

Lower bounds to the Weizsäcker correction

Shridhar R. Gadre and Rajeev K. Pathak

Department of Chemistry, University of Poona, Pune-411 007, India

(Received 2 February 1981)

Two rigorous lower bounds to T_2 , the Weizsäcker correction, have been derived: $T_2 \geq (\pi^{4/3} 2^{2/3} / 24) \times (\int \rho^3(\vec{r}) d\vec{r})^{1/3} = T_2^{B1}[\rho]$ and $T_2 > (1/72) \langle r^{-2} \rangle = T_2^{B2}[\rho]$. The first bound is universal, while the second holds only for spherically symmetric bound systems. Numerical comparisons employing the Hartree-Fock atomic densities reveal that the bounds are not very tight; however, the ratios T_2/T_2^{B1} and T_2/T_2^{B2} , though decreasing slowly with increasing Z , remain fairly constant for $Z = 2$ through 24. The implications of these bounds in the variational context are discussed.

I. INTRODUCTION

Since its introduction, there has been a wide-spread interest in the density-functional (DF) formalism first put forth by Hohenberg and Kohn¹ (hereafter termed HK), which has furnished an approach to treat many-electron systems on a footing that ascribes the electron density ρ a status of a basic variable. Within the DF framework the exact many-particle ground state is a functional of $\rho(\vec{r})$, which in turn can be shown to be a unique functional of the applied external potential $V(\vec{r})$. The total energy, which is the sum of the ingredients

$$E \equiv E[\rho] = T[\rho] + U[\rho] + V[\rho], \tag{1}$$

becomes a functional of ρ . In Eq. (1) the terms represent, respectively, the kinetic energy, the electron-electron interaction energy, and that due to the external potential. $T[\rho]$ and $U[\rho]$ are universal functionals of ρ . Their forms, however, are not known exactly. In particular, from HK (and the references therein) it follows that the kinetic energy functional can be expressed as

$$T[\rho] = T_0[\rho] + T_2[\rho] + T_4[\rho] + \dots \tag{2}$$

The first term is the Thomas-Fermi^{2,3} contribution to the kinetic energy, which forms the major part of $T[\rho]$. The second term is the Weizsäcker or the first inhomogeneity correction.⁴ Employing the Hartree-Fock atomic densities, $T_0[\rho] + T_2[\rho]$ serves as a fairly good approximation to $T[\rho]$, as has been demonstrated from the recent work of Murphy *et al.*⁵ Explicitly written, one has (in hartree units)

$$T_0[\rho] + T_2[\rho] = \frac{3}{10} (3\pi^2)^{2/3} \int \rho^{5/3}(\vec{r}) d\vec{r} + \frac{1}{72} \int \frac{|\vec{\nabla}\rho(\vec{r})|^2}{\rho(\vec{r})} d\vec{r}. \tag{3}$$

(The term T_2 here is $\frac{1}{3}$ th the original Weizsäcker

term.) In the realm of the variational technique, the approximation $T[\rho] \approx T_0[\rho]$ leads to Thomas-Fermi or Thomas-Fermi-Dirac and related theories,⁶ wherein the value of the density at the nucleus $\rho(0)$ is infinite and hence unphysical. With the inclusion of T_2 , $\rho(0)$ becomes finite and the total energies for atomic systems are estimated fairly accurately, unlike the overestimated ones from the Thomas-Fermi and related theories. The cusp condition⁷ is well obeyed upon the incorporation of T_2 . Following the earlier work of Goodisman,⁸ recently Parr *et al.*⁹ have advocated that the full Weizsäcker correction (i.e., 9 times the present T_2) should be taken, whereas the coefficient appearing in the expression for T_0 should be replaced by some other constant which they have reported from their studies of atomic systems.

The above remarks make it evident that the inclusion of the Weizsäcker term serves far more than merely a "correction" alone. It is of further interest to note that this correction term is bounded from below, which forms the theme of this paper.

