



Research paper

Trivial constraints on orbital-free kinetic energy density functionals

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ABSTRACT

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 ν -representable densities is not restored by appeal to the density-potential bijection.

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1. 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.,

$$T_s[n] := \int d\mathbf{r} t_s[n(\mathbf{r})], \quad (1)$$

instead of the familiar orbital-dependent version

$$\begin{aligned} T_s[\{\varphi_i\}_{i=1}^{N_e}] &:= \frac{1}{2} \sum_{i=1}^{N_e} \int d\mathbf{r} |\nabla \varphi_i(\mathbf{r})|^2 \\ &\equiv \int d\mathbf{r} t_s^{\text{orb}}(\mathbf{r}) \end{aligned} \quad (2)$$

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

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

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 $T_s[n]$ without explicit use of the KS orbitals. If one restricts attention to single-point approximations, $t_s^{\text{approx}}[n(\mathbf{r})]$, 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 Balin [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 $v_{\text{ext}} = \delta E_{\text{ext}} / \delta n$.

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].

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Brief consideration to show that a seemingly plausible Hohenberg-Kohn bijectivity argument does not alter the result concludes the presentation.

2. Differential virial constraint-1D

2.1. Euler equation

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

$$E[n] = T_s[n] + E_{\text{ext}}[n] + E_H[n] + E_{\text{xc}}[n], \quad (4)$$

with $T_s[n]$ the non-interacting kinetic energy functional as defined above, $E_{\text{ext}}[n]$ the external field interaction energy, $E_H[n]$ the Hartree energy (classical electron-electron repulsion), and $E_{\text{xc}}[n]$ the exchange-correlation (XC) energy functional. (Remark: any external system configurational energy, e.g., ion-ion repulsion, is omitted as irrelevant here.) Minimization gives a single Euler equation,

$$\frac{\delta T_s[n]}{\delta n(\mathbf{r})} + v_{\text{KS}}([n]; \mathbf{r}) = \mu. \quad (5)$$

Here $v_{\text{KS}} = \delta(E_{\text{ext}} + E_H + E_{\text{xc}})/\delta n$ is the KS potential and μ is the chemical potential such that the minimizing density n_0 yields the correct N_e . Explicit use of the KS KE orbital dependence renders the Euler equation as the familiar KS equation

$$\left\{ -\frac{1}{2} \nabla^2 + v_{\text{KS}}([n]; \mathbf{r}) \right\} \varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r}). \quad (6)$$

2.2. Original differential virial argument

The original argument of Ref. [11] follows in our notation. Consider a 1D system and its KS potential and states. For it the differential virial theorem (Eq. (13) of Ref. [15]) is

$$\frac{dt_s(x)}{dx} = \frac{1}{8} \frac{d^3 n(x)}{dx^3} - \frac{1}{2} n(x) \frac{dv_{\text{KS}}}{dx} \quad (7)$$

or in primed notation as used in Ref. [11],

$$t'_s(x) = \frac{n'''(x)}{8} - \frac{1}{2} n(x) v'_{\text{KS}}(x). \quad (8)$$

(Remark: To get to the Euler equation equivalent to our Eq. (5), Eq. (7) of Ref. [11] writes the supposed equivalent of our Eq. (4) in 1D as

$$E[n] = \int_{-\infty}^{\infty} dx t_s(x) + \int_{-\infty}^{\infty} dx n(x) v_{\text{KS}}(x). \quad (9)$$

This is incorrect since v_{KS} is not solely the external potential but the error is inconsequential for the discussion at hand.)

