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# Laurent series expansions in density functional theory

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**Abstract**

It is shown that various energy functionals in density functional theory, including the total correlation functional $E_c[\rho]$, its kinetic-energy component $T_c[\rho]$, and its electron–electron repulsion component $V_c[\rho]$, can be expanded to good accuracy in Laurent series in terms of a common set of homogeneous functionals of different specific degrees in coordinate scaling: $\ldots, (1+n), \ldots, 2, 1, 0, -1, -2, \ldots, (1-n), \ldots$. From the asymptotic behavior of the Kohn–Sham effective potential, it is further argued that the local approximation to such Laurent series requires a complete truncation of the Taylor-like component of the Laurent series, and the remaining series are combinations of functionals $\langle \rho^k \rangle$ homogeneous in $\rho$ of degrees $k = 4/3, 5/3, 2, 7/3, \ldots, (4+n)/3, \ldots$. Numerical results on atoms confirm the soundness of this theory. Several exact integro-differential relations are derived within the adiabatic connection formulation.

## 1. Introduction

As shown by Lieb and Levy [1,2], the Hohenberg–Kohn universal functional $F_\lambda[\rho]$, defined within an extended domain via the constrained-search formulation [2,3],

$$F_\lambda[\rho] = \langle \Psi^\lambda | \hat{T} + \lambda \hat{V}_{ee} | \Psi^\lambda \rangle , \tag{1}$$

always has a minimum for an antisymmetric N-electron wavefunction $\Psi^\lambda$, which generates an $N$- and $v$-representable electron density $\rho(r)$, with a specific electron–electron interaction coupling constant $\lambda$. It was later revealed [4–6] that $\Psi^\lambda$ is an eigenstate of the coupled Hamiltonian

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

where $\hat{T}$, $\hat{V}_{ee}$, and $\hat{V}_{ext}^\lambda$ are the kinetic-energy, the electron–electron repulsion, and the external potential operators, respectively. In the spirit of the Kohn–Sham (KS) theory [7], $F_\lambda[\rho]$ is partitioned into three main pieces:

$$F_\lambda[\rho] = T_s[\rho] + \lambda J[\rho] + \lambda E_{xc}^\lambda[\rho] , \tag{3}$$

where $T_s[\rho]$ is the noninteracting ($\lambda = 0$) kinetic-energy functional, $J[\rho]$ is the classical electron–electron Coulomb repulsion functional, and $E_{xc}^\lambda[\rho]$ is the exact exchange–correlation functional. $E_{xc}^\lambda[\rho]$ in turn can be decomposed into two components [8]:

$$E_{xc}^\lambda[\rho] = E_x[\rho] + E_c^\lambda[\rho] ; \tag{4}$$

namely, the $\lambda$-independent exchange functional $E_x[\rho]$,

$$E_x[\rho] = \langle \Psi^{\lambda=0} | \hat{V}_{ee} | \Psi^{\lambda=0} \rangle - J[\rho]$$
$$= V_{ee}^0[\rho] - J[\rho] , \tag{5}$$


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and the $\lambda$-dependent correlation functional $E_c^\lambda[\rho]$,

$$E_c^\lambda[\rho] = (1/\lambda)T_c^\lambda[\rho] + V_c^\lambda[\rho], \tag{6}$$

where

$$T_c^\lambda[\rho] = \langle\Psi^\lambda|\hat{T}|\Psi^\lambda\rangle - \langle\Psi^{\lambda=0}|\hat{T}|\Psi^{\lambda=0}\rangle = T^\lambda[\rho] - T_s[\rho], \tag{7}$$

and

$$V_c^\lambda[\rho] = \langle\Psi^\lambda|\hat{V}_{ee}|\Psi^\lambda\rangle - \langle\Psi^{\lambda=0}|\hat{V}_{ee}|\Psi^{\lambda=0}\rangle = V_{ee}^\lambda[\rho] - V_{ee}^0[\rho]. \tag{8}$$

In a discussion of the virial theorem, Levy and Perdew [8] found three integro-differential relations for $E_x[\rho]$, $E_c^\lambda[\rho]$ and $T_c^\lambda[\rho]$:

$$\hat{S}_c E_x[\rho] = E_x[\rho], \tag{9}$$

$$-\lambda E_c^\lambda[\rho] + \lambda\hat{S}_c E_c^\lambda[\rho] = T_c^\lambda[\rho], \tag{10}$$

and

$$\hat{S}_c E_c^\lambda[\rho] = E_c^\lambda[\rho] - \lambda\frac{dE_c^\lambda[\rho]}{d\lambda}. \tag{11}$$

