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Padé approximants in density functional theory

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Abstract

Padé approximants are used to represent the total correlation functional $E_c^\lambda[\rho]$ and its kinetic-energy component $T_c^\lambda[\rho]$, where the parameter λ is the electron–electron interaction coupling constant within the adiabatic connection formalism. The exact relations between $E_c^\lambda[\rho]$ and $T_c^\lambda[\rho]$ are employed to generate the associated $T_c^\lambda[\rho]$ functional from its parent $E_c^\lambda[\rho]$ functional. Numerical results (with $\lambda = 1$) on the first 18 neutral atoms confirm the soundness of this procedure. It is proved that no local representations of these functionals can be exact for the nonuniform electron gas. However, it is still useful to design local functionals that are as accurate as possible.

1. Introduction

Based on density scaling, coordinate scaling, homogeneity, and locality properties of density functionals, several studies on the correlation-energy density functional $E_c[\rho]$ and its kinetic-energy component $T_c[\rho]$ have been recently undertaken [1] [1][2] [2] [3]. Within the adiabatic connection formalism (see, e.g. [5]), the correlation functional $E_c^\lambda[\rho]$ is commonly defined as [6]

$$E_c^\lambda[\rho] = (1/\lambda)T_c^\lambda[\rho] + V_c^\lambda[\rho], \tag{1}$$

whose kinetic-energy component $T_c^\lambda[\rho]$ and potential-energy component $V_c^\lambda[\rho]$ are

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

$$V_c^\lambda[\rho] = \langle\Psi^\lambda|\hat{V}_{ee}|\Psi^\lambda\rangle - \langle\Psi^{\lambda=0}|\hat{V}_{ee}|\Psi^{\lambda=0}\rangle. \tag{2}$$

Here, the antisymmetric N-electron wavefunction Ψ^λ generates an N-representable electron density $\rho(\boldsymbol{r})$ and minimizes the generalized Hohenberg–Kohn functional $\langle\Psi|\hat{T}+\lambda\hat{V}_{ee}|\Psi\rangle$ for a specific inter-electron interaction coupling constant λ (which must be set equal to 1 for real systems with a full Coulomb interaction).

It has been shown that if $E_c^\lambda[\rho]$ can be expanded as a full Taylor series in powers of λ, in the vicinity of $\lambda = 0$ [1,3,7,8],

$$E_c^\lambda[\rho] = \sum_{n=1}^{\infty} \frac{1}{n!} A_n[\rho]\lambda^n, \tag{3}$$

then, the $A_n[\rho]$ are homogeneous functionals of degree $(1-n)$ in coordinate scaling [1,9]

$$A_n[\rho_\gamma] = \gamma^{1-n} A_n[\rho], \tag{4}$$

[1] In this paper (according to the authors), the 4-term fitted results should be interpreted as assuming all species are in a large box of finite volume. The same for the 4-term results in Ref. [2]. For more discussion on this matter, see Ref. [3].

[2] In this paper, according to Ref. [4] the value of the parameter κ of Eq. (12) should be 2.8350, instead of 1.0910. Some of their results might be affected by this error.

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where the uniformly scaled density is defined as [6,10]

$$\rho_\gamma(\boldsymbol{r}) = \gamma^3 \rho(\gamma \boldsymbol{r}) . \tag{5}$$

The corresponding Taylor series expansion for $T_c^\lambda[\rho]$ is [1],

$$T_c^\lambda[\rho] = \sum_{n=1}^{\infty} \frac{-1}{(n-1)!} A_n[\rho] \lambda^{n+1} . \tag{6}$$

Under an assumption of locality, the $A_n[\rho]$ are homogeneous functionals of degree $(4-n)/3$ in density scaling [1],

$$\left\langle \rho(\boldsymbol{r}) \middle| \frac{\delta A_n[\rho]}{\delta \rho(\boldsymbol{r})} \right\rangle = \frac{4-n}{3} A_n[\rho] . \tag{7}$$

Consequently [1], $E_c^\lambda[\rho]$ and $T_c^\lambda[\rho]$ are combinations of local functionals homogeneous in $\rho(\boldsymbol{r})$ of degrees: $1, 2/3, 1/3, 0, -1/3, \cdots$,

$$E_c^\lambda[\rho] = \sum_{n=1}^{\infty} a_n \left\langle \rho(\boldsymbol{r})^{\frac{4-n}{3}} \right\rangle \lambda^n , \tag{8}$$

$$T_c^\lambda[\rho] = \sum_{n=1}^{\infty} (-n) a_n \left\langle \rho(\boldsymbol{r})^{\frac{4-n}{3}} \right\rangle \lambda^{n+1} , \tag{9}$$

where $\{a_n\}$ are undetermined expansion coefficients and $\langle \rho(\boldsymbol{r})^k \rangle$ are simple integrals of $\rho(\boldsymbol{r})^k$. Numerical results for atomic and molecular species based on the first three terms in the local Taylor series expansion are encouraging [1,2], albeit the Kohn–Sham (KS) correlation potential [11]

$$v_c(\boldsymbol{r}) = \frac{\delta E_c[\rho]}{\delta \rho(\boldsymbol{r})} \tag{10}$$

derived from Eq. (8) diverges asymptotically [3],

$$\lim_{r \to \infty} |v_c(\boldsymbol{r})| = \infty , \tag{11}$$

for $E_c[\rho]$ expansions of any finite length longer than 1.

