Positivity constraints and information-theoretical kinetic energy functionals

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Positivity Constraints and Information-theoretical Kinetic Energy Functionals

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Recently several variants of a new orbital-free density functional for the total N_e-electron kinetic energy (KE) have been proposed. These are based on a systematically constructed (N_e-1)-electron conditional probability function and Monte Carlo evaluation of the associated conditional expectation of the KE operator in the case of the homogeneous electron gas. Because the resulting functionals depend on $n \ln n$ ($n =$ the electron number density), they have been interpreted as being the leading term in a Shannon information power expression for the non-von Weizsäcker part of the total KE. We show that these functionals violate known positivity constraints, are inconsistent with known results for the correlation energy of the homogeneous electron gas, and that the Shannon information power interpretation also violates known constraints. We consider both the full KE and Kohn-Sham KE cases. Possible corrections and extensions are considered, including a possible new form for parametrization.

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I. INTRODUCTION AND BASICS

In density functional theory[1–5], one of the key challenges to direct implementation of the variational principle is the N_e-electron kinetic energy in state Ψ,

$$T[n_\Psi] = \langle \Psi | \hat{T} | \Psi \rangle \tag{1}$$

with $n(\mathbf{r})$ the electron number density (normalized to N_e). The notation is a reminder of the difficulty: T is indeed a functional of n but the general functional form is unknown. Analysis of this problem from an information theory-based decomposition of $T[n_\Psi]$ has been considered sporadically over the history of DFT, beginning apparently with Sears, Parr, and Dinur[6] in 1980. A survey through 2001 is found in Sect. 3 of Ref. 7.

The information-theoretical decomposition begins from writing the N_e-body density as

$$N_e \Psi^*(\mathbf{r}_1 \ldots \mathbf{r}_{N_e}) \Psi(\mathbf{r}_1 \ldots \mathbf{r}_{N_e}) = n(\mathbf{r}_1) f(\mathbf{r}_2 \ldots \mathbf{r}_{N_e} \| \mathbf{r}_1) \; . \tag{2}$$

(This and similar factorizations have a long history[8,9].) The positive-definite form of T (in Hartree atomic units) then decomposes into

$$\begin{aligned} T[\Psi] &= \frac{1}{8} \int d\tau_{N_e} \frac{|\nabla_1 n f|^2}{n f} \\ &= T_W[n] \\ &+ \frac{1}{8} \int d\mathbf{r}_1 \int d\tau_{N_e - 1} \frac{|\nabla_1 f(\tau_{N_e-1} \| \mathbf{r}_1)|^2}{f(\tau_{N_e-1} \| \mathbf{r}_1)} \; , \end{aligned} \tag{3}$$

where $d\tau_{N_e} = d\mathbf{r}_1 \ldots d\mathbf{r}_{N_e}$ and the von Weizsäcker kinetic energy[10] is

$$T_W[n] = \frac{1}{8} \int d\mathbf{r} \, \frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})} \equiv \int d\mathbf{r} \, t_W[n(\mathbf{r})] \; . \tag{4}$$

The von Weizsäcker term is identified with the Fisher information entropy, a measure of localization. The remaining, non-local contribution is called the correlation part in Ref. 11 or the kinetic correlation term in Refs. 12,13 and is discussed in terms of the Shannon information entropy.

When used variationally, this factorization has a direct interpretation[11,13] in terms of Levy-Lieb constrained search[14,15] DFT. In notation essentially parallel with that of Refs. 11,13, the electronic total energy is

$$\begin{aligned} E[n,f] &= T_W[n] + \int d\mathbf{r}_1 n(\mathbf{r}_1) v_{ext}(\mathbf{r}_1) \\ &\quad + K_{corr}[n] + \mathcal{E}_{corr}[n] \end{aligned}$$

$$\begin{aligned} K_{corr}[n] &+ \mathcal{E}_{corr}[n] = \min_f \Gamma[f,n] \\ \Gamma[f,n] &:= \frac{1}{8} \int d\mathbf{r}_1 n(\mathbf{r}_1) \int d\tau_{N_e-1} \frac{|\nabla_1 f(\tau_{N_e-1})|^2}{f(\tau_{N_e-1})} \\ &\quad + \frac{(N_e-1)}{2} \int d\mathbf{r}_1 n(\mathbf{r}_1) \\ &\quad \times \int d\tau_{N_e-1} \frac{f(\tau_{N_e-1})}{|\mathbf{r}_1 - \mathbf{r}_2|} \; . \end{aligned} \tag{5}$$

Here K_{corr} and $\mathcal{E}_{corr}$ correspond in order to the terms on the RHS of the definition of $\Gamma[f,n]$ and v_{ext} is the external potential, usually the nuclear-electron attraction. Observe that, by construction,

$$K_{corr} \geq 0 \; . \tag{6}$$

Remarks: (i) Despite the useful notation, K_{corr} is not the conventional correlation kinetic energy, $T - T_{RHF} \geq 0$ with T_{RHF} the restricted Hartree-Fock KE and T the total KE. Nor is K_{corr} the DFT correlation kinetic energy, which is $T_{c,DFT} = T - T_s$, with T_s the Kohn-Sham KE as defined below at Eq. (11). Instead $K_{corr} = T - T_W$. It is useful to keept this in mind. At various points in the discussion, we point out which correlation energy is being calculated. (ii) The $(|\nabla_1 f|^2/f)$ term has been studied by Ayers[16] in the context of a bounding sequence of generalized von Weizsäcker type terms.