Ref. [11] then considers a one-point approximation for t_s that depends on spatial derivatives of n through g^{th} order:

$$t_s(x) := f(n, n', n'', n''', \dots, n^{(g)}). \quad (10)$$

Straightforwardly one gets

$$t'_s(x) = \sum_{v=0}^g \frac{\partial f}{\partial n^{(v)}} \frac{dn^{(v)}}{dx} = \sum_{v=0}^g \frac{\partial f}{\partial n^{(v)}} n^{(v+1)} \quad (11)$$

which is Eq. (11) in Ref. [11]. Alternatively, repeated integration by parts gives Eq. (6) of that reference,

$$\frac{\delta T_s}{\delta n} = \sum_{v=0}^g (-1)^v \frac{d^v}{dx^v} \left[\frac{\partial f}{\partial n^{(v)}} \right]. \quad (12)$$

Ref. [11] then rewrites the Euler equation (5) with (12) and takes one spatial derivative to get

$$v'_{\text{KS}}(x) = \sum_{v=0}^g (-1)^{v+1} \frac{d^{v+1}}{dx^{v+1}} \left[\frac{\partial f}{\partial n^{(v)}} \right]. \quad (13)$$

Substitution of both this result and the result from (11) in Eq. (8) then gives

$$\sum_{v=0}^g \left[(-1)^v n \frac{d^{v+1}}{dx^{v+1}} \left(\frac{\partial f}{\partial n^{(v)}} \right) - 2n^{(v+1)} \frac{\partial f}{\partial n^{(v)}} \right] = -\frac{1}{4} n'''. \quad (14)$$

Ref. [11] then says that "...this equation has to be looked upon as a relation to be satisfied identically with respect to the variables $n, n', \dots, n^{(g)}$ occurring in it" and that the equation "is a condition to be imposed on the dependence of f upon the variables $n, n', \dots, n^{(g)}$ ". There follows an examination of functions f which depend on $n^{(g)}$ through $g = 2$ with the conclusion that the only allowable form consists of the full von Weizsäcker term [16] plus an arbitrarily scaled Thomas-Fermi term [17,18].

2.3. Difficulty

There are two consequential flaws in the foregoing argument that seem not to have been recognized heretofore. They have a common stem. First, the differential virial relation from which Eq. (8) is derived holds *only* for the exact eigenstates of the given Hamiltonian. In the KS case with fixed external potential, that differential virial relation therefore properly reads

$$t'_s(n_0(x)) = \frac{n_0'''(x)}{8} - \frac{1}{2} n_0(x) v'_{\text{KS}}(n_0(x)). \quad (15)$$

The same error occurs in use of the Euler equation to get the spatial derivative of the potential. The Euler equation is not a general functional relation for arbitrary density n . Rather it is a relationship between the minimizing density n_0 and the unique (up to a constant) external potential which is paired with that n_0 . Thus Eq. (13) must be replaced by

$$v'_{\text{KS}}(n_0(x)) = \sum_{v=0}^g (-1)^{v+1} \frac{d^{v+1}}{dx^{v+1}} \left[\frac{\partial f}{\partial n^{(v)}} \right]_{n_0}. \quad (16)$$

As a consequence, the purported constraint on functional dependence becomes

$$\sum_{v=0}^g \left[(-1)^v n_0 \frac{d^{v+1}}{dx^{v+1}} \left(\frac{\partial f}{\partial n^{(v)}} \right)_{n_0} - 2n_0^{(v+1)} \frac{\partial f}{\partial n^{(v)}} \right]_{n_0} = -\frac{1}{4} n_0'''. \quad (17)$$

This is a requirement on the behavior of f at a single point n_0 in the space of one-body densities and paired with a specific v_{ext} . Contrary to Ref. [11], Eq. (17) is *not* a condition on the dependence of f upon the variables $n, n', \dots, n^{(g)}$ for arbitrary density n given a v_{ext} . Rather, given a dependence through order $n^{(g)}$, and a particular v_{ext} , the requirement is to find the equilibrium density n_0 that satisfies (17).

3. 1D Examples

Just as with the original argument, early examples of the implications of the purported constraint were for 1D systems. We analyze two of those early 1D cases as particularly clear instances of the trivial nature of the supposed constraint.