In an effort to diffuse this divergence problem of the Taylor series expansion of $E_c^\lambda[\rho]$ in terms of local homogeneous functionals, Wang et al. [3] introduced general Laurent series expansions in powers of λ centered at $\lambda = 0$,

$$E_c^\lambda[\rho] = \sum_{-\infty}^{\infty} B_n[\rho] \lambda^n , \tag{12}$$

and

$$T_c^\lambda[\rho] = \sum_{-\infty}^{\infty} (-n) B_n[\rho] \lambda^{n+1} , \tag{13}$$

where the $B_n[\rho]$ possess the same scaling properties as the $A_n[\rho]$ displayed in Eqs. (4) and (7) under the same conditions [3]. If the $B_n[\rho]$ are local, the correct long-range behavior of $v_c(\boldsymbol{r})$ [12,13] requires a complete truncation of the positive terms (the Taylor-like series), and the final surviving Laurent series are combinations of local functionals homogeneous in $\rho(\boldsymbol{r})$ of degrees: $4/3, 5/3, 2, 7/3, \cdots$ [3],

$$E_c^\lambda[\rho] = \sum_{-\infty}^{0} B_n[\rho] \lambda^n = \sum_{n=0}^{\infty} C_n[\rho] \lambda^{-n} , \tag{14}$$

$$T_c^\lambda[\rho] = \sum_{-\infty}^{0} (-n) B_n[\rho] \lambda^{n+1} = \sum_{n=1}^{\infty} n C_n[\rho] \lambda^{1-n} , \tag{15}$$

where

$$C_n[\rho] = B_{-n}[\rho] = c_n \left\langle \rho(\boldsymbol{r})^{\frac{4+n}{3}} \right\rangle , \tag{16}$$

and $\{c_n\}$ are undetermined coefficients. With this new truncated Laurent series, the short-range and long-range properties of $v_c(\boldsymbol{r})$ appear to be better represented than by the Taylor series expansion in Eq. (8). Although there are no clear indications as to when such Laurent series are going to terminate and as to how fast they converge, numerical results (with only the first few terms of the truncated Laurent series) on the first-eighteen neutral atoms are quite satisfactory [3].

The Taylor series and the Laurent series are not free of other difficulties [1,3]. For example, the Taylor series expansion as shown in Eq. (8) does not satisfy the low-γ limit coordinate scaling conditions [10], such as

$$\lim_{\gamma \to 0} \gamma^{-1} E_c[\rho_\gamma] = \text{finite} , \tag{17}$$

while interestingly, the truncated Laurent series expansion as shown in Eq. (14) does not agree with the high-γ limit coordinate scaling properties [10], including

$$\lim_{\gamma \to \infty} E_c[\rho_\gamma] > -\infty . \tag{18}$$

The complementary scaling properties satisfied by the Taylor series, Eq. (8), and the truncated Laurent series, Eq. (14), argue for a general attractiveness of the full Laurent series expansions, Eqs. (12) and (13) [3]. However, this contradicts the necessity of completely deleting the Taylor-like component from the full Laurent series. In addition, the truncated Laurent series, Eqs. (14) and (15), cannot recover their defined null value at $\lambda = 0$ [12,13]: $E_c^{\lambda=0} = T_c^{\lambda=0} = 0$.

In order to reconcile the various inconsistencies mentioned above, Padé approximants [14] may be used to re-express all the series. In consequence, the Taylor series expansion and the truncated Laurent series expansion become the high-density limit and the low-density limit, respectively, of the functionals defined with Padé approximants. More importantly, the coordinate scaling properties of the low-γ limit and the high-γ limit [10] can be both satisfied, without either sacrificing the correct asymptotic behavior of $v_c(\boldsymbol{r})$ or missing the defined null value at $\lambda = 0$.

Table 1
Restrictions on the highest power of the numerator (K) and the highest power of the denominator (M) of the Padé approximants defined in Eq. (20).

Desired condition [a]	Restriction on {K,M}
$\lim_{\rho \to 0} E_c^\lambda[\rho] = 0$	any $\{K,M\}$
$\lim_{\rho \to 0} T_c^\lambda[\rho] = 0$	any $\{K,M\}$
$\lim_{\rho \to \infty} E_c^\lambda[\rho] = \text{finite}(<0)$	$K > M - 4$
$\lim_{\rho \to \infty} T_c^\lambda[\rho] = \text{finite}(>0)$	$K > M - 4$
$\lim_{\rho \to 0} v_c^\lambda(\boldsymbol{r}) = 0$	any $\{K,M\}$
$\lim_{\rho \to \infty} v_c^\lambda(\boldsymbol{r}) = \text{cons.}$	$K = M - 1$
$E_c^{\lambda=0}[\rho] = 0$	$K < M$
$T_c^{\lambda=0}[\rho] = 0$	$K < M + 1$
$\lim_{\gamma \to \infty} E_c^\lambda[\rho_\gamma] = \text{cons.}$	$K = M - 1$
overall	$K = M - 1$

[a] See for example, Refs. [10], [12] and [13].

