Lower bounds to the first-order gradient corrections in the gradient expansion of the kinetic- and exchange-energy functionals

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Lower bounds for the first-order gradient corrections to the kinetic- and exchange-energy functionals in atoms are derived using Benson's inequality. They are formulated in terms of the expectation values and the momentum expectation value in a simple manner, namely,

$$T_2[\rho] = \frac{1}{72} \int \frac{|\boldsymbol{\nabla}\rho(\mathbf{r})|^2}{\rho(\mathbf{r})} \, d\mathbf{r} \geq \frac{n^2}{72} \langle r^{n-3} \rangle^2 \langle r^{2n-4} \rangle^{-1}$$

and

$$|K_2[\rho]| = \beta \int \frac{|\boldsymbol{\nabla}\rho(\mathbf{r})|^2}{\rho^{4/3}(\mathbf{r})} \, d\mathbf{r} \geq 0.051\,05 \langle r^{-1} \rangle^2 \langle p \rangle^{-1},$$

where n is the natural number, $\langle r^{n-3} \rangle$ and $\langle r^{2n-4} \rangle$ are the expectation values, $\langle p \rangle$ is the momentum value, and $\rho(\mathbf{r})$ is the electron density with the normalization condition of $\int \rho(\mathbf{r}) d\mathbf{r} = N$, the number of electrons. The bounds derived in this work are tested for atoms $Z = 1-36$. A comparison is also made with the previously derived lower bound estimates for $T_2[\rho]$ and $K_2[\rho]$. The bounds presented are sharper than the previous ones given by Pathak and Gadre [Phys. Rev. A **25**, 3426 (1982); **24**, 2906 (1981)] (atomic units are used throughout the paper). [S1050-2947(96)01711-8]

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I. INTRODUCTION

Since Hohenberg, Kohn, and Sham [1,2] made a suggestion that ascribed the electron density $\rho(\mathbf{r})$ as a basic variable to study the electronic properties of many-electron systems, density-functional theory has been widely and successfully applied to atoms, molecules, solids, etc. However, the exact forms of the kinetic- and exchange-energy functionals $T[\rho]$ and $\mathcal{E}[\rho]$ have not been known so far. In the study of density-functional theory, much effort has been devoted to the gradient expansions of $T[\rho]$ and $\mathcal{E}[\rho]$ using the gradient-expansion technique [3–5].

In the gradient-expansion approximation, the kinetic- and exchange-energy functionals take the forms [3–5]

$$T[\rho] = T_0[\rho] + T_2[\rho] \tag{1}$$

and

$$\mathcal{E}[\rho] = K_0[\rho] + K_2[\rho], \tag{2}$$

where

$$T_0[\rho] = \tfrac{3}{10}(3\pi^2)^{2/3} \int \rho^{5/3}(\mathbf{r}) d\mathbf{r} \tag{3}$$

is the zeroth-order kinetic-energy functional,

$$T_2[\rho] = \frac{1}{72} \int \frac{|\boldsymbol{\nabla}\rho(\mathbf{r})|^2}{\rho(\mathbf{r})} \, d\mathbf{r} \tag{4}$$

is the first-order gradient (or Weizsäcker) correction [6],

$$K_0[\rho] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} \int \rho^{4/3}(\mathbf{r}) d\mathbf{r} \tag{5}$$

is the zeroth-order or Salter exchange-energy functional [7], and

$$K_2[\rho] = -\beta \int \frac{|\boldsymbol{\nabla}\rho(\mathbf{r})|^2}{\rho^{4/3}(\mathbf{r})} \, d\mathbf{r} \tag{6}$$

is the first-order gradient correction to the zeroth-order exchange-energy functional. The coefficient β in Eq. (6) has a value of $7/144(3\pi^2)^{4/3} = 0.001\,667$, reported by Sham [5]. Recently, Engel and Vosko have argued that this value should be multiplied by $\frac{10}{7}$ and this is generally accepted [8]. In the following calculation, we will take $\beta = 5.5 \times 10^{-3}$ given emperically by Shih, Murphy, and Wang [9].

