

Expansion of the density-functional energy components E_c and T_c in terms of moments of the electron density

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Starting from known identities in density-functional theory, it is shown that for finite electronic systems the density functionals $E_c^\lambda[\rho]$ and $T_c^\lambda[\rho]$ can be expanded in terms of powers of the classical moments $\langle x^q y^r z^s \rho \rangle$ of the electron density, with the expansion coefficients of the two series related in a simple way. For neutral atoms and coupling constant $\lambda = 1$, two-term universal linear expansions are demonstrated to be reasonably accurate: $E_c[\rho] = -0.1659\langle \rho \rangle \ln Z + 0.00040\langle r\rho \rangle Z$ and $T_c[\rho] = 0.1659\langle \rho \rangle \ln Z - 0.00080\langle r\rho \rangle Z$, where Z is the atomic number. The factors $\ln Z$ and Z in these formulas are rationalized. [S1050-2947(99)02702-X]

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I. INTRODUCTION

Important quantities in the density-functional theory of the electronic structure are $T_c^\lambda[\rho]$, the excess of the true total kinetic energy over the kinetic energy of the corresponding noninteracting system, $E_c^\lambda[\rho]$, the sum of $T_c^\lambda[\rho]$ and the nonclassical part of the electron-electron repulsion, and λ , the coupling parameter in the electron repulsion part of the Hamiltonian. $T_c^\lambda[\rho]$ and $E_c^\lambda[\rho]$ are defined by

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

and

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

respectively. The system of interest has $\lambda = 1$ and $T_c[\rho] = T_c^1[\rho]$, $E_c[\rho] = E_c^1[\rho]$.

A major difficulty in density-functional theory is the determination of T_c and E_c , and a host of papers have been written on this subject. Here we shall develop some of the promise of three basic formulas that relate T_c and E_c as functions of λ and functionals of the density ρ ; namely [1,2],

$$\lambda \frac{\partial E_c^\lambda[\rho]}{\partial \lambda} = E_c^\lambda[\rho] + \int \rho(\mathbf{r}) \mathbf{r} \cdot \nabla \frac{\delta E_c^\lambda[\rho]}{\delta \rho(\mathbf{r})} d\mathbf{r}, \quad (1)$$

$$\lambda \frac{\partial T_c^\lambda[\rho]}{\partial \lambda} = 2T_c^\lambda[\rho] + \int \rho(\mathbf{r}) \mathbf{r} \cdot \nabla \frac{\delta T_c^\lambda[\rho]}{\delta \rho(\mathbf{r})} d\mathbf{r}, \quad (2)$$

and

$$T_c^\lambda[\rho] = -\lambda^2 \frac{\partial E_c^\lambda[\rho]}{\partial \lambda}. \quad (3)$$

Previously [2], for finite systems we studied these equations using linear expansions in terms of the generalized moments

$\langle \rho^k \rangle$. In the present paper, we propose use of the simpler classical electrostatic moments $\langle x^q y^r z^s \rho \rangle$, or for spherical atoms just $\langle r^p \rho \rangle$.

II. EXPANSIONS IN MOMENTS

First, let us consider the equation one gets by functionally differentiating Eq. (1) with respect to ρ ,

$$\lambda \frac{dv_c^\lambda}{d\lambda} - v_c^\lambda = \mathbf{r} \cdot \nabla v_c^\lambda + \int d\mathbf{r}_1 \rho(\mathbf{r}_1) \mathbf{r}_1 \cdot \nabla_1 \frac{\delta v_c^\lambda}{\delta \rho(\mathbf{r}_1)}, \quad (4)$$

where

$$v_c^\lambda \equiv v_c^\lambda(\mathbf{r}, [\rho]) = \frac{\delta E_c^\lambda[\rho]}{\delta \rho(\mathbf{r})} \quad (5)$$

is the correlation potential. The last term in Eq. (4) is the second-order quantity

$$\int d\mathbf{r}_1 \rho(\mathbf{r}_1) \mathbf{r}_1 \cdot \nabla_1 \frac{\delta^2 E_c^\lambda[\rho]}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}_1)} \quad (6)$$

and is hopefully small. If we assume spherical symmetry and neglect it, we find

$$\lambda \frac{dv_c^\lambda}{d\lambda} - v_c^\lambda = r \nabla v_c^\lambda, \quad (7)$$

of which the solution is immediate,

$$v_c^\lambda = A \lambda^{p+1} r^p, \quad (8)$$

where A and p are constants. The corresponding E_c , from Eq. (1), is

$$E_c^\lambda[\rho] = A \lambda^{p+1} \langle r^p \rho \rangle, \quad (9)$$

so that

$$E_c[\rho] = A \langle r^p \rho \rangle. \quad (10)$$

But Eqs. (4) and (7) are homogeneous, so that a linear combination of solutions is a solution. Hence we obtain, as a more general solution of Eq. (7),