Reduction of this formulation to a local functional was begun by Ghiringhelli and Delle Site[17]. They presented a Monte Carlo sampling of Eq. (5) for a model $f(\tau_{N_e-1})$ constructed from necessary conditions on the N_e-fermion wave function. The Monte Carlo sampling was done for the homogeneous electron gas (HEG) over a finite range of densities. From those calculations they proposed (see Ref. 17 at Eq. (12)) that for slowly-varying densities a new functional "ready for OFDFT-based codes" is

$$T_{GDS08}[n] = T_W[n] + \int d\mathbf{r} n(\mathbf{r})[A_1 + B_1 \ln n(\mathbf{r})] \tag{7}$$

with $A_1 = 0.860 \pm 0.022$ and $B_1 = 0.224 \pm 0.012$. In what follows, we refer to this functional and the associated paper as GDS08.

In the Erratum to Ref. 11, the GDS08 form was rationalized as being the leading-order term of a more general form, namely

$$\begin{aligned} K_{corr,SIP} &= \xi \exp\left\{\frac{m}{3}\mathcal{S}\right\}, \quad 0 < m < 2 \\ \mathcal{S}[\sigma] &:= -\int d\mathbf{r} \sigma(\mathbf{r}) \ln \sigma(\mathbf{r}) \\ \sigma(\mathbf{r}) &:= \frac{n(\mathbf{r})}{N_e}, \end{aligned} \tag{8}$$

with ξ a constant. Such a form was introduced in Refs. 18,19 with the signs as shown. (Somewhat confusingly, the Erratum to Ref. 11 has the sign in the exponent wrong at both Eqs. (3) and (4). The corresponding sign in Eq. (23) of Ref. 11 is correct.) The quantity $\mathcal{S}$ is recognized as the Shannon information and $K_{corr,SIP}$ with $m = 2$ is recognized as the Shannon information power. We focus on the DFT aspects and do not discuss the information-theoretical aspects further.

To improve upon GDS08, Ref. 13 refined the trial conditional probability function to model the behavior of high-density fermion pairing. From a Monte Carlo procedure closely analogous with that of GDS08, they obtained what we denote as the GHDS10 functional,

$$\begin{aligned} T_{GHDS10}[n] =& T_W + T_{TF} \\ &+ \int d\mathbf{r} n(\mathbf{r})[A_2 + B_2 \ln n(\mathbf{r})]. \end{aligned} \tag{9}$$

The constants are $A_2 = 1.02$ and $B_2 = 0.163$ (after combining like terms in Eq. (34) of Ref. 13). Here the Thomas-Fermi KE is

$$\begin{aligned} T_{TF}[n] &:= c_0 \int d\mathbf{r}\, n^{5/3}(\mathbf{r}) \\ c_0 &:= \frac{3}{10}(3\pi^2)^{2/3} \approx 2.8712 \end{aligned} \tag{10}$$

One other introductory point is needed. Commonly the objective of orbital-free kinetic energy approximation development is to replace the explicitly orbital-dependent Kohn-Sham kinetic energy

$$\begin{aligned} T_s[\{\phi_i\}_{i=1}^N] &= \frac{1}{2}\sum_{i=1}^N \int d\mathbf{r} \nabla\phi_i^*(\mathbf{r})\nabla\phi_i(\mathbf{r}) \\ &\equiv \int d\mathbf{r} t_s[n(\mathbf{r})], \end{aligned} \tag{11}$$

not the full N_e-body KE T. Though there is mention in the works by Delle Site and co-workers about OFKE approximations to T_s, (*e.g.* introduction to Ref. 17, discussion toward the end of Section 2 of Ref. 12, as well as the suggestive quotation above about existing OFDFT codes), the GDS08 functional[17] is for the full T, not T_s[20]. The same is true for the GHDS10 functional; see page 3 of Ref. 13. We return to issues of T_s briefly below.

II. POSITIVITY AND THE GDS08 AND GHDS10 FUNCTIONALS

There are several positivity problems with Eqs. (7), (8), and (9). We consider numerical values first, then formal properties.