The first-order gradient corrections $T_2[\rho]$ and $K_2[\rho]$ to the zeroth-order kinetic- and exchange-energy functionals $T_0[\rho]$ and $K_0[\rho]$ are large for a nonuniform system. Therefore, the first-order gradient corrections are crucial for studying atoms and molecules. It would seem of obvious interest to study $T_2[\rho]$ and $K_2[\rho]$ defined in Eqs. (4) and (6).

Studies on the bounds to the first-order gradient corrections $T_2[\rho]$ and $K_2[\rho]$ are of interest [10,11]. Pathak and Gadre [11] derived the lower bounds for $T_2[\rho]$ and $|K_2[\rho]|$ using Sobolev's inequality in three dimensions in conjunction with Hölder's inequality

$$T_2[\rho] \geq \tfrac{10}{72}(\tfrac{2}{3})^{2/3} N^{-2/3} T_0[\rho] \qquad (7)$$

and

$$|K_2[\rho]| \geq 3\pi(6\pi)^{2/3}\beta N^{-2/3}|K_0[\rho]|, \qquad (8)$$

where β appearing in Eq. (8) is inserted there to make the value of $K_2[\rho]$ in Ref. [11] equal to that of $K_2[\rho]$ in the present context. However, the numerical test shows that the bounds for $T_2[\rho]$ and $|K_2[\rho]|$ in Eqs. (7) and (8) are not tight.

In the present work, lower bounds to the first-order gradient corrections $T_2[\rho]$ and $|K_2[\rho]|$ in atoms are derived and a better relationship between $|K_0[\rho]|$ and $|K_2[\rho]|$ is proposed. Numerical investigations on the bounds are made for comparison.

II. BOUNDS TO THE FIRST-ORDER GRADIENT CORRECTIONS

The fundamental inequality—Benson's inequality [12]—employed in this work is given as Benson's theorem, which is quite useful in finding rigorous bounds involving moments of the electron density.

Benson's theorem. If $u(r)$, $P(u,r)$, and $G(u,r)$ are continuously differentiable for r in $[a,b]$ and $P(u,r) > 0$, the following inequality holds:

$$\int_a^b (Pu'^2 + P^{-1}G_u^2 + 2G_r)dr \geq 2[G(u(b),b) - G(u(a),a)], \qquad (9)$$

where $G_u = (\partial/\partial u)G(u,r)$ and $G_r = (\partial/\partial r)G(u,r)$.

If we let $P = \alpha r^2$ and $G = \tfrac{1}{2}u^2 g(r)$, then we can readily derive the following inequality from Eq. (9):

$$\int_a^b \left[\alpha r^2 u'^2 + \frac{1}{\alpha} r^{-2} u^2 g^2(r) + u^2 g'(r) \right] dr \geq u^2(b)g(b) - u^2(a)g(a), \qquad (10)$$

where α is an arbitrary positive parameter and $g(r)$ is assumed to be any continuously differentiable function. With the substitutions $u = \rho^{1/2}(r)$, $g(r) = -r^n$ ($n = 1,2,3,\dots$), and letting $a = 0$, $b \to \infty$, we obtain

$$\frac{\alpha}{4} \int_0^\infty \frac{1}{\rho} \left(\frac{d}{dr}\rho \right)^2 r^2 dr + \frac{1}{\alpha} \int_0^\infty r^{2n-2}\rho \, dr - n\int_0^\infty r^{n-1}\rho \, dr \geq \rho(r)r^n \big|_\infty^0, \qquad (11)$$

where $\rho(r)$ is assumed to be radially symmetric. Since the term on the right-hand side of Eq. (11) vanishes for atomic densities, we obtain from Eq. (11)

$$\frac{\alpha}{4} \int \frac{1}{\rho}\left(\frac{d}{dr}\rho \right)^2 r^2 dr + \frac{1}{\alpha} \langle r^{2n-4}\rangle \geq n\langle r^{n-3}\rangle. \qquad (12)$$

