The impossibility of expanding the square root of the electron density as a linear combination of elements of a complete set of basis functions

Omololu Akin-Ojo

*ICTP East African Institute for Fundamental Research, University of Rwanda, Kigali, Rwanda and Department of Physics, University of Ibadan, Ibadan, Nigeria*

(Dated: April 3, 2018)

In orbital-free density functional theory (OFDFT), an equation exists for \( \psi = \sqrt{n} \), the square root of the ground state electron density \( n \). We show that \( \psi \) cannot be expanded as a linear combination of elements of a complete set of basis functions except in the case of one or two electron systems. This is unlike the case for the ground state of a system of identical bosons in which the square root of the ground state bosonic density can have an expansion as a linear combination of elements of a complete set of basis functions.
I. INTRODUCTION

The original density functional theory (DFT), which is orbital-free DFT (OFDFT), expresses all functionals in terms of the electron ground state density. This is in contrast to the popular version of DFT, Kohn-Sham DFT (KSDFT), in which the kinetic energy density functional is written in terms of one-electron orbitals. Research is ongoing to discover an accurate kinetic energy density functional (KEDF) given only in terms of the ground state density \( n \) of the system. In this work, it is shown that another issue that should be considered seriously in OFDFT research is the proper mathematical representation of the square root of the density.

OFDFT writes the total energy of the system \( E \) as a functional of the density \( n \):

\[
E[n] = T[n] + W[n]
\]  

where \( T \) is the kinetic energy density functional and \( W \) is the total potential energy of the electrons. Optimization of Eq. 1 with respect to the density \( n \), subject to the condition that \( n \) integrates to the total number of electrons \( N \), gives the Euler equation:

\[
\frac{\delta T[n]}{\delta n} + v_{\text{eff}}[n] = \mu,
\]  

where \( v_{\text{eff}} = \delta W/\delta n \) and \( \mu \) is a Lagrange multiplier, which happens to be the chemical potential of the system. Although Eq. 2 can be solved to obtain \( n \), the solutions, however, are not guaranteed to be non-negative everywhere. In order to have non-negative solutions, the optimization is often done with respect to \( \sqrt{n} \) and Eq. 2 is written in the form:

\[
\left[ \frac{\delta T[n]}{\delta n} + v_{\text{eff}}[n] \right] \sqrt{n} = \mu \sqrt{n},
\]  

from which, after solving for \( \sqrt{n} \), the density \( n = (\sqrt{n})^2 \) is easily obtained.

In another vein, one can simply go the route of Ref. 1 who showed that the exact ground state density satisfies the equation:

\[
-\frac{\hbar^2}{2m} \nabla^2 + u_s(r) \sqrt{n} = \mu \sqrt{n}
\]  

in which \( m \) is the electron mass. Expressions for the effective potential \( u_s \) are given in the same paper. Perhaps, because Eqs. 2 and 4 appear similar to single-particle Schrödinger
equations, they are often solved by expanding $\psi = \sqrt{n}$ as a linear combination of elements of a complete basis set of functions, $\{g_k\}$, i.e.,

$$\psi = \sqrt{n} = \sum_\alpha d_\alpha g_\alpha(r)$$  \hspace{1cm} (5)

where, the coefficients $d_k$ are simply scalars.

Because of the difficulty in obtaining an accurate KEDF or, equivalently, an accurate effective potential $u_s$, Kohn and Sham replaced the kinetic energy of the many-electron system with that of a non-interacting system and wrote the latter in terms of single-particle orbitals $\phi_i$. This led to the Kohn-Sham equations:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + v_{\text{eff}}(r)\right] \phi_i = \epsilon_i \phi_i.$$  \hspace{1cm} (6)

In terms of the orbitals, the ground state electron density is given as: $n = \sum^{\text{occ}}_i |\phi_i|^2$, where the sum is over occupied electron states. Since $v_{\text{eff}}(r)$ is real, the orbitals can also be chosen to be real. Now, each orbital $\phi_i$ can be written as a linear combination of elements of a complete basis set of functions, $\{g_k\}$, i.e.,

$$\phi_i = \sum_\alpha c^{(i)}_\alpha g_\alpha(r)$$  \hspace{1cm} (7)