II. BOUNDS TO THE WEIZSÄCKER CORRECTION

A Sobolev inequality,¹⁰ in three dimensions, for any bounded $\phi(\vec{r})$ such that $\int \phi(\vec{r}) d\vec{r}$ is finite, is

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

With the substitution

$$\phi(\vec{r}) = 2[\rho(\vec{r})]^{1/2} \tag{5}$$

one has $\vec{\nabla}\phi(\vec{r}) = \vec{\nabla}\rho(\vec{r})/[\rho(\vec{r})]^{1/2}$, so that from the inequality (4) it turns out that

$$T_2[\rho] = \frac{1}{72} \int \frac{|\vec{\nabla}\rho(\vec{r})|^2}{\rho(\vec{r})} d\vec{r} \geq \frac{\pi^{4/3} 2^{2/3}}{24} \left(\int \rho^3(\vec{r}) d\vec{r}\right)^{1/3} = T_2^{B1}[\rho]. \tag{6}$$

It is noteworthy that the lower bound $T_2^{B1}[\rho]$ appears in a much simpler form compared to T_2 since it (i.e., $T_2^{B1}[\rho]$) is free of the gradients of ρ . Above all, it is also gratifying to note that the inequality (6) does *not* need any special assumptions such as spherical symmetry of ρ and hence, furnishes a universal lower bound to T_2 .

Yet another lower bound to T_2 can be obtained for spherically symmetric densities $\rho(r)$ by virtue of the inequality¹¹

$$J[y] = \int_0^\infty \left[4 \left(\frac{dy(r)}{dr} \right)^2 - \frac{y^2(r)}{r^2} \right] dr > 0 \quad (7)$$

for all $y(r)$ such that $y(0) = 0$. The prescription

$$y(r) = r\sqrt{\rho(r)} \quad (8)$$

is compatible with these conditions and the inequality (7) leads to

$$\int_0^\infty \frac{r^2}{\rho(r)} \left(\frac{d\rho(r)}{dr} \right)^2 dr + 3 \int_0^\infty \rho(r) dr + 4 \int_0^\infty r \frac{d\rho(r)}{dr} dr > 0. \quad (9)$$

A partial integration yields

$$\begin{aligned} \int_0^\infty \rho(r) dr &= \rho(r)r \Big|_0^\infty - \int_0^\infty \rho'(r)r dr \\ &= - \int_0^\infty r \frac{d\rho(r)}{dr} dr, \end{aligned} \quad (10)$$

since the integrated term vanishes for all atomic densities. With Eqs. (9) and (10) one is led to

$$\frac{1}{72} \int_0^\infty \frac{4\pi r^2}{\rho(r)} \left(\frac{d\rho(r)}{dr} \right)^2 dr > \frac{1}{72} \int_0^\infty \rho(r) 4\pi dr = T_2^{B2}[\rho] \quad (11)$$

for all spherically symmetric densities. The quantity on the right-hand side of Eq. (11) is $\frac{1}{72}\langle r^{-2} \rangle$, whereas that on the left-hand side is T_2 . With the use of

$$\frac{16}{15} \langle r^{-1} \rangle^2 < N \langle r^{-2} \rangle, \quad (12)$$

as shown by Gadre¹² for monotonically decreasing densities (N being the total number of electrons), it follows that

$$T_2 > T_2^{B2} = \frac{1}{72} \langle r^{-2} \rangle > \frac{2}{135} \frac{\langle r^{-1} \rangle^2}{N} = \frac{2}{135} \frac{V_{ne}^2}{NZ^2}, \quad (13)$$

V_{ne} being the nuclear-electron attraction. It has been observed¹³ that the Hartree-Fock densities are monotonically decreasing, even though a rigorous proof to this effect is lacking.