Here,

$$\hat{S}_c = -\int d\tau\,\rho(r)(r\cdot\nabla)\frac{\delta}{\delta\rho(r)}, \tag{12}$$

is the *functional coordinate-scaling operator*, which delivers the degree of the homogeneity in coordinate scaling of a well-behaved functional $Q[\rho]$ upon acting on $Q[\rho]$ [9,10]:

$$\hat{S}_c Q[\rho] = mQ[\rho], \tag{13}$$

with

$$Q[\rho_\gamma] = \gamma^m Q[\rho], \tag{14}$$

and

$$\rho_\gamma(r) = \gamma^3\rho(\gamma r). \tag{15}$$

Working from Eqs. (10) and (11), one can readily show [Appendix A] the following exact identities for $E_c^\lambda[\rho]$, $T_c^\lambda[\rho]$ [10,11], and $T^\lambda[\rho]$:

$$T_c^\lambda[\rho] = -\lambda^2\frac{dE_c^\lambda[\rho]}{d\lambda}, \tag{16}$$

$$\hat{S}_c T_c^\lambda[\rho] = 2T_c^\lambda[\rho] - \lambda\frac{dT_c^\lambda[\rho]}{d\lambda}, \tag{17}$$

and

$$\hat{S}_c T^\lambda[\rho] = 2T^\lambda[\rho] - \lambda\frac{dT^\lambda[\rho]}{d\lambda}. \tag{18}$$

Similarly, one can further prove [Appendix B] exact identities for $V_{ee}^0[\rho]$, $V_{ee}^\lambda[\rho]$, and $V_c^\lambda[\rho]$:

$$\hat{S}_c V_{ee}^0[\rho] = V_{ee}^0[\rho], \tag{19}$$

$$\frac{dV_{ee}^\lambda[\rho]}{d\lambda} = \frac{dV_c^\lambda[\rho]}{d\lambda} = -\frac{1}{\lambda}\frac{dT_c^\lambda[\rho]}{d\lambda} = -\frac{1}{\lambda}\frac{dT^\lambda[\rho]}{d\lambda}, \tag{20}$$

$$\lambda\frac{dV_{ee}^\lambda[\rho]}{d\lambda} = V_{ee}^\lambda[\rho] - \hat{S}_c V_{ee}^\lambda[\rho], \tag{21}$$

and

$$\lambda\frac{dV_c^\lambda[\rho]}{d\lambda} = V_c^\lambda[\rho] - \hat{S}_c V_c^\lambda[\rho]. \tag{22}$$

Here, Eqs. (9), (11), (17), (18), (19), (21), and (22) involve only $E_x[\rho]$, $E_c^\lambda[\rho]$, $T_c^\lambda[\rho]$, $T^\lambda[\rho]$, $V_{ee}^0[\rho]$, $V_{ee}^\lambda[\rho]$, and $V_c^\lambda[\rho]$, respectively.

## 2. General Taylor series expansion near $\lambda = 0$

If one postulates [8,10,12,13] that $E_c^\lambda[\rho]$ can be expanded as a full Taylor series in powers of $\lambda$ in the vicinity of $\lambda = 0$,

$$E_c^\lambda[\rho] = \sum_{n=1}^{\infty}\frac{1}{n!}A_n[\rho]\lambda^n, \tag{23}$$

where the $A_n[\rho]$ are homogeneous functionals of degree $(1-n)$ in coordinate scaling [10,14]

$$A_n[\rho_\gamma] = \gamma^{1-n}A_n[\rho]. \tag{24}$$

Consequently, Eq. (16) delivers a corresponding Taylor series expansion for $T_c^\lambda[\rho]$ [10],

$$T_c^\lambda[\rho] = \sum_{n=1}^{\infty}\frac{-1}{(n-1)!}A_n[\rho]\lambda^{n+1}. \tag{25}$$

Eqs. (6) and (20) lead to [13,18]

$$V_c^\lambda[\rho] = \sum_{n=1}^{\infty}\frac{(n+1)}{n!}A_n[\rho]\lambda^n, \tag{26}$$

and Eqs. (5), (8), and (19) yield

$$V_{ee}^{\lambda}[\rho] = J[\rho] + E_x[\rho] + \sum_{n=1}^{\infty} \frac{(n+1)}{n!} A_n[\rho]\lambda^n . \quad (27)$$

With $\lambda = 1$, Eqs. (23) and (25–27) become

$$E_c[\rho] = \sum_{n=1}^{\infty} \frac{A_n[\rho]}{n!} , \quad (28)$$

$$T_c[\rho] = \sum_{n=1}^{\infty} \frac{-A_n[\rho]}{(n-1)!} , \quad (29)$$

$$V_c[\rho] = \sum_{n=1}^{\infty} \frac{(n+1)}{n!} A_n[\rho] , \quad (30)$$

and

$$V_{ee}[\rho] = J[\rho] + E_x[\rho] + \sum_{n=1}^{\infty} \frac{(n+1)}{n!} A_n[\rho] . \quad (31)$$

