i^*(x'y'z')\phi_i(xyz)\ ,$$

and where the ϕ_i are the Kohn-Sham orbitals of which the determinant $\Phi_n^{\min}$ is composed. From Eqs. (45) and (9), one finds

$$E_x[n_\lambda^x]=-\tfrac{1}{4}\int\int\frac{|\lambda\gamma(\lambda x,y,z;\lambda x',y'z')|^2}{[(x-x')^2+(y-y')^2+(z-z')^2]^{1/2}}dx\,dy\,dz\,dx'dy'dz'$$

$$=-\tfrac{1}{4}\int\int\frac{|\gamma(\mathbf{r},\mathbf{r}')|^2}{[\lambda^{-2}(x-x')^2+(y-y')^2+(z-z')^2]^{1/2}}d^3r\,d^3r'\ . \tag{46}$$

With some algebra, it can be shown that

$$\lim_{\lambda\to\infty}E_x[n_\lambda^x]=\lim_{\lambda\to 0}\frac{\partial}{\partial\lambda}E_x[\lambda^2n(x,\lambda y,\lambda z)]$$

$$=\int\int\frac{|\gamma(\mathbf{r},\mathbf{r}')|^2}{[(y-y')^2+(z-z')^2]^{1/2}}d^3r\,d^3r'\ , \tag{47}$$

$$\lim_{\lambda\to 0}\frac{\partial}{\partial\lambda}E_x[n_\lambda^x]=\lim_{\lambda\to\infty}E_x[\lambda^2n(x\lambda y,\lambda z)]$$

$$=\int\int\frac{|\gamma(\mathbf{r},\mathbf{r}')|^2d^3r\,d^3r'}{|(x-x')|}\ , \tag{48}$$

and

$$\lim_{\lambda\to 1}\frac{\partial}{\partial\lambda}(E_x[n_\lambda^x]+E_x[n_\lambda^y]+E_x[n_\lambda^z])=E_x[n]\ . \tag{49}$$

Equations (46)–(48) give

$$\lim_{\lambda\to\infty} E_x[n_\lambda^x] \neq \lim_{\lambda\to\infty} E_x[n_\lambda^y] \neq \lim_{\lambda\to\infty} E_x[n_\lambda^z] < \infty \quad (50)$$

and

$$\lim_{\lambda\to 0} \frac{\partial}{\partial\lambda} E_x[n_\lambda^x] \neq \lim_{\lambda\to 0} \frac{\partial}{\partial\lambda} E_x[n_\lambda^y] \neq \lim_{\lambda\to 0} \frac{\partial}{\partial\lambda} E_x[n_\lambda^z] < \infty \ . \quad (51)$$

Both Eqs. (50) and (51) lead to

$$E_x[n_\lambda^x] \neq E_x[n_\lambda^y] \neq E_x[n_\lambda^z] \ . \quad (52)$$

Equations (50)–(52) are violated by $E_x^{\mathrm{LDA}}[n]$.

We now identify two types of densities where Eq. (9) applies, which guarantees the validity of our results derived in this section. Firstly, consider a density whose noninteracting Hamiltonian is

$$\hat{H} = \sum_{i=1}^{N} [-\tfrac{1}{2}\nabla_i^2 + v_x(x_i) + v_y(y_i) + v_z(z_i)] \ . \quad (53)$$

The exact $T_s[n]$ for this system (assumed for simplicity to consist of only doubly occupied orbitals) is

$$T_s[n] = 2\sum_{i=1}^{M} \int \phi_i^*(-\tfrac{1}{2}\nabla^2)\phi_i d^3r \ , \quad (54)$$

where ϕ_i satisfies the following equations:

$$[-\tfrac{1}{2}\nabla^2 + v_x(x) + v_y(y) + v_z(z)]\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r}), \quad i = 1, 2, \ldots, M \quad (55)$$

with $M = N/2$. Equation (55) can be solved by separation of variables:

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial x^2} + v_x(x)\right]\phi_k^x(x) = \varepsilon_k^x\phi_k^x(x) \ , \quad (56)$$

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial y^2} + v_y(y)\right]\phi_l^y(y) = \varepsilon_l^y\phi_l^y(y) \ , \quad (57)$$

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial z^2} + v_z(z)\right]\phi_m^z(z) = \varepsilon_m^z\phi_m^z(z) \ , \quad (58)$$

with $\varepsilon_i = \varepsilon_k^x + \varepsilon_l^y + \varepsilon_m^z$, and $\phi_i(\mathbf{r}) = \phi_k^x(x)\phi_l^y(y)\phi_m^z(z)$, where k, l, and m are understood to depend on i.

