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Expansions of the correlation-energy density functional $E_c[\rho]$ and its kinetic-energy component $T_c[\rho]$ in terms of homogeneous functionals

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Based on the constrained-search formulation of a coupled Hamiltonian, new formulas are given involving the correlation-energy density functional $E_c[\rho]$ and its kinetic component $T_c[\rho]$, starting from two relations of Levy and Perdew. Consequences are examined of assuming (following earlier authors) the existence of a Taylor series expansion of $E_c^\lambda[\rho]$ in the coupling parameter λ. If one truncates the series at the linear term, one finds that $E_c[\rho]$ and $T_c[\rho]$ are homogeneous of degree zero with respect to coordinate scaling, and if local, they are homogeneous of degree one in the density scaling. More generally, it is shown that $E_c[\rho]$ and $T_c[\rho]$ are linear combinations of homogeneous functionals of different specific degrees in coordinate scaling: $0,-1,-2,-3,\ldots,(1-n),\ldots$. If the functionals also are local, both $E_c[\rho]$ and $T_c[\rho]$ are combinations of functionals $\langle\rho^k\rangle$ homogeneous in ρ of degrees $k=1,\frac{2}{3},\frac{1}{3},0,\ldots,(4-n)/3,\ldots$. For atoms and molecules, $k\geqslant 0$, and so E_c and T_c take the form $X_c[\rho]=aN+b\int\rho^{2/3}(\mathbf{r})d^3r+c\int\rho^{1/3}(\mathbf{r})d^3r+d$, where a, b, c, and d are constants to be determined. Numerical tests are given that demonstrate the effectiveness of such series of local functionals. We also give definitions of density scaling, coordinate scaling, and homogeneities, and relations among them.

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I. INTRODUCTION

The Hohenberg-Kohn universal functional $F_\lambda[\rho]$ is defined within an extended domain via the constrained-search formulation [1,2] by the prescription

$$\begin{aligned}F_\lambda[\rho]&=\langle\Psi^\lambda|\hat{T}+\lambda\hat{V}_{ee}|\Psi^\lambda\rangle\\&=T_s[\rho]+\lambda J[\rho]+\lambda E_x[\rho]+\lambda E_c^\lambda[\rho],\end{aligned}\tag{1}$$

where Ψ^λ is the antisymmetric N-electron function that yields $\rho(\mathbf{r})$, minimizes $\langle(\hat{T}+\lambda\hat{V}_{ee})\rangle$, and is an eigenstate of some Hamiltonian of the form [3]

$$\hat{H}_\lambda=\hat{T}+\lambda\hat{V}_{ee}+\hat{V}_{ne,\lambda},\tag{2}$$

where

$$\hat{T}=\sum_{i=1}^{N}-\frac{1}{2}\boldsymbol{\nabla}_i^2,\tag{3}$$

$$\hat{V}_{ee}=\frac{1}{2}\sum_i\sum_{j\neq i}|\mathbf{r}_i-\mathbf{r}_j|^{-1},\tag{4}$$

and

$$\hat{V}_{ne,\lambda}=\sum_{i=1}^{N}\nu_\lambda(\mathbf{r}_i),\tag{5}$$

where λ is the coupling constant that measures the interaction strength between electrons of the system. The correlation-energy density functional $E_c^\lambda[\rho]$ can then be defined as [4]

$$\lambda E_c^\lambda[\rho]=\langle\Psi^\lambda|\hat{T}+\lambda\hat{V}_{ee}|\Psi^\lambda\rangle-\langle\Psi^{\lambda=0}|\hat{T}+\lambda\hat{V}_{ee}|\Psi^{\lambda=0}\rangle,\tag{6}$$

which can be decomposed into two components, namely, the kinetic-energy part $T_c^\lambda[\rho]$ and the potential-energy part $V_c^\lambda[\rho]$:

$$\lambda E_c^\lambda[\rho]=T_c^\lambda[\rho]+\lambda V_c^\lambda,\tag{7}$$

with

$$T_c^\lambda[\rho]=\langle\Psi^\lambda|\hat{T}|\Psi^\lambda\rangle-\langle\Psi^{\lambda=0}|\hat{T}|\Psi^{\lambda=0}\rangle,\tag{8}$$

and

$$V_c^\lambda[\rho]=\langle\Psi^\lambda|\hat{V}_{ee}|\Psi^\lambda\rangle-\langle\Psi^{\lambda=0}|\hat{V}_{ee}|\Psi^{\lambda=0}\rangle.\tag{9}$$

Here, ρ is any specific N and ν representable electron density.

Some time ago, Levy and Perdew [4] derived two relations for $E_c^\lambda[\rho]$ and $T_c^\lambda[\rho]$,

$$-\lambda E_c^\lambda[\rho]-\lambda\int\rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\nabla}\left(\frac{\delta E_c^\lambda[\rho]}{\delta\rho(\mathbf{r})}\right)d^3r=T_c^\lambda[\rho],\tag{10}$$

and

$$\int\rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\nabla}\left(\frac{\delta E_c^\lambda[\rho]}{\delta\rho(\mathbf{r})}\right)d^3r=-E_c^\lambda[\rho]+\lambda\frac{dE_c^\lambda[\rho]}{d\lambda}.\tag{11}$$

Eliminating the integral term between these equations, one obtains [5]

$$T_c^\lambda[\rho]=-\lambda^2\frac{dE_c^\lambda[\rho]}{d\lambda}.\tag{12}$$

Consequently, using Eq. (8), we have [5,6]

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$$E_c[\rho] = -\int_0^1 \frac{d\lambda}{\lambda^2}\, T_c^\lambda[\rho] = -\int_0^1 \frac{d\lambda}{\lambda^2}\, (\langle \Psi^\lambda|\hat{T}|\Psi^\lambda\rangle - \langle \Psi^{\lambda=0}|\hat{T}|\Psi^{\lambda=0}\rangle). \tag{13}$$