These series do not satisfy the low-$\gamma$-limit scaling properties put forward by Levy and Perdew [8,12,15], such as

$$\lim_{\gamma \to 0} \gamma^{-1} E_c[\rho_\gamma] = \text{finite} . \quad (32)$$

Under an assumption of locality, the $A_n[\rho]$ have been shown to be homogeneous functionals of degree $(4-n)/3$ in density scaling [10],

$$\int \rho(r) \frac{\delta A_n[\rho]}{\delta \rho(r)} d\tau = \frac{4-n}{3} A_n[\rho] . \quad (33)$$

In other words [10], if the Taylor series expansions in Eqs. (23) and (25, 26) are valid, the present derivation suggests that $E_c[\rho]$, $T_c[\rho]$, and $V_c[\rho]$ are (to some level of accuracy) combinations of local functionals homogeneous in $\rho(r)$ of degrees: 1, 2/3, 1/3, 0, −1/3, ...,

$$X_c[\rho] = \sum_{n=1}^{\infty} a_n \int \rho(r)^{(4-n)/3} d\tau , \quad (34)$$

where $X_c[\rho]$ is a dummy symbol standing for $E_c[\rho]$, $T_c[\rho]$, or $V_c[\rho]$, and $\{a_n\}$ are undetermined expansion coefficients. Numerical results for atomic and molecular species based on this local Taylor series expansion are encouraging [10,16]. Generalizations to include the current-density functional theory have been given [17], and nonlocal explicit forms for $A_n[\rho]$ recently have been proposed [18].

However, the power series in Eq. (34) has to be truncated from at least the fourth order on, since these negative-power terms will 'self-explode' for any exponentially decaying density,

$$|a_n| \int \rho(r)^{(4-n)/3} d\tau = \infty, \ (n = 4, 5, 6, \ldots) , \quad (35)$$

unless, either every coefficient or the sum of these terms is zero. This reduces the infinite series in Eq. (34) to a three-term summation [10,16],

$$X_c[\rho] = \sum_{n=1}^{3} a_n \int \rho(r)^{(4-n)/3} d\tau . \quad (36)$$

Furthermore, even this three-term summation is not acceptable if the asymptotic behavior of the KS correlation potential [7]

$$v_c(r) = \frac{\delta E_c[\rho]}{\delta \rho(r)} , \quad (37)$$

comes into play. It is known that $v_c(r)$ has a very short-range and so is strongly vanishing at large distance [19–22],

$$\lim_{r \to \infty} v_c(r) = 0 . \quad (38)$$

Therefore, Eq. (36) is formally disqualified, since

$$\frac{\delta X_c[\rho]}{\delta \rho(r)} = a_1 + \tfrac{2}{3} a_2 \rho^{-1/3} + \tfrac{1}{3} a_3 \rho^{-2/3} , \quad (39)$$

where $a_1$ introduces a constant shift into the KS effective potential [7], while the last two terms involving $\rho^{-1/3}$ and $\rho^{-2/3}$ diverge asymptotically.

## 3. General Laurent series expansion in the parameter $\lambda$

To overcome the problem facing the Taylor series expansion of $E_c^{\lambda}[\rho]$ in terms of local homogeneous functionals, in the present paper special attention is given to the point $\lambda = 0$, where $E_c^{\lambda}[\rho]$ may not be analytic. In that case, there may exist a general

Laurent series expansion [23] in powers of $\lambda$ centered at $\lambda = 0$,

$$E_c^{\lambda}[\rho] = \sum_{-\infty}^{\infty} B_n[\rho]\lambda^n, \tag{40}$$

where the $B_n[\rho]$ possess the same scaling properties as the $A_n[\rho]$ displayed in Eqs. (24) and (33) under the same conditions. Eqs. (25–27) similarly transform into

$$T_c^{\lambda}[\rho] = \sum_{-\infty}^{\infty} (-n) B_n[\rho]\lambda^{n+1}, \tag{41}$$

$$V_c^{\lambda}[\rho] = \sum_{-\infty}^{\infty} (n+1) B_n[\rho]\lambda^n, \tag{42}$$

and

$$V_{ee}^{\lambda}[\rho] = J[\rho] + E_x[\rho] + \sum_{-\infty}^{\infty} (n+1) B_n[\rho]\lambda^n. \tag{43}$$

