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LETTER TO THE EDITOR

The kinetic energy density functional for fast-varying densities

Y C Lee[†] and D S Chuu

Department of Electrophysics, National Chiao Tung University, Hsinchu, Taiwan,
Republic of China

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Abstract. The expression of the von Weizsäcker term consisting of the kinetic energy density of an inhomogeneous fermion gas is derived from a variational standpoint when the density varies rapidly. It may provide insight or serve as a starting point for a Kohn–Sham-type self-consistent calculation in density functional theory.

When a system of fermions is under an external potential, the spatial distribution $n(\mathbf{r})$ of particles will be non-uniform. The particle density gradient is particularly important near surfaces, or close to the force centre in the case of an impurity. In the theory of density functional pioneered by Kohn, Hohenberg, Sham (Hohenberg and Kohn 1964, Kohn and Sham 1965) and others (Lundqvist and March 1983), an important quantity is the kinetic energy density $t_s(n(\mathbf{r}))$ as a functional of $n(\mathbf{r})$ under the condition of non-interacting fermions, aside from the additional exchange–correlation energy functional $E_{xc}(n)$ which is usually calculated in the local density approximation (LDA). In situations where the density gradient is large, $t_s(n(\mathbf{r}))$ may actually account for a major part of the total energy density. In turn, this large $t_s(n(\mathbf{r}))$ would play a significant role in determining the distribution function $n(\mathbf{r})$ itself in the context of the Kohn–Hohenberg variational principle (Hohenberg and Kohn 1964). Unlike $E_{xc}(n)$, it is obvious that this $t_s(n)$ cannot be accurately obtained by the LDA under these situations. One then usually resorts to a perturbation expansion in powers of the density gradient (Hohenberg and Kohn 1964). The so-called von Weizsäcker correction (von Weizsäcker 1935) was indeed given in this form (Kirzhnits 1957):

$$t_s(n(\mathbf{r})) = (\hbar^2/m) \left[\frac{3}{10} (3\pi^2 n(\mathbf{r}))^{2/3} + \frac{1}{2} |\nabla n|^2/n^2 \right] \quad (1)$$

in which the coefficient $\frac{1}{2}$ was first obtained by Kirzhnits (1957) for cases of mildly varying densities or small density gradients. The original Thomas–Fermi approximation (Thomas 1927, Fermi 1927) assumes that particle wavefunctions may be replaced locally by plane waves. The von Weizsäcker correction introduces an explicit account of the deviation from plane waves. This correction, whose original derivation was not satisfactory, has preoccupied many scientists (Lieb 1981, 1982, Bamzai and Deb 1981). It is not *a priori* clear whether such an expansion would even exist for cases of large density

[†] Permanent address: Physics Department, SUNY at Buffalo, Amherst, NY 14260, USA.

gradients. It appears as the first term in a gradient expansion for a 'reasonably slowly varying' density, with or without the $\frac{1}{2}$ factor, depending on the type of density variation (Hodges 1973). If one could express the density in the form

$$n(\mathbf{r}) = n_0 + n_1 \cos(qz) \quad (2)$$

with $|n_1| \ll n_0$ and $q \geq \overline{k_F(\mathbf{r})}$, the average local Fermi wavevector, one can show that the total kinetic energy functional $T_s(n)$ is given by

$$T_s(n) = \int d\mathbf{r} n(\mathbf{r}) t_s(n(\mathbf{r})) \quad (3a)$$

$$t_s(n(\mathbf{r})) = (\hbar^2/m) \left[\frac{3}{10} (3\pi^2 n(\mathbf{r}))^{2/3} + \frac{1}{8} |\nabla n|^2/n^2 \right] \quad (3b)$$

where the coefficient is $\frac{1}{8}$ rather than $\frac{1}{2}$. Alonso and Girifalco (1978) derive this $\frac{1}{8}$ -factor correction in a LDA without resorting to a gradient expansion. However, the major source of error in their kinetic energy formula arises from regions of rapidly varying electron density and inaccurate knowledge of the correlation factor involved. Many other works (Tal and Bader 1978, Wang and Parr 1977, Deb and Ghosh 1983, Krivine and Treiner 1979, Herring 1986) have been devoted to the derivation of the correct expression of the von Weizsäcker term; however, no clearly conclusive result can be obtained. One may doubt that for a general $n(\mathbf{r})$ that varies rapidly, the correction term $\frac{1}{8} |\nabla n|^2/n^2$ may not necessarily yield the correct results.

In this Letter we shall derive an expression for $t_s(n(\mathbf{r}))$ for large density gradients from a variational point of view. The reason that we employ the variational approach is that for the cases of large density gradients the perturbational technique is unsuitable. We shall show that for a general $n(\mathbf{r})$ that varies rapidly, equation (3b) is of a much more general validity.