2. Theoretical formulation

For the sake of later use, one defines two new variables

$$\beta(\boldsymbol{r}) = \rho(\boldsymbol{r})^{1/3}, \quad x = \beta(\boldsymbol{r})/\lambda, \tag{19}$$

and Padé approximants [14]

$$P_M^K = [K,M] = \frac{1 + b_1 x + b_2 x^2 + \cdots + b_K x^K}{1 + c_1 x + c_2 x^2 + \cdots + c_M x^M} = \frac{\sum_{k=0}^{K} b_k x^k}{\sum_{m=0}^{M} c_m x^m}. \tag{20}$$

Here, $\{b_1, \cdots, b_K, c_1, \cdots, c_M\}$ are coefficients yet to be determined, and both of the denominator and the numerator are polynomials of ascending power series. Then, a straightforward but laborious derivation [15] reveals that correlation-energy density functionals $E_c^\lambda[\rho]$ from the general Padé approximants P_M^K,

$$E_c^\lambda[\rho] = -a\langle \beta^4 P_M^K \rangle, \tag{21}$$

where $\{a\}$ is a positive coefficient, are legitimate solutions of the exact integro-differential relation for $E_c^\lambda[\rho]$ [6]

$$E_c^\lambda[\rho] = \lambda \frac{\mathrm{d}E_c^\lambda[\rho]}{\mathrm{d}\lambda} - \left\langle \rho(\boldsymbol{r}) |(\boldsymbol{r} \cdot \boldsymbol{\nabla}) \frac{\delta E_c^\lambda[\rho]}{\delta \rho(\boldsymbol{r})} \right\rangle, \tag{22}$$

within a locality assumption. However, according to further analysis, K has to be $(M-1)$ in order to meet all the preconditions displayed in Table 1.

With a little more manipulation, one can readily show that the defined representation,

$$E_c^\lambda[\rho] = -a\langle \beta^4 P_M^{M-1} \rangle, \tag{23}$$

does indeed reproduce the Taylor series, Eq. (8), at the high-density limit, and the truncated Laurent series, Eq. (14), at the low-density limit. Except for the case of $M = 1$, Eq. (23) yields the full Laurent series, Eq. (12), for intermediate density.

A direct utilization of the exact relation between $E_c^\lambda[\rho]$ and $T_c^\lambda[\rho]$ [1,16],

$$T_c^\lambda[\rho] = -\lambda^2 \frac{\mathrm{d}E_c^\lambda[\rho]}{\mathrm{d}\lambda} = \frac{\mathrm{d}E_c^\lambda[\rho]}{\mathrm{d}(1/\lambda)}, \tag{24}$$

yields a corresponding equation for $T_c^\lambda[\rho]$:

$$T_c^\lambda[\rho] = a\left\langle \beta^5 \left[\left(\sum_{k=0}^{M-1} \sum_{m=1}^{M} m b_k c_m x^{k+m-1} \right) - \left(\sum_{k=1}^{M-1} \sum_{m=0}^{M} k b_k c_m x^{k+m-1} \right) \right] \times \left[\left(\sum_{m=0}^{M} c_m x^m \right)^2 \right]^{-1} \right\rangle, \quad (25)$$

which stems from the Padé approximant $P_{2M}^{2(M-1)}$. The same result can also be achieved by using the coordinate scaling relation

$$T_c^\lambda[\rho] = -\lambda E_c^\lambda[\rho] + \lambda \left(\frac{\partial E_c^\lambda[\rho_\gamma]}{\partial \gamma} \right)_{\gamma=1}, \quad (26)$$

which is the generalized version (for arbitrary positive λ values) of the original Levy–Perdew equation (with $\lambda = 1$) [6].

3. Results and discussion

The effectiveness of the local functionals with Padé approximants may be tested with $M = 1$ and 2. The simplest functionals of the form shown in Eqs. (23) and (25) are the Wigner-type correlation functional [17–20] [3] and its associated kinetic-energy correlation functional:

$$E_c^\lambda[\rho]_{\mathrm{Wigner}} = E_c^\lambda[\rho]_{[0,1]} = -a\left\langle \beta^4 \frac{1}{1+bx} \right\rangle, \quad (27)$$

$$T_c^\lambda[\rho]_{\mathrm{Wigner}} = T_c^\lambda[\rho]_{[0,1]} = ab\left\langle \beta^5 \frac{1}{(1+bx)^2} \right\rangle. \quad (28)$$

Increasing M by 1, one obtains the general P_2^1 representations:

$$E_c^\lambda[\rho]_{[1,2]} = -a\left\langle \beta^4 \frac{1+dx}{1+bx+cx^2} \right\rangle, \quad (29)$$

$$T_c^\lambda[\rho]_{[1,2]} = a\left\langle \beta^5 \frac{(b-d)+2cx+cdx^2}{(1+bx+cx^2)^2} \right\rangle. \quad (30)$$

Here, $\{a, b, c, d\}$ are undetermined coefficients. If the integrands and $-v_c(\mathbf{r})$ are assumed to be everywhere positive and continuous, it is necessary for all the coefficients and $(b-d)$ to be positive.