The $\Phi_n^{\min}$ constructed from the $\phi_i(\mathbf{r})$ minimizes $\langle \hat{T} \rangle$. We now prove that the scaled wave function

$$\lambda^{N/2}\Phi_n^{\min}(\lambda x_1 y_1 z_1, \ldots, \lambda x_N y_N z_N)$$

constructed from the $\lambda^{1/2}\phi_i(\lambda x, y, z)$ also minimizes $\langle \hat{T} \rangle$. The equivalent problem is to show that $\lambda^{1/2}\phi_i(\lambda x, y, z)$ is an eigenfunction of $(-\frac{1}{2}\nabla^2 + v_{\mathrm{eff}})$, where v_{eff} is a single-particle potential. To do so, we transform Eq. (56) into a new form:

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial(\lambda x)^2} + v_x(\lambda x)\right]\phi_k^x(\lambda x) = \varepsilon_k^x\phi_k^x(\lambda x)$$

or

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial x^2} + \lambda^2 v_x(\lambda x)\right]\lambda^{1/2}\phi_k(\lambda x) = (\lambda^2\varepsilon_k^x)\lambda^{1/2}\phi_k^x(\lambda x) \ . \quad (59)$$

Combining Eqs. (57)–(59), one obtains

$$\left[-\frac{1}{2}\nabla^2 + v_{\mathrm{eff}}\right]\lambda^{1/2}\phi_i(\lambda x, y, z) = \varepsilon_i'\lambda^{1/2}\phi_i(\lambda x, y, z) \ , \quad (60)$$

where $v_{\mathrm{eff}} = \lambda^2 v_x(\lambda x) + v_y(y) + v_z(z)$, and where $\varepsilon_i' = \lambda^2\varepsilon_k^x + \varepsilon_l^y + e_m^z$.

The second example is embodied by the one- and two-electron systems where the scaled wave function yields the scaled density n_λ^x and also minimizes $\langle \hat{T} \rangle$. Proof for this statement is similar to the one given above.

VI. CONCLUDING REMARKS

We summarize the main results achieved in this paper. First of all, we have introduced nonuniform coordinate scaling into density-functional theory. A set of nonuniform scaling relations concerning the exact kinetic energy $T_s[n]$ has been derived. It has been proven here that the Thomas-Fermi functional, the von Weizsäcker term, the fourth-order gradient term, and the whole gradient expansion through fourth order all fail to satisfy these exact nonuniform scaling conditions for $T_s[n]$. For some special cases, we have obtained even more stringent conditions for both $T_s[n]$ and $E_x[n]$, which are, once again, violated by the LDA. Finally it should be noted that the gradient expansion through second order, $T_s^{\mathrm{TF}} + \frac{1}{9}T_s^W$, satisfies Eq. (15), (16), and (23), but this expansion violates[5] the condition that the Pauli potential be nonnegative[6,7] for all $\mathbf{r}$. The Pauli potential is defined[8] as $\delta(T_s[n] - T_w[n])/\delta n$. In closing, we emphasize that an important challenge for an approximate T_s is its capability of generating reasonably accurate molecular binding energies.[9] With this in mind, we feel that proper behavior with respect to nonuniform scaling is necessary because bonding causes nonuniform distortions in the density.

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[3]T_s may be defined in slightly different ways. See, for instance, the discussion and references in the chapter by M. Levy and J. P. Perdew in *Density Functional Methods in Physics*, edited by R. M. Dreizler and J. da Providencia (Plenum, New York, 1985). In any case $\Phi_{n_\lambda^x}^{\min}$ is the original Kohn-Sham determined when $\Phi_{n_\lambda^x}^{\min}$ is a nondegenerate ground-state single

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