One can formally split the Laurent series in Eqs. (40–42) into two infinite series,

$$X_c^{\lambda}[\rho] = \sum_{n=1}^{\infty} x_n B_n[\rho]\lambda^n + \sum_{n=0}^{-\infty} x_n B_n[\rho]\lambda^n. \tag{44}$$

Here, the first sum is a Taylor-like series, and the second sum may be called the 'Laurent-minus-Taylor-like' (L − T) series. Generally, the Taylor-like series converges within its radius of convergence $R_{TI}$, while the L − T series converges outside its radius of convergence $R_{LT}$. If $R_{TI} \geqslant R_{LT}$, Eqs. (40–43) will have a non-empty domain of convergence, and these equations will be valid only for those $\lambda$ values between $R_{TI}$ and $R_{LT}$ [23].

At $\lambda = 1$, if the $B_n[\rho]$ are approximated by local homogeneous functionals, the requirement of the correct asymptotic behavior of $v_c(r)$ [19–22] results in a complete truncation of the positive terms (the Taylor-like series), giving

$$E_c[\rho] = \sum_{-\infty}^{0} B_n[\rho] = \sum_{n=0}^{\infty} C_n[\rho], \tag{45}$$

$$T_c[\rho] = \sum_{-\infty}^{0} (-n) B_n[\rho] = \sum_{n=1}^{\infty} n C_n[\rho], \tag{46}$$

$$V_c[\rho] = \sum_{-\infty}^{0} (n+1) B_n[\rho] = \sum_{n=0}^{\infty} (1-n) C_n[\rho], \tag{47}$$

and

$$V_{ee}[\rho] = J[\rho] + E_x[\rho] + \sum_{n=0}^{\infty} (1-n) C_n[\rho], \tag{48}$$

where

$$C_n[\rho] = B_{-n}[\rho] = c_n \int \rho(r)^{(4+n)/3}\, d\tau \quad (n = 0, 1, 2, \ldots), \tag{49}$$

and $\{c_n\}$ are coefficients yet to be determined. Interestingly, in this representation, $T_c[\rho]$ does not have a $\langle \rho^{4/3} \rangle$ term, while $V_c[\rho]$ lacks a contribution from $\langle \rho^{5/3} \rangle$.

With this new L − T series, the short-range and long-range properties of $v_c(r)$ appear to be better represented than by the Taylor series expansion in Eq. (23). While fulfilling Eq. (32), Eq. (45) does not satisfy the high-$\gamma$-limit scaling properties advocated by Levy and Perdew [8,12,15], for example,

$$\lim_{\gamma \to \infty} E_c[\rho_\gamma] > -\infty. \tag{50}$$

## 4. Results and discussion

There are two possible reasons that the Taylor series expansions in Eqs. (23) and (25–27) might diverge at $\lambda = 1$. First, the Taylor series might not even exist because of a singularity at $\lambda = 0$, and the general Laurent series in Eqs. (40–43) would then have to be introduced. Second, the radius of convergence of the Taylor series expansions could be less than 1: $R_T < \lambda = 1$. Similarly, if the radius of convergence of the Taylor-like series expansions are less than 1: $R_{TI} < \lambda = 1$, the complete elimination of such Taylor-like series from the general Laurent series expansions, Eqs. (40–43), will be legitimate. In this case, the assumption of locality [10], together with the argument from the long-range behavior [19–22] of the KS effective potential [7], strongly indicates $R_{TI} < R_{LT} \leqslant \lambda = 1$. More detailed informa-

Table 1
Convergence properties of the various series for a specific value of $\lambda$ [a]

| Domain of convergence | Convergent series | Corresponding equations |
|---|---|---|
| $0 \leqslant \lambda \leqslant R_T$ | Taylor series | Eqs. (23) and (25–27) |
| $R_{LT} \leqslant \lambda \leqslant R_{TI}$ | Laurent series | Eqs. (40–43) |
| $\lambda \leqslant R_{TI} < R_{LT}$ | Taylor-like series | first sum in Eq. (44) |
| $R_{TI} < \lambda < R_{LT}$ | none | none |
| $R_{TI} < R_{LT} \leqslant \lambda$ | L − T series | second sum in Eq. (44) [b] |

[a] $R_T$, $R_{TI}$, and $R_{LT}$ are the radii of convergence of the Taylor series, the Taylor-like series and the L − T series, respectively.
[b] For the special case of $\lambda = 1$, the corresponding equations are Eqs. (45–48).

tion about the convergence property of the infinite series here discussed is collected in Table 1.

