Brief Reports

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Gradient-free representation of the Weizsäcker term for atoms

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(Received 28 February 1983)

It has been demonstrated that the Weizsäcker inhomogeneity term may be replaced by a gradient-free form for atomic systems. This forms a realization of a previous conjecture made by the authors [Phys. Rev. A 25, 668 (1982)]. In the variational context, numerical computations have been performed with such a representation with the first-row atoms employed as test cases. The resulting energies are seen to match very well with their Hartree-Fock counterparts.

The Weizsäcker term,[1] or the first inhomogeneity term in the gradient expansion of the kinetic-energy functional $T[\rho]$, namely $T_2[\rho]$, given by

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

is a rather significant correction[2-11] to the zeroth-order or the Thomas-Fermi kinetic-energy functional $T_0[\rho]$:

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

This term, therefore, has retained interest especially within the realm of the density-functional theory of Hohenberg and Kohn[2] (T_2 employed here is actually $\frac{1}{9}$ of the original Weizsäcker term[6]). Further, the present authors have recently derived two rigorous bounds to T_2,[12,13]

$$\begin{aligned}T_2[\rho]&=\frac{1}{72}\int|\vec{\nabla}\rho(\vec{r})|^2d\tau/\rho(\vec{r})\\ &\geqslant\frac{\pi^{4/3}2^{2/3}}{24}\left[\int\rho^3(\vec{r})\,d\tau\right]^{1/3}\\ &\equiv T_2^{B1}[\rho]\geqslant\frac{10}{72}\left[\frac{2}{3}\right]^{2/3}\frac{T_0[\rho]}{N^{2/3}} \ ,\end{aligned} \qquad (3)$$

for any non-negative normalizable density $\rho(\vec{r})$, and

$$T_2[\rho]>\frac{4\pi}{72}\int\rho(r)\,dr\equiv\frac{1}{72}\langle r^{-2}\rangle\equiv T_2^{B2}>\frac{2\langle r^{-1}\rangle^2}{135N} \qquad (4)$$

for any spherically symmetric monotonically decreasing $\rho(\vec{r})\equiv\rho(r)$. Recently, Csavinszky[14] has done an exhaustive numerical analysis of these lower bounds. The spirit underlying the present report is to bring out a simple gradient-free representation of the Weizsäcker inhomogeneity term. For this purpose, the tighter of these lower bounds, T_2^{B2} (from Ref. 12), will be employed. Even though an upper bound is apt for use in a variational context, such a usage is justified on the lines that the ratio T_2/T_2^{B2} is fairly constant for a given row of atoms in the periodic table. Thus, as stipulated by the authors in Ref. (12), the representation of T_2 for spherically symmetric atomic densities in terms of T_2^{B2} would be given by

$$\begin{aligned}T_2[\rho]&=\frac{1}{72}\int_0^\infty\frac{1}{\rho(r)}\left[\frac{d\rho}{dr}\right]^2\\ &\simeq1.840\int_0^\infty4\pi\rho(r)\,dr\equiv T_2'[\rho] \ .\end{aligned} \qquad (5)$$

The number 1.840 is appropriately chosen to be the mean of the (fairly constant[12]) ratios T_2/T_2^{B2} for the first-row atoms in the periodic table. Evidently, $T_2'[\rho]$ scales correctly as the kinetic energy in the sense of Szàsz, Berrios-Pagan, and McGin.[15]

Now, the well-known Thomas-Fermi-Dirac—von Weizsäcker[7] energy functional is

$$E[\rho]=T_0[\rho]+T_2[\rho]+V_C[\rho]+V_{\rm ne}[\rho]+E_x[\rho] \ , \qquad (6)$$

with

$$V_C=\int\int\frac{\rho(\vec{r})\rho(\vec{r}')}{2|\vec{r}-\vec{r}'|}d\tau d\tau' \ ,$$

the Coulomb repulsion energy,

$$V_{\rm ne}=-Z\int\frac{\rho(\vec{r})}{r}d\tau \ ,$$

TABLE I. Total energies for the atoms Li through Ne, within the representations T_2', the exact T_2, compared with their Hartree-Fock counterparts. (See text for further details.)

Atom	$-E'$ Present[a]	$-E$[b]	$-E_{\rm HF}$[c]
Li	7.414	7.61	7.432
Be	14.65	14.98	14.57
B	24.85	25.37	24.53
C	38.27	39.00	37.68
N	55.1	56.1	54.4
O	75.6	76.9	74.8
F	99.9	101.5	99.4
Ne	128.3	130.2	128.5

[a]See Eqs. (7) and (8).
[b]See Eqs. (6) and (8).
[c]Hartree-Fock energies, Ref. 21.