A. Quantitative Behavior

If the GDS08 functional is a reasonable approximation for the total KE $T[n]$ of the HEG, then the conventional correlation KE it yields for the HEG

$$T_{c,GDS08}[n] = T_{GDS08}[n] - T_{TF}[n] \tag{12}$$

should be reasonable. (Observe that $T_{TF} = T_{RHF}$ for the HEG.) Fig. 1 shows the HEG kinetic energy per electron for the Thomas-Fermi model and for GDS08, Eq. (7), with the published values[17] of A_1, B_1. The Thomas-Fermi values always are above those from Eq. (7), hence the correlation kinetic energy produced by Eq. (12) is negative, *i.e.* $T_{c,GDS08}$ for the HEG has the wrong sign. Because the values of A_1, B_1 were obtained over the range $0.04 \leq n \leq 1.4$ (see Fig. 2 of Ref. 17), a fairer assessment is to consider Eq. (12) only on that domain. But even there the imputed $T_{c,GDS08}$ is negative.

The GDS08 and GHDS10 functional form suggests consideration of high densities. For roughly $n \geq 1.9$, the asymptotic expansion in r_s of the HEG correlation energy is a fair approximation[21] which improves as the density increases. The asymptotic correlation KE density from that expansion is

$$t_{c,asymp} = 0.0103 \ln n + 0.02066 \tag{13}$$

This expression is properly positive for $n > 0.135$, a density far below the range for which the asymptotic expansion is accurate. The GDS08 functional has that

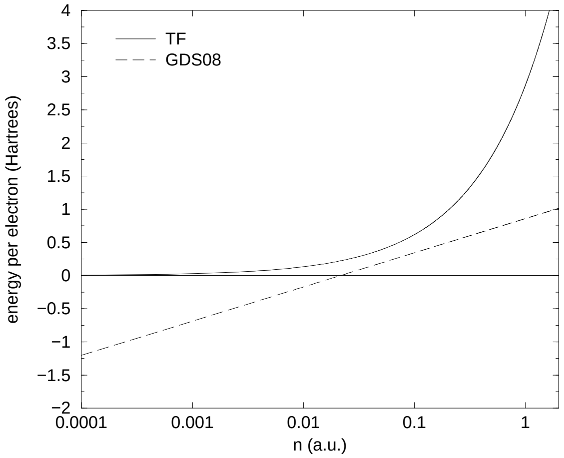

FIG. 1: Kinetic energy per electron.

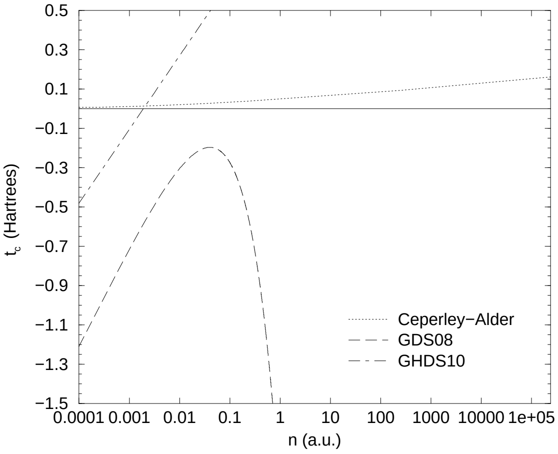

FIG. 2: Correlation kinetic energy per electron for GDS08, GHDS10, and the parametrized Ceperley-Alder Monte Carlo results. See text.

asymptotic form but because the constants are quite different, GDS08 goes negative at a much lower density, $n < 0.0215$; again see Fig. 1. Such failure of positivity is suggestive of an N-representability problem[22] with the specific form of f used in Ref. 17 at least for this density range. In retrospect, an N-representability problem might have been expected, since the form for f used in GDS08 is identical for bosons and fermions. Recognition of that difficulty is one way to formulate the motivation for GHDS10[13].

Similarly the GHDS10 KE, Eq. (9) goes negative for an HEG density such that

$$\ln n = -(A_2 + c_0\, n^{2/3})/B_2 \tag{14}$$

which has a solution $n_{crit,1} \approx 0.00152$. The density range for which the MC calculations were done to determine A_2 and B_2 is not reported in Ref. 13 but Fig. 1 of that paper shows that 0.01 or 0.02 apparently was the lowest density used. The failure of N-representability therefore is below the expected range of valid densities for the GHDS10 functional.

In Fig. 2, we compare the GHDS10, GDS08, and Ceperley-Alder correlation kinetic[23] energies. The CA values were obtained from the parametrization in Ref. 24, which used essentially the same virial relation as used just above for the asymptotic correlation KE. Note that neither GHDS10 nor GDS08 resembles the exact result even qualitatively, except in the limited sense that the exact result is dominantly logarithmic.