Furthermore, the complementary scaling properties satisfied by the Taylor series, Eq. (23), and the L − T series, Eq. (45), argue for a general attractiveness of the full Laurent series expansions, Eqs. (40–43). However, it seems that going beyond the assumption of locality will be necessary to resolve the paradox presented by the necessity of completely truncating the Taylor-like series expansions. At the present stage of understanding, the effectiveness of a particular series should be judged by its numerical performance.

To test the validity of Eqs. (45–46), one may keep only terms with $n < 3$,

$$E_{c3}[\rho] \cong \sum_{n=0}^{2} C_n[\rho] = c_0\langle\rho^{4/3}\rangle + c_1\langle\rho^{5/3}\rangle + c_2\langle\rho^2\rangle, \quad (51)$$

$$T_{c3}[\rho] \cong \sum_{n=1}^{2} nC_n[\rho] = c_1\langle\rho^{5/3}\rangle + 2c_2\langle\rho^2\rangle, \quad (52)$$

and with $n < 4$,

$$E_{c4}[\rho] \cong \sum_{n=0}^{3} C_n[\rho] = c_0\langle\rho^{4/3}\rangle + c_1\langle\rho^{5/3}\rangle + c_2\langle\rho^2\rangle + c_3\langle\rho^{7/3}\rangle, \quad (53)$$

$$T_{c4}[\rho] \cong \sum_{n=1}^{3} nC_n[\rho] = c_1\langle\rho^{5/3}\rangle + 2c_2\langle\rho^2\rangle + 3c_3\langle\rho^{7/3}\rangle. \quad (54)$$

Least-square fitting is employed to determine coefficients. The data for the density functional theory (DFT) $E_c$ of the first eighteen atoms were taken from a recent optimized-effective-potential (OEP) calculation by Grabo and Gross [24]; and for $T_c$, from Morrison and Zhao [25]. Due to its peculiar value, the $T_c$ value for Ar was excluded from the $T_c$ data set [25] used in the fitting. All these data are enumerated in Table 3. Densities were taken as the accurate RHF results of Clementi and Roetti [26].

Three types of least-square fitting have been performed over these three data sets. First, the $E_c$ scheme fits Eq. (51) to the DFT $E_c$ data set; second, the $(E_c + T_c)_3$ scheme simultaneously fits Eqs. (51) and (52) to the DFT $E_c$ data set and the $T_c$ data set; and finally, the $(E_c + T_c)_4$ scheme fits Eqs. (53) and (54) to the DFT $E_c$ data set and the $T_c$ data set. Results are compared in Tables 2 and 3: Table 2 displays the expansion coefficients $\{c_n,\ n < 4\}$ for the truncated L − T series in Eqs. (51–54), and Table 3 shows the fitted $E_c$ and $T_c$ values. Figs. 1 and 2 depict some of the results.

From Table 3 and Fig. 1, one sees that the $E_c$ scheme faithfully reproduces the DFT $E_c$ data with a mean absolute deviation of only 0.0074 hartree. This is better than the previous results of the Taylor series

Table 2
Fitted expansion coefficients for the truncated L − T series in Eqs. (51–54) [a,b]

| Scheme | $c_0$ | $c_1$ | $c_2$ | $c_3$ |
|---|---|---|---|---|
| $E_c$ | $-0.4036 \times 10^{-1}$ | $0.7584 \times 10^{-2}$ | $-0.4255 \times 10^{-3}$ | |
| $(E_c + T_c)_3$ | $-0.5268 \times 10^{-1}$ | $0.1286 \times 10^{-1}$ | $-0.7688 \times 10^{-3}$ | |
| $(E_c + T_c)_4$ | $-0.6177 \times 10^{-1}$ | $0.2078 \times 10^{-1}$ | $-0.2226 \times 10^{-2}$ | $0.6963 \times 10^{-4}$ |

[a] All values are in atomic units.
[b] $(E_c + T_c)_3$ and $(E_c + T_c)_4$ stand for the results from the 3-term and 4-term least-square-fittings to the DFT $E_c$ and the $T_c$ data sets, respectively. $E_c$ stands for the result from the $E_c$ scheme of the 3-term least-square-fitting to the DFT $E_c$ data set.

