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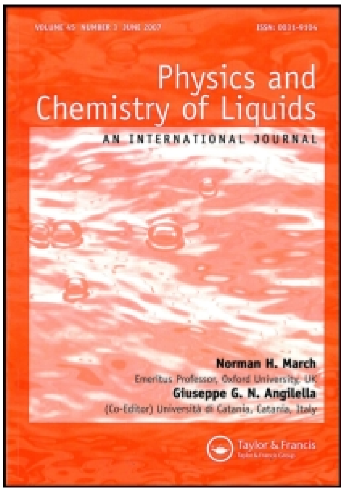

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HOMOGENEITY PROPERTIES OF KINETIC ENERGY IN DENSITY FUNCTIONAL THEORY OF AN INHOMOGENEOUS ELECTRON LIQUID

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The work of Parr and Liu has prompted a further study of the homogeneity properties of the kinetic energy functional of an inhomogeneous electron liquid. The exact results are confirmed by the example of the self-consistent Thomas-Fermi atom.

Keywords: Chemical potential; eigenvalue sum

1. BACKGROUND

One of us [1] has recently demonstrated 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 this investigation is to discuss, motivated by Eq. (1) and the treatment of its homogeneity properties by Parr and Liu [2],

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more generally the kinetic energy in the above context. Parr and Liu [2] showed that both the interacting

$$T = \int \varrho(\mathbf{r}) \frac{\delta T}{\delta \varrho(\mathbf{r})} d\mathbf{r} \tag{2}$$

and the noninteracting

$$T_s = \int \varrho(\mathbf{r}) \frac{\delta T_s}{\delta \varrho(\mathbf{r})} d\mathbf{r} \tag{3}$$

kinetic energy is a functional homogeneous of degree one in density scaling.

These results, however, lead to certain difficulties, as they emphasized in their third paper [3]. Presenting it in somewhat different form, we will study it in the following.

2. HOMOGENEITY PROPERTIES OF KINETIC ENERGY

Using the Kohn-Sham equations

$$\left[-\frac{1}{2}\nabla^2 + v_{KS} \right] \phi_i = \varepsilon_i \phi_i \tag{4}$$

the noninteracting kinetic energy has the form:

$$T_s = E_s - \int \varrho(\mathbf{r}) v_{KS}(\mathbf{r}) d\mathbf{r}, \tag{5}$$

where

$$E_s = \sum_i \varepsilon_i \tag{6}$$

is the eigenvalue sum. Making use of the Euler equation

$$\frac{\delta T_s}{\delta \varrho(\mathbf{r})} + v_{KS}(\mathbf{r}) = \mu \tag{7}$$

we readily obtain

$$T_s = E_s - \mu N + \int \varrho(\mathbf{r}) \frac{\delta T_s}{\delta \varrho(\mathbf{r})} d\mathbf{r}. \tag{8}$$

As the chemical potential μ is not equal to E_s/N there is a contradiction between Eqs. (3) and (8). (For more discussion of the chemical potential see [3].)

In a similar way, we can notice a contradiction between Eqs. (1), (3) and the Thomas-Fermi kinetic expression. It is shown in the Appendix that applying Eq. (1), that is true on the minimum,

$$\int \varrho(\mathbf{r}) \frac{\delta T_{TF}}{\delta \varrho(\mathbf{r})}\bigg|_{\min} d\mathbf{r} = (T_{TF})_{\min}. \tag{9}$$

On the other hand, making use of the well-known Thomas-Fermi expression

$$T_{TF} = c_k \int \varrho(\mathbf{r})^{5/3} d\mathbf{r} \tag{10}$$

and its functional derivative

$$\frac{\delta T_{TF}}{\delta \varrho(\mathbf{r})} = \frac{5}{3} c_k \varrho(\mathbf{r})^{2/3}, \tag{11}$$

we arrive at the result

$$\int \varrho(\mathbf{r}) \frac{\delta T_{TF}}{\delta \varrho(\mathbf{r})} d\mathbf{r} = \frac{5}{3} c_k \int \varrho(\mathbf{r})^{5/3} d\mathbf{r} = \frac{5}{3} T_{TF}, \tag{12}$$

which is again different from Eq. (3). Parr and Liu, in their third paper [3] proposed a way to resolve this contradiction which we are going to discuss in the following and illustrate with the example of the self-consistent Thomas-Fermi atom.

3. KINETIC ENERGY WITH CONSTRAINT

Parr and Liu, in their third paper [3] emphasize that for any differentiable functional $Q[n]$, one has

$$\frac{\delta Q}{\delta \varrho} = \left(\frac{\delta Q}{\delta \varrho}\right)_N + \mathit{constant}, \tag{13}$$

i.e., the functional derivative taken at constant N is different from the general functional derivative considered above. The constant in Eq. (13) is completely arbitrary, which follows from the fact that we can always add a constant to the functional derivative, since $\delta\varrho$ integrates to 0. However, in a particular case, *e.g.*, the noninteracting kinetic energy of a given system, we can ascribe the constant a definite value. (It is analogous to the determination of a constant in the integration of a function.)