These behaviors draw attention to the range of densities over which the GDS08 and GHDS10 fits were obtained, $0.04 \leq n \leq 1.4$ e/au^3 for the former, $0.01-0.02 \leq n \leq 2.0$ e/au^3 for the latter. In terms of the Wigner-Seitz radius, these ranges are $0.55 \leq r_s \leq 1.81$ and $0.49 \leq r_s \leq 2.88$, respectively. Compared to metallic equilibrium, these are rather high densities, especially for GDS08. Insight comes from the text of Ref. 17, which says that densities 0.04, 0.2, and 1.0 e/au^3 correspond approximately to Na, Ti, and Pt, respectively. That correspondence is not the conventional choice of valence electrons only. If one works back to the effective number of valence electrons[25]

$$Z_{val} = 11.2055 \frac{n\,A}{\rho_m} \tag{15}$$

with ρ_m the mass density in gm/cm^3, A the atomic mass, and n in e/au^3, the three densities quoted give $Z_{val} =$ 10.6, 23.84, and 102.1, respectively. More typical values for determining the appropriate equivalent HEG for those three elements would be $Z_{val} = 1$, 3, and 2 (or 4), which give densities 0.0038, 0.0025, and 0.0019 (or 0.0039), respectively. Of course, developers of approximate functionals may choose the domain in which fitting to results on the HEG is done. The point here is that the failures identified above are in the range of realistic equilibrium metallic densities, whereas the GDS08 fitting range and much of the GHDS10 fitting range correspond to compressions of 10-200 or more.

Returning to Fig. 2, note that the CA correlation kinetic energy density t_c has almost logarithmic dependence on the density, at least qualitatively similar to the GDS10 functional, as remarked above. Hence we can use the parametrized CA form for t_c given in Ref. 24 to reparametrize the GHDS10 total KE functional, Eq. (9). Our values of parameters are $\tilde{A}_2 = 0.61434 \times 10^{-1}$ and $\tilde{B}_2 = 0.61317 \times 10^{-2}$. Closer inspection of Fig. 2 shows that the CA t_c depends non-linearly on $\ln n$, hence we fit to a total KE functional with a quadratic term,

$$\begin{aligned} T_{TKVln}[n] \;&=\; T_W + T_{TF} \\ &+ \int d\mathbf{r} n(\mathbf{r})[A_3 + B_3 \ln n(\mathbf{r}) + C_3 \ln^2 n(\mathbf{r})] \,. \end{aligned} \tag{16}$$

The resulting parameters are $A_3 = 0.45960 \times 10^{-1}$, $B_3 = 0.65545 \times 10^{-2}$, and $B_3 = 0.23131 \times 10^{-3}$.

Table I compares the valence kinetic energy per atom delivered by the GDS08, GHDS10, GHDS10 re-parametrized, TKVln, and second-order gradient approximate functionals to the Kohn-Sham value for two crystalline systems. The approximate functional values are from evaluation at the KS valence density. The KS calculations used numerical atomic orbitals as implemented in the SIESTA code[26] with Troulier-Martins non-local pseudopotentials[27], and the Perdew, Burke and Ernzerhof[28] exchange-correlation functional.

If we use the DFT definition of correlation kinetic energy, $T_{c,DFT}[n] = T[n] - T_s[n] \geq 0$, the result should be approximately the value from the third term in Eq. (16). This is the value shown in the table as T_c^{estim}. Consistent with the positivity discussion above, GDS08 strongly underestimates the valence KE, with a negative value for Li, and a negative T_c for Al. In contrast, GHDS10 strongly overestimates the valence KE, with the result that predicted T_c is too large by a factor of roughly 2-3.

As might be expected, both the re-parametrized GHDS10 and new TKVln functionals predict reasonable valence total KEs. They would not be expected to be applicable for all-electron densities however. There are formal problems with constraints (discussed in the next Subsection) and there is the problem that the $T_W + T_{TF}$ functional in these two forms strongly over-estimates the non-interacting (KS) KE, so that the third term would have to be spuriously negative.

B. Formal Issues

There also is a formal problem with the forms of both the GDS08 and GHDS10 functionals. Levy, Perdew, and Sahni[29] (LPS hereafter) studied

$$\begin{aligned} G[n] :=& K_{corr}[n] + \mathcal{E}_{corr} \\ & - \tfrac{1}{2}\int d\mathbf{r}_1 d\mathbf{r}_2 n(\mathbf{r}_1)n(\mathbf{r}_2)/r_{12} \end{aligned} \tag{17}$$

and showed that $\delta G/\delta n \geq 0$. They also showed that

$$\begin{aligned} \frac{\delta K_{corr}}{\delta n} &= \frac{1}{8}\int d\tau_{N_e-1}\frac{|\nabla_1 f(\tau_{N_e-1})|^2}{f(\tau_{N_e-1})} \\ &\quad + \frac{1}{8}\int d\mathbf{r}_1 n(\mathbf{r}_1)\frac{\delta}{\delta n}\int d\tau_{N_e-1}\frac{|\nabla_1 f(\tau_{N_e-1})|^2}{f(\tau_{N_e-1})} . \\ &\geq 0 \end{aligned} \tag{18}$$

The first term of this expression is itself manifestly positive. It corresponds to the third term on the right-hand side of LPS Eq. (17). The LPS argument also provides a proof that the second term of our Eq. (18) is positive. Simply take the kinetic energy contribution to the second term on the right-hand side of their Eq. (17).