Table 3
Fitted $T_c$ and $E_c$ values compared with previous published $T_c$ and DFT $E_c$ data [a,b,c,d]

| Atom | $Z$ | $T_c$ | DFT $E_c$ | $E_c$ | $T_{c3}$ | $E_{c3}$ | $T_{c4}$ | $E_{c4}$ |
|---|---|---|---|---|---|---|---|---|
| H | 1 | 0.000 | 0.0000 | −0.0109 | 0.0012 | −0.0139 | 0.0019 | −0.0158 |
| He | 2 | 0.037 | −0.0416 | −0.0419 | 0.0103 | −0.0522 | 0.0153 | −0.0571 |
| Li | 3 | 0.038 | −0.0509 | −0.0667 | 0.0251 | −0.0808 | 0.0353 | −0.0853 |
| Be | 4 | 0.074 | −0.0934 | −0.0953 | 0.0459 | −0.1126 | 0.0612 | −0.1159 |
| B | 5 | 0.095 | −0.1289 | −0.1275 | 0.0714 | −0.1475 | 0.0904 | −0.1494 |
| C | 6 | 0.12 | −0.1608 | −0.1650 | 0.1018 | −0.1875 | 0.1225 | −0.1883 |
| N | 7 | 0.15 | −0.1879 | −0.2081 | 0.1369 | −0.2326 | 0.1574 | −0.2327 |
| O | 8 | 0.19 | −0.2605 | −0.2548 | 0.1758 | −0.2806 | 0.1939 | −0.2802 |
| F | 9 | 0.24 | −0.3218 | −0.3070 | 0.2188 | −0.3333 | 0.2329 | −0.3326 |
| Ne | 10 | 0.30 | −0.3757 | −0.3643 | 0.2658 | −0.3903 | 0.2749 | −0.3894 |
| Na | 11 | 0.31 | −0.4005 | −0.4044 | 0.3066 | −0.4243 | 0.3065 | −0.4217 |
| Mg | 12 | 0.34 | −0.4523 | −0.4458 | 0.3425 | −0.4589 | 0.3326 | −0.4560 |
| Al | 13 | 0.35 | −0.4905 | −0.4870 | 0.3714 | −0.4925 | 0.3530 | −0.4902 |
| Si | 14 | 0.36 | −0.5265 | −0.5310 | 0.3914 | −0.5293 | 0.3691 | −0.5284 |
| P | 15 | 0.41 | −0.5594 | −0.5783 | 0.4006 | −0.5698 | 0.3823 | −0.5707 |
| S | 16 | 0.39 | −0.6287 | −0.6282 | 0.3964 | −0.6138 | 0.3940 | −0.6160 |
| Cl | 17 | 0.41 | −0.6890 | −0.6824 | 0.3772 | −0.6635 | 0.4072 | −0.6657 |
| Ar | 18 | 0.21 | −0.7435 | −0.7416 | 0.3406 | −0.7198 | 0.4254 | −0.7196 |
| $\delta$ | | | | 0.0074 | 0.0177 | 0.0178 | 0.0087 | 0.0180 |
| $\delta$ [e] | | | | 0.0160 | 0.0216 | 0.0197 | | |

[a] All values are in hartree.
[b] The DFT $E_c$ data and the $T_c$ data are from Refs. [23,24], respectively. The previous published $T_c$ value of Ar has been excluded from the data set due to its abnormal value.
[c] $T_{c3}$ and $E_{c3}$ stand for the results from the $(E_c + T_c)_3$ scheme. Similarly, $T_{c4}$ and $E_{c4}$ stand for the results from the $(E_c + T_c)_4$. $E_c$ stands for the result from the $E_c$ scheme.
[d] $\delta$ denotes the mean absolute deviation from the corresponding literature values.
[e] From Ref. [10], the results of the three-term Taylor series expansions, Eq. (36).

expansions Eq. (36) [10] on the same set of atoms. However, the final judgement has to be made based on much more extended ionic and molecular systems. The results in Table 3 also identify several atoms where better account of spin polarization may be needed: Li, N, and P.

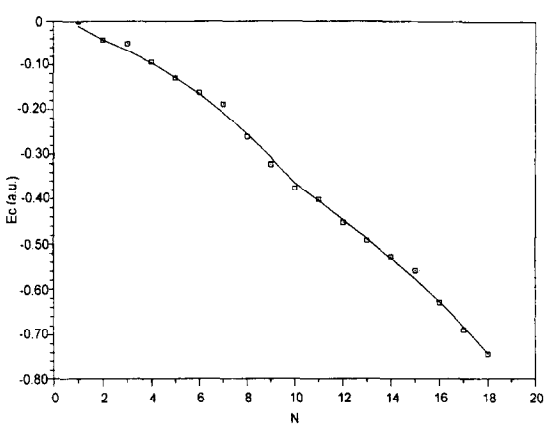


Fig. 1. The 3-term least-square fitting results (solid line) for the DFT $E_c$ data set (□) for the first two-row neutral atoms.

