Relationships between the terms in the gradient expansion:
Kinetic and exchange energy functionals

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Rigorous lower bounds for all bound-state systems, for the first-gradient corrections to the kinetic and exchange energy functionals, viz., (i)

$$T_2[\rho] = \frac{1}{72} \int \frac{|\vec{\nabla}\rho(\vec{r})|^2}{\rho(\vec{r})} d\vec{r} \geq \frac{\pi^{4/3} 2^{2/3}}{24 N^{2/3}} \int \rho^{5/3}(\vec{r}) d\vec{r} = \frac{10}{72} \left[\frac{2}{3}\right]^{2/3} \frac{T_0[\rho]}{N^{2/3}}$$

and (ii)

$$|K_2[\rho]| = \int \frac{|\vec{\nabla}\rho(\vec{r})|^2}{\rho^{4/3}(\vec{r})} d\vec{r} \geq \frac{27(\pi/2)^{4/3}}{N^{2/3}} \int \rho^{4/3}(\vec{r}) d\vec{r} = \frac{3\pi(6\pi)^{2/3}}{N^{2/3}} |K_0[\rho]|$$

have been derived [N is the number of electrons and $\rho(\vec{r})$ is the electron density]. Numerical investigations on these bounds employing Hartree-Fock atomic-electron densities have been carried out. An empirical relationship between the Hartree-Fock T_2 and T_0 for neutral atoms has also been presented.

In a recent paper,[1] the present authors have established that T_2, the first-gradient (or Weizsäckar) correction,[2] viz.,

$$T_2[\rho] = \frac{1}{72} \int \frac{|\vec{\nabla}\rho(\vec{r})|^2}{\rho(\vec{r})} d\vec{r} \qquad (1)$$

to the zeroth-order kinetic-energy functional

$$T_0[\rho] = \frac{3}{10}(3\pi^2)^{2/3} \int \rho^{5/3}(\vec{r}) d\vec{r} \qquad (2)$$

is bounded from below

$$T_2[\rho] \geq \frac{\pi^{4/3} 2^{2/3}}{24} \left[\int \rho^3(\vec{r}) d\vec{r} \delta\right]^{1/3}. \qquad (3)$$

The inequality (3) is valid for *any* given electron density $\rho(\vec{r})$ for a bound-state problem. The derivation of (3) originates from a three-dimensional Sobolev inequality,[3,4]

$$\int |\vec{\nabla}\phi(\vec{r})|^2 d\vec{r} \geq 3 \left[\frac{\pi}{2}\right]^{4/3} \left[\int |\phi(\vec{r})|^6 d\vec{r}\right]^{1/3} \qquad (4)$$

for all $\phi(\vec{r})$ such that $\int |\phi(\vec{r})| d\vec{r}$ exists. The prescription $\phi(\vec{r}) = 2[\rho(\vec{r})]^{1/2}$ leads to the inequality (3) above, connecting T_2 to a gradient-free form.

The spirit of the present work is to establish a relationship between T_0 and T_2 for all well-behaved densities. For this purpose, the Hölder inequality,[5] viz.,

$$\int f(\vec{r})g(\vec{r})d\vec{r} \leq \left[\int |f(\vec{r})|^p d\vec{r}\right]^{1/p}$$

$$\times \left[\int |g(\vec{r})|^q d\vec{r}\right]^{1/q} \qquad (5)$$

(where $p \geq 1$, $1/p + 1/q = 1$, and the required integrals exist) can be employed. Substituting

TABLE I. The ratios $R_1 = T_2 N^{2/3}/T_0$ and $R_2 = C \, |K_2| \, N^{2/3} / |K_0|$ [a] for a few atoms derived from near Hartree-Fock densities.[b]

Atom	R_1	R_2	Atom	R_1	R_2
Li	0.0197	0.499	K	0.0489	0.826
B	0.0291	0.676	Sc	0.0507	0.842
N	0.0366	0.768	V	0.0524	0.847
F	0.0390	0.717	Mn	0.0537	0.847
Na	0.0409	0.753	Ni	0.0550	0.848
Al	0.0431	0.769	Cu	0.0502	0.837
P	0.0452	0.793	Zn	0.0536	0.838
Cl	0.0472	0.808			

[a] $C = 5.5 \times 10^{-3}$, thus $C \, |K_2| \, N^{2/3} \geq 0.367 \, 14 \, |K_0|$.
[b] The near Hartree-Fock densities derived from the tables of Clementi and Roetti, At. Data Nucl. Data Tables **14**, 177 (1974).