For the sake of comparison, the Taylor series expansions, Eqs. (8) and (9), with the first three terms [1,2]

$$E_c[\rho]_{\mathrm{Taylor}} \cong \sum_{n=1}^{3} A_n[\rho] = a\langle \beta^3 \rangle + b\langle \beta^2 \rangle + c\langle \beta \rangle, \quad (31)$$

$$T_c[\rho]_{\mathrm{Taylor}} \cong \sum_{n=1}^{3} (-n) A_n[\rho] = -a\langle \beta^3 \rangle - 2b\langle \beta^2 \rangle - 3c\langle \beta \rangle, \quad (32)$$

have been reparameterized, and the truncated Laurent series expansions, Eqs. (14) and (15) [3], with the first five terms

$$E_c[\rho]_{\mathrm{Laurent}} \cong \sum_{n=0}^{4} C_n[\rho] = a\langle \beta^4 \rangle + b\langle \beta^5 \rangle + c\langle \beta^6 \rangle + d\langle \beta^7 \rangle + e\langle \beta^8 \rangle, \quad (33)$$

$$T_c[\rho]_{\mathrm{Laurent}} \cong \sum_{n=0}^{4} n C_n[\rho] = b\langle \beta^5 \rangle + 2c\langle \beta^6 \rangle + 3d\langle \beta^7 \rangle + 4e\langle \beta^8 \rangle, \quad (34)$$

are presented. Here, $\{a, b, c, d, e\}$ are undetermined coefficients.

Least-square fitting is employed to determine the coefficients. The data for the conventional E_c of the first eighteen atoms were taken from the latest ab initio calculation by Chakravorty and Davidson [22]; for the Density Functional Theory (DFT) E_c, from a recent optimized-effective-potential (OEP) calculation by Grabo and Gross [23]; and for T_c, from Morrison and Zhao [24]. Due to its peculiar value, the T_c value for Ar was excluded from the T_c data set used in the fitting. These data are enumerated in

[3] The conventional E_c values of eight closed shell atomic systems (He, Li^+, Be^{2+}, Be, B^+, Ne, Mg, and Ar) are from Ref. [21].

Table 2
Least-square-fitted coefficients [a,b]

$(\text{Scheme})_{\text{Type}}$	a	b	c	d	e
$(E_c^{\text{con}})_{\text{Taylor}}$	-0.5966×10^{-1}	0.1781×10^{-1}	-0.5722×10^{-3}		
$(E_c^{\text{DFT}})_{\text{Taylor}}$	-0.6105×10^{-1}	0.1837×10^{-1}	-0.6123×10^{-3}		
$(E_c+T_c)_{\text{Taylor}}$	-0.5210×10^{-1}	0.1106×10^{-1}	-0.3181×10^{-3}		
$(E_c^{\text{con}})_{\text{Laurent}}$	-0.4433×10^{-1}	0.1942×10^{-1}	-0.6094×10^{-2}	0.8179×10^{-3}	-0.3531×10^{-4}
$(E_c^{\text{DFT}})_{\text{Laurent}}$	-0.3615×10^{-1}	0.7976×10^{-2}	-0.2129×10^{-2}	0.3295×10^{-3}	-0.1591×10^{-4}
$(E_c+T_c)_{\text{Laurent}}$	-0.6398×10^{-1}	0.2348×10^{-1}	-0.3018×10^{-2}	0.1507×10^{-3}	-0.2720×10^{-5}
$(E_c^{\text{con}})_{\text{Wigner}}$	0.5406×10^{-1}	0.6200			
$(E_c^{\text{DFT}})_{\text{Wigner}}$	0.4762×10^{-1}	0.4580			
$(E_c+T_c)_{\text{Wigner}}$	0.1010	1.6559			
$(E_c^{\text{con}})_{[1,2]}$	0.6228×10^{-1}	1.2944	0.2047	0.3342	
$(E_c^{\text{DFT}})_{[1,2]}$	0.4717×10^{-1}	0.6041	0.7636×10^{-1}	0.1638	
$(E_c+T_c)_{[1,2]}$	0.1659	3.9971	0.3224×10^{-3}	0.8854×10^{-1}	

[a] All values in atomic units. $E-n$ indicates a number to be multiplied by 10^{-n}.
[b] See text for functional forms in terms of the parameters $\{a, b, c, d, e\}$.

Tables 4–6. Densities were taken as the accurate RHF results of Clementi and Roetti [4].