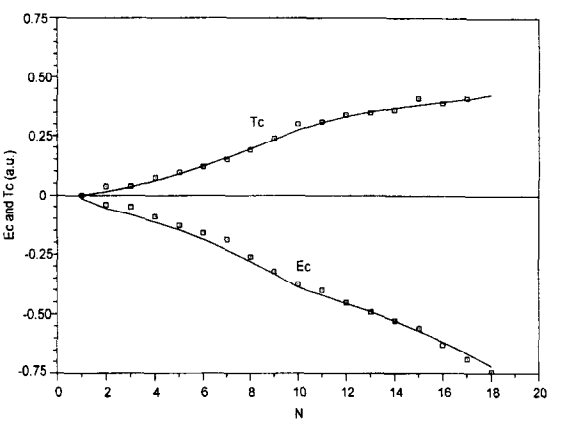


Fig. 2. The 4-term least-square fitting $(E_c + T_c)_4$ results (solid line) for the $T_c$ and DFT $E_c$ data sets (□) for the first two-row neutral atoms.

The quality of fitting (especially for the first-row atoms) deteriorates once the $T_c$ data set is included, and the $(E_c + T_c)_3$ scheme has mean absolute deviations of more than 0.0176 hartree for the whole set of $T_c$ and $E_c$ values. With one more term in the expansion, the $(E_c + T_c)_4$ scheme shows big improvement over the $(E_c + T_c)_3$ scheme. With little sacrifice in the overall quality of the fitted $E_c$ values, the $(E_c + T_c)_4$ scheme cuts by more than one half the mean absolute deviation of the $T_c$ values from those given by the $(E_c + T_c)_3$ scheme. More importantly, the $(E_c + T_c)_4$ scheme predicts a monotonically increasing trend in the values of $T_c$ as one progresses toward the heavier atoms, while the $(E_c + T_c)_3$ scheme fails to do this after the P atom.

Moreover, as shown in Tables 2 and 3, when going from the $(E_c + T_c)_3$ scheme to the $(E_c + T_c)_4$ scheme, the fitted expansion coefficients have a large fluctuation, and both the $(E_c + T_c)_3$ and $(E_c + T_c)_4$ schemes have bigger mean absolute deviations than the $E_c$ scheme does. This is probably due to the fact that the $T_c$ data set [25] is only reliable with two significant figures and less reliable for heavier atoms which dominate the globe minimum searching process. Further studies along the line of improving the literature $E_c$ and $T_c$ data sets are crucial.

Based upon the good performance of the L − T series with local homogenous functionals, one ought to be optimistic about molecular applications. Furthermore, the simplicity of the form of the functionals and better short-range and long-range behaviors will enhance the capability of the present theory. However, it would appear to be very desirable to try to gain additional understanding of the analytic properties of the various functionals $X_c^\lambda[\rho]$, especially in the region near $\lambda = 0$.

## 5. Conclusion

The numerical performance of the L − T series expansions, as shown in Eqs. (45–48), adequately demonstrates the effectiveness of the present proposal. These Laurent series expansions (both full and truncated) are well worth further investigation. More profound understanding of their convergence properties and the effects of the locality assumption will be essential to settle precisely which series is the best. Although this primary comparison shows that the L − T series expansions perform better than the Taylor series expansions [10], it is quite necessary to further test them for molecular systems [16].

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## Appendix A

### *A.1. Exact equations for $E_c^\lambda[\rho]$, $T_c^\lambda[\rho]$, and $T^\lambda[\rho]$*

Eliminating the common terms between Eqs. (10, 11) yields Eq. (16) [10,11]

$$T_c^\lambda[\rho] = -\lambda^2 \frac{dE_c^\lambda[\rho]}{d\lambda}. \tag{A1}$$

Acting with $\hat{S}_c$ on both sides of Eq. (A1) and substituting Eqs. (11) and (A1) into the right-hand side of Eq. (A1), one finds Eq. (17) [10]

$$\hat{S}_c T_c^\lambda[\rho] = 2T_c^\lambda[\rho] - \lambda \frac{dT_c^\lambda[\rho]}{d\lambda}. \tag{A2}$$

Furthermore, knowing $T_s[\rho]$ is homogeneous of degree two in the coordinate scaling [8],

$$T_s[\rho_\gamma] = \gamma^2 T_s[\rho], \tag{A3}$$

one has

$$\hat{S}_c T_s[\rho] = 2T_s[\rho]. \tag{A4}$$

Then, combining Eqs. (A2) and (A4) with the help from Eq. (7), one obtains Eq. (18),

$$\hat{S}_c T^\lambda[\rho] = 2T^\lambda[\rho] - \lambda \frac{dT^\lambda[\rho]}{d\lambda}. \tag{A5}$$