Instead of Eq. (3), we take an equation in which the general functional derivative is replaced by the functional derivative taken at constant N. Thus we arrive, using Eq. (13) with $Q = T_s$ at the result

$$T_s = \int \varrho(\mathbf{r}) \left(\frac{\delta T_s}{\delta \varrho(\mathbf{r})} \right)_N d\mathbf{r} + bN. \tag{14}$$

Comparing Eqs. (8) and (14) we obtain the physical meaning of the constant b:

$$b = \bar{\varepsilon} - \mu \tag{15}$$

$$\bar{\varepsilon} = \frac{E_s}{N}. \tag{16}$$

(We mention in passing that the constant b had already implicitly been used in the work of Parr and Liu [3].)

We now return to the self-consistent Thomas-Fermi atom characterized by an electron density satisfying the Euler equation:

$$\left[\frac{\nabla^2 \varrho}{\varrho} - \frac{1}{3} \left(\frac{\nabla \varrho}{\varrho} \right)^2 \right] = \frac{\varrho^{1/3}}{l}. \tag{17}$$

Using again Eq. (13) with $Q = T_{TF}$ one finds, by subsequent multiplication of Eq. (13) by ϱ and integration that for

$$\int \varrho(\mathbf{r}) d\mathbf{r} = N, \tag{18}$$

$$\int \varrho(\mathbf{r}) \frac{\delta T_{TF}}{\delta \varrho(\mathbf{r})} d\mathbf{r} = \int \varrho(\mathbf{r}) \frac{\delta T_{TF}}{\delta \varrho(\mathbf{r})} \bigg|_N d\mathbf{r} + constant\ N. \tag{19}$$

Hence from Eqs. (10) and (11) we obtain

$$\frac{2}{3}T_{TF} = -b_{TF}N, \tag{20}$$

denoting the constant by b_{TF}. But for the neutral Thomas-Fermi atom under constraint

$$T_{TF} = -E_{TF}, \tag{21}$$

and hence

$$b_{TF}N = \frac{2}{3}E_{TF}. \tag{22}$$

The final step is to use the relation between the eigenvalue sum and the total energy for the Thomas-Fermi atom, first given by March and Plaskett [4]:

$$E_s = \frac{2}{3}E_{TF} \tag{23}$$

and hence

$$b_{TF} = \frac{E_s}{N}. \tag{24}$$

This agrees with Eq. (15).

The constant b in Eqs. (15) and (24) is expressed by Lagrange multiplicators, they are considered to be really constants, so the homogeneity of order one is preserved.

In summary, we have emphasized that the constant b in the Parr-Liu treatment of the kinetic energy functional expressed in terms of the eigenvalue sum and the highest occupied eigenvalue resolves the discrepancy in the Kohn-Sham and Hohenberg-Kohn treatment of the kinetic energy. The result is confirmed by the example of the neutral Thomas-Fermi atom.

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[1] March, N. H. (1997). *Phys. Rev.*, **A56**, 1025.
[2] Liu, S. and Parr, R. G. (1997). *Chem. Phys. Lett.*, **278**, 341.
[3] Parr, R. G. and Liu, S. (1997). *Chem. Phys. Lett.*, **280**, 159.
[4] March, N. H. and Plaskett, J. S. (1956). *Proc. Roy. Soc.*, **A235**, 419.
[5] Baltin, R. (1987). *J. Phys.*, **A20**, 111, who however, restricts his arguments to closure at order ϱ' in 1 dimension.

APPENDIX A. ONE-DIMENSIONAL CASE

In this one-dimensional example, the customary procedure of the calculus of variations [5] allows us to write, with a generalized *TF* (*TFG*) assumption that the kinetic energy t/unit length is a function only of ϱ, ϱ' and ϱ'',

$$\frac{\delta T_{TFG}}{\delta\varrho(x)} = \frac{\partial t_{TFG}}{\partial\varrho} + \sum_{i=1}^{2}(-i)^i \frac{d}{dx}\frac{\partial t_{TFG}}{\partial\varrho^{(i)}}. \tag{25}$$

Motivated by a very recent study of Parr and Liu [2], we multiply of both sides of Eq. (25) by $\varrho(x)$ and integrate from $-\infty$ to ∞. Then, after integration by parts and subject to the vanishing of contributions at the limits one readily finds

$$\int \varrho(x)\frac{\delta T_{TFG}}{\delta\varrho(x)}dx = \int \varrho(x)\frac{\partial t_{TFG}}{\partial\varrho}dx + \sum_{i=1}^{2}\int \varrho^{(i)}\frac{\partial t_{TFG}}{\partial\varrho^{(i)}}dx. \tag{26}$$

Of course, the restriction to just three terms on the RHS of Eq. (26) is explicitly the result of the assumed closure of the kinetic energy density

t at ϱ'' in writing Eq. (25). If we now, again following Parr and Liu [2], require that T is homogeneous in ϱ of degree one, then it is a straightforward matter to recover Eq. (9) for our admittedly limited case of truncation at ϱ''. With the above one-dimensional case as motivation, let us turn to the explicit three-dimensional form of the functional derivative of the noninteracting kinetic energy in the self-consistent Thomas-Fermi atom, already displayed in Eq. (1).