Three types of least-square fitting have been performed for these two data sets. The E_c^{con} and E_c^{DFT} schemes fit all the above $E_c[\rho]$ formulas to the conventional E_c data set and the DFT E_c data set, respectively; and the (E_c+T_c) scheme simultaneously fits these $E_c[\rho]$ and $T_c[\rho]$ formulas to the DFT E_c data set and the T_c data set. Results are collected in Tables 2–6: Table 2 displays the fitted coefficients, Table 3 compares the various parametrizations of the $E_c[\rho]_{\text{Wigner}}$ functional [17–20] and Tables 4–6 exhibit the fitted E_c and T_c values. Table 2 shows that with some minor deviations in the expansion coefficients, the reparameterized 3-term Taylor series expansions are essentially the same as before [1,2]. Figs. 1 and 2 depict the results from the functionals with the Padé approximant P_2^1.

The first impression on viewing Tables 4 and 5 is the closeness of the DFT E_c data and the conventional E_c data, whose differences are less than 0.023 E_h, despite the distinction in their definitions. Consequently, the fitted E_c^{con} and E_c^{DFT} data are also quite similar. However, a close scrutiny of the mean absolute deviations reveals that the E_c^{DFT} scheme performs much better than the E_c^{con} scheme, except for the case with the Taylor series expansion. This is more likely due to the inner coherence between the definition of the DFT E_c and its data [23], although the conventional E_c data by Chakravorty and Davidson are much more reliable [22] and numerically

Table 3
Different parametrizations of the Wigner-type E_c functional [a,b]

Parameter	Wigner [c]	McWeeny [d]	Brual–Rothstein [e]	Süle–Nagy [g]	$(E_c^{\text{DFT}})_{\text{Wigner}}$	$(E_c^{\text{con}})_{\text{Wigner}}$
a	0.7093	0.3394	0.04665	0.04398	0.04762	0.05406
b	12.5735	3.2763	0.4576	0.3527	0.4580	0.6200

[a] All values in atomic units.
[b] All the different formulas are brought into the same form as Eq. (27), in terms of the parameters $\{a, b\}$.
[c] From Ref. [17].
[d] From Ref. [18].
[e] From Ref. [19].
[g] From Ref. [20].

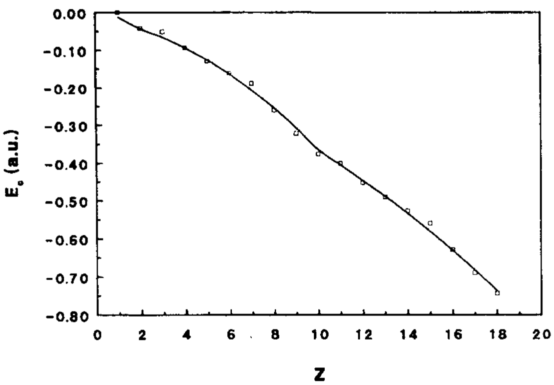

Fig. 1. Least-square-fitted $(E_c^{DFT})_{[1,2]}$ results (solid line) for the DFT E_c data set (□) for the first two-row neutral atoms.

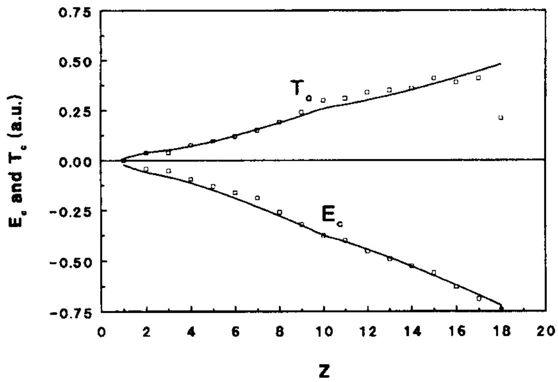

Fig. 2. Least-square-fitted $(E_c+T_c)_{[1,2]}$ results (solid line) for the DFT E_c and T_c data sets (□) for the first two-row neutral atoms.

close to the former ones. Therefore, the results of the (E_c+T_c) scheme will be reported here only for the DFT E_c data set.

Also from Tables 4–6, one sees that the Taylor series expansions, Eqs. (31) and (32), and the truncated Laurent series expansions, Eqs. (33) and (34), are the poorest and the best, respectively, among the four types of local functionals discussed heretofore. Even worse, the Taylor series expansions do not predict a smoothly increasing trend in the T_c values as Z becomes larger [1]. For example, the trend of the T_c values from Li to B, and from Na to Al is unreasonable. Additionally, the negative T_c value for H is not acceptable. As was found previously [3], the truncated Laurent series expansion Eq. (34) is an especially good approximation for the $T_c[\rho]$ functional, with a mean absolute deviation of only 0.0087 E_h.

