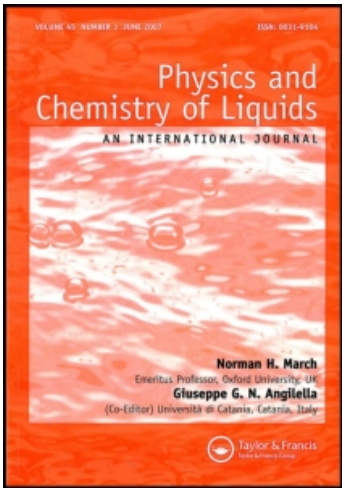

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Letter

HOMOGENEITY PROPERTIES OF PAULI ENERGY IN DENSITY FUNCTIONAL THEORY OF AN ELECTRON LIQUID

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In a recent paper of the authors the homogeneity properties of the kinetic energy functional have been studied prompted by the work of Parr and Liu. This then motivates a similar study of the Pauli energy. A new expression for the electron density is derived.

Keywords: Inhomogeneous electron liquid; Pauli energy; Legendre transform

It has recently been demonstrated [1] that the functional derivative $\delta T/\delta\varrho(\mathbf{r})$ of the kinetic energy T with respect to the electron density $\varrho(\mathbf{r})$ takes the form for the self-consistent Thomas-Fermi (TF) atom

$$\frac{\delta T}{\delta\varrho(\mathbf{r})} = \frac{5}{3}c_k l^2 \left[\frac{\nabla^2\varrho}{\varrho} - \frac{1}{3}\left(\frac{\nabla\varrho}{\varrho}\right)^2\right]^2, \tag{1}$$

where $c_k = (3h^2/10m)(3/8\pi)^{2/3}$ and $l = (1/4)(\pi/3)^{1/3}a_0$; $a_0 = \hbar^2/me^2$.

The purpose of the study of Nagy and March [2] was to discuss, motivated by Eq. (1) and the treatment of its homogeneity properties

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by Parr and Liu [3], more generally the kinetic energy in the above context. Now, a similar study follows for the Pauli energy.

The total non-interacting kinetic energy can be separated into two terms:

$$T = T_w + T_p, \tag{2}$$

where the T_w is the full Weizsäcker kinetic energy [4]

$$T_w = \frac{1}{8}\int \frac{|\nabla \varrho|^2}{\varrho} d\mathbf{r} \tag{3}$$

and the term T_p is called the Pauli energy [5]. The functional derivatives are

$$\frac{\delta T_w}{\delta \varrho} = \frac{1}{8}\left|\frac{\nabla \varrho}{\varrho}\right|^2 - \frac{1}{4}\frac{\nabla^2 \varrho}{\varrho} = \varrho^{-1/2}\left(-\frac{1}{2}\nabla^2\right)\varrho^{1/2} \tag{4}$$

and

$$v_p = \frac{\delta T_p}{\delta \varrho}. \tag{5}$$

It can be easily seen [3] that the Weizsäcker kinetic energy fulfils the Liu–Parr relation:

$$T = \int \varrho(\mathbf{r}) \frac{\delta T}{\delta \varrho(\mathbf{r})} d\mathbf{r}. \tag{6}$$

The Pauli potential can be written as [5]

$$v_p = \frac{t_p}{\varrho} + \frac{1}{\varrho}\sum_i f_i(\varepsilon_M - \varepsilon_i)\varrho_i, \tag{7}$$

where t_p, ε_i, f_i and ϱ_i are the Pauli kinetic energy density, the orbital energies, the occupation numbers and orbital energy densities, respectively. (Double occupation is assumed: $M = N/2$.)

Inserting Eq. (7) into the left hand side of Eq. (6) one can readily obtain

$$\int \varrho(\mathbf{r}) v_p(\mathbf{r}) d\mathbf{r} = T_p + \sum_i f_i(\varepsilon_M - \varepsilon_i), \tag{8}$$

or

$$\int \varrho(\mathbf{r}) v_p(\mathbf{r}) d\mathbf{r} = T_p + \mathrm{N}(\varepsilon_M - \bar{\varepsilon}), \tag{9}$$

where

$$\bar{\varepsilon} = \frac{\sum_i f_i \varepsilon_i}{\mathrm{N}}. \tag{10}$$

Parr and Liu [6] Emphasize that for any differentiable functional $Q[n]$, one has

$$\frac{\delta G}{\delta \varrho} = \left(\frac{\delta G}{\delta \varrho}\right)_{\mathrm{N}} + \text{constant}, \tag{11}$$

i.e., the functional derivative taken at constant N is different from the general functional derivative considered above. When the general functional derivative is replaced by the functional derivative taken at constant N, then using Eq. (11) with $G = T$ we arrive at the result

$$T = \int \varrho(\mathbf{r}) \left(\frac{\delta T}{\delta \varrho(\mathbf{r})}\right)_{\mathrm{N}} d\mathbf{r} + \mathrm{bN}. \tag{12}$$

Comparing Eqs. (9) and (12) the physical meaning of the constant b can be obtained [6, 2]:

$$\mathrm{b} = \bar{\varepsilon} - \varepsilon_M. \tag{13}$$

Now, we turn to the Euler equation:

$$\frac{\delta T[\varrho]}{\delta \varrho(\mathbf{r})} + v_{\mathrm{KS}}(\mathbf{r}) = \mu, \tag{14}$$

where v_{KS} and μ are the Kohn-Sham potential and the chemical potential, respectively. The functional Legendre transform of the non-interacting kinetic energy T is defined [7] by

$$Q[\tilde{u}] = T[\varrho] + \int d\mathbf{r} \varrho(\mathbf{r}) \tilde{u}(\mathbf{r}), \tag{15}$$

where

$$\tilde{u} = v_{\mathrm{KS}} - \mu. \tag{16}$$

The Legendre transform of the total kinetic energy can be again separated into two terms:

$$Q = Q_w + Q_p. \tag{17}$$

As the Weizsäcker kinetic energy fulfils the Liu–Parr relation (6) we can immediately see that

$$Q = Q_p. \tag{18}$$

and

$$Q_w = 0. \tag{19}$$

Equation (18) can also be written as

$$Q_p = T_p - \int \varrho(\mathbf{r}) \frac{\delta T_p}{\delta \varrho(\mathbf{r})} d\mathbf{r} = T_p - \int \varrho(\mathbf{r}) v_p(\mathbf{r}) d\mathbf{r}. \tag{20}$$

Comparing this relation with Eq. (9) we arrive at

$$Q = Q_p = \mathrm{N}(\bar{\varepsilon} - \varepsilon_M). \tag{21}$$

(Observe that the original form of the Liu–Parr relation would lead to the result that $Q_p = 0$.) On the other hand, making use of the relation

$$\frac{\delta Q[\tilde{u}]}{\delta \tilde{u}(\mathbf{r})} = \varrho(\mathbf{r}) \tag{22}$$

that follows from the fact that Q is defined by a Legendre transformation, we obtain

$$\frac{\delta}{\delta \tilde{u}(\mathbf{r})} [\mathrm{N}(\bar{\varepsilon} - \varepsilon_M)] = \varrho(\mathbf{r}). \tag{23}$$

This appears to be an interesting relation giving the density as the functional derivative of the Legendre transform of the Pauli energy that is expressed by an orbital energy difference.

In conclusion, the homogeneity properties of the Pauli energy functional are studied and consequences of the work of Parr and Liu are investigated. A new expression for the electron density is derived.

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