Without loss of generality, suppose the density changes rapidly in the z direction, with its magnitude dropping from maximum to nearly zero within a short distance $\Delta z = 1/q$, where $g \geq \overline{k_F(\mathbf{r})}$, the average being over a local region larger than Δz . For example, in the case of a surface-type discontinuity of a bulk metal, the z direction may be taken to be the direction normal to the surface. For the shells of electrons surrounding an atomic nucleus, the z direction is just the radial direction which is normal to the shells. Of course, densities may also vary along the metallic surface or over each atomic shell, but such variations are generally milder and their contributions are already adequately treated by the $\frac{1}{2} |\nabla n|^2/n^2$ term in equation (1). Hence we shall focus our attention on this sharpest density variation in the z direction. How does such a piling-up of fermions occur? Variationally we try a class of single-particle wavefunctions of the form

$$\Psi_{k_x k_y}(x, y, z) = \frac{\exp(ik_x x) \exp(ik_y y)}{\sqrt{A}} \Phi_0(z) \quad (4)$$

with a fixed but as yet undetermined $\Phi_0(z)$ that is primarily responsible for the fast density variation, i.e. $\Phi_0(z)$ might behave like $\cos(qz)$ over the distance Δz , within which it is real and has no nodes. Again the use of plane waves in the other two directions does not really imply that there is no density change in these directions in the actual case. Rather we have relegated their contributions to equation (1) and, consequently, plane waves along the x and y axes must be assumed to avoid double counting. When particles fill up states with the same $\Phi_0(z)$ but different k_x, k_y , Pauli's principle is satisfied. We certainly do not want particles to occupy other $\Phi_v(z)$ states with faster spatial variation or more wiggle than $\Phi_0(z)$ since they would raise the energy unnecessarily. Mixing $\Phi_0(z)$

with states that vary more slowly in z would serve no useful purpose either, since they would not help in producing the necessary sharp density variations. In other words, if we broaden the class of functions of equation (4) by mixing it with other orthogonal functions that have slower spatial variations and use the mixing coefficients as variational parameters, these coefficients would turn out to be zero upon minimising the resulting energy. The adoption of single-particle wavefunctions rather than correlated many-particle functions is also in conformity with the spirit of the Kohn–Sham self-consistent single-particle equations (Kohn and Sham 1965). Accordingly the density of $\mathbf{r} \equiv (x, y, z)$ is

$$n(\mathbf{r}) = \sum_{k_x, k_y} |\Psi_{k_x, k_y}(\mathbf{r})|^2 = \frac{1}{A} \sum_{k_x, k_y} |\Phi_0(z)|^2 = \frac{N(\Delta z)}{A} |\Phi_0(z)|^2 \quad (5)$$

where

$$N(\Delta z) = \sum_{k_x, k_y} 1$$

is the number of particles within the slab Δz . Their total kinetic energy in the z direction is then

$$\begin{aligned} \langle \text{KE} \rangle_{\Delta z} &= \frac{\hbar^2}{2m} N(\Delta z) \int \left| \frac{\partial}{\partial z} \left(\Phi_0(z) \frac{\exp(ik_x x) \exp(ik_y y)}{\sqrt{A}} \right) \right|^2 d\mathbf{r} \\ &= \frac{\hbar^2}{2m} N(\Delta z) \int \frac{dx dy}{A} \int_{\Delta z} dz \left| \frac{d\Phi_0(z)}{dz} \right|^2 \end{aligned} \quad (6)$$

where A is the cross-sectional area of the slab. Recalling that $\Phi_0(z)$ is assumed to be real, having no nodes, we may express $\Phi_0(z)$ in terms of $n(\mathbf{r})$ by means of equation (5). Thus

$$\begin{aligned} \langle \text{KE} \rangle_{\Delta z} &= \frac{\hbar^2}{2m} N(\Delta z) \int_{\Delta z} dz \left[\frac{\partial}{\partial z} \left(\frac{An(\mathbf{r})}{N(\Delta z)} \right)^{1/2} \right]^2 \\ &= \frac{\hbar^2}{2m} A \int_{\Delta z} dz \left(\frac{1}{2n^{1/2}} \frac{\partial n}{\partial z} \right)^2 \\ &= \frac{\hbar^2}{8m} \int_{\Delta z} d\mathbf{r} \left(\frac{\nabla n(\mathbf{r})}{n(\mathbf{r})} \right)^2 n(\mathbf{r}) \end{aligned} \quad (7)$$

from which we identify the correction term due to a rapid density variation as†

$$\Delta t_s(n(\mathbf{r})) = (\hbar^2/8m) |\nabla n(\mathbf{r})/n(\mathbf{r})|^2. \quad (8)$$

It is noted that while equation (8) reconfirms (3b), no restrictions (Kohn and Vashishta 1983) on the form of equation (2) with $n_1 \ll n_0$ nor on the specific form of $\Phi_0(z)$ have

† More precisely one might add the small contribution from the slower density variation in the other directions to equation (8), which then becomes

$$\Delta t_s(n(\mathbf{r})) = \frac{\hbar^2}{8m(n(\mathbf{r}))^2} \left(\left| \frac{\partial n}{\partial z} \right|^2 + \frac{1}{9} \left| \frac{\partial n}{\partial x} \right|^2 + \frac{1}{9} \left| \frac{\partial n}{\partial y} \right|^2 \right).$$

If the density varies rapidly along all three axes, we just have to rename the direction of this large $\nabla n(\mathbf{r})$ vector as the z axis in that local region and equation (8) will again be valid.

been imposed, i.e. our result of equation (8) is of a much more general validity. One may thus employ equation (8) together with some approximated (such as LDA) form of the exchange–correlation energy functional $E_{xc}(n)$ in the Euler condition that results from the Kohn–Hohenberg variational principle to solve for $n(\mathbf{r})$ directly and possibly analytically. Although in most current applications of the density functional theory the self-consistent set of Kohn–Sham equations that bypasses the necessity of an explicit $t_s(n(\mathbf{r}))$ is solved numerically, one is often faced with such a labyrinth of computational details that renders the physical picture rather obscure. The former approach with our explicit form of $t_s(n(\mathbf{r}))$ may constitute a welcome alternative, or provide at least an approximate initial $n(\mathbf{r})$ to start the self-consistency scheme in the latter approach.

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