Table 4
Fitted E_c values (via the E_c^{con} scheme) compared with previous published con-E_c data [a,b,c]

Atom	Z	con-E_c	$(E_c^{con})_{Taylor}$	$(E_c^{con})_{Laurent}$	$(E_c^{con})_{Wigner}$	$(E_c^{con})_{[1,2]}$
H	1	0.0000	−0.0047	−0.0110	−0.0129	−0.0137
He	2	−0.0420	−0.0490	−0.0398	−0.0449	−0.0459
Li	3	−0.0453	−0.0593	−0.0616	−0.0677	−0.0683
Be	4	−0.0944	−0.0711	−0.0885	−0.0950	−0.0958
B	5	−0.1248	−0.1118	−0.1213	−0.1268	−0.1280
C	6	−0.1564	−0.1623	−0.1612	−0.1645	−0.1660
N	7	−0.1883	−0.2183	−0.2074	−0.2076	−0.2090
O	8	−0.2580	−0.2760	−0.2573	−0.2541	−0.2552
F	9	−0.3248	−0.3349	−0.3110	−0.3051	−0.3055
Ne	10	−0.3912	−0.3951	−0.3674	−0.3603	−0.3596
Na	11	−0.3965	−0.4143	−0.4054	−0.3975	−0.3962
Mg	12	−0.4394	−0.4252	−0.4424	−0.4370	−0.4356
Al	13	−0.4706	−0.4574	−0.4766	−0.4767	−0.4754
Si	14	−0.5057	−0.4999	−0.5120	−0.5192	−0.5183
P	15	−0.5409	−0.5509	−0.5508	−0.5644	−0.5641
S	16	−0.6062	−0.6011	−0.5962	−0.6111	−0.6113
Cl	17	−0.6683	−0.6600	−0.6549	−0.6605	−0.6612
Ar	18	−0.7261	−0.7194	−0.7351	−0.7125	−0.7135
δ			0.0117	0.0093	0.0108	0.0110

[a] All values in E_h.
[b] Con-E_c data from Ref. [22].
[c] δ denotes the mean absolute deviation from corresponding literature values.

Table 5
Fitted E_c values (via the E_c^{DFT} scheme) compared with previous published DFT-E_c data [a,b,c]

Atom	Z	DFT-E_c	$(E_c^{DFT})_{Taylor}$	$(E_c^{DFT})_{Laurent}$	$(E_c^{DFT})_{Wigner}$	$(E_c^{DFT})_{[1,2]}$
H	1	0.0000	−0.0056	−0.0097	−0.0119	−0.0118
He	2	−0.0416	−0.0502	−0.0376	−0.0429	−0.0428
Li	3	−0.0509	−0.0648	−0.0610	−0.0661	−0.0660
Be	4	−0.0934	−0.0748	−0.0896	−0.0935	−0.0935
B	5	−0.1289	−0.1157	−0.1229	−0.1254	−0.1254
C	6	−0.1608	−0.1666	−0.1623	−0.1633	−0.1633
N	7	−0.1879	−0.2235	−0.2074	−0.2069	−0.2069
O	8	−0.2605	−0.2823	−0.2563	−0.2543	−0.2543
F	9	−0.3218	−0.3424	−0.3099	−0.3068	−0.3068
Ne	10	−0.3757	−0.4038	−0.3677	−0.3640	−0.3641
Na	11	−0.4005	−0.4278	−0.4089	−0.4042	−0.4043
Mg	12	−0.4523	−0.4374	−0.4497	−0.4463	−0.4465
Al	13	−0.4905	−0.4704	−0.4888	−0.4885	−0.4886
Si	14	−0.5265	−0.5129	−0.5294	−0.5334	−0.5335
P	15	−0.5594	−0.5643	−0.5731	−0.5810	−0.5811
S	16	−0.6287	−0.6152	−0.6214	−0.6302	−0.6302
Cl	17	−0.6890	−0.6752	−0.6787	−0.6821	−0.6820
Ar	18	−0.7435	−0.7356	−0.7496	−0.7367	−0.7365
δ			0.0160	0.0073	0.0079	0.0079

[a] All values in E_h.
[b] DFT-E_c data from Ref. [23].
[c] δ denotes the mean absolute deviation from corresponding literature values.

Table 6
Fitted E_c and T_c values (via the $(E_c + T_c)$ scheme) compared with previous published DFT-E_c and T_c data[a,b,c]