Even though one is restricted to spherically symmetric densities, the second bound connects T_2 via an inequality to the major energy ingredient V_{ne} , which is an interesting feature in itself. In

the next section the two bounds $T_2^{B1}[\rho]$ and $T_2^{B2}[\rho]$ will be investigated for tightness.

III. NUMERICAL TESTS AND DISCUSSION

For an initial orientation the tightness of these bounds has been tested for simple density profiles, viz., the Slater-type orbitals (STO), the Gaussian-type orbitals (GTO), and $\rho(r) = \exp(-\alpha\sqrt{r})$. The results have been reported in Table I, from which it is clear that with the profiles used, the first bound is fairly tight whereas the second one is not as tight. In the Hartree-Fock context, both bounds $T_2^{B1}[\rho]$ and $T_2^{B2}[\rho]$ are valid since the Hartree-Fock densities are known to be monotonically decreasing. When applied to atomic systems it turns out that both the bounds are not very tight. However, the ratios $T_2[\rho]/T_2^{B1}[\rho]$ and $T_2[\rho]/T_2^{B2}[\rho]$ remain fairly constant for the Hartree-Fock atomic densities although they decrease slowly with increasing Z . For elements He through Ne the average ratios are 2.59 and 1.84, respectively, with a maximum mean deviation of 4%. For elements Na through Ar they are 2.50 and 1.71, respectively, with a maximum mean deviation of about 2%. Table II displays the ratios for $Z=2$ through 22 for a comparison. It may be noted from Table II that the bound $T_2^{B2}[\rho]$ is much tighter than $T_2^{B1}[\rho]$ for spherically averaged Hartree-Fock densities.

It would be worthwhile to investigate the consequences of the constancy of ratios T_2/T_2^{B1} and T_2/T_2^{B2} in the variational context. It may be stipulated here that if $T_2[\rho]$ is replaced by $(\text{const})T_2^{B1}[\rho]$ or by $(\text{const})T_2^{B2}[\rho]$ and the variational technique applied (the constants chosen appropriately for the first and the second row atoms), one is assured of obtaining good estimates for the total energy without having to compute $\vec{\nabla}[\rho(\vec{r})]$ at all. For molecular systems, of course only $T_2^{B1}[\rho]$ would be appropriate, and Balázs theorem¹⁴ [which states that "when the electrostatic potential at a point is a function (*not* functional) of ρ , molecules cannot be stable"] does not deny the possibility of obtaining good estimates of total energies with the replacement $T_2[\rho] \rightarrow (\text{const})T_2^{B1}[\rho]$ and the variational technique employed. Strictly speaking, however, it would be apt to employ an upper bound in a

TABLE I. The ratios $T_2[\rho]/T_2^{B1}[\rho]$ and $T_2[\rho]/T_2^{B2}[\rho]$ for some model densities. See text (Sec. III) for details.

Density	Ratio	$\frac{T_2[\rho]}{T_2^{B1}[\rho]}$	$\frac{T_2[\rho]}{T_2^{B2}[\rho]}$
$\exp(-\alpha r)$		1.175	2
$\exp(-\alpha r^2)$		1.183	3
$\exp(-\alpha\sqrt{r})$		1.072	1.5

TABLE II. The ratios T_2/T_2^{B1} and T_2/T_2^{B2} employing the Hartree-Fock densities for atoms [see the text (Sec. III) for further details].

Atom	T_2/T_2^{B1}	T_2/T_2^{B2}
He	2.659	1.909
Li	2.644	1.902
Be	2.634	1.897
B	2.607	1.871
C	2.581	1.841
N	2.559	1.812
O	2.540	1.789
F	2.525	1.767
Ne	2.515	1.763
Na	2.507	1.735
Mg	2.503	1.725
Al	2.498	1.717
Si	2.495	1.710
P	2.492	1.703
S	2.488	1.696
Cl	2.486	1.690
Ar	2.484	1.684
K	2.481	1.679
Ca	2.479	1.675
Sc	2.476	1.669

variational principle, but a simple form for an upper bound to T_2 is hard to find.

