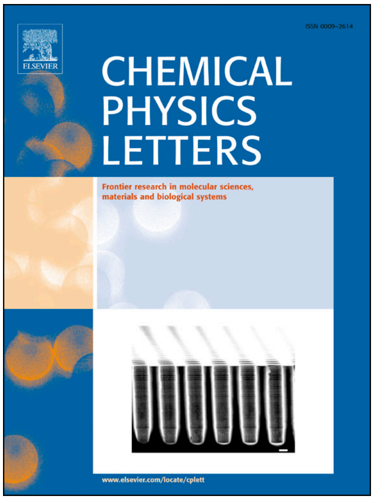

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Trivial Constraints on Orbital-free Kinetic Energy Density Functionals

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Approximate kinetic energy density functionals (KEDFs) are central to orbital-free density functional theory. Limitations on the spatial derivative dependencies of KEDFs have been claimed from differential virial theorems. We identify a central defect in the argument: the relationships are not true for an arbitrary density but hold only for the minimizing density and corresponding chemical potential. Contrary to the claims therefore, the relationships are not constraints and provide no independent information about the spatial derivative dependencies of approximate KEDFs. A simple argument also shows that validity for arbitrary v-representable densities is not restored by appeal to the density-potential bijection.

I. INTRODUCTION

Unarguably the dominant contemporary form of many-electron theory for computing the properties of complicated molecules, clusters, and almost all extended systems is density functional theory (DFT) in its Kohn-Sham (KS) form[1]. Conventionally the KS scheme is used to render the DFT Euler equation in the form of a mean-field orbital eigenvalue problem, the KS equations. Though enormously successful, this approach has the standard computational cost barrier of any eigenvalue problem, namely cubic cost scaling with the number of electrons (or equivalent, the number of basis functions). That motivates long-standing interest in orbital-free DFT (OF-DFT)[2,3], which in principle scales with system size.

OF-DFT, however, introduces the challenge of approximating the KS kinetic energy (KE) as an explicit density functional, e.g.,

$$T_{\rm s}[n] := \int d\mathbf{r}\, t_{\rm s}[n(\mathbf{r})] \ , \tag{1}$$

instead of the familiar orbital-dependent version

$$\begin{aligned} T_{\rm s}[\{\varphi_i\}_{i=1}^{N_e}] &:= \tfrac{1}{2}\sum_{i=1}^{N_e}\int d\mathbf{r}\, |\nabla\varphi_i(\mathbf{r})|^2 \\ &\equiv \int d\mathbf{r}\, t_{\rm s}^{\rm orb}(\mathbf{r}) \end{aligned} \tag{2}$$

in Hartree atomic units. [Remark: In this form the integrand is manifestly positive definite. The more common Laplacian form is not. The difference is a surface integral which ordinarily is zero.] Here N_e is the number of electrons and the ground state number density is

$$n_0(\mathbf{r}) = \sum_i^{N_e} f_i\, |\varphi_i(\mathbf{r})|^2 \, . \tag{3}$$

where the spin-orbital occupation numbers, f_i, at zero temperature are 0 or 1, except for the case of degeneracy at the Fermi level[4].

Orbital-free DFT aims to provide useful approximations to $T_{\rm s}[n]$ without explicit use of the KS orbitals. If one restricts attention to single-point approximations, $t_{\rm s}^{approx}[n(\mathbf{r})]$, a basic issue is the maximum order of spatial derivative dependence to be included. Generalized gradient approximations[5] (GGA) and Laplacian-level functionals[6–9] are the practical limits so far. Various dimensionless spatial derivative combinations (reduced density derivatives) have been proposed[10] but little is known about how to select from among them. An exception would seem to be papers by Baltin[11] and co-workers[12] and others[13,14]. Those use differential virial theorems to derive constraints on the order of spatial derivative that can appear.

Here we show that those relationships are not constraints but trivial identities of complicated form satisfied only by the equilibrium density (i.e. ground-state density) for a given external potential $v_{\rm ext} = \delta E_{\rm ext}/\delta n$.

We begin the next section with the pertinent aspects of the KS Euler equation. Then we rehearse the original arguments from Ref. [11] using the one-dimensional (1D) case presented there. (The three-dimensional case uses identical logic but is more cumbersome, so we do not treat it explicitly.) In the subsequent section, we discuss two related omissions in those arguments which significantly alter the claimed consequences to the point of triviality. We illustrate by reconsidering two cases originally treated in Ref. [11]. Brief consideration to show that a seemingly plausible Hohenberg-Kohn bijectivity argument does not alter the result concludes the presentation.

II. DIFFERENTIAL VIRIAL CONSTRAINT- 1D

A. Euler Equation

The KS decomposition of the universal ground-state total electronic energy density functional is[1]

$$E[n] = T_{\rm s}[n] + E_{\rm ext}[n] + E_{\rm H}[n] + E_{\rm xc}[n] \ , \tag{4}$$

with $T_{\rm s}[n]$ the non-interacting kinetic energy functional as defined above, $E_{\rm ext}[n]$ the external field interaction