

# ON THE SINGLE-PARTICLE KINETIC ENERGY DENSITY FUNCTIONAL IN HYPERSPHERICAL REPRESENTATION

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The properties of hyperspherical representation where the one-body orbitals are expressed in terms of the square root of the electron density,  $\rho(\mathbf{r})$  and the angle functions  $\{\theta_i(\mathbf{r})\}_{i=1,\dots,N-1}$ , (R.F. Nalewajski, P.M. Kozłowski, *Acta Phys. Pol.* A74, 287 (1988)) are discussed, and the expression for the kinetic energy density functional is analyzed. This expression contains the Weizsäcker term plus a correction determined by the angle functions. Taking into account both the limit of only one occupied level and the slowly varying electron density with large  $N$ , it is shown that the kinetic energy density functional interpolates correctly between the known results. Finally, an example of a linear harmonic oscillator is given and the relation between the usual orbital pictures is discussed.

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Density Functional Theory (DFT) has some advantages in the theory of many body systems such as atoms, molecules and the solid state. One of the most important problems in DFT is to derive the single-particle kinetic energy density functional  $T_s[\rho(\mathbf{r})]$  in terms of the electron density  $\rho(\mathbf{r})$  and its lowest derivatives. The simplest and most basic formulation of DFT is embodied in Thomas-Fermi (TF) theory, since the kinetic energy is approximated by that corresponding to a free electron gas *e.g.* a homogeneous system [1]. Construction of an adequate kinetic energy density functional is closely related to the problem of  $N$ -representability, namely, for a given density  $\rho(\mathbf{r})$  with  $\rho(\mathbf{r}) \geq 0$  and  $\int \rho(\mathbf{r})d\mathbf{r} = N$ , is it always possible to find antisymmetric,  $N$ -electron wave function leading to this density? The usual approach is based on construction of a set of orthonormal functions which are continuous, smooth, and extended over all space. This approach has been discussed in the literature by many authors, for example Macke [2], Gilbert

[3], Harriman [4] and Lieb [5]. In terms of these functions, the one-body orbitals are given as the square root of the electron density times a phase factor which particularly depends on the construction, however, the first practical realization has been put forward by Harriman. In this construction, the orbitals are expressed as follows (in one-dimension)

$$\phi_k(x) = \sqrt{\rho(x)/N} \exp(ikh(x)), \quad (1)$$

where

$$h(x) = \frac{2\pi}{N} \int^x \rho(s) ds, \quad (2)$$

and all of which yield the same probability density

$$|\phi_k(x)| = \frac{\rho(x)}{N}. \quad (3)$$

There are two important points in relation to this construction. The first is that Harriman's orbitals lead to approximate expressions for energy functional. This universal functional is strictly valid within the context of the independent particle model and it is not possible to obtain a unique energy functional [6]. The second point is that all one-body orbitals have the same electron density independent of orbital quantum numbers. The purpose of the present paper is to demonstrate, that construction based on hyperspherical representation [7, 8] removes these basic difficulties.

Following Refs [7] and [8], one has the relation between one-body orbitals in terms of the square root of the electron density  $\rho(\mathbf{r})$  and the angle functions  $\{\theta_i(\mathbf{r})\}_{i=1, \dots, N-1}$ , of the hyperspherical function frame (for simplicity we also assume an occupancy of one electron per orbital):

$$\begin{aligned} \phi_1(\mathbf{r}) &= \sqrt{\rho(\mathbf{r})} \sin(\theta_1(\mathbf{r})) \sin(\theta_2(\mathbf{r})) \dots \sin(\theta_{N-1}(\mathbf{r})) = \sqrt{\rho(\mathbf{r})} K_1(\mathbf{r}), \\ \phi_2(\mathbf{r}) &= \sqrt{\rho(\mathbf{r})} \cos(\theta_1(\mathbf{r})) \sin(\theta_2(\mathbf{r})) \dots \sin(\theta_{N-1}(\mathbf{r})) = \sqrt{\rho(\mathbf{r})} K_2(\mathbf{r}), \\ \phi_3(\mathbf{r}) &= \sqrt{\rho(\mathbf{r})} \cos(\theta_2(\mathbf{r})) \dots \sin(\theta_{N-1}(\mathbf{r})) = \sqrt{\rho(\mathbf{r})} K_3(\mathbf{r}), \\ &\vdots \\ \phi_N(\mathbf{r}) &= \sqrt{\rho(\mathbf{r})} \cos(\theta_{N-1}(\mathbf{r})) = \sqrt{\rho(\mathbf{r})} K_N(\mathbf{r}). \end{aligned} \quad (4)$$