The corresponding terms from $T_{GDS08}[n]$ are

$$\begin{aligned} v_{corr,GDS08} &= \frac{\delta(T_{GDS08} - T_W)}{\delta n} \\ &= \frac{\delta}{\delta n}\int d\mathbf{r} n(\mathbf{r})[A_1 + B_1 \ln n(\mathbf{r})] \\ &= A_1 + B_1 + B_1 \ln n . \end{aligned} \tag{19}$$

For the published values of A_1, B_1, at sufficiently small densities

$$n_{crit,2} = \exp(-(1 + A_1/B_1)) = 0.0079 , \tag{20}$$

this potential goes negative. Once again, however, the critical density is outside the range of the GDS08 Monte Carlo data fit.

But a focus on the range of valid densities begs the question of the meaning of the constant shift $A_1 + B_1$ in the potential. That shift cannot be correct. LPS showed that the potential v_{corr} is part of the effective potential for a one-body eigenvalue problem for the square root of the density. The eigenvalue for that problem is the negative of the ionization potential. Therefore the zero of the potential must be zero, not the constant $A_1 + B_1$ in Eq. (19). If we eliminate that potential shift, then the critical density below which the potential from a KE of the form $\int n \ln n$ goes negative is just

$$n_{crit,2} = 1 . \tag{21}$$

Essentially the same arguments can be made with regard to the GHDS10 correlation potential, which is

$$\begin{aligned} v_{corr,GHDS10} &= \frac{\delta(T_{GHDS10} - T_W)}{\delta n} \\ &= \frac{\delta}{\delta n}\int d\mathbf{r} n(\mathbf{r})[c_0 n^{2/3}(\mathbf{r}) + A_2 + B_2 \ln n(\mathbf{r})] \\ &= \frac{5}{3}n^{2/3} + A_2 + B_2 + B_2 \ln n . \end{aligned} \tag{22}$$

We eschew obvious detail.

Next, consider the Shannon information power form, Eq. (8). First, the change of variables, n to $\sigma = n/N_e$, introduces size-extensivity difficulties via the highly non-linear explicit N_e dependence. Second, though it might seem plausible, it is not true that $\sigma \leq 1$. A counter-example is a hydrogenic density for a neutral atom, $N_e = Z$, which satisfies the Kato cusp condition[4,30–33]. (sufficiently close to the nucleus $n(\mathbf{r}) \propto 1 - 2Z|\mathbf{r}| + \ldots$). Such a spherical density is

$$n_H(r) = \frac{N_e^4}{\pi}\exp(-2N_e r) \tag{23}$$

This density integrates to N_e over $\mathbb{R}^3$, as it should, but even for $N_e = 2$ has a maximum value ≈ 5.093, or $\sigma \leq 2.54$.

This little example illustrates an underlying difficulty with using a Shannon entropy form such as Eq. (8) in

TABLE I: Comparison of approximate and Kohn-Sham valence kinetic energies (eV) per atom for two solids. See text.

	GDS08	GHDS10	GHDS10(repar)	TKVln	SGA	T_s	T_c^{estim}
bcc-Li (a=3.44Å)	-6.257	9.221	4.085	3.760	3.007	3.626	0.527
fcc-Al (a=4.05Å)	5.271	57.532	25.492	24.351	21.346	22.102	2.067

DFT. A physical σ as defined above is not a probability mass function for a discrete random variable. Hence, such a σ is not bounded by unity and therefore the Shannon entropy $\mathcal{S}(\sigma)$ is not of one sign for all possible σ. This point was recognized by Sears, Parr, and Dinur[6]. The consequence, once again, is positivity violation for v_{corr}, even though the contribution to the total KE given by Eq. (8) is positive. This follows from

$$\begin{aligned} v_{corr,SIP} &= \frac{\delta K_{corr,SIP}}{\delta n} \\ &= \frac{m}{3} K_{corr,SIP} \frac{\delta \mathcal{S}}{\delta n} . \end{aligned} \tag{24}$$

Since $\mathcal{S}$ has the same form as T_{GDS08}, the same kind of non-positivity problems will arise, except at different critical densities.

III. RE-INTERPRETATION?

The Monte Carlo minimization which yielded the GDS08 and GHDS10 functionals was for the HEG, so one may ask if, after all, those functionals can be interpreted as an approximation for the Kohn-Sham KE T_s, not T. It is straightforward to see that this interpretation is not workable. The difficulty is exposed via an exact result called the Pauli KE decomposition[34–37], to wit

$$\begin{aligned} T_s[n] &= T_W[n] + T_\theta[n] \\ T_\theta[n] &\geq 0 . \end{aligned} \tag{25}$$

Critically for the present discussion, it is known that the Pauli potential must be positive semi-definite[29,37,38]:

$$v_\theta([n]; \mathbf{r}) = \delta T_\theta[n]/\delta n(\mathbf{r}) \geq 0 , \ \ \forall \, \mathbf{r} . \tag{26}$$

These conditions have been shown[39,40] to be important to the construction of reasonable approximations to T_s. But the GDS08, GHDS10, and Shannon information power functionals violate the Pauli potential constraint for the same reason that they violate the LPS constraint discussed above. And the GDS08 and GHDS10 functionals also violate Pauli KE positivity for sufficiently small densities.