If one takes the functional derivative of Eq. (12) with respect to $\rho(\mathbf{r})$, multiples by $\rho(\mathbf{r})\mathbf{r}\cdot\nabla$, and then integrates over all space, there results

$$\int \rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\nabla}\left(\frac{\delta T_c^\lambda[\rho]}{\delta\rho(\mathbf{r})}\right)d^3r = -\lambda^2 \frac{d}{d\lambda}\left\{\int \rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\nabla}\left(\frac{\delta E_c^\lambda[\rho]}{\delta\rho(\mathbf{r})}\right)d^3r\right\}. \tag{14}$$

After Eq. (11) is employed to eliminate the integral on the right-hand side, this becomes

$$\int \rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\nabla}\left(\frac{\delta T_c^\lambda[\rho]}{\delta\rho(\mathbf{r})}\right)d^3r = -2T_c^\lambda[\rho] + \lambda\,\frac{dT_c^\lambda[\rho]}{d\lambda}. \tag{15}$$

Notice that Eqs. (11) and (15), respectively, involve only $E_c^\lambda[\rho]$ and $T_c^\lambda[\rho]$. These formulas all are exact identities.

II. FIRST-ORDER APPROXIMATIONS FOR $E_c[\rho]$ AND $T_c[\rho]$

Following Levy and Perdew [4], we first suppose that $E_c^\lambda[\rho]$ can be expanded in a Taylor series in λ up to the first order, i.e.,

$$E_c^\lambda[\rho] = E_c^{\lambda=0} + \lambda\left(\frac{dE_c^\lambda[\rho]}{d\lambda}\right)_{\lambda=0} = E_c^{\lambda=0} + \lambda E_c'. \tag{16}$$

Here E_c' is by definition the λ-independent derivative $(dE_c^\lambda[\rho]/d\lambda)_{\lambda=0}$. However, $E_c^{\lambda=0}[\rho]=0$ [4], so that

$$E_c^\lambda[\rho] = \lambda\,\frac{dE_c^\lambda[\rho]}{d\lambda}, \tag{17}$$

and Eq. (11) becomes

$$\int \rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\nabla}\left(\frac{\delta E_c^\lambda[\rho]}{\delta\rho(\mathbf{r})}\right)d^3r = 0, \tag{18}$$

as was already given by Levy and Perdew [4]. Inserting Eq. (17) into Eq. (12), one finds

$$T_c^\lambda[\rho] = \frac{\lambda}{2}\,\frac{dT_c^\lambda[\rho]}{d\lambda}. \tag{19}$$

Combination of Eqs. (15) and (19) gives

$$\int \rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\nabla}\left(\frac{\delta T_c^\lambda[\rho]}{\delta\rho(\mathbf{r})}\right)d^3r = 0. \tag{20}$$

Equations (18) and (20) mean that in the first-order approximation $E_c^\lambda[\rho]$ and $T_c^\lambda[\rho]$ are homogeneous of degree zero in *coordinate* scaling (see Appendix for discussion).

Consider now the case that $E_c^\lambda[\rho]$ and $T_c^\lambda[\rho]$ are local functionals, which means (see Appendix) that

$$E_c^\lambda[\rho] = \int e_c^\lambda(\rho(\mathbf{r}))d^3r, \tag{21}$$

and

$$T_c^\lambda[\rho] = \int t_c^\lambda(\rho(\mathbf{r}))d^3r. \tag{22}$$

The locality condition then implies [7]

$$E_c^\lambda[\rho] = -\frac{1}{3}\int \mathbf{r}\cdot\boldsymbol{\nabla}\rho(\mathbf{r})\,\frac{\delta E_c^\lambda[\rho]}{\delta\rho(\mathbf{r})}\,d^3r, \tag{23}$$

and

$$T_c^\lambda[\rho] = -\frac{1}{3}\int \mathbf{r}\cdot\boldsymbol{\nabla}\rho(\mathbf{r})\,\frac{\delta T_c^\lambda[\rho]}{\delta\rho(\mathbf{r})}\,d^3r. \tag{24}$$

By partially integrating Eqs. (18) and (20) and using the above relations, one arrives at the conclusion that $E_c^\lambda[\rho]$ and $T_c^\lambda[\rho]$ are homogeneous of degree one with respect to *density* scaling, i.e.,

$$E_c^\lambda[\rho] = \int \rho(\mathbf{r})\,\frac{\delta E_c^\lambda[\rho]}{\delta\rho(\mathbf{r})}\,d^3r \tag{25}$$

and

$$T_c^\lambda[\rho] = \int \rho(\mathbf{r})\,\frac{\delta T_c^\lambda[\rho]}{\delta\rho(\mathbf{r})}\,d^3r. \tag{26}$$

See the Appendix for a discussion of homogeneity with respect to coordinate scaling and homogeneity with respect to density scaling. These are different concepts.

As shown in the Appendix, the only way a functional $X[\rho]$ can be homogeneous of degree one in density scaling and homogeneous of degree zero in coordinate scaling is for it to be of the form $X[\rho]=CN[\rho]=CN$. The first-order assumption of Eq. (16) would therefore suggest that both E_c and T_c might be proportional to N. Indeed, actual data demonstrate that these proportionalities hold roughly. This is shown in Figs. 1 and 2, in which E_c and T_c values are plotted against N for the atoms He through Ar. The data for E_c were obtained from the very recent optimized-effective-potential (OEP) calculation by Grabo and Gross [8]. The data for T_c were taken from Morrison and Zhao [9]. It is clear that the homogeneities of Eqs. (18) and (20) and (25) and (26) are approximately satisfied.

One sees from the figures that there certainly is an approximate proportionality between E_c and N and also between T_c and N, though, not surprisingly, the proportionality assumption is better satisfied if one replaces N with $N-1$. Best fits give $E_c=-0.0377N$ and $E_c=-0.040(N-1)$, with regression coefficients 0.957 and 0.984, respectively; $T_c=0.0257N$ and $0.028(N-1)$, with regression coefficient 0.956 and 0.974, respectively.