Varying the density and the angle functions one can derive the set of Euler-Lagrange equations as has been demonstrated previously [7, 8]. From the solution of these equations the optimal density and the set of angle functions can be determined. According to Eq. (4), the orbital densities are equal to

$$\begin{aligned}
 |\phi_1(\mathbf{r})|^2 &= \rho(\mathbf{r})K_1^2(\mathbf{r}), \\
 |\phi_2(\mathbf{r})|^2 &= \rho(\mathbf{r})K_2^2(\mathbf{r}), \\
 &\vdots \\
 |\phi_N(\mathbf{r})|^2 &= \rho(\mathbf{r})K_N^2(\mathbf{r}).
 \end{aligned} \tag{5}$$

Evidently, in this construction, orbitals have different densities due to angle functions. The second goal of the present work is to demonstrate that the single-particle kinetic energy density functional obtained from this transformation interpolates correctly between known results. Therefore, from this point of view this approach is of some importance for density functional theory.

In this representation the kinetic energy density functional takes the form

$$T_s = -\frac{1}{2} \sum_{n=1}^N \int \phi_n^*(\mathbf{r}) \nabla^2 \phi_n(\mathbf{r}) d\mathbf{r} = T_W + T_\theta, \tag{6}$$

where  $T_W$  is the familiar von Weizsäcker term

$$T_W = \frac{1}{8} \int \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})} d\mathbf{r}, \tag{7}$$

solely determined by the electron density and its gradient. The second contribution  $T_\theta$  is equal to

$$T_\theta = \int \rho(\mathbf{r}) u_\theta(\mathbf{r}) d\mathbf{r}, \tag{8}$$

with the function  $u_\theta(\mathbf{r})$  defined as follows

$$u_\theta(\mathbf{r}) = -\frac{1}{2} \sum_{n=1}^N K_n(\mathbf{r}) \nabla^2 K_n(\mathbf{r}). \tag{9}$$

For one level occupied only, the function  $u_\theta(\mathbf{r})$  becomes identically zero, and Eq. (5) simplifies to  $T_s = T_W$ . The fact that the kinetic energy density functional could be expressed as in Eq. (6) has been discussed by many authors in the literature, for example by Herring and co-workers [9, 10]. The mean kinetic energy is never less than the Weizsäcker energy,  $T_W$ , calculated from the mean particle density and,  $T_\theta > 0$ . On the other hand, it is very reasonable to consider that the exact kinetic energy density functional can be written as a sum of the Weizsäcker term, which is the local contribution to the kinetic energy plus a correction which involves nonlocal contributions arising from the Fermi and Coulomb holes. From this point of view our approach is fully consistent with the general consideration.

Next, let us consider that  $N$  electrons are moving in a one-body effective potential  $V(\mathbf{r})$  which includes the relevant exchange and correlation terms. For a given potential  $V(\mathbf{r})$  the minimum principle of  $E[\rho(\mathbf{r})]$  subject to

$$\int \rho(\mathbf{r}) d\mathbf{r} = N, \tag{10}$$

leads to the Euler equation

$$\frac{1}{8} \left( \frac{\nabla \rho(\mathbf{r})}{\rho(\mathbf{r})} \right)^2 - \frac{1}{4} \frac{\nabla^2 \rho(\mathbf{r})}{\rho(\mathbf{r})} + \frac{\delta T_\theta}{\delta \rho(\mathbf{r})} = \mu - V(\mathbf{r}), \quad (11)$$

where the Lagrange multiplier  $\mu$  is the chemical potential. If the electron density is considered to be slowly varying in the spirit of semiclassical theory, we may neglect it in the Euler equation derivatives of the electron density

$$\frac{\delta T_\theta}{\delta \rho(\mathbf{r})} \approx \mu - V(\mathbf{r}). \quad (12)$$