Atom	Z	DFT-E_c	T_c	$(E_c)_{Taylor}$	$(T_c)_{Taylor}$	$(E_c)_{Laurent}$	$(T_c)_{Laurent}$	$(E_c)_{Wigner}$	$(T_c)_{Wigner}$	$(E_c)_{[1,2]}$	$(T_c)_{[1,2]}$
H	1	0.0000	0.000	−0.0158	−0.0021	−0.0162	0.0021	−0.0188	0.0064	−0.0215	0.0110
He	2	−0.0416	0.037	−0.0593	0.0247	−0.0578	0.0166	−0.0568	0.0287	−0.0582	0.0371
Li	3	−0.0509	0.038	−0.0736	0.0637	−0.0857	0.0377	−0.0803	0.0448	−0.0814	0.0517
Be	4	−0.0934	0.074	−0.0986	0.0388	−0.1159	0.0640	−0.1104	0.0625	−0.1129	0.0707
B	5	−0.1289	0.095	−0.1400	0.0602	−0.1491	0.0929	−0.1459	0.0838	−0.1492	0.0944
C	6	−0.1608	0.12	−0.1875	0.0935	−0.1880	0.1242	−0.1871	0.1101	−0.1897	0.1226
N	7	−0.1879	0.15	−0.2382	0.1358	−0.2325	0.1580	−0.2326	0.1413	−0.2333	0.1541
O	8	−0.2605	0.19	−0.2893	0.1835	−0.2802	0.1932	−0.2798	0.1756	−0.2782	0.1869
F	9	−0.3218	0.24	−0.3414	0.2324	−0.3329	0.2315	−0.3299	0.2138	−0.3253	0.2216
Ne	10	−0.3757	0.30	−0.3941	0.2830	−0.3896	0.2734	−0.3822	0.2553	−0.3744	0.2579
Na	11	−0.4005	0.31	−0.4132	0.3366	−0.4218	0.3048	−0.4138	0.2831	−0.4063	0.2781
Mg	12	−0.4523	0.34	−0.4368	0.3163	−0.4560	0.3313	−0.4499	0.3110	−0.4445	0.3012
Al	13	−0.4905	0.35	−0.4716	0.3363	−0.4901	0.3529	−0.4868	0.3387	−0.4839	0.3251
Si	14	−0.5265	0.36	−0.5144	0.3584	−0.5282	0.3704	−0.5275	0.3682	−0.5273	0.3522
P	15	−0.5594	0.41	−0.5623	0.3920	−0.5705	0.3845	−0.5714	0.4000	−0.5734	0.3818
S	16	−0.6287	0.39	−0.6093	0.4272	−0.6157	0.3956	−0.6166	0.4332	−0.6206	0.4126
Cl	17	−0.6890	0.41	−0.6615	0.4753	−0.6656	0.4049	−0.6641	0.4688	−0.6697	0.4452
Ar	18	−0.7435	0.21	−0.7139	0.5233	−0.7201	0.4133	−0.7137	0.5067	−0.7205	0.4794
δ				0.0197	0.0216	0.0180	0.0087	0.0167	0.0197	0.0162	0.0170

[a] All values in E_h.
[b] DFT-E_c data and T_c data from Refs. [23] and [24], respectively. The previous published T_c value of Ar has been excluded from the data set due to its abnormal value.
[c] δ denotes the mean absolute deviation from corresponding literature values.

It should also be noted that contrary to the results of an earlier study [2], the present Wigner-type functionals perform better than the Taylor series expansions, for both of the E_c^{con} and E_c^{DFT} schemes. This situation is probably due to the difference in the fitted parameters [2,20]. An inspection on Table 3 verifies that the present parametrizations of the Wigner-type functional, especially from the E_c^{DFT} scheme, are most compatible with the work of Brual and Rothstein [19], which is the best [25] among all the existing ones [17–20].

If one ignores the results from the Taylor series expansion, Table 5 and Fig. 1 show that the E_c scheme faithfully reproduces the DFT-E_c data with a mean absolute deviation of less than 0.0080 E_h for the remaining three types of functionals, although for several atoms (e.g., Li, N, and P), better theoretical understanding is needed. Compared to the $E_c[\rho]_{Laurent}$, both the $E_c[\rho]_{Wigner}$ and the $E_c[\rho]_{[1,2]}$ perform comfortably well, with somewhat better results from the latter formula. There will not be much benefit if the Padé approximants with larger M values are used to represent $E_c[\rho]$.

However, as illustrated in Table 6 and Fig. 2, the quality of fitting (especially the E_c values for the first-row atoms) deteriorates once the T_c data set is included. In addition, as shown in Table 2, when going from the E_c scheme to the $(E_c + T_c)$ scheme, the fitted coefficients exhibit large changes. This is probably due to the fact that the T_c data set is only reliable with two significant figures and is less reliable for heavier atoms (see the fitted T_c results in Fig. 2) which dominate the globe minimum searching process [3]. Further studies toward improving the literature E_c and T_c data sets are needed.

4. Properties of local functionals

Table 1 also shows that the $v_c(\boldsymbol{r})$ originating from Eq. (23) will vanish asymptotically,

$$\lim_{r \to \infty} v_c(\boldsymbol{r}) = 0, \tag{35}$$

and $E_c^\lambda[\rho]$ and $T_c^\lambda[\rho]$ recover their defined value at $\lambda = 0$. In opposite to an earlier claim [25], besides holding [25,26] most of the uniform coordinate scaling properties [10], the $E_c^\lambda[\rho]$ defined in Eq. (23) indeed satisfies few nonuniform coordinate scaling conditions [27–29], including

$$\lim_{\alpha \to 0} E_c[\rho_\alpha^x] = 0. \tag{36}$$

Here the nonuniformly scaled density is defined as

$$\rho_\alpha^x(\boldsymbol{r}) = \alpha\rho(\alpha x, y, z). \tag{37}$$

Another important conclusion can be drawn from Table 1: $v_c(\boldsymbol{r})$ will become a constant at high-density limit (the same for different systems). This is satisfied by neither the Taylor series expansion nor the Laurent series expansion. Moreover, the fact that $v_c(\boldsymbol{r})$ derived from Eq. (31) or 33 is not single-signed may cause trouble if one tries to plug it into the KS effective potential [11] and to solve the KS equation [11] self-consistently. In contrast, the functionals with Padé approximants will not suffer from this problem as long as all the coefficients, as listed in Table 2, are *positive*.