IV. POSSIBLE MODIFICATIONS

All acceptable densities n satisfy relatively mild conditions[41], to wit:

$$\begin{aligned} n(\mathbf{r}) > 0 & \qquad \text{almost everywhere} \\ \int d\mathbf{r} |\nabla \sqrt{n(\mathbf{r})}|^2 &< \infty \\ \int d\mathbf{r} n^3(\mathbf{r}) &< \infty . \end{aligned} \tag{27}$$

The essential point is that every physical density has a maximum (it may be a supremum, that does not matter for the level of this discussion). Denote that maximum, which is clearly a functional of n, as $M[n] = \max n$. If we suppose, on practical grounds regarding the density properties just listed, that there is an upper bound N_m to $M[n]$, then we have $N_m \geq M[n]$ for all acceptable densities. Remarks: [i] We have disallowed delta-function and other singular densities. This restriction includes the conventional Thomas-Fermi atom. However, Parr and Ghosh[42] have shown that imposition of conditions akin to Eqs. (27) on the TF atom gives physically plausible results with a non-singular density. [ii] Note that N_m is a *density, not a number.* With this definition, redefine

$$\sigma := n/N_m \ \leq \ 1 \ , \tag{28}$$

whence $\mathcal{S}[\sigma] \geq 0$ in Eq. (8). This redefinition also gets rid of, or at least hides, the size-extensivity problem in the original σ definition.

However, the leading-order argument about the Shannon information power $\mathcal{S}$ summarized above still may fail because the correlation potential $v_{corr,1}$ from $\mathcal{S}$ itself (not from the full K_{corr}) is

$$\begin{aligned} v_{corr,1} &= -\frac{1}{N_m} (\ln \sigma + 1) \\ &> 0 \ \text{ for } \ n < N_m \exp(-1) . \end{aligned} \tag{29}$$

(The index on $v_{corr,1}$ is simply to distinguish this result from similar ones that follow.) Once again the range of allowed densities is restricted, a violation of the universality of the functional. In practice, one might argue that N_m may be large, *e.g.* of the order of N_e^4 per unit volume for the hydrogenic density just mentioned, and the restriction then might not be too severe. But that argument is difficult to use in practice, since N_m cannot be determined *a priori*.

Returning to the GDS08 functional from Eq. (7), even if one shifts to $\sigma \leq 1$ as the variable, there is still a positivity problem except for one special case, namely changing the parameters to $A' = -B' > 0$. The prime is to recognize the fact that the variable is different (σ, not n). This choice automatically eliminates the difficulty with the zero of v_{corr} discussed above, though it does not match the Monte Carlo result from Ref. 17. Then the counterpart of Eq. (7) is

$$T_{corr,2} := B' \int d\mathbf{r}\sigma(\mathbf{r})[-1 + \ln\sigma(\mathbf{r})] \tag{30}$$

which is manifestly positive. The counterpart potential to Eq. (19) also is positive:

$$v_{corr,2} = \frac{B'}{N_m} \ln\sigma \ . \tag{31}$$

Continuing with the modified definition of σ, Eq. (28), (thus forestalling for the moment the problem of using N_m rather than $M[n]$), one may ask what modification of $\mathcal{S}$ in Eq. (8) would yield a properly positive-definite v_{corr} as well as T_{corr}. We have found one such modification. Consider

$$\mathcal{S}_3[\sigma] := -A_3 \int d\mathbf{r}\sigma(\mathbf{r}) \ln(\sigma(\mathbf{r}) + B_3\sigma^2(\mathbf{r})) \tag{32}$$

with $A_3 > 0$, $-1 < B_3 < 0$. Then $\sigma^2 < \sigma \ \forall\mathbf{r}$, the argument of the logarithm is everywhere less than unity but positive, and $\mathcal{S}_3 \geq 0$. The effective potential which results is

$$\begin{aligned} v_{corr,3} = &-\frac{A_3}{N_m}\left\{\ln(\sigma + B_3\sigma^2)\right. \\ &\left. + \left(\frac{1}{1+B_3\sigma}\right)(1 + 2B_3\sigma)\right\} \ . \end{aligned} \tag{33}$$

The choice $B_3 = -\frac{1}{2}$ gives

$$\begin{aligned} v_{corr,3} = &-\frac{A_3}{N_m}\left\{\ln(\sigma - \tfrac{1}{2}\sigma^2)\right. \\ &\left. + \left(\frac{1}{1-\frac{1}{2}\sigma}\right)(1 - \sigma)\right\} \end{aligned} \tag{34}$$

which has the interesting consequence that

$$\begin{aligned} v_{corr,3}(\sigma = 1) &= -\frac{A_3}{N_m}\ln(\tfrac{1}{2}) = \frac{A_3 \ln 2}{N_m} \\ v_{corr,3}(\sigma = 0) &= -\frac{A_3}{N_m}\ln(0) = \infty \ . \end{aligned} \tag{35}$$

It is easy to show that the first term on the RHS of Eq. (34) is smaller than the second for the entire range, $0 \leq \sigma \leq 1$. Again, since N_m seems likely to scale at least as some power of N_e, the practical effect would be $0 \lesssim v_{corr,3} \leq \infty$.