Comparing right hand side of Eq. (12) with the usual semiclassical relation between density  $\rho(\mathbf{r})$  and potential  $V(\mathbf{r})$  (see, for example [1])

$$\rho(\mathbf{r}) = \frac{8\pi}{3h^2} (2m)^{\frac{2}{3}} (\mu - V(\mathbf{r}))^{\frac{2}{3}}, \quad (13)$$

one obtains the result for large  $N$

$$\frac{\delta T_\theta}{\delta \rho(\mathbf{r})} \approx \text{const } \rho^{\frac{2}{3}}(\mathbf{r}). \quad (14)$$

The above relation is fulfilled if the function  $u_\theta(\mathbf{r})$  has the form

$$u_\theta(\mathbf{r}) = c_k \rho^{\frac{2}{3}}(\mathbf{r}). \quad (15)$$

It should be also noted that similar analysis in one-dimension gives  $u_\theta(x) = c'_k \rho^2(x)$ . As we intuitively expect, for large  $N$  the Thomas-Fermi theory comes into its own and the Thomas-Fermi term becomes a simple correction to the Weizsäcker energy.

$$T_s = \frac{1}{8} \int \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})} d\mathbf{r} + c_k \int \rho^{\frac{5}{3}}(\mathbf{r}) d\mathbf{r}. \quad (16)$$

The nature of the nonlocal contribution has also been analyzed by many authors in the literature. In the context of a plane-wave approximation, Ludeña has demonstrated that an explicit expression for the nonlocal term leads to the Thomas-Fermi energy [11], similar to the hyperspherical representation.

Let us illustrate this somewhat formal result by the example of a linear harmonic oscillator. For only two-levels occupied the density is

$$\rho(x) = \pi^{-\frac{1}{2}} \exp(-x^2)(1 + 2x^2). \quad (17)$$

In terms of this density and angle function the first and second orbitals become,

$$\begin{aligned} \psi_0(x) &= \sqrt{\rho(x)} \sin(\theta(x)), \\ \psi_1(x) &= \sqrt{\rho(x)} \cos(\theta(x)), \end{aligned} \quad (18)$$

with the angle function

$$\theta(x) = \arcsin \left( \frac{1}{\sqrt{1 + 2x^2}} \right). \quad (19)$$

It should be pointed out that the above phase is solely determined by the density and its first derivative as the solution of the following differential equation [12].

$$\theta'' + \frac{\rho'}{\rho} \theta' = 2\xi \sin(2\theta); \quad \xi = (\epsilon_1 - \epsilon_2)/2. \quad (20)$$

The above transformation can be performed for an arbitrary number of levels recovering the appropriate angle functions. However, for this particular model the expression for single-particle kinetic energy is known for an arbitrary number of levels [12, 13],

$$T_s = \int t_s(x) dx, \quad (21)$$

with

$$t_s = \frac{1}{8} \frac{(\rho')^2}{\rho} + \frac{1}{2} \int \frac{(\rho')^3}{\rho^5} dy, \quad (22)$$

and, as we demonstrated previously, this equation contains as limit both the Weizsäcker form for  $N = 1$  and the Thomas-Fermi limit as  $N \rightarrow \infty$  [12]. Of course, the above relations hold only for a particular harmonic oscillator model which is known to be local [14]. For the general atomic or molecular case, the similar relations are more complicated and nonlocal.

The main object of this paper was to demonstrate that the hyperspherical approach gives a very reasonable representation of the kinetic energy density functional. This functional behaves correctly between the known limiting results. However, in order to describe any atomic or molecular system in terms of the electron density we have to solve a set of nonlinear differential equations presumably in a self-consistent scheme [7, 8]. This formulation is very parallel to the standard Schroedinger formulation, where in order to obtain an optimal set of one-body orbitals we have to solve a set of Hartree-Fock equations. This similarity is even more explicit in the example of the harmonic oscillator model, which can be alternatively formulated in terms of the density.

Finally, it would be worthwhile to obtain a practical scheme for the determination of the set of angle functions in the hyperspherical representation discussed in the present paper. We believe that the present approach can find several applications in density functional theory, for example the properties of the Pauli potential [7, 8, 15].

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