## Appendix B

### *B.1. Exact equations for $V_{ee}^\lambda[\rho]$ and $V_c^\lambda[\rho]$*

Levy and Perdew [8] derived a direct relation between $T^\lambda[\rho]$ and $V_{ee}^\lambda[\rho]$,

$$2T^\lambda[\rho] - \hat{S}_c T^\lambda[\rho] = \lambda\left(-V_{ee}^\lambda[\rho] + \hat{S}_c V_{ee}^\lambda[\rho]\right), \tag{B1}$$

which is of a combined form of Eqs. (28, 29) of Ref. [8]. Eq. (7) partitions the left-hand side of Eq. (B1) into two contributions, from $T_s[\rho]$ and $T_c^\lambda[\rho]$, with the $T_s[\rho]$ contribution identically zero due to Eq. (A4). Then, substitution of Eq. (A2) into the remaining left-hand side of Eq. (B1) gives a direct relation between $T_c^\lambda[\rho]$ and $V_{ee}^\lambda[\rho]$,

$$\frac{dT_c^\lambda[\rho]}{d\lambda} = -V_{ee}^\lambda[\rho] + \hat{S}_c V_{ee}^\lambda[\rho]. \tag{B2}$$

Since according to Eq. (45) of Ref. [8] and Eq. (4)

$$\begin{aligned} V_{ee}^\lambda[\rho] &= J[\rho] + E_{xc}^\lambda[\rho] + E_c^\lambda[\rho] - \hat{S}_c E_c^\lambda[\rho] \\ &= J[\rho] + E_x[\rho] + 2E_c^\lambda[\rho] \\ &\quad - \hat{S}_c E_c^\lambda[\rho], \end{aligned} \tag{B3}$$

one finds

$$\frac{dV_{ee}^\lambda[\rho]}{d\lambda} = \frac{d}{d\lambda}\left(2E_c^\lambda[\rho] - \hat{S}_c E_c^\lambda[\rho]\right). \tag{B4}$$

Eqs. (11) and (A1) help simplify Eq. (B4) to

$$\begin{aligned} \frac{dV_{ee}^\lambda[\rho]}{d\lambda} &= 2\frac{dE_c^\lambda[\rho]}{d\lambda} + \lambda\frac{d^2E_c^\lambda[\rho]}{d^2\lambda} \\ &= -\frac{1}{\lambda}\frac{dT_c^\lambda[\rho]}{d\lambda}. \end{aligned} \tag{B5}$$

Combination of Eqs. (B2) and (B5) now produces an identity [Eq. (21)] involving $V_{ee}^\lambda[\rho]$ alone,

$$\lambda\frac{dV_{ee}^\lambda[\rho]}{d\lambda} = V_{ee}^\lambda[\rho] - \hat{S}_c V_{ee}^\lambda[\rho]. \tag{B6}$$

Interestingly, this is of the same form as Eq. (11) for $E_c^\lambda[\rho]$.

Moreover, Eqs. (5) and (8) indicate a three-way partition for $V_{ee}^\lambda[\rho]$,

$$V_{ee}^\lambda[\rho] = J[\rho] + E_x[\rho] + V_c^\lambda[\rho], \tag{B7}$$

in which $E_x[\rho]$ and $J[\rho]$ are both homogeneous of degree one in the coordinate scaling [8],

$$E_x[\rho_\gamma] = \gamma E_x[\rho], \tag{B8}$$

$$J[\rho_\gamma] = \gamma J[\rho]. \tag{B9}$$

These quantities respectively satisfy Eq. (9) and

$$\hat{S}_c J[\rho] = J[\rho]. \tag{B10}$$

Thus, Eq. (B6) reduces to an identity [Eq. (22)] involving only $V_c^\lambda[\rho]$

$$\lambda\frac{dV_c^\lambda[\rho]}{d\lambda} = V_c^\lambda[\rho] - \hat{S}_c V_c^\lambda[\rho]. \tag{B11}$$

Similarly in Eq. (B5), the $\lambda$-independence of $J[\rho]$, $E_x[\rho]$, and $T_s[\rho]$ leads to Eq. (20),

$$\begin{aligned} \frac{dV_{ee}^\lambda[\rho]}{d\lambda} = \frac{dV_c^\lambda[\rho]}{d\lambda} &= -\frac{1}{\lambda}\frac{dT_c^\lambda[\rho]}{d\lambda} \\ &= -\frac{1}{\lambda}\frac{dT^\lambda[\rho]}{d\lambda}. \end{aligned} \tag{B12}$$

Then, subtracting Eq. (B11) from Eq. (B6) yields Eq. (19),

$$\hat{S}_c V_{ee}^0[\rho] = V_{ee}^0[\rho]. \tag{B13}$$

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