Return to the Shannon information power form of K_{corr} as defined in Eq. (8), but, again, with the *revised* definition of $\sigma = n/N_m$. The kinetic-correlation potential which results is

$$\begin{aligned} v_{corr,4} &= \frac{\delta K_{corr}}{\delta n} = \frac{m}{3N_m}K_{corr}\frac{\delta\mathcal{S}}{\delta\sigma} \\ &= -\frac{m}{3N_m}K_{corr}[n]\,(\ln\sigma + 1) \end{aligned} \tag{36}$$

which has, of course, the same limitation as $v_{corr,1}$, Eq. (29).

An obvious question is, what happens if we use $M[n]$, the density maximum functional, rather than N_m? Of course, this choice also resolves the explicit size-extensivity problem from N_e introduced in the original Romera and Dehesa[18] type of definition. Moreover, this modification helps show what is missing from the purely information-theoretical formulation in a more systematic way than the somewhat *ad hoc* illustration provided by the construction of $\mathcal{S}_3$, Eq. (32).

Thus, we consider a modified version of K_{corr}, namely

$$\begin{aligned} \bar{K}_{corr} &= \xi \exp\left\{\frac{m}{3}\tilde{\mathcal{S}}[\sigma']\right\} \ , \quad 0 < m < 2 \\ \tilde{\mathcal{S}}[\sigma'] &:= -\int d\mathbf{r}\sigma'(\mathbf{r}) \ln\sigma'(\mathbf{r}) \\ \sigma'(\mathbf{r}) &:= \frac{n(\mathbf{r})}{M[n]} \ . \end{aligned} \tag{37}$$

Then the question becomes the behavior of the functional derivatives of $M[n]$, because v_{corr} now is

$$\begin{aligned} v_{corr,5} &= \frac{\delta\bar{K}_{corr}}{\delta n} \\ &= -\frac{m}{3}\bar{K}_{corr}\frac{1}{M[n]}\left(1 - \frac{n}{M[n]}\frac{\delta M}{\delta n}\right) \\ &\quad \times \left\{\ln\left(\frac{n}{M[n]}\right) + 1\right\} \ . \end{aligned} \tag{38}$$

In fact, we may generalize the problem into asking what functional $\mathcal{M}[n]$ might be introduced as in Eq. (37), with the redefinition $\sigma' := n/\mathcal{M}$, to satisfy constraints on v_{corr} without stipulating that $\mathcal{M}[n]$ be the maximum functional used in Eq. (37), but with the stipulation $\sigma' \leq 1$.

The problem simplifies a bit if we consider a function of n rather than a functional of n, $M(n)$ rather than $M[n]$ or $\mathcal{M}[n]$. Two obvious positivity constraints then follow from Eq. (38), namely that

$$1 - \frac{n}{M(n)}\frac{\partial M}{\partial n} > 0 \tag{39}$$

and

$$M(n) > \exp{(+1)}\, n \ . \tag{40}$$

That such a function exists is trivial, for example

$$M(n) = \exp{(+1)}n + \Delta \ , \ \Delta = \text{constant } > 0 \ . \tag{41}$$

This trivial result, however, illustrates what we believe to be a general fact. Introduction of $M(n)$ has a significant effect on the interpretation of $\tilde{\mathcal{S}}$, namely a shift away from being a straightforward Shannon information. We have not explored the consequences of other seemingly plausible choices of $M(n)$ (*e.g.*

$M(n) = n\exp(+1) + \Delta\exp(-\alpha n)$, $\alpha > 0$, $\Delta > 0$) to date.