More interestingly, it can be easily shown [14] that the truncated Laurent series expansions, Eqs. (14) and (15), and the Taylor series expansions, Eqs. (8) and (9), are actual functional expansions [20] (in terms of homogeneous functionals $\langle \beta^4 x^n \rangle$ and $\langle \beta^4 x^{-n} \rangle$, respectively) of the local functionals, Eqs. (23) and (25), with the Padé approximants. The above-stated arguments imply strongly that *a combination of finite terms of such a homogeneous functional expansion will lose many merits* (e.g., the coordinate scaling properties) of the original inhomogeneous functional. For instance, Eqs. (14) and (15) become singular at $\lambda = 0$ [3].

On the other hand, the good performance of these local functionals with Padé approximants should not make one over-optimistic about their correctness. Not long ago, Levy and Ou-Yang [27,28] showed that the local-density approximation to the $E_c[\rho]$ functional is independent of the direction of the nonuniform coordinate scaling in Eq. (37), while the exact $E_c[\rho]$ functional *might* not be so in general. However, as shown in Eq. (36), this statement does *not* preclude local functionals satisfying some of the nonuniform coordinate scaling conditions [29]. The following general theorem may help settle this issue.

Theorem: For the nonuniform electron gas, the exact $E_c[\rho]$ functional cannot be a local functional nor a product [30] of local functionals, if the local functional is defined as $\langle f(\rho)\rangle$, where $f(\rho)$ is a suitable function of $\rho(\boldsymbol{r})$, without any explicit dependence on $\boldsymbol{r}$ and the gradients (of any order) of $\rho(\boldsymbol{r})$.

Proof: With the nonuniformly scaled density is defined as [29]

$$\rho_{\alpha\xi}^{xy}(\boldsymbol{r}) = \alpha\xi\rho(\alpha x,\xi y,z), \tag{38}$$

one has the identity for the local functional

$$\langle f(\rho_{\alpha\xi}^{xy})\rangle = \left\langle \frac{f(\alpha\xi\rho)}{\alpha\xi} \right\rangle. \tag{39}$$

On setting ξ to $1/\alpha$, one then has an invariant

$$\langle f(\rho_{\alpha 1/\alpha}^{xy})\rangle = \langle f(\rho)\rangle, \tag{40}$$

for the local functional. Thus, the exact nonuniform coordinate scaling conditions [29]

$$\begin{aligned} \lim_{\alpha\to 0} E_c\left[\rho_{\alpha 1/\alpha}^{xy}\right] &= \lim_{\alpha\to 0} \frac{E_c\left[\rho_{\alpha 1/\alpha}^{xy}\right]}{\alpha} \\ &= \lim_{\alpha\to\infty} E_c\left[\rho_{\alpha 1/\alpha}^{xy}\right] \\ &= \lim_{\alpha\to\infty} \alpha E_c\left[\rho_{\alpha 1/\alpha}^{xy}\right] = 0 \end{aligned} \tag{41}$$

will never be satisfied by such a local functional with the invariance property. Similar conclusions hold for the product of local functionals [30]. Therefore, local functionals and the products of local functionals cannot be exact [QED]. One can further show that any functional (including product) of the basic form $\langle f(\rho,\ \boldsymbol{r}\cdot\boldsymbol{\nabla}\rho)\rangle$ cannot be the correct $E_c[\rho]$ functional either. Here, the function $f(\rho,\ \boldsymbol{r}\cdot\boldsymbol{\nabla}\rho)$ does not contain higher-order gradients of $\rho(\boldsymbol{r})$.

Of course, the exactness of the local-density approximation for the uniform electron gas is well known [12,13]. The high- and low-density limits for this system [31] cannot be correctly described by Eqs. (21) and (23), and the exact E_c and T_c data of the uniform electron gas were also extracted from local and gradient-corrected density functionals [32].

Nonetheless, one should not be too pessimistic about the performance of the local functionals. Even though local functionals can never be exact for the nonuniform electron gas, they can be designed to be quite accurate as shown by this work and previous works [1–3,30,33–35]. There is a good feeling about the simplicity of the functional forms proposed in this work, and they can serve as the seeds to generate more accurate and rational nonlocal functionals [25,26,34,36]. Based upon past experience [2,35], it is reasonable to hope that such functionals will yield satisfactory results in molecular applications.

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Erratum

Padé approximants in density functional theory (Chem. Phys. Letters 268 (1997) 76) [1]

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The following corrections to the above-mentioned article have to be made:

(1) On page 76, in footnote 2, "Ref. [4]" should read "Ref. [20]".

(2) On page 79, footnote 3 is only directed to Ref. [20], not for Refs. [17–20] as published.

(3) On page 80, in footnote a of Table 2, "$E-n$ indicates a number to be multiplied by 10^{-n}" should be eliminated, since the numbers are already in this format in the final publication.

(4) On page 83, in the 6th line after Eq. (37), "Eq. (31) or 33" should read "Eq. (31) or (33)".

(5) On page 83, in the 16th line after Eq. (37), "[20]" should be "[30]".

(6) Some references can be updated:

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