Consequently, the electron density $n$ becomes:

$$n = \sum_{i}^{\text{occ}} |\phi_i|^2 = \sum_{i}^{\text{occ}} \sum_\alpha \sum_\beta c^{(i)}_\alpha c^{(i)}_\beta g_\alpha(r)g_\beta(r)$$  \hspace{1cm} (8)

$$= \sum_\alpha \sum_\beta \left(\sum_{i}^{\text{occ}} c^{(i)}_\alpha c^{(i)}_\beta\right) g_\alpha(r)g_\beta(r)$$  \hspace{1cm} (9)

At the same time, we obtain from Eq. (5)

$$n = \psi^2 = \sum_\alpha \sum_\beta d_\alpha d_\beta g_\alpha(r)g_\beta(r)$$  \hspace{1cm} (10)

Comparing Equations (9) and (10) one concludes that:

$$d_\alpha d_\beta = \sum_{i}^{\text{occ}} c^{(i)}_\alpha c^{(i)}_\beta$$  \hspace{1cm} (11)

from which one can get:

$$d_\alpha^2 = (d_\alpha d_\alpha) = \sum_{i}^{\text{occ}} c^{(i)}_\alpha c^{(i)}_\alpha = \sum_{i}^{\text{occ}} (c^{(i)}_\alpha)^2$$  \hspace{1cm} (12)
and:
\[(d_\alpha d_\beta)^2 = \left( \sum_{i=1}^{\text{occ}} c^{(i)}_\alpha c^{(i)}_\beta \right)^2 \]  \hspace{1cm} (13)

Application of the Cauchy-Schwartz inequality gives:
\[(d_\alpha d_\beta)^2 = \left( \sum_{i=1}^{\text{occ}} c^{(i)}_\alpha c^{(i)}_\beta \right)^2 \leq \sum_{i=1}^{\text{occ}} (c^{(i)}_\alpha)^2 \sum_{i=1}^{\text{occ}} (c^{(i)}_\beta)^2 = d^2_\alpha d^2_\beta \]  \hspace{1cm} (14)

The equality holds if and only if, for given \(\alpha\) and \(\beta\), \(c^{(i)}_\alpha = \text{Constant} \times c^{(i)}_\beta\) for each orbital \(\phi_i\). This only occurs for a bosonic system (in which all the particles are in the same state). It also occurs if there is only one term in the sum, i.e., for a single-electron system (or two-electron system in which the two electrons are in the same spatial orbital state but different spin states – “spin up and spin down” / singlet spin state).

Expression (14) is the main result of this work which establishes that \((d_\alpha d_\beta)^2 < d^2_\alpha d^2_\beta\) for all systems with identical particles, except those enumerated above. This contradiction implies that the square root of the electron density cannot be written as a linear combination of elements of a complete set of basis functions, except for one- or two-electron systems. This may explain why attempts to solve Eq. 3 or 4 by linear expansions of \(\psi = \sqrt{n}\) often leads to difficulties in convergence of the iterative self consistent field approach typically used for DFT calculations. Attempts to minimize the energy functional Eq. 1 directly with respect to \(\psi\), the square root of the density, are also bound to be unsuccessful if \(\psi\) is expanded as a linear combination of elements of a complete set of basis functions whose coefficients are the variables of the optimization procedure. However, the use of other non-expansion methods, such as the finite-difference method can succeed. This work does not imply that no solution of Eq. 4 can be found but that such solutions will not correspond to the ground state density (of non-interacting electrons) in the general case if \(\psi\) is expanded as a linear combination of elements of a complete set of basis functions.

II. CONCLUSIONS

This work shows that the square root of the electron density cannot be expanded as a linear combination of elements of a complete set of basis functions except in the case of one or two electron systems.
1 M. Levy, J. P. Perdew, and V. Sahni, Phys. Rev. A 30, 2745 (1984).
2 W. Kohn and L. J. Sham, Phys. Rev. 140, 1133 (1965).
3 G. K.-L. Chan, A. J. Cohen, and N. C. Handy, J. Chem. Phys. 114, 1063 (2001).
4 V. Karasiev and S. Trickey, Computer Physics Communications 183, 2519 (2012).