$$v_c^\lambda = \sum_p A_p \lambda^{p+1} r^p, \quad (11)$$

with which goes

$$E_c^\lambda[\rho] = \sum_p A_p \lambda^{p+1} \langle r^p \rho \rangle, \quad (12)$$

and

$$E_c[\rho] = \sum_p A_p \langle r^p \rho \rangle. \quad (13)$$

This last formula gives $E_c[\rho]$ as a linear combination of the classical electrostatic moments of the electron density. From Eq. (3) there also follows

$$T_c[\rho] = - \sum_p (p+1) A_p \langle r^p \rho \rangle. \quad (14)$$

At this point the p values need not be integer. The constants A_p are yet to be determined.

This procedure can be iterated, to give a series of hierarchical equations [3,4], of which Eq. (4) is the first. Taking the functional derivative of Eq. (4) with respect to the density gives the second equation of the hierarchy. Neglecting the third-order functional derivative of E_c^λ yields an equation of which the solution is Eq. (12) above plus a correction. Specifically,

$$v_c^\lambda = \sum_{p1} A_{p1} \lambda^{p1+1} r^{p1} + \sum_{p2} A_{p2} r^{p2} \lambda^{2p2+1} \langle r^{p2} \rho \rangle, \quad (15)$$

so that

$$E_c^\lambda[\rho] = \sum_{p1} A_{p1} \lambda^{p1+1} \langle r^{p1} \rho \rangle + \frac{1}{2} \sum_{p2} A_{p2} \lambda^{2p2+1} \langle r^{p2} \rho \rangle^2 \quad (16)$$

and

$$E_c[\rho] = \sum_{p1} A_{p1} \langle r^{p1} \rho \rangle + \frac{1}{2} \sum_{p2} A_{p2} \langle r^{p2} \rho \rangle^2. \quad (17)$$

We now have a linear combination of the moments and their squares. Continuing, the next equation of the hierarchy brings in the third powers, and so on. The final results, upon truncation at order K are

$$v_c^\lambda = \sum_p \sum_{k=1}^K \frac{1}{k} A_{pk} \lambda^{pk+1} r^2 \langle r^p \rho \rangle^{k-1}, \quad (18)$$

$$E_c^\lambda[\rho] = \sum_p \sum_{k=1}^K \frac{1}{k} A_{pk} \lambda^{pk+1} \langle r^p \rho \rangle^k, \quad (19)$$

$$E_c[\rho] = \sum_p \sum_{k=1}^K \frac{1}{k} A_{pk} \langle r^p \rho \rangle^k. \quad (20)$$

Also,

$$T_c^\lambda[\rho] = - \sum_p \sum_{k=1}^K \left(p + \frac{1}{k} \right) A_{pk} \lambda^{pk+2} \langle r^p \rho \rangle^k, \quad (21)$$

and

$$T_c[\rho] = - \sum_p \sum_{k=1}^K \left(p + \frac{1}{k} \right) A_{pk} \langle r^p \rho \rangle^k. \quad (22)$$

Constants A_{pk} are yet to be determined.

If the system is not spherically symmetrical, the formulas analogous to Eqs. (20) and (22) turn out to be

$$E_c[\rho] = \sum_{qrs} \sum_{k=1}^K \frac{1}{k} A_{qrsk} \langle x^q y^r z^s \rho \rangle^k \quad (23)$$

and

$$T_c[\rho] = - \sum_{qrs} \sum_{k=1}^K \left(q + \frac{1}{k} \right) \left(r + \frac{1}{k} \right) \left(s + \frac{1}{k} \right) A_{qrsk} \langle x^q y^r z^s \rho \rangle^k, \quad (24)$$

with various relations among A_{qrsk} if any symmetry is present.

While we have employed a hierarchical procedure—differentiate, truncate, and solve; repeat—to arrive at the above formulas, we need not have. For a simple guess that any quantity $\langle x^q y^r z^s \rho \rangle$ or $\langle r^p \rho \rangle$ satisfies Eqs. (1) or (2) is readily verified by direct substitution in Eq. (1) or Eq. (2). That is, every one of Eqs. (9), (12), (16), and (19) is a solution of Eq. (1), and correspondingly for the T_c formulas.

Other solutions of Eqs. (1) and (2) might exist. Nevertheless, Eqs. (21) and (22) may suffice because of the vast number of terms in them.

III. FIRST-ORDER APPROXIMATIONS FOR ATOMS

Accurate E_c and T_c values are sorely needed, for atoms and molecules, so that the equations above can be extensively tested. We confine ourselves here to the neutral atoms H through Ar, for which reasonably good values are available for both E_c [5] and T_c [6].