APPENDIX B. THREE-DIMENSIONAL CASE

As the first step, let us construct the 3-dimensional generalization of Eq. (25)

$$\frac{\delta T_{TF}}{\delta \varrho} = \frac{\partial t_{TF}}{\partial \varrho} - \sum_{i=1}^{3} \frac{\partial}{\partial x_i} \frac{\partial t_{TF}}{\partial\left(\frac{\partial \varrho}{\partial x_i}\right)} + \sum_{i=1}^{3} \frac{\partial^2}{\partial x_i^2} \frac{\partial t_{TF}}{\partial\left(\frac{\partial^2 \varrho}{\partial x_i^2}\right)}, \tag{27}$$

and hence

$$\begin{aligned} \int \varrho \frac{\delta T_{TF}}{\delta \varrho} d\mathbf{r} = \int \varrho \frac{\partial t_{TF}}{\partial \varrho} d\mathbf{r} + \sum_{i=1}^{3} \int \frac{\partial t_{TF}}{\partial\left(\frac{\partial \varrho}{\partial x_i}\right)} \frac{\partial \varrho}{\partial x_i} d\mathbf{r} \\ + \sum_{i=1}^{3} \int \frac{\partial t_{TF}}{\partial\left(\frac{\partial^2 \varrho}{\partial x_i^2}\right)} \frac{\partial^2 \varrho}{\partial x_i^2} d\mathbf{r}. \end{aligned} \tag{28}$$

We now assume, consistently with Eq. (9) that in the 3 dimensional case the kinetic energy density $t_{TF}(\mathbf{r})$ is given by

$$t_{TF} = \varrho \left[\frac{\nabla^2 \varrho}{\varrho} - c \left(\frac{\nabla \varrho}{\varrho} \right)^2 \right]^2 : c = 1/3, \tag{29}$$

where use has been of Eq. (1). Hence

$$t_{TF} = \frac{(\nabla^2 \varrho)^2}{\varrho} - 2c \frac{\nabla^2 \varrho (\nabla \varrho)^2}{\varrho^2} + c^2 \frac{(\nabla \varrho)^4}{\varrho^3}. \tag{30}$$

Taking the terms of the right hand side of Eq. (28) in turn, one then finds

$$\int \varrho \frac{\partial t_{TF}}{\partial \varrho} d\mathbf{r} = -\int \frac{(\nabla^2 \varrho)^2}{\varrho} d\mathbf{r} + 4c \int \frac{\nabla^2 \varrho (\nabla \varrho)^2}{\varrho^2} d\mathbf{r} - 3c^2 \int \frac{(\nabla \varrho)^4}{\varrho^3} d\mathbf{r}, \tag{31}$$

$$\sum_{i=1}^{3} \int \frac{\partial t_{TF}}{\partial \left(\frac{\partial \varrho}{\partial x_i}\right)} \frac{\partial \varrho}{\partial x_i} d\mathbf{r} = -\int \left[-4c \frac{\nabla^2 \varrho (\nabla \varrho)^2}{\varrho^2} + 4c^2 \frac{(\nabla \varrho)^4}{\varrho^3} \right] d\mathbf{r}, \tag{32}$$

and

$$\sum_{i=1}^{3} \int \frac{\partial t_{TF}}{\partial \left(\frac{\partial^2 \varrho}{\partial x_i^2}\right)} \frac{\partial^2 \varrho}{\partial x_i^2} d\mathbf{r} = \int \left[2 \frac{(\nabla^2 \varrho)^2}{\varrho} - 2c \frac{\nabla^2 \varrho (\nabla \varrho)^2}{\varrho^2} \right] d\mathbf{r}. \tag{33}$$

Hence returning to Eq. (28) one sums Eqs. (31)–(33) to find

$$\int \varrho \frac{\delta T_{TF}}{\delta \varrho} d\mathbf{r} = -\int \left[\frac{(\nabla^2 \varrho)^2}{\varrho} - 2c \frac{\nabla^2 \varrho (\nabla \varrho)^2}{\varrho^2} + c^2 \int \frac{(\nabla \varrho)^4}{\varrho^3} \right] d\mathbf{r}, \tag{34}$$

which is simply again the Parr-Liu relation (9).

However, while the above argument strongly points to the correctness of the expression (29) for the kinetic energy density $t_{TF}(\mathbf{r})$ of the Thomas-Fermi atom, direct formation of the functional derivative $\delta T_{TF}/\delta \varrho(\mathbf{r})$ leads one to higher partial derivatives, which we have not, to date succeeded in eliminating. We expect that the differentiated Thomas-Fermi Euler equation will have to be used for such elimination.