Scaling analysis of a physics-guided kinetic energy density expansion

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Abstract. An approach guided by physical consistency in determining the general forms of $D$-dimensional kinetic energy density functionals (KEDF) has been demonstrated previously, producing an expansion which contains the majority of the known one-point KEDF forms. It is known that any noninteracting KEDF shall necessarily have a homogeneity degree of 2 in coordinate scaling. This paper demonstrates that this condition is already satisfied in the general expansion despite not being conceived with the scaling as a constraint.

1. Introduction

One of the most commonly used and relatively efficient computational approaches that exist today for calculations related to quantum chemistry is density-functional theory (DFT) [1–4]. It was first put on solid theoretical footing by Hohenberg and Kohn in their seminal paper [1], which stated that the total energy of any electronic system can be calculated as a functional of the system’s electron density $\rho(x)$. Thus, the ground state can be found by minimizing the total energy. In that paper [1], Hohenberg and Kohn introduced a universal energy density functional $F[\rho(x)]$ composed of the sum of the kinetic energy density functional (KEDF) $T[\rho(x)]$ and the Hartree energy of the correlated electronic system. While the latter is known as a functional of density, $T[\rho(x)]$ is not known completely yet. Thus, practical implementation of this method was initially difficult due to $F[\rho(x)]$ being unknown. This led Kohn and Sham [3] to develop an alternative method of approximating $F[\rho(x)]$ that allowed $T[\rho(x)]$ to be separated into a non-interacting KEDF and a correction term. This came at the cost of reintroducing orbitals back into the calculations. Numerically, this resulted in reduced computational efficiency as $N D$-dimensional coupled equations should be solved instead of just a $D$-dimensional problem in the Hohenberg-Kohn formulation, where $N$ is the number of electrons in the system and $D$ is the spatial dimension of the problem. An important aspect of the original work of Hohenberg and Kohn was to avoid relying on orbitals and instead use only electron density $\rho(x)$ for their calculations.

There have since been many attempts to return to form and propose expressions for the KEDF that are accurate in terms of their computational ability, but are also free of orbitals
in their arguments [5–7], creating the field commonly known as orbital-free density functional theory (OF-DFT). Many of the proposed KEDF forms are density gradient-based expansions. One such expansion was proposed recently [7] through an axiomatic approach relying on physical constraints, with one of the primary results being:

\[ t(x) \equiv t(\rho(x)) = \sum_{s=0}^{D+1} \sum_{n=0}^{D+1-s} a_{sn} \frac{1}{r_d} \rho^{\frac{1}{2}[(2-s-n)+(1-n)D]}(\nabla \rho \cdot \nabla \rho)^{n/2} \]  

(1)

where \( t(x) \) is the kinetic energy density, \( r_d \) corresponds to the extension of electron density over space, and \( a_{sn} \) are the expansion coefficients.

\[ T[\rho(x)] = \int t(x) \, dx = \int t(\rho(x)) \, dx. \]  

(2)

Multiple approaches for analysis exist when it comes to determining the accuracy and efficacy of a particular KEDF. The most common and straightforward approach is to compare the obtained calculation results with established ones in order to confirm the precision of the KEDF. This is supplemented by theoretical constraints that can be enforced on it, the sources of which typically stem from mathematical or physical reasoning. One of the critical constraints is the fulfilment of proper coordinate scaling, which must be satisfied for physical consistency. Levy and Perdew [8] established a set of inequalities concerning this constraint for \( F[\rho(x)] \) and it’s component functionals. The most relevant inequalities concerning general KEDFs are:

\[ T[\rho_{\gamma}] > \gamma^2 T[\rho] \quad (\gamma < 1), \]

\[ T[\rho_{\gamma}] < \gamma^2 T[\rho] \quad (\gamma > 1), \]

where \( \gamma \) is the scaling factor, and:

\[ \rho_{\gamma}(x) \equiv \gamma^D \rho(\gamma x). \]  

(3)

This is made into an exact equality when limiting ourselves only to the non-interacting KEDF, as is the case with the KED introduced in Eq. (1). The condition then becomes:

\[ T_s[\rho_{\gamma}] = \gamma^2 T_s[\rho], \]  

(4)

which is equivalent to stating that the non-interacting KEDF must be homogeneous of degree 2 in spacial coordinate scaling. The goal of this paper is to confirm that Eq. (1) (and therefore Eq. (2)) satisfies the scaling constraint as it is and without need for additional modification to the elements or range of the expansion.