Equation (12) can be recast in the form

$$\frac{\alpha}{4}\int \frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})}d\mathbf{r} + \frac{1}{\alpha}\langle r^{2n-4}\rangle \geq n\langle r^{n-3}\rangle, \qquad (13)$$

where $\rho(\mathbf{r})$ is the electron density subject to the normalization condition $\int\rho(\mathbf{r})d\mathbf{r} = N$ (the total number of electrons) and $\langle r^{n-3}\rangle$ and $\langle r^{2n-4}\rangle$ are the expectation values in atoms. For the case of $n = 3$, $\langle r^{n-3}\rangle = \int\rho(\mathbf{r})d\mathbf{r} = N$ and for the case of $n = 2$, $\langle r^{2n-4}\rangle = \int\rho(\mathbf{r})d\mathbf{r} = N$.

The optimum value for the parameter α is readily determined to be

$$\alpha = \left(\langle r^{2n-4}\rangle \Big/ \frac{1}{4}\int \frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})}d\mathbf{r} \right)^{1/2}. \qquad (14)$$

Substituting the optimized parameter α of Eq. (14) into Eq. (13) leads to the desirable result

$$\int \frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})}d\mathbf{r} \geq n^2 \langle r^{n-3}\rangle^2 \langle r^{2n-4}\rangle^{-1}, \qquad (15)$$

namely,

$$T_2[\rho] \geq \frac{n^2}{72}\langle r^{n-3}\rangle^2 \langle r^{2n-4}\rangle^{-1}. \qquad (16)$$

For the cases of $n = 1, 2$, and 3, the inequality (16) gives the following lower bounds for $T_2[\rho]$:

$$T_2[\rho] \geq \tfrac{1}{72}\langle r^{-2}\rangle \quad (n = 1), \qquad (17\text{a})$$

$$T_2[\rho] \geq \frac{1}{18N}\langle r^{-1}\rangle^2 \quad (n = 2), \qquad (17\text{b})$$

$$T_2[\rho] \geq \frac{N^2}{8}\langle r^2\rangle^{-1} \quad (n = 3). \qquad (17\text{c})$$

Likewise, a lower bound for the first-order gradient correction $K_2[\rho]$ to the zeroth-order exchange-energy functional $K_0[\rho]$ can readily be obtained along the same line as above. This can be accomplished in the following way by using the same inequality (10). With the substitutions $u = \rho^{1/3}(r)$, $g(r) = -r^2\rho^{1/3}(r)$ and letting $a = 0$, $b \to \infty$, we may obtain from the inequality (10)

$$\frac{\alpha}{9}\int_0^\infty r^2 \frac{1}{\rho^{4/3}}\left(\frac{d}{dr}\rho \right)^2 dr + \frac{1}{\alpha}\int_0^\infty r^2\rho^{4/3}dr - 2\int_0^\infty r\rho \, dr$$
$$- \frac{1}{3}\int_0^\infty r^2\left(\frac{d}{dr}\rho \right)dr \geq r^2\rho(r)\big|_\infty^0, \qquad (18)$$

which yields, upon a partial integration for the fourth term of the left-hand-side,

$$\frac{\alpha}{9}\int_0^\infty r^2 \frac{1}{\rho^{4/3}}\left(\frac{d}{dr}\rho \right)^2 dr + \frac{1}{\alpha}\int_0^\infty r^2\rho^{4/3}dr \geq \frac{4}{3}\int_0^\infty r\rho \, dr \qquad (19)$$

since $r^2\rho(r)$ vanishes when $r = 0$ or $r \to \infty$ in atomic systems.

Our next objective is to recast Eq. (19) in terms of more readily available quantities. For this purpose, we assume $\rho(r)$ to be radially symmetric, so Eq. (19) can be recast in the form

TABLE I. Bounds for $T_2[\rho]$. (All values are in a.u.)