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the nuclear-electron attraction energy, and

$$E_x = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\left(\frac{2}{3}\right)^{-1}\alpha\int \rho^{4/3}(\vec{r})d\tau \ ,$$

the exchange energy in the Slater approximation[16] with $\alpha=\frac{2}{3}$ as given by Kohn and Sham.[17] With the prescription (5) that T_2 be replaced by its simpler, gradient-free functional form $T_2'[\rho]$, the total energy functional $E'[\rho]$ emerges as

$$E'[\rho] = T_0[\rho] + T_2'[\rho] + V_C[\rho] + V_{\text{ne}}[\rho] + E_x[\rho] \ . \tag{7}$$

Employing the above total energy functional E', a variational form for the density profile was chosen as[18,19]

$$\rho(r) = A[C_1\exp(-\alpha_1 r) + C_2\exp(-\alpha_2 r)]^3 \ , \tag{8}$$

where the C_i and the α_i are the variation parameters and $A(\alpha_i, C_i)$ is determined by the normalization constraint

$$\int_0^\infty \rho(r)4\pi r^2 dr = N \ , \tag{9}$$

N being the total number of electrons. Substituting Eq. (8) into Eq. (7) one obtains after some algebra

$$\begin{aligned}
E' \equiv E'(\alpha_i, C_i) = {} & \tfrac{12}{5}\pi(3\pi^2)^{2/3}A^{5/3}\sum_{i,j,\ldots,m}\frac{C_iC_jC_kC_lC_m}{(\alpha_i+\alpha_j+\alpha_k+\alpha_l+\alpha_m)^3} \\
& + \frac{1.840}{18}\pi A\sum_{i,j,k}\frac{C_iC_jC_k\alpha_j\alpha_k}{(\alpha_i+\alpha_j+\alpha_k)^3} - 4\pi AZ\sum_{i,j,k}\frac{C_iC_jC_k}{(\alpha_i+\alpha_j+\alpha_k)^2} \\
& + 16\pi^2A^2\sum_{i,j,\ldots,n}C_iC_jC_kC_lC_mC_n\frac{1}{(\alpha_i+\alpha_j+\alpha_k+\alpha_l+\alpha_m)^3} \\
& \times\left[\frac{1}{(\alpha_l+\alpha_m+\alpha_n)^2} + \frac{1}{(\alpha_i+\alpha_j+\alpha_k)^2} + 3\frac{1}{(\alpha_l+\alpha_m+\alpha_n)}\frac{1}{(\alpha_i+\alpha_j+\alpha_k)}\right] \\
& - 6\alpha\pi A^{4/3}\left(\frac{3}{\pi}\right)^{1/3}\sum_{i,j,k,l}\frac{C_iC_jC_kC_l}{(\alpha_i+\alpha_j+\alpha_k+\alpha_l)^3} \ ,
\end{aligned} \tag{10}$$

where

$$A = \left(\frac{8\pi}{Z}\sum_{i,j,k}\frac{C_iC_jC_k}{(\alpha_i+\alpha_j+\alpha_k)^3}\right)^{-1} \ . \tag{11}$$

For comparison, the functional E of Eq. (6) incorporating the exact T_2 in conjunction with the form (7) was also evaluated independently. Both these computations were carried out employing a versatile minimization routine STEPIT.[20] Table I displays the results for the total energies E' and E for the first-row atoms ($Z=3-10$). It is to be noted that the values E' (with the representation T_2') match fairly well with their corresponding E values; employing the correct T_2, both these (E and E'), in turn, agree with the exact Hartree-Fock (HF) energies. The mean deviation between E' and E_{HF} values is merely 0.7%.

Incidentally, it must be remarked that the present scheme allows only a description of atomic systems. The theorem due to Balàzs[10] rules out the existence of stable molecules if the replacement $T_2 \rightarrow T_2'$ is made. However, as inferred from Table I such replacements indeed yield decent estimates for atomic systems while they simplify computations, for the total atomic energies. The present computation for the first-row atoms is purely illustrative; one could proceed for the second and third rows using appropriate constants.[12] Thus, the conjecture expressed in Ref. (12) has been verified to be true.

One of the authors (R.K.P.) wishes to express his indebtedness to Professor R. G. Parr for his encouragement and support in the form of a fellowship at the University of North Carolina at Chapel Hill. This research was aided in part by the National Institutes of Health.

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