Several factors argue for first trying the simple linear expansions in the moments $\langle \rho \rangle$, $\langle r \rho \rangle$, etc. This is the simplest thing to try. It is the only expansion of the ones we have given that is size consistent. It is the only one that is homogeneous of degree one in the density [7,8]. So we set out to test Eqs. (13) and (14) in their simplest possible forms,

$$E_c[\rho] = A_0 \langle \rho \rangle + A_1 \langle r \rho \rangle \quad (25)$$

and

$$T_c[\rho] = -A_0 \langle \rho \rangle - 2A_1 \langle r \rho \rangle. \quad (26)$$

What we hope is that these formulas can fit the data well with universal values A_0 and A_1 . They do not. However, some scaling and other arguments, given in Sec. IV below,

TABLE I. Accurate and fitted values of the correlation energy E_c and its kinetic component T_c for first 18 neutral atoms. Accurate E_c and T_c values are from Refs. [5] and [6], respectively. The three parameters in Ref. [2] are refitted. See footnote for the fitted parameters. Atomic units.

Atom	E_c	T_c	E_c Present fit ^a	T_c Present fit ^b	E_c Ref. [2] ^c	T_c Ref. [2] ^d
H	0	0	0.000 6	−0.001 2	−0.023 9	0.006 6
He	−0.042	0.0374	−0.021 5	0.020 0	−0.068 1	0.045 6
Li	−0.051	0.0421	−0.048 6	0.042 5	−0.081 5	0.044 6
Be	−0.093	0.0710	−0.082 0	0.072 2	−0.119 2	0.066 3
B	−0.129	0.0977	−0.119 7	0.106 0	−0.162 5	0.103 3
C	−0.161	0.1247	−0.160 9	0.143 7	−0.209 1	0.146 6
N	−0.188	0.1547	−0.205 0	0.184 4	−0.256 7	0.192 9
O	−0.261	0.2074	−0.251 2	0.226 8	−0.303 5	0.239 0
F	−0.322	0.2601	−0.299 6	0.271 5	−0.351 0	0.286 2
Ne	−0.376	0.3028	−0.349 8	0.318 2	−0.398 7	0.334 0
Na	−0.401	0.3304	−0.389 2	0.341 3	−0.413 7	0.337 6
Mg	−0.452	0.3622	−0.435 1	0.376 0	−0.449 1	0.356 8
Al	−0.491	0.402	−0.480 9	0.409 4	−0.486 3	0.385 2
Si	−0.527	0.436	−0.530 8	0.449 5	−0.530 8	0.423 9
P	−0.559	0.483	−0.582 9	0.492 8	−0.577 6	0.467 7
S	−0.629	0.541	−0.635 6	0.536 2	−0.623 3	0.510 1
Cl	−0.689	0.597	−0.690 1	0.582 1	−0.671 0	0.557 5
Ar	−0.744	0.663	−0.745 9	0.629 8	−0.719 0	0.605 4
Residue			0.000 187	0.000 242	0.000 873	0.000 630

$$^a E_c = -0.165\,69\,N \ln Z + 0.000\,401Z\langle r\rho\rangle.$$

$$^b T_c = 0.165\,69\,N \ln Z - 0.000\,802Z\langle r\rho\rangle.$$

$$^c E_c = -0.046\,82N + 0.005\,753\langle \rho^{2/3}\rangle - 0.000\,96\langle \rho^{1/3}\rangle.$$

$$^d T_c = 0.046\,82N - 2 \times 0.005\,753\langle \rho^{2/3}\rangle + 3 \times 0.000\,96\langle \rho^{1/3}\rangle.$$

suggest introducing the atomic numbers Z (themselves functionals of the density) into the formulas, by setting $A_0 = C_0 \ln Z$ and $A_1 = C_1 Z$:

$$E_c[\rho] = C_0 \ln Z\langle \rho \rangle + C_1 Z\langle r\rho \rangle \quad (27)$$

and

$$T_c[\rho] = -C_0 \ln Z\langle \rho \rangle - 2C_1 Z\langle r\rho \rangle. \quad (28)$$

The results are very good, as given in Table I and exhibited in Fig. 1. Hartree-Fock densities [9] are used in the calculations of $\langle r\rho \rangle$; $\langle \rho \rangle$ is of course the number of electrons N . The fit with $C_0 = -0.1657$ and $C_1 = 0.000\,40$ is better than the earlier linear fits in the quantities $\langle \rho \rangle$, $\langle \rho^{2/3} \rangle$, $\langle \rho^{1/3} \rangle$ [2].