Next, we test the validity of the first-order approximation. We may expand $E_c^\lambda[\rho]$ to second order and use known data to check whether the second-order term is smaller than the first-order term. In place of Eq. (16), write

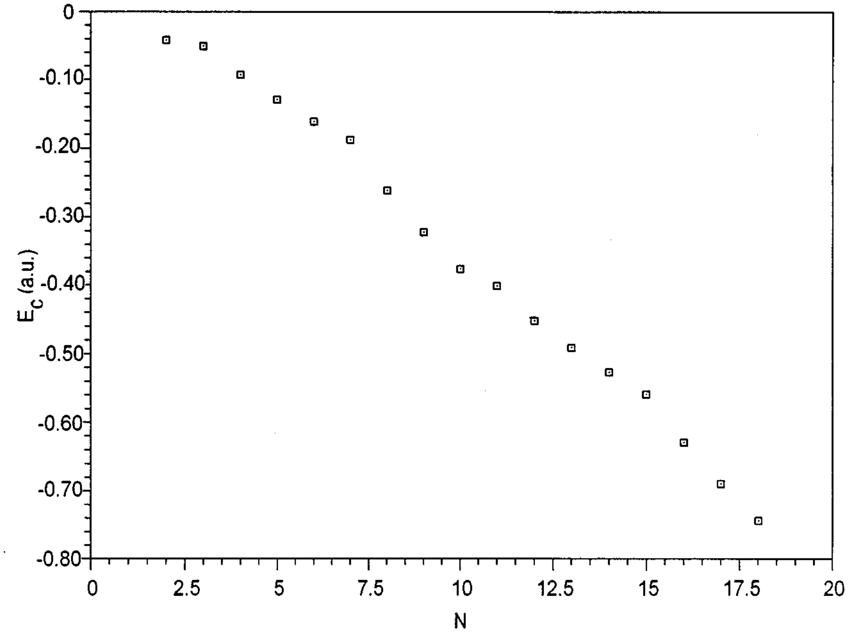

FIG. 1. Correlation energy E_c of neutral atoms as function of number of electrons N. See text.

$$E_c^\lambda[\rho]=\lambda\left(\frac{dE_c^\lambda}{d\lambda}\right)_{\lambda=0}+\lambda^2\left(\frac{1}{2}\,\frac{d^2E_c^\lambda}{d\lambda^2}\right)_{\lambda=0}=\lambda E_c'+\lambda^2E_c''. \tag{27}$$

Given $\lambda=1$, Eq. (27) becomes

$$E_c=E_c'+E_c''. \tag{28}$$

Inserting Eq. (27) into Eq. (12), one obtains

$$\begin{aligned}T_c^\lambda[\rho]&=-\lambda^2\left(\frac{dE_c^\lambda}{d\lambda}\right)_{\lambda=0}-2\lambda^3\left(\frac{1}{2}\,\frac{d^2E_c^\lambda}{d\lambda^2}\right)_{\lambda=0}.\\&=-\lambda^2E_c'-2\lambda^3E_c''.\end{aligned} \tag{29}$$

With $\lambda=1$, Eq. (29) becomes

$$T_c=-E_c'-2E_c''. \tag{30}$$

Employing reference values of E_c [8] and T_c [9], from Eqs. (28) and (30) one can estimate magnitudes of E_c' and E_c''. Table I shows the results for the atoms from H to Ar. The magnitude of E_c'' is roughly 20% of that of E_c', which shows that Eq. (16) gives reasonably good approximations for both $E_c^\lambda[\rho]$ and $T_c^\lambda[\rho]$. Note that the only approximation here is that $E_c^\lambda[\rho]$ is quadratic in λ; no locality assumption has been made.

III. GENERAL EXPANSIONS OF $E_c^\lambda[\rho]$ AND $T_c^\lambda[\rho]$ IN TERMS OF HOMOGENEOUS FUNCTIONALS

Now, following Görling and Levy [10], let us make the general postulate that there exists a full Taylor series expansion of E_c^λ in powers of λ,

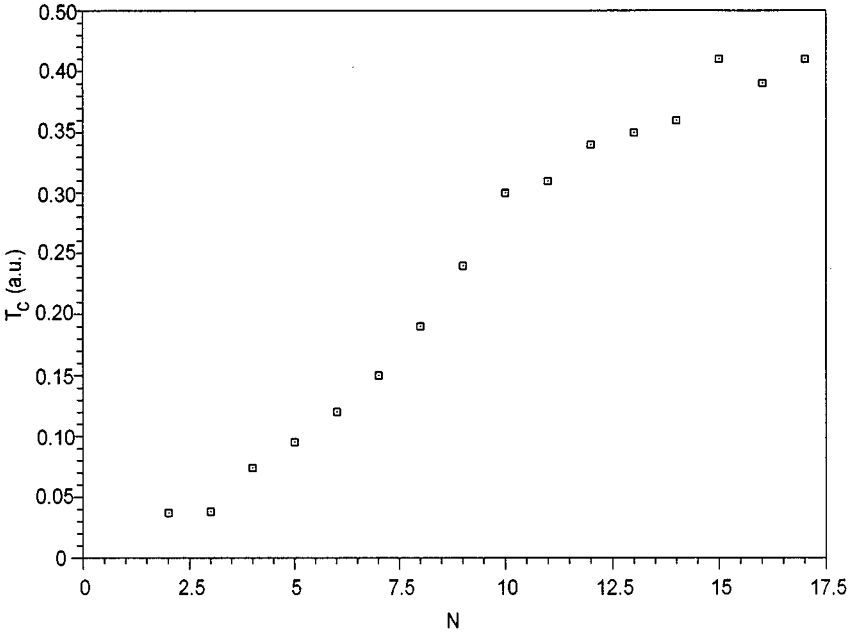

FIG. 2. Kinetic-energy contribution T_c to correlation energy of neutral atoms as a function of number of electrons N. See text.