Atom	N	$\langle r^{-1}\rangle$[a]	$T_0[\rho]$[a]	$T_2[\rho]$[a] exact	$T_2[\rho]$ Eq. (7)	$T_2[\rho]$ Eq. (17b)
H	1	1.00	0.289	0.211	0.031	0.056
He	2	3.375	2.56	0.32	0.171	0.316
Li	3	5.730	6.38	1.23	0.325	0.608
Be	4	8.396	12.84	2.14	0.540	0.979
B	5	11.374	22.07	3.30	0.800	1.437
C	6	14.864	34.32	4.68	1.102	1.996
N	7	18.332	49.83	6.29	1.443	2.667
O	8	22.260	68.30	8.61	1.810	3.441
F	9	26.526	91.41	10.14	2.239	4.343
Ne	10	31.128	117.84	12.37	2.691	5.383
Ar	18	69.73	490.6	34.3	7.571	15.007
Kr	36	182.85	2594	142	25.217	51.596

[a]From Ref. [14].

$$\frac{\alpha}{9}\int\frac{|\nabla\rho(\mathbf{r})|^2}{\rho^{4/3}(\mathbf{r})}\,d\mathbf{r}+\frac{1}{a}\int\rho^{4/3}(\mathbf{r})\,d\mathbf{r}\geq\frac{4}{3}\langle r^{-1}\rangle,\quad(20)$$

where $\rho(\mathbf{r})$ is the electron density of atomic systems with the normalization condition $\int\rho(\mathbf{r})\,d\mathbf{r}=N$ (the total number of electrons) and $\langle r^{-1}\rangle$ is the expectation value in atomic systems.

The optimum value of the parameter α in Eq. (20) is readily determined to be

$$\alpha=\left(\int\rho^{4/3}(\mathbf{r})\,d\mathbf{r}\bigg/\frac{1}{9}\int\frac{|\nabla\rho(\mathbf{r})|^2}{\rho^{4/3}(\mathbf{r})}\,d\mathbf{r}\right)^{1/2}.\quad(21)$$

Substituting the optimized parameter α of Eq. (21) in conjunction with the definitions of $K_0[\rho]$ and $K_2[\rho]$ in Eqs. (5) and (6) into Eq. (20) leads to the result

$$|K_0[\rho]|\,|K_2[\rho]|\geq3\left(\frac{3}{\pi}\right)^{1/3}\beta\langle r^{-1}\rangle^2\equiv0.016\,25\langle r^{-1}\rangle^2,\tag{22}$$

where $\beta=5.5\times10^{-3}$.

Within the Burkhardt-Kònya-Coulson-March procedure [13], Pathak and Gadre established an approximate relationship between $|K_0[\rho]|$ and the momentum expectation value $\langle p\rangle$ [14]:

$$|K_0[\rho]|=\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int\rho^{4/3}(\mathbf{r})\,d\mathbf{r}\approx\frac{\langle p\rangle}{\pi}.\tag{23}$$

Substituting Eq. (23) into Eq. (22) yields the expected result

$$|K_2[\rho]|\geq(9\pi)^{2/3}\beta\langle r^{-1}\rangle^2\langle p\rangle^{-1}\equiv0.051\,05\langle r^{-1}\rangle^2\langle p\rangle^{-1}.\tag{24}$$

III. NUMERICAL RESULTS FOR THE BOUNDS TO $T_2[\rho]$ AND $K_2[\rho]$

In order to test the tightness of the bounds in Eq. (17b), the bound estimates are evaluated for neutral atoms $Z=1-36$. The results are presented in Table I. The bound estimates for $T_2[\rho]$ in Eq. (7) given by Pathak and Gadre [11] have

TABLE II. Bounds for $|K_2[\rho]|$. (All values are in a.u.)