3.1. 1D homogeneous electron gas

For the 1D homogeneous electron gas (HEG), the Thomas-Fermi functional, T_{TF}

$$T_{\text{TF}} = c_{\text{TF}} \int dx n^3(x) \quad (18)$$

is exact. Secure in that knowledge, one can put it aside for a moment and simply consider T_{TF} as a candidate approximate KE functional. The associated kinetic energy density and partial derivative are

$$t_{TF} = c_{TF} n^3 := f(n) \quad (19)$$

$$\frac{\partial f}{\partial n} = 3c_{TF} n^2. \quad (20)$$

Then Eq. (17) becomes

$$n_0 \frac{d}{dx} (3c_{TF} n_0^2) - 2n_0^{(1)} (3c_{TF} n_0^2) = -\frac{1}{4} n_0^{(3)}. \quad (21)$$

Its solution is

$$n_0(x) = \frac{1}{2} ax^2 + bx + c, \quad (22)$$

with coefficients to be determined. An appropriate boundary condition is periodic

$$n_0(x+L) = n_0(x) \quad (23)$$

where L is a suitable length. As a result

$$a = b = 0. \quad (24)$$

The constant c is set by imposition of the desired value of the uniform density. The outcome of the supposed constraint is simply to demonstrate that t_{TF} is compatible with the HEG.

If, on the other hand, one imposes box boundary (BB) conditions

$$n_0(0) = n_0(L) = 0 \quad (25)$$

one has $c = 0$ and

$$n_{0,BB}(x) = \frac{6N_e}{L^3} x(L-x). \quad (26)$$

This density, however is unacceptable, since it violates Lieb's condition [19] for the finitude of the KE:

$$\int_0^L dx \left(\frac{d\phi}{dx} \right)^2 < \infty \quad (27)$$

$$\phi(x) := \sqrt{n_{0,BB}(x)} \quad (28)$$

Alternatively, one may see the problem with $n_{0,BB}$ by attempting direct inversion of the Schrödinger equation for ϕ in the $N_e = 1$ case to recover the one-body potential. Up to a constant, the purported potential is negative definite with poles at $x = 0, L$: $(-L^2/[8x^2(L-x)^2])$, i.e., $n_{0,BB}$ is not ν -representable. There is nothing special about $N_e = 1$ to rescue the case.

Thus, all that Eq. (17) yields in the T_{TF} case is confirmation that T_{TF} is indeed correct for the 1D HEG. One also learns that Eq. (17) has solutions which upon detailed inspection do not correspond to any potential, but that says nothing about limits on the validity of T_{TF} as an approximate functional. For cases in which ν_{ext} does exist, Eq. (17) has no information about it and provides no information on the accuracy of the approximation $t_s \approx t_{TF}$. Thus, contrary to Ref. [11], no general requirement on the dependence of $T_s[n]$ upon spatial derivative order is obtained from Eq. (17) when T_{TF} is put to the test.

3.2. One electron in 1D

For a 1-electron system, the von Weizsäcker functional T_W

$$T_s = T_W = \int dx t_W(x) \quad (29)$$

is exact. Its kinetic energy density is

$$t_W = \frac{[n'(x)]^2}{8n(x)} := f_W(n, n'). \quad (30)$$

For convenience, the relevant partial derivatives for use of Eq. (17) are

$$\begin{aligned} \frac{\partial f_W}{\partial n} &= -\frac{(n')^2}{8n^2} \\ \frac{\partial f_W}{\partial n'} &= \frac{n'}{4n} \end{aligned}$$

Substitution of these results in the left-hand side of Eq. (17) gives

$$\begin{aligned} &\left(n_0 \frac{d}{dx} \frac{-(n'_0)^2}{8n_0^2} - 2n'_0 \frac{-(n'_0)^2}{8n_0^2} \right) + \left(-n_0 \frac{d^2}{dx^2} \frac{n'_0}{4n_0} - 2n'_0 \frac{n'_0}{4n_0} \right) \\ &= \left(-\frac{n'_0 n''_0}{4n_0} + \frac{(n'_0)^3}{4n_0^2} + \frac{(n'_0)^3}{4n_0^2} \right) \\ &\quad + \left(-\frac{1}{4} n_0^{(3)} + \frac{3n'_0 n''_0}{4n_0} - \frac{(n'_0)^3}{2n_0^2} - \frac{n'_0 n''_0}{2n_0} \right) = -\frac{1}{4} n_0^{(3)} \end{aligned}$$