TABLE I. Values of the Kohn-Sham correlation energy E_c, its kinetic component T_c, and expansion coefficients of the first- and second-order Taylor series of E_c^λ and T_c^λ for atoms from He to Ar (atomic units). E_c and T_c values from Refs. [8] and [9], respectively.

Atom	E_c	T_c	E_c'	E_c''
He	−0.042	0.037	−0.047	0.005
Li	−0.051	0.038	−0.064	0.013
Be	−0.093	0.074	−0.112	0.019
B	−0.129	0.095	−0.163	0.034
C	−0.161	0.12	−0.202	0.041
N	−0.188	0.15	−0.226	0.038
O	−0.261	0.19	−0.332	0.071
F	−0.322	0.24	−0.404	0.082
Ne	−0.376	0.30	−0.452	0.076
Na	−0.401	0.31	−0.492	0.091
Mg	−0.452	0.34	−0.564	0.112
Al	−0.491	0.35	−0.532	0.141
Si	−0.527	0.36	−0.694	0.167
P	−0.559	0.41	−0.708	0.149
S	−0.629	0.39	−0.868	0.239
Cl	−0.689	0.41	−0.968	0.279
Ar	−0.744	0.21[a]	−1.278	0.543

[a] The value of T_c for Ar is rather suspicious as discussed in Ref. [9].

$$E_c^\lambda[\rho]=\sum_{n=1}^{\infty}\frac{\lambda^n}{n!}\left(\frac{d^nE_c^\lambda[\rho]}{d\lambda^n}\right)_{\lambda=0}=\sum_{n=1}^{\infty}\frac{\lambda^n}{n!}A_n[\rho]. \tag{31}$$

Then

$$\lambda\frac{dE_c^\lambda[\rho]}{d\lambda}=\sum_{n=1}^{\infty}\frac{\lambda^n}{(n-1)!}A_n[\rho]. \tag{32}$$

Inserting this into Eq. (12), one gets

$$T_c^\lambda[\rho]=-\sum_{n=1}^{\infty}\frac{\lambda^{n+1}}{(n-1)!}A_n[\rho], \tag{33}$$

so that

$$\lambda\frac{dT_c^\lambda[\rho]}{d\lambda}=-\sum_{n=1}^{\infty}\frac{(n+1)\lambda^{n+1}}{(n-1)!}A_n[\rho]. \tag{34}$$

On insertion of Eqs. (31) and (32) into Eq. (11), and Eqs. (33) and (34) into Eq. (15), there result

$$\sum_{n=1}^{\infty}\frac{\lambda^n}{n!}\left\{\int\rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\nabla}\left(\frac{\delta A_n[\rho]}{\delta\rho(\mathbf{r})}\right)d^3r-(n-1)A_n[\rho]\right\}=0, \tag{35}$$

and

$$\sum_{n=1}^{\infty}\frac{\lambda^{n+1}}{(n-1)!}\left\{\int\rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\nabla}\left(\frac{\delta A_n[\rho]}{\delta\rho(\mathbf{r})}\right)d^3r-(n-1)A_n[\rho]\right\}=0 \tag{36}$$

for any λ. The important consequence is that

$$-\int\rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\nabla}\left(\frac{\delta A_n[\rho]}{\delta\rho(\mathbf{r})}\right)d^3r=(1-n)A_n[\rho]. \tag{37}$$

This is to say, provided that the Taylor series of Eq. (31) exists and admits of the operations we have made on it, the nth component of the Taylor series for $E_c^\lambda[\rho]$ and $T_c^\lambda[\rho]$ is a homogeneous functional of degree $(1-n)$ in coordinate scaling; that is[1]

$$A_n[\rho_\gamma]=\gamma^{1-n}A_n[\rho],\quad n=1,2,3,\ldots, \tag{38}$$

where

$$\rho_\gamma=\gamma^3\rho(\gamma\mathbf{r}). \tag{39}$$

In contrast, recall the fact that the kinetic-energy density functional $T_s[\rho]$ is homogeneous of degree two in coordinate scaling [4],

$$T_s[\rho_\gamma]=\gamma^2T_s[\rho], \tag{40}$$

and that the exchange-energy density functional $E_x[\rho]$ is homogeneous of degree one in coordinate scaling [4],

$$E_x[\rho_\gamma]=\gamma E_x[\rho]. \tag{41}$$

With λ=1, Eq. (31) becomes

$$E_c[\rho]=\sum_{n=1}^{\infty}\frac{A_n[\rho]}{n!}, \tag{42}$$

and Eq. (33) becomes

$$T_c[\rho]=-\sum_{n=1}^{\infty}\frac{A_n[\rho]}{(n-1)!}, \tag{43}$$

where $A_n[\rho]$ is homogeneous of degree $(1-n)$ in coordinate scaling. We conclude that $E_c[\rho]$ and $T_c[\rho]$ must be combinations of homogeneous functionals of various specific degrees in coordinate scaling: $0,-1,-2,\ldots,(1-n),\ldots$.

As a confirmation of Eqs. (42) and (43), recall the relationship of Levy and Perdew [4],

$$E_c[\rho]+T_c[\rho]=\left(\frac{dE_c[\rho_\gamma]}{d\gamma}\right)_{\gamma=1}, \tag{44}$$

which holds only at $\gamma=1$. Using Eqs. (38) and (42), one obtains

$$E_c[\rho_\gamma]=\sum_{n=1}^{\infty}\frac{\gamma^{1-n}}{n!}A_n[\rho]. \tag{45}$$

This expansion was earlier generated by Levy and by Levy and Görling [10, 11].

Differentiating Eq. (45) with respect to γ and setting $\gamma=1$, we obtain

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[1] In a paper that has appeared since the present paper was submitted [Phys. Rev. A **52**, 4493 (1995)], A. Görling and M. Levy also have derived this result.