Atom	$\langle r^{-1}\rangle$[a]	$\langle p\rangle$[b]	$|K_2[\rho]|$[c] exact	$|K_2[\rho]|$[d] Eq. (8)	$|K_2[\rho]|$ Eq. (24)
H	1.00	0.67	0.10	0.08	0.08
He	3.375	2.80	0.28	0.21	0.21
Li	5.715	4.91	0.44	0.28	0.34
N	18.34	18.86	1.2	0.60	0.91
Ne	31.11	35.20	1.7	0.89	1.40
Na	35.43	40.73	1.9	0.96	1.57
P	54.15	66.18	2.7	1.27	2.26
Cl	64.36	80.65	3.1	1.43	2.62
Ar	69.73	88.70	3.3	1.51	2.80
K	74.89	96.22	3.5	1.58	2.98
Cr	103.99	142.5	4.5	2.00	3.87
Ni	123.58	185.3	5.3	2.35	4.56
Br	175.84	268.9	6.8	2.94	5.87
Kr	182.85	281.4	7.0	3.02	6.07

[a]From Ref. [16].
[b]From Ref. [17].
[c]From Ref. [9].
[d]The bound for $|K_2[\rho]|$ in Eq. (8) is $0.1169N^{-2/3}\langle P\rangle$, obtained by substituting Eq. (23) into Eq. (8), where we take $\beta=5.5\times10^{-3}$.

also been carried out in terms of $T_0[\rho]$ and N as displayed in Table I for comparison.

For the case of $n=2$ examined in Table I, the lower bound to $T_2[\rho]$ given by Eq. (17b) is observed to be better than that obtained by Pathak and Gadre [11]. However, the bound given by Eq. (17b) typically still underestimates by a factor of 2. It is interesting to note that within the Thomas-Fermi theory, the atomic kinetic energy T has the well-known $Z^{1/3}$ dependence (Z is the atomic number and $Z=N$, the total number of electrons) and $T_2[\rho]$, the first-order gradient correction to the kinetic energy, also has such a dependence because the atomic expectation value $\langle r^{-1}\rangle$ has the $Z^{1/3}$ dependence [15].

In order to test the quality of the lower bound to $K_2[\rho]$ given by Eq. (24), numerical investigations on neutral atoms for $Z=1-36$ have been made, as shown in Table II. The bound given by Pathak and Gadre [11] is also examined for comparison.

It is clear from Table II that Eq. (24) is considerably sharper than Eq. (8). The lower bound to $|K_2[\rho]|$ given by Eq. (24) is observed to be in better agreement with the exact $|K_2[\rho]|$. One observes that the relative error of the bound (24) is at most 0.25, which occurs for $Z=2$, and then it slowly decreases for larger atomic numbers. This suggests that there is a close reciprocal relationship between the leading term $K_0[\rho]$ and the first-order gradient correction $K_2[\rho]$ in the gradient expansion of the exchange energy. So we can estimate the error caused by the first-order gradient correction to the exchange energy from the reciprocal relationship (22).

IV. CONCLUSION

In conclusion, we have found the lower bounds for the first-order gradient corrections in the gradient expansion of the kinetic- and exchange-energy functionals. The bounds

proposed in this work are not only extremely simple to evaluate since they depend only on the expectation values and the momentum expectation value in atoms, but also are sharper than the bounds derived by Pathak and Gadre [11]. The bound to $K_2|[\rho]|$, given by Eq. (24), is particularly good, as seen from Table II. According to the reciprocal relationship between the zeroth-order exchange-energy functional $K_0[\rho]$ and the first-order gradient correction $K_2[\rho]$ given by Eq. (22), we may conjecture that the results of various physical quantities of atomic systems calculated in the Thomas-Fermi (TF) theory or the local-density approximation (LDA) of density-functional theory (DFT) will become more and more accurate if the atoms are heavier. The reason is that the relative errors caused by neglecting the first-order gradient correction $K_2[\rho]$ to the zeroth-order or Slater exchange-energy functional $K_0[\rho]$ become smaller for heavier atoms because $K_0[\rho]$ becomes larger for heavier atoms, whereas $K_2[\rho]$ becomes smaller according to Eq. (22). We conclude that the TF theory and the LDA of the DFT are more applicable to heavier atoms.

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