This is the same as the right hand side of Eq. (17) so that equation reduces to a trivial identity for all equilibrium densities associated with the combination T_W , some E_{xc} , and some E_{ext} . Therefore, no information is provided by the differential virial constraint, Eq. (17), about the functional dependence of T_s upon spatial derivatives except that t_W is a valid form. Note also that unlike the 1D HEG or box-bounded t_{TF} cases considered above, there are infinitely many densities that lead to the trivial identity because there are infinitely many single-electron external potentials. Thus, there is no access to a unique solution n_0 provided by the purported constraint.

4. Discussion and conclusions

Examination of the 3D version of the differential virial constraint argument as summarized, for example, in Ref. [14], shows that the same critical mis-use of the Euler equation occurs in 3D as in 1D. The preceding analysis therefore holds unchanged.

It might seem that Hohenberg-Kohn bijectivity between ν_{ext} and n_0 could rescue the argument by making the Euler equation true for an arbitrary ν -representable density. Note that even if that were the case, the differential virial theorem part of the argument itself still would hold only for the extremalizing density. But HK bijectivity does not remove the Euler equation restriction either. Bijectivity is true for an arbitrary density precisely and only in the case that the arbitrarily chosen density is paired with the unique external potential for which it is the *minimizing* density n_0 . Bijectivity is irrelevant for the case of interest, namely a *fixed* ν_{ext} and *arbitrary* $n(\mathbf{r})$. The required pairing of density and potential is missing. Thus, though the Euler equation holds for arbitrary n_0 with the associated $\nu_{\text{ext}}[n_0]$ and corresponding $\mu[n_0]$, the flaw identified above persists. Spatial differentiation of the Euler equation to replace ν'_{KS} (recall Eq. (13)) in the differential virial relation still ties the result to equilibrium densities n_0 , not arbitrary ones.

It is worth noting that the non-uniqueness of KE densities [20] (indeed, any energy density) should raise suspicions about the validity of any supposed constraint on the spatial derivative dependence of an approximation for t_s . The well-known vanishing of $\nabla^2 n$ terms is an example. In fact, it is the counterexample to the Ref. [11] argument (just after Eq. (48) of that reference) that the approximate KE density must obey $t_s^{\text{approx}} \geq 0$. That constraint is highly valuable but it is a choice of gauge. The issue is discussed in detail in Refs. [21,22]. A related issue is that it is not self-evident that a function having up through g^{th} order derivatives, Eq. (11), necessarily is itself differentiable for arbitrary densities. Nor is it always true that one can do the repeated integration by

parts, Eq. (12) with vanishing surface terms; see Ref. [23] for counterexamples.

The present analysis resolves at least one other peculiar finding in Refs. [11,12]. Those claim to show that through second-order spatial derivatives the only KE density form consistent with the supposed differential virial constraint is $t_s^{approx} = \lambda t_{TF} + t_W$ with λ an undetermined constant. This restriction is suspect on its face because of the Lieb conjecture [24] that $T_s \leq T_{TF} + T_W$. That conjecture is consistent with the $N_e \rightarrow \infty$ limit of the bound found by Gázquez and Robles [25]. (See also Acharya et al. [26] for a heuristic formulation with number dependence that has the Lieb bound as the $N_e \rightarrow \infty$ limit.) For finite systems, the only straightforward way to make the peculiar result consistent with the Gázquez-Robles expression would be for λ to be number-dependent, thereby raising an obvious problem of size-consistency. There is no obvious simple way to make the result consistent with the Lieb bound in the thermodynamic limit. The analysis presented here removes that problem by showing that all the supposed constraint really does is to confirm that for a specific n_0 one always can find a λ which makes the claim true. Just pick

$$\lambda[n_0] = \frac{T_s[n_0] - T_W[n_0]}{T_{TF}[n_0]}. \quad (31)$$

While true, it is essentially tautological, hence useless.

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