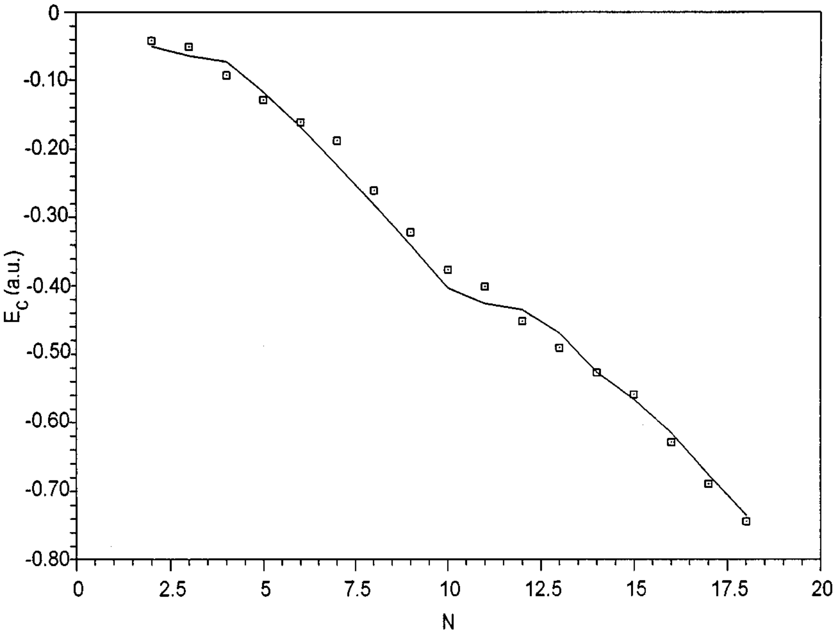

FIG. 3. Curve of E_c vs N. The fitted curve is $E_c = -0.0603N + 0.0175\int \rho^{2/3} d^3r - 0.000\,53\int \rho^{1/3} d^3r$. The correlation coefficient is 0.997.

$$\left(\frac{dE_c[\rho_\gamma]}{d\gamma}\right)_{\gamma=1} = \sum_{n=1}^{\infty} \frac{1-n}{n!} A_n[\rho] = E_c[\rho] + T_c[\rho]. \tag{46}$$

One can readily confirm that Eqs. (42) and (43), together with the scaling property of A_n, satisfy various other identities of $E_c[\rho]$ and its components proposed by Levy and Perdew [5,11].

A. Case of local functionals

If one assumes that $A_n[\rho]$ is a local functional, that is,

$$A_n[\rho] = \int a_n(\rho(\mathbf{r})) d^3r, \tag{47}$$

then (see Appendix)

$$A_n[\rho] = -\frac{1}{3} \int \mathbf{r} \cdot \boldsymbol{\nabla} \rho(\mathbf{r}) \frac{\delta A_n[\rho]}{\delta \rho(\mathbf{r})} d^3r. \tag{48}$$

Using Eqs. (37), we will have

$$\int \rho(\mathbf{r}) \frac{\delta A_n[\rho]}{\delta \rho(\mathbf{r})} d^3r = \frac{4-n}{3} A_n[\rho], \tag{49}$$

which means that, if it is local, $A_n[\rho]$ is a homogeneous functional of degree $(4-n)/3$ in density scaling, with $n = 1,2,3,\ldots$. Recall that for homogeneous systems under the locality approximation, $T_s[\rho]$ is homogeneous of degree $\frac{5}{3}$ in density scaling, and $E_x[\rho]$ is homogeneous of degree $\frac{4}{3}$. From the present derivation, we now know that $E_c[\rho]$ and $T_c[\rho]$ are combinations of functionals homogeneous in ρ of degrees: $1, \frac{2}{3}, \frac{1}{3}, 0, -\frac{1}{3}, \ldots$.

Since the only form of a local functional $X[\rho]$ that is homogeneous of degree k with respect to density scaling and homogeneous of degree $m = 3k-3$ (see Appendix) in coordinate scaling is $C\int \rho^k(\mathbf{r}) d^3r$ (see Appendix for a detailed proof), where C is a constant to be determined, if one considers the Taylor expansion up to the third order, one would have, for both E_c and T_c,

$$X_c[\rho] = aN + b\int \rho^{2/3}(\mathbf{r}) d^3r + c\int \rho^{1/3}(\mathbf{r}) d^3r. \tag{50}$$

If, however, one considers the expansion up to the fourth order, then one would have

$$X_c[\rho] = aN + b\int \rho^{2/3}(\mathbf{r}) d^3r + c\int \rho^{1/3}(\mathbf{r}) d^3r + d, \tag{51}$$

where a, b, c, and d are coefficients to be determined somehow. For atoms and molecules, n values greater than 4 are not allowed, because exponential decay of the density then will cause divergence.

Figures 3 and 4 show the results for E_c and T_c, respectively, obtained using least squares to determine the coefficients in Eq. (50). The correlation coefficients for the two figures are 0.997 and 0.984, respectively. The results in Figs. 3 and 4 show quite conclusively that Eq. (50) is a rather good approximation. Note in particular the decreasing values of the coefficients in the series. Notice also, however, that Eqs. (42) and (43), with all A_n local, very probably are not exact, because it has been previously demonstrated that $E_{\mathrm{xc}}[\rho]$ is not completely local and for all the nonlocality to be contained in the exchange would be most unlikely [12]. Note also that the values of $E_c[\rho]$ we have used here are not the exact Kohn-Sham values, and for larger atoms, for instance, Ar, very accurate numerical calculations of T_c have not yet been achieved.