$f(\vec{r}) = \rho(\vec{r})$, $g(\vec{r}) = \rho^{2/3}(\vec{r})$, $p = 3$, and $q = \frac{3}{2}$, and using the inequality (5) in conjunction with the inequality (3), one arrives at

$$T_2[\rho] \geq \frac{10}{72} \left[\frac{2}{3} \right]^{2/3} \frac{1}{N^{2/3}} T_0[\rho] = \frac{0.010\,599}{N^{2/3}} T_0[\rho] \; .$$

(6)

N, the total number of electrons $= \int \rho(\vec{r}) \, d\vec{r}$. Likewise, a bound for

$$K_2[\rho] = -\int \frac{|\vec{\nabla}\rho(\vec{r})|^2 d\vec{r}}{\rho^{4/3}(\vec{r})}$$

(apart from a numerical coefficient), the first-gradient correction[6] to the zeroth-order or Slater[7] exchange-energy functional $K_0[\rho] = -(\frac{3}{4})(3/\pi)^{1/3} \times \int \rho^{4/3}(\vec{r}) \, d\vec{r}$, can readily be obtained. This can be accomplished with the substitution $\phi(\vec{r}) = 3[\rho(\vec{r})]^{1/3}$ in the inequality (3) and subsequently with $f(\vec{r}) = g(\vec{r}) = \rho^{2/3}(\vec{r})$, $p = 3$, and $q = \frac{2}{3}$ in the inequality (5). The result is

$$|K_2[\rho]| \geq \frac{3\pi(6\pi)^{2/3}}{N^{2/3}} |K_0[\rho]|$$

$$\equiv \frac{66.7531}{N^{2/3}} |K_0[\rho]| \; .$$

(7)

If the Thomas-Fermi densities are employed and the ratios T_2/T_0 and $|K_2| / |K_0|$ computed, it turns out that both of these ratios are proportional to $N^{-2/3}$ for neutral atoms. A similar dependence on N is exhibited in the inequalities (6) and (7). Further, it is remarkable that the gradient corrections T_2 and $|K_2|$ are bounded from below in terms of the corresponding leading contributions

T_0 and $|K_0|$ themselves.

Numerical investigations for the two lower bounds (6) and (7) have been carried out as displayed in Table I. Note that the bounds are not very tight and that the ratios $T_2 N^{2/3}/T_0$ and $|K_2| \, N^{2/3} / |K_0|$ gradually increase as one proceeds from He through Ni. Then, a slight decrease is exhibited and once again, the ratios continue to increase from Zn onwards.

An empirical investigation on the N dependence of the ratio T_0/T_2 for neutral atoms from He through Zn has also been done. A plot of T_0 vs $T_2 N^{1/3}$ employing Hartree-Fock densities has been depicted in Fig 1. The fit of these quantities is remarkably linear with a correlation coefficient
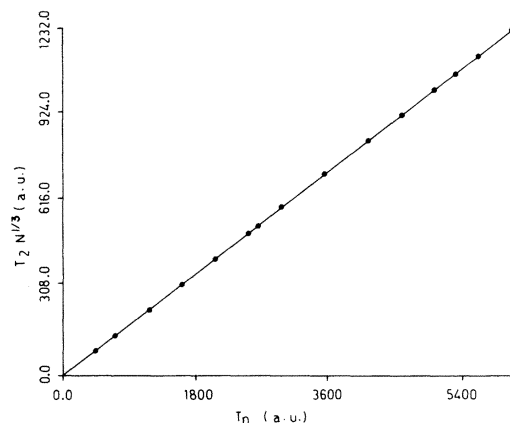

FIG. 1. A graph of $T_2 N^{1/3}$ vs T_0 for neutral atoms using Hartree-Fock densities. All values in atomic units.

0.999 99 from a least-squares analysis, the value of the slope being 0.1795. Thus $T_0 N^{1/3}$ may gainfully be employed as a gradient-free expansion of the Weizsäcker correction. The consequences of this would be worth investigating within the Thomas-Fermi and local-density functional[8] models.

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