2. Spatial Scaling Analysis

It is important to clarify that the expected homogeneity in coordinate scaling is unrelated to the spatial dimension \( D \). Therefore, the KEDF should be homogeneous of degree 2 for any \( D \). We will begin by analyzing how \( r_d \) transforms with coordinate scaling, where it explicitly takes the following form:

\[ r_d^2 = \frac{1}{D} \frac{\int \int \rho(x)\rho(x')x \cdot (x - x')\,dx\,dx'}{\left[ \int \rho(x)\,dx \right]^2}. \]  

(5)

Upon using the scaled expression (Eq. (3)) in the above form Eq. (5), the denominator is unchanged, since an integration purely over \( \rho(x) \) will give a physically significant result that cannot be affected by our scaling choice:
\[ \int \gamma^D \rho(\gamma x) dx = \int \rho(\gamma x) d(\gamma x). \] (6)

The numerator will be effected due to the presence of spatial terms that are not simply functions of the electron density:

\[ \int \gamma^D \rho(\gamma x) \gamma^D \rho(\gamma x') x \cdot (x - x') dx dx' = \gamma^{-2} \int \rho(\gamma x) \rho(\gamma x') \gamma x \cdot (\gamma x - \gamma x') d(\gamma x) d(\gamma x'). \] (7)

Combining these two results, it is clear that \( r_d^s \) is homogeneous of degree \(-s\) in coordinate scaling, meaning that the \( 1/r_d^s \) term will contribute a scaling factor of \( \gamma^s \) in the final expression.

In order to examine the validity of the constraint on Eq. (2), it suffices to check the scaling condition on any arbitrary term of the KED expansion. Indeed, the homogeneity of an arbitrary term is expected to be free of any dependence on the summation indices in order for the total sum to be homogeneous in coordinate scaling. Also, the transformation will generate an additional factor of \( \gamma \) for every gradient operator. We now perform the analysis used on \( r_d \) on the KED:

\[
t_{sn}(x) \rightarrow a_{sn} \frac{\gamma^s}{r_d^s} \gamma^{2-s-n+D-nD} \left[ \rho(\gamma x) \right]^{\frac{1}{2}(2-s-n)+(1-n)D} (\gamma^D \nabla \rho(\gamma x) \cdot \gamma^D \nabla \rho(\gamma x))^{n/2},
\] (8)

\[
t_{sn}(x) \rightarrow a_{sn} \frac{\gamma^2 D}{r_d^s} \left[ \rho(\gamma x) \right] \left[ (\nabla \rho(\gamma x) \cdot \nabla \rho(\gamma x))^{n/2} = \gamma^{2+D} t_{sn}(\gamma x). \right.
\] (9)

Therefore, the KED scales as \( 2 + D \) in spatial coordinate scaling, and has no dependence on either of the summation indices. However, the dependence of the homogeneity on the dimension number is critical, as we can observe by applying the condition now to the full KEDF as follows:

\[ T[\rho] \rightarrow \int \gamma^D t(\gamma x) dx = \gamma^2 \int t(\gamma x) d(\gamma x) = \gamma^2 T[\rho], \] (10)

thereby proving that this KEDF expansion form is homogeneous of degree 2 in coordinate scaling, satisfying the necessary constraint that all non-interacting KEDFs must fulfill.

3. Conclusion

It was shown that the KEDF form presented in Eqs. (1) and (2) satisfies the spatial coordinate scaling constraint required of all physically reasonable non-interacting KEDFs. It is worth noting that this gradient-based KEDF expansion was not formulated with the scaling constraint as a prerequisite, and yet satisfied it without any need for modification. Thus, this KEDF shows promise in its accuracy and generality, but it remains to be seen whether or not other constraints can be applied successfully to this form without altering it. These other conditions are being investigated with the requirement that any alterations do not cause the KEDF to violate the spatial scaling constraint.

References

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