Since Eqs. (42) and (43) predict that $E_c[\rho]$ and $T_c[\rho]$ share the same expansion coefficients, in Fig. 5, we report the results when they are fitted together in the form of Eq. (51) with one set of coefficients as predicted from Eqs. (42)

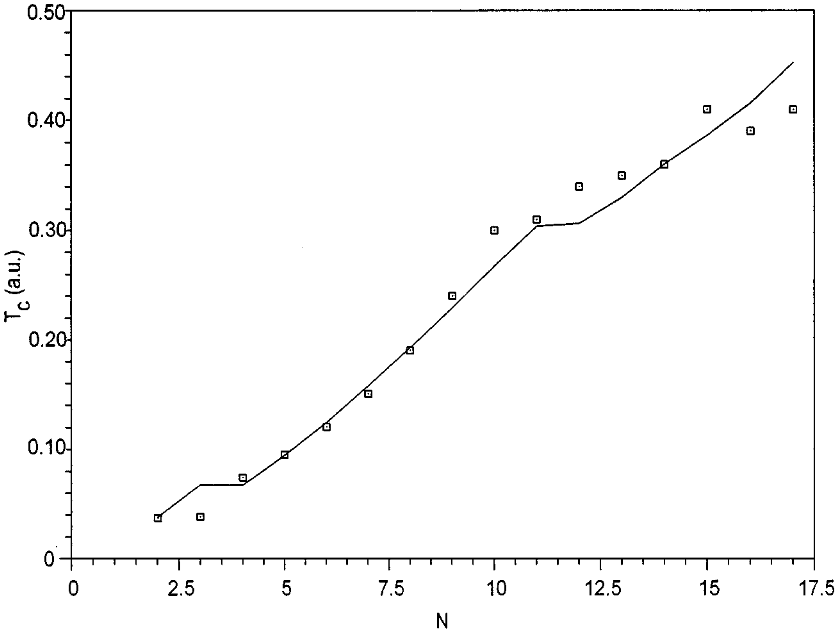

FIG. 4. Curve of T_c vs N. The fitted curve is $T_c = 0.037\,77N - 0.010\,02\int\rho^{2/3}d^3r + 0.000\,39\int\rho^{1/3}d^3r$. The correlation coefficient is 0.984.

and (43). The accuracy is remarkable, confirming the general validity of Eqs. (42) and (43) and a surprising accuracy for the local approximation.

B. More general cases

If one supposes that the functionals of $A_n[\rho]$ take form

$$A_n[\rho] = \int a_n(\mathbf{r},\rho(\mathbf{r}),\boldsymbol{\nabla}\rho(\mathbf{r}))d^3r. \tag{52}$$

Then the following identity holds (see Appendix):

$$A_n[\rho] + \frac{1}{3}\int d^3r\mathbf{r}\cdot\boldsymbol{\nabla}\rho(\mathbf{r})\,\frac{\delta A_n[\rho]}{\delta\rho(\mathbf{r})}$$

$$= \frac{1}{3}\int d^3r\left[\rho_j(\mathbf{r})\,\frac{\partial a_n}{\partial\rho_j(\mathbf{r})} - \mathbf{r}\cdot\,\frac{\partial a_n}{\partial\mathbf{r}}\right]. \tag{53}$$

Integrating Eq. (37) by parts, and using this identity, one thus obtains

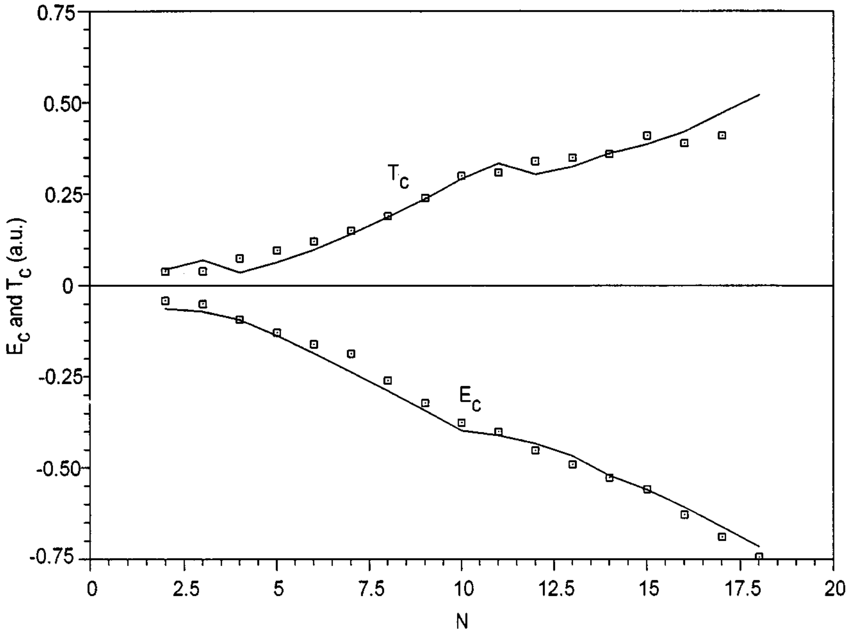

FIG. 5. Curves of E_c vs N and T_c vs N. The fitted curves are $E_c = -0.0532N + 0.0121\int\rho^{2/3}d^3r - 0.0003\int\rho^{1/3}d^3r - 0.0070$, $T_c = 0.0532N - 2\times0.0121\int\rho^{2/3}d^3r + 3\times0.0003\int\rho^{1/3}d^3r + 4\times0.0070$.

$$A_n[\rho]=\frac{3}{4-n}\int d^3r\rho(\mathbf{r})\,\frac{\delta A_n[\rho]}{\delta\rho(\mathbf{r})}+\frac{1}{4-n}\int d^3r\left[\rho_j(\mathbf{r})\,\frac{\partial a_n}{\partial\rho_j(\mathbf{r})}-\mathbf{r}\cdot\,\frac{\partial a_n}{\partial\mathbf{r}}\right]. \tag{54}$$

In the generalized-gradient-approximation framework, in which $A_n[\rho]$ is expressed as

$$A_n[\rho]=\int a_n(\rho(\mathbf{r}),\boldsymbol{\nabla}\rho(\mathbf{r}))d^3r, \tag{55}$$

Eq. (54) becomes

$$A_n[\rho]=\frac{3}{4-n}\int d^3r\rho(\mathbf{r})\,\frac{\delta A_n[\rho]}{\delta\rho(\mathbf{r})}+\frac{1}{4-n}\int d^3r\left[\rho_j(\mathbf{r})\,\frac{\partial a_n}{\partial\rho_j(\mathbf{r})}\right]. \tag{56}$$