IV. DISCUSSION

There is a good argument for expanding E_c and T_c in terms of the moments, either as in Eqs. (13) and (14) or as in the more complex Eqs. (20) and (22). The moments determine the density, by the classical theory of determination of a density from moments [10], and the density determines everything, by the Hohenberg-Kohn theorem. Therefore, the moments determine everything. What is more, the formulas we have obtained, in terms of moments, arise naturally from the basic exact Eqs. (1)–(3), as we have shown. The reason for preferring the linear forms of Eqs. (13) and (14) were given above.

The rationale for the factor Z in the second terms of Eqs. (27) and (28) is that one expects universality in such things

for an atom when one transforms r into Zr (as in the traditional $1/Z$ expansion method). We offer three arguments for the factor $\ln Z$ in the first terms of Eqs. (27) and (28): (1) The hydrogenlike system has $\ln \rho = 3 \ln Z$ + other terms. Real atomic densities are piecewise exponentially decaying and so

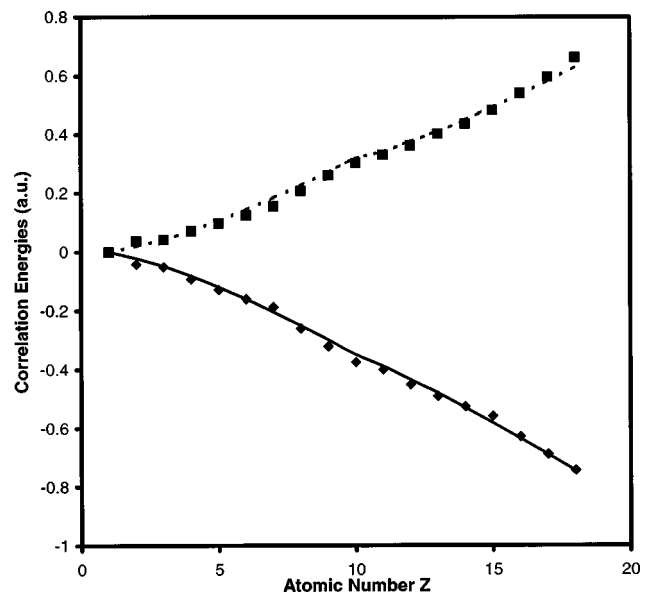


FIG. 1. Curves of the true and fitted E_c and T_c results vs the atomic number Z . The solid line is the fitted E_c results and the dashed line is the fitted T_c results. The accurate E_c and T_c data from Refs. [5,6] are in symbols \blacklozenge and \blacksquare , respectively. The fitted equations are Eqs. (27) and (28) of the text.

in a sense hydrogenlike [11]. E_c and T_c are linked to the density through Eqs. (1) and (2). (2) The classical high-density formula for E_c for a uniform gas has a leading term proportional to $\ln r_s$, and $\ln r_s$ for an exponentially decaying normalized density will contain a term proportional to $\ln Z$. An atom has fairly large density at the nucleus and fairly small r_s ; there $r_s(0) \approx 0.72Z^{-1}$. (3) Very recent work by March and co-workers [12] argues that a term $Z \ln Z$ may enter the correlation energy formula for a high density, large N , Thomas-Fermi atom.

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- [1] M. Levy and J. P. Perdew, Phys. Rev. A **32**, 2010 (1985).
 - [2] S. Liu and R. G. Parr, Phys. Rev. A **53**, 2211 (1996).
 - [3] Á. Nagy, Phys. Rev. A **47**, 2715 (1993).
 - [4] Á. Nagy, Phys. Rev. A **52**, 984 (1995).
 - [5] T. Grabo and E. K. U. Gross, Chem. Phys. Lett. **240**, 141 (1995).
 - [6] R. C. Morrison and Q. Zhao, Phys. Rev. A **51**, 1980 (1995); Y. A. Wang and R. C. Morrison (unpublished).
 - [7] R. G. Parr and S. Liu, Chem. Phys. Lett. **276**, 164 (1997).
 - [8] S. Liu and R. G. Parr, Chem. Phys. Lett. **278**, 341 (1997).
 - [9] T. Koga, H. Tatewaki, and A. J. Thakkar, Phys. Rev. A **47**, 4510 (1993).
 - [10] For example, S. B. Sears, R. G. Parr, and U. Dinur, Isr. J. Chem. **19**, 165 (1980).
 - [11] S. Liu and R. G. Parr, J. Comput. Chem. (to be published).
 - [12] A. Grassi, G. M. Lombardo, N. H. March, and R. Pucci, Int. J. Quantum Chem. **69**, 721 (1998). See also, N. H. March, Phys. Rev. A **55**, 3935 (1997), last paragraph. These authors compute the Shannon information entropy for the Thomas-Fermi atom and then they proceed to show how the Gell-Mann-Brueckner high-density total correlation energy is $-0.021Z \ln Z + 0.005Z$.