Of special interest is a recent model developed by Parr and co-workers¹⁵ wherein local functionals have been employed for the energy ingredients. It is noteworthy that their $E[\rho]$ is *not* a rigorous upper bound to the true energy functional. With a proper choice of the parameters, however, this model yields reasonable energies for atomic systems. With simpler forms for T_2 offered by the two bounds when utilized in conjunction with the

work of Ref. (9), the energy functional would assume simple forms

$$E[\rho] = A \int \rho^{5/3}(\vec{r}) d\vec{r} + B \left(\int \rho^3(\vec{r}) d\vec{r} \right)^{1/3} + C \left(\int \rho^{4/3}(\vec{r}) d\vec{r} \right) N^{2/3} - \sum_{\alpha} Z_{\alpha} \int \frac{\rho(\vec{r})}{|\vec{r} - \vec{r}_{\alpha}|} d\vec{r} + V_{nn} \quad (14)$$

for molecular systems and

$$E[\rho] = A' \int \rho^{5/3} 4\pi r^2 dr + B' \int 4\pi \rho(r) dr + C' \left(\int \rho^{4/3}(r) 4\pi r^2 dr \right) N^{2/3} - Z \int 4\pi r \rho(r) dr \quad (15)$$

for spherically symmetric densities; A, B, C and A', B', C' being the appropriately chosen constants. The $E[\rho]$ in Eqs. (14) and (15) do *not* provide rigorous upper bounds to the true energy. In light of the work of Parr *et al.*¹⁵ it may, however, be anticipated that reasonable energies (for example, compared to their Hartree-Fock counterparts) can be obtained from Eqs. (14) and (15) with an appropriate choice of parameters. The variational technique can be subsequently applied to obtain decent and rather quick estimates of the total energy. All these investigations are being done.

ACKNOWLEDGMENTS

One of the authors (S.R.G.) is grateful to Dr. Danny R. Murphy for providing him with a copy of his computer program to evaluate various integrals involved in this work. We thank the University Grants Commission, New Delhi for a grant for computer time and financial support to one of us (R.K.P.).

¹P. Hohenberg and W. Kohn, Phys. Rev. 136B, 864 (1964).

²L. H. Thomas, Proc. Cambridge Philos. Soc. 23, 542 (1927).

³E. Fermi, Z. Phys. 48, 73 (1928); 49, 550 (1928).

⁴C. F. von Weizsäcker, Z. Phys. 96, 431 (1935).

⁵D. R. Murphy and R. G. Parr, Chem. Phys. Lett. 60, 377 (1979); W.-P. Wang and R. G. Parr, Phys. Rev. A 16, 891 (1977).

⁶P. Gombás, *Die Statistische Theorie des Atoms und Ihre Anwendungen* (Springer, Berlin, 1949).

⁷T. Kato, Commun. Pure Appl. Math. 10, 151 (1957).

⁸J. Goodisman, Phys. Rev. A 1, 1574 (1970).

⁹P. K. Acharya, L. J. Bartolotti, S. B. Sears, and R. G. Parr, Proc. Nat. Acad. Sci. (U.S.A.) (in press).

¹⁰S. L. Sobolev, Math. Sbornik 4, 471 (1938); G. Rosen, SIAM J. Appl. Math. 21, 30 (1971).

¹¹G. H. Hardy, J. E. Littlewood, and G. Polya, *Inequalities* (Cambridge University Press, Cambridge, 1964).

¹²S. R. Gadre, J. Chem. Phys. 71, 1510 (1979).

¹³H. Weinstein, P. Politzer, and S. Srebrenik, Theor. Chim. Acta 38, 159 (1975).

¹⁴N. L. Balázs, Phys. Rev. 156, 42 (1967).

¹⁵R. G. Parr, S. R. Gadre, and L. J. Bartolotti, Proc. Nat. Acad. Sci. (U.S.A.) 76, 2522 (1979).