In the weighted-density-approximation approach, $A_n[\rho]$ takes the form

$$A_n[\rho]=\int a_n(\mathbf{r},\rho(\mathbf{r}))d^3r. \tag{57}$$

Here, Eq. (54) becomes

$$A_n[\rho]=\frac{3}{4-n}\int d^3r\rho(\mathbf{r})\,\frac{\delta A_n[\rho]}{\delta\rho(\mathbf{r})}-\frac{1}{4-n}\int d^3r\left[\mathbf{r}\cdot\,\frac{\partial a_n}{\partial\mathbf{r}}\right]. \tag{58}$$

IV. CONCLUDING REMARKS

In summary, in this paper, we have examined the consequences of two exact relations, Eqs. (12) and (15), for the correlation energy density functional $E_c[\rho]$ and its kinetic component $T_c[\rho]$. Working from known identities and the assumption that $E_c^{\lambda}[\rho]$ can be expanded in a Taylor series in λ, we have arrived at the conclusion that $E_c[\rho]$ and $T_c[\rho]$ are expressible as combinations of homogeneous functionals of different degrees in coordinate scaling, starting from $0,-1,-2,\dots,(1-n),\dots$. Furthermore, we have shown that when E_c and T_c are local functionals, for atoms and molecules, they are linear combinations of homogeneous functionals of the density of degrees, 1, 2/3, 1/3, and 0. More specifically, E_c and T_c each has the form of $X_c[\rho]=aN+b\int\rho^{2/3}(\mathbf{r})d^3r+c\int\rho^{1/3}(\mathbf{r})d^3r+d$, where a, b, c, and d are constants. Numerical results show the effectiveness of such series of local functionals.

It may be noted that some of the ‘‘allowed’’ components in these various series could vanish identically, or could be very small. Thus from Eq. (7) and the results we have obtained, the potential component V_c of the correlation energy density functional can be expressed as a combination of homogeneous functionals. Morrison and Parr [13] recently suggested that the principal component of V_c is approximately a local homogeneous functional of degree one in the density, and the principal component of T_c is approximately a local homogeneous functional of degree zero in the density. These homogeneities accord with the results we here found in the present paper. A final interesting point is that terms $\langle\rho^{4/3}\rangle$ are missing from the expressions we have obtained for E_c and T_c. This is traceable to the presumption [4] that as λ approaches zero, E_c goes to zero.

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APPENDIX: SCALING, HOMOGENEITY, AND LOCALITY PROPERTIES OF DENSITY FUNCTIONALS

1. Scaling and homogeneity

The homogeneity property of a density functional is related to a scaling process. In density functional theory, there are two types of scalings that are met. One is the density scaling, and the other is the coordinate scaling.

(i) Density scaling. A functional is homogeneous of degree k in (or ‘‘with respect to’’) density scaling if the functional $Q[\rho]$ satisfies following condition:

$$Q[\zeta\rho]=\zeta^kQ[\rho]. \tag{A1}$$

Another definition of the homogeneity with respect to density scaling is

$$\int\,\rho(\mathbf{r})\,\frac{\delta Q[\rho]}{\delta\rho(\mathbf{r})}\,d^3r=kQ[\rho]. \tag{A2}$$

These two definitions are equivalent except when $k=0$. If $k=0$, Eq. (A1) implies Eq. (A2), but Eq. (A2) does not necessarily yield Eq. (A1). Instead, one then has

$$\frac{dQ[\zeta\rho]}{d\zeta}=0, \tag{A3}$$

which means that

$$Q[\zeta\rho]=X[\rho], \tag{A4}$$

where $X[\rho]$ is an arbitrary function or functional of ρ such that

$$\int\,\rho(\mathbf{r})\,\frac{\delta X[\rho]}{\delta\rho(\mathbf{r})}\,d^3r=0. \tag{A5}$$

This implies only that $\delta X/\delta\rho$ is orthogonal to ρ, so that $X[\rho]$ is not necessarily a constant. As an example, one may have

$$X[\rho]=\int\,\frac{|\boldsymbol{\nabla}\rho(\mathbf{r})|}{\rho(\mathbf{r})}\,d^3r. \tag{A6}$$

(ii) Coordinate scaling. Homogeneity of a functional $Q[\rho]$ of degree m in coordinate scaling is defined as

$$Q[\rho_\gamma]=\gamma^mQ[\rho], \tag{A7}$$

where

$$\rho_\gamma(\mathbf{r}) = \gamma^3 \rho(\gamma \mathbf{r}). \tag{A8}$$

It has been proved [14] that, for any well-behaved $Q[\rho]$ that obeys Eq. (A7),

$$-\int \rho(\mathbf{r})\mathbf{r}\cdot \boldsymbol{\nabla}\left(\frac{\delta Q[\rho]}{\delta\rho(\mathbf{r})}\right) d^3r = mQ[\rho]. \tag{A9}$$

Notice that equivalence of Eqs. (A7) and (A9) also requires $m\neq 0$. If $m=0$, it can be shown that Eq. (A7) implies Eq. (A9), but from Eq. (A9), one cannot derive Eq. (A7). Instead, one obtains

$$\frac{dQ[\rho_\gamma]}{d\gamma} = 0, \tag{A10}$$

which means that

$$Q[\rho_\gamma] = Y[\rho], \tag{A11}$$

where $Y[\rho]$ is an arbitrary functional such that

$$\int \rho(\mathbf{r})\mathbf{r}\cdot \boldsymbol{\nabla}\frac{\delta Y[\rho]}{\delta\rho(\mathbf{r})}\, d^3r = 0. \tag{A12}$$

$Y[\rho]$ is not necessarily a constant. For instance, one might have

$$Y[\rho] = \int \frac{|\boldsymbol{\nabla}\rho(\mathbf{r})|}{\rho^{4/3}(\mathbf{r})}\, d^3r. \tag{A13}$$

2. Locality

A energy density functional $Q[\rho]$ is local if it can be expressed in the form

$$Q[\rho] = \int q(\rho(\mathbf{r}))d^3r, \tag{A14}$$

where q is a function of the density $\rho(\mathbf{r})$. It has been shown [7,12] that for any well-behaved local functional $Q[\rho]$,

$$-\frac{1}{3}\int \mathbf{r}\cdot \boldsymbol{\nabla}\rho(\mathbf{r})\,\frac{\delta Q[\rho]}{\delta\rho(\mathbf{r})}\, d^3r = Q[\rho]. \tag{A15}$$

Note that "well-behavedness" requires ρ to vanish strongly at infinity [12].