Instead, explore the formal structure of $M(n)$. A clue is the fact that the coefficients for the GDS08 functional, Eq. (7), were obtained for the HEG, but that it does not have the Thomas-Fermi contribution. (TF is introduced in GHDS10 by choice of a constant.) Thus we consider, as an *ansatz*, the von Weizsäcker plus parametrized Thomas-Fermi model,

$$\begin{aligned} T_{WTF}[n] &= T_W[n] + \gamma T_{TF}[n] \\ 0 &\leq \gamma \leq 1\,. \end{aligned} \tag{42}$$

From the expansion

$$n^{1+\alpha} = n + \alpha n \ln n + \tfrac{1}{2} n(\alpha \ln n)^2 + \ldots \tag{43}$$

with $\alpha = 2/3$, we have

$$\begin{aligned} T_{TF} =& c_0 \int d\mathbf{r} \left(n + \frac{2}{3} n \ln n \right) \\ &+ c_0 \int d\mathbf{r} \frac{2}{3} n \ln n \sum_{j=1}^{\infty} \frac{1}{(j+1)!} \left(\frac{2}{3} \ln n \right)^j \\ :=& c_0 \int d\mathbf{r} \left(n + \frac{2}{3} n \ln n \right) \\ &+ \frac{2}{3} c_0 \int d\mathbf{r}\, n \ln n \mathcal{L}(n)\,. \end{aligned} \tag{44}$$

To compare with the GDS08 form, pull out the constant and $n \ln n$ terms and write

$$\begin{aligned} T_{WTF} &= T_W + \gamma c_0 \left\{ N_e + \frac{2}{3} \int d\mathbf{r} n \ln n \right\} \\ &+ \frac{2}{3} \gamma c_0 \int d\mathbf{r}\, n \ln n \mathcal{L}(n) \\ &= T_{GDS08} + \Delta T\,. \end{aligned} \tag{45}$$

The difference ΔT between parametrized WTF and GDS08 follows by comparison with Eq. (7) as

$$\begin{aligned} \Delta T &= (\gamma c_0 - A_1) N_e + \left(\frac{2\gamma c_0}{3} - B_1 \right) \int d\mathbf{r} n \ln n \\ &+ \frac{2}{3} \gamma c_0 \int d\mathbf{r}\, n \ln n \mathcal{L}(n)\,. \end{aligned} \tag{46}$$

Unsurprisingly, for the published values[17] of A_1, B_1, no single value of γ will eliminate the first two terms of ΔT. However, the choice $\gamma = A_1/c_0 \approx 3/10$ will eliminate the explicit number dependence, while $\gamma = 0.117$ will eliminate the "excess" Shannon-entropy-like term. Either way, there is a complicated density functional left.

At least formally, the form of the function $M(n)$ can be recovered by this line of argument. From the definition in Eq. (44) we have $\mathcal{L} > 0$ for both $n > 1$ and $n < 1$. For $n = 0$, $\mathcal{L} = 0$. Therefore, when the Shannon term in Eq. (44) goes negative, so does the $\mathcal{L}$ term. Then with $\gamma = 1$, the full KE is

$$\begin{aligned} T[n] &= T_W[n] + T_{TF}[n] + T_R[n] \\ &:= T_W[n] + T_{TF}[n] + \int d\mathbf{r} n(\mathbf{r}) t_R[n] \end{aligned} \tag{47}$$

with T_R the (in general unknown) remainder functional. By comparison with the last line of Eq. (44), we have

$$\begin{aligned} T[n] &= T_W[n] + c_0 \int d\mathbf{r} n \left(1 + \frac{2}{3} \ln n \right) \\ &+ \int d\mathbf{r} n(\mathbf{r}) \left\{ \frac{2}{3} c_0 \ln n \mathcal{L}(n) + t_R[n] \right\} \\ &:= T_W[n] + c_0 \int d\mathbf{r} n \left(1 + \frac{2}{3} \ln n \right) \\ &- \frac{2}{3} c_0 \int d\mathbf{r} n(\mathbf{r}) \ln M(n) \\ &= T_W[n] + c_0 \int d\mathbf{r} n(\mathbf{r}) \left(1 + \frac{2}{3} \ln \frac{n}{M(n)} \right)\,. \end{aligned} \tag{48}$$

The complexity of M is evident. This may be a caution against assuming simple forms of $M(n)$. For example, one might return to the HEG, assume a form of M, impose positivity on the resulting v_{corr}, and parametrize to the GDS08 or GHDS10 Monte Carlo results. But without detailed knowledge of the behavior of M from the structure in Eq. (48), it would be hard to know whether the resulting approximate M was of any generality for use in calculations.

V. CONCLUDING REMARKS

Despite the intriguing form and connection with Monte Carlo sampled data, we have shown that the GDS08 and GHDS10 KE functionals are limited by violation of important positivity constraints. We have also shown in a new way how the Shannon information entropy form comes into the KE functional, namely as part of the TF contribution. The von Weizsäcker term enters as a lower bound. The remainder is a renormalization of the Shannon term.

Finally, there is a cautionary note from the Coulomb virial theorem. For the N_e electron with equilibrium ground state density n_0, the ground state total energy $E[n_0] = -T[n_0]$. Finding a widely valid approximate $T[n]$ functional therefore would be equivalent to finding a functional which gives the same equilibrium results (same solution for its Euler equation) as the Hohenberg-Kohn functional. The history of DFT shows that finding such a functional is a truly formidable task. A more profitable use of the information-theoretical structure may be in building T_θ in Eq. (25) along lines parallel with the discussion of the formal structure of $M(n)$ just given, Eq. (48). We have this approach under investigation.

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