3. Relationship between homogeneity and locality

Theorem 1. If $Q[\rho]$ is local, homogeneity in coordinate scaling is equivalent to homogeneity in density scaling.

Proof. Suppose $Q[\rho]$ is homogeneous of degree k in density scaling. From Eqs. (A2) and (A15), it follows that $Q[\rho]$ is homogeneous of degree $3k-3$ in coordinate scaling. Conversely, if one suppose that $Q[\rho]$ is homogeneous of degree m in coordinate scaling, then using Eqs. (A9) and (A15), it follows that $Q[\rho]$ is homogeneous of degree $(m+3)/3$ in density scaling. In general, in the locality assumption, homogeneities of degree k in density scaling and degree m in coordinate scaling are related by

$$3k = m + 3. \tag{A16}$$

Theorem 2. If $Q[\rho]$ is local and homogeneous with respect to coordinate scaling and density scaling, it has the form

$$Q[\rho] = C\int \rho^k(\mathbf{r})d^3r, \tag{A17}$$

where C is the constant to be determined. The homogeneity in density scaling is k; the homogeneity in coordinate scaling is $m=3k-3$.

Proof. If $k\neq 0$, we have both Eq. (A2) and Eq. (A14). Taking functional derivative of Eq. (A2) with respect to the density, and since $\delta Q[\rho]/\delta\rho = dq/d\rho$, one has

$$\rho\frac{d^2q}{d\rho^2} - (k-1)\,\frac{dq}{d\rho} = 0. \tag{A18}$$

The only solution of above equation for the well-behaved functional $Q[\rho]$ is Eq. (A17).

If $k=0$, however, according to Eq. (A16), $m=-3$. By using Eqs. (A9) and (A15), there results

$$\int \rho(\mathbf{r})\,\frac{\delta Q[\rho]}{\delta\rho(\mathbf{r})}\, d^3r = 0. \tag{A19}$$

Using the same procedure as above, one has $q(\rho(\mathbf{r}))=\text{const}$, which is a special case of $k=0$ in Eq. (A17).

Comments. Note that the equivalence of the two kinds of scaling does not in general hold if $Q[\rho]$ is not local. Notice also that it has been well known that in the local density approximation (LDA) the kinetic-energy density functional $T_s[\rho]$ and the exchange-only density functional $E_x[\rho]$ are homogenous of degree $\frac{5}{3}$ and $\frac{4}{3}$, respectively, with respect to density scaling. According to above theorem, the only forms of them are

$$T_s[\rho] = C_F\int \rho^{5/3}(\mathbf{r})d^3r \tag{A20}$$

and

$$E_x[\rho] = C_X\int \rho^{4/3}(\mathbf{r})d^3r, \tag{A21}$$

respectively, where C_F and C_X are constants to be determined.

4. Functional expansions

It has been shown recently [7] that a well-behaved functional can be expanded in terms of its functional derivatives up to a constant. If $Q[\rho]$ takes a form

$$Q[\rho] = \int q(\mathbf{r},\rho(\mathbf{r}),\boldsymbol{\nabla}\rho(\mathbf{r}))d^3r, \tag{A22}$$

where q is a function of $\mathbf{r}$, $\rho(\mathbf{r})$, and $\nabla\rho(\mathbf{r})$, then [7]

$$Q[\rho]+\frac{1}{3}\int d^3r\mathbf{r}\cdot\boldsymbol{\nabla}\rho(\mathbf{r})\,\frac{\delta Q[\rho]}{\delta\rho(\mathbf{r})}=\frac{1}{3}\int d^3r\left[\rho_j(\mathbf{r})\,\frac{\partial q}{\partial p_j(\mathbf{r})}-\mathbf{r}\cdot\,\frac{\partial q}{\partial\mathbf{r}}\right], \tag{A23}$$

where

$$\rho_j\equiv\frac{\partial\rho(\mathbf{r})}{\partial x_j}. \tag{A24}$$

Equation (A23) includes two important special cases. One is the gradient expansion approximation or the generalized gradient approximation, in which $Q[\rho]$ takes the form

$$Q[\rho]=\int q(\rho(\mathbf{r}),\boldsymbol{\nabla}\rho(\mathbf{r}))d^3r. \tag{A25}$$

Here Eq. (A23) becomes

$$Q[\rho]+\frac{1}{3}\int d^3r\mathbf{r}\cdot\boldsymbol{\nabla}\rho(\mathbf{r})\,\frac{\delta Q[\rho]}{\delta\rho(\mathbf{r})}=\frac{1}{3}\int d^3r\left[\rho_j(\mathbf{r})\,\frac{\partial q}{\partial\rho_j(\mathbf{r})}\right]. \tag{A26}$$

The other case is the so-called weighted-density approximation, in which $Q[\rho]$ has the form

$$Q[\rho]=\int q(\mathbf{r},\rho(\mathbf{r}))d^3r, \tag{A27}$$

where q is only a function of $\mathbf{r}$ and $\rho(\mathbf{r})$. Equation (A23) consequently becomes

$$Q[\rho]+\frac{1}{3}\int d^3r\mathbf{r}\cdot\boldsymbol{\nabla}\rho(\mathbf{r})\,\frac{\delta Q[\rho]}{\delta\rho(\mathbf{r})}=-\frac{1}{3}\int d^3r\left[\mathbf{r}\cdot\,\frac{\partial q}{\partial\mathbf{r}}\right]. \tag{A28}$$

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