

# Extension of the Universal Density Functional to the Domain of Unnormalized Densities

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*Abstract:* Since the early 1980's, there have been numerous attempts to generalize the variational density domain of the Hohenberg-Kohn universal density functional to unnormalized densities. Recently, several papers by Lindgren and Salomonson [Phys. Rev. A **67**, 056501 (2003); **70**, 032509 (2004); and Adv. Quantum Chem. **43**, 95 (2003)] and by Gál [Phys. Rev. A **63**, 022506 (2001); **64**, 062503 (2001); J. Phys. A **35**, 5899 (2002)] appeared in the literature. We point out that all such efforts do not agree with some results of density functional theory.

*Keywords:* Universal density functional, Density functional theory, Density domain, Functional derivative

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## 1 Results of Lindgren and Salomonson

Many people have worked on the Hohenberg-Kohn (HK) universal density functional [1, 2, 3] in the domain of unnormalized densities [3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16]. In particular, Lindgren and Salomonson recently published three papers on density-functional differentiability [4, 5, 6], whose results resemble those of Nguyen-Dang *et al.* [7], Bergmann and Hinze [8], Gál [9, 10, 11], and Parr and Liu [12].

Taking Eq. (10) in their first paper in *Phys. Rev. A* by Lindgren and Salomonson [4]

$$\left[ \frac{\delta T[\rho]}{\delta \rho(\mathbf{r})} \right]_{\rho=\rho_0} + v(\mathbf{r}) - \mu = 0, \quad (1)$$

and Eq. (21) in the same paper [4]

$$\left[ \frac{\delta T[\rho]}{\delta \rho(\mathbf{r})} \right]_{\rho=\rho_0} = \frac{E_0}{N} - v(\mathbf{r}), \quad (2)$$

we immediately have

$$\mu = \frac{E_0}{N}, \quad (3)$$

where  $\rho_0(\mathbf{r})$  is the ground-state (GS) density,  $E_0$  is the Kohn-Sham (KS) energy for  $N$  noninteracting electrons [2, 3],  $v(\mathbf{r})$  is the total KS effective potential, and  $T[\rho]$  is the KS kinetic energy or

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$T_s[\rho]$  in the conventional notation. Eq. (3) foretold Eq. (34) of the latest paper in *Phys. Rev. A* by these two authors [6], which has been confuted recently [16].

Let us focus on Eq. (2), multiply both sides of this equation by  $\rho_0(\mathbf{r})$ , integrate over the entire space, and get the following result:

$$\left\langle \rho_0(\mathbf{r}) \left[ \frac{\delta T[\rho]}{\delta \rho(\mathbf{r})} \right]_{\rho=\rho_0} \right\rangle = \left\langle \left[ \frac{E_0}{N} - v(\mathbf{r}) \right] \rho_0(\mathbf{r}) \right\rangle = E_0 - \langle v(\mathbf{r}) \rho_0(\mathbf{r}) \rangle = T[\rho_0], \quad (4)$$

or simply put: the KS kinetic energy is homogeneous in density of order 1. Similar result [16] can be derived based upon Eqs. (59) and (69) of their second paper in *Adv. Quantum Chem.* [5]:

$$\left\langle \rho_0(\mathbf{r}) \left[ \frac{\delta F[\rho]}{\delta \rho(\mathbf{r})} \right]_{\rho=\rho_0} \right\rangle = F[\rho_0], \quad (5)$$

where  $F[\rho]$  is the HK universal density functional [1, 2, 3].

In fact, Eq. (4) is the same result first advocated by Parr and Liu [12], and then refuted by Wang [15], Joubert [13], Chan and Handy [14], and Gál [9, 10, 11]. Interestingly, identical statements like Eqs. (3)-(5) have been proposed by Nguyen-Dang *et al.* [7], of Bergmann and Hinze [8], and of Parr and Liu [12] before, Lindgren and Salomonson just reached the same result in a different context.

In this talk, we are going to comment on such proposals by these authors [3, 4, 5, 6, 7, 8, 9, 10, 11, 12] and reveal some subtleties in their derivation.

## 2 Gál's Proposal

Following some earlier efforts [3], Gál worked out an explicit way to define a functional derivative in Hilbert space of  $N$  electrons [10], without an extension of the density domain of the universal functional followed by a subsequent inclusion of a Lagrangian multiplier term that enforces the normalization of the density of the stationary solution.

The idea is to separate the shape of the density from its normalization through the following generalization of the density domain [3, 17, 10]:

$$\rho^N(\mathbf{r}) = N \frac{g(\mathbf{r})}{\langle g(\mathbf{r}) \rangle} = N \sigma(\mathbf{r}), \quad (6)$$

where positive function  $g(\mathbf{r})$  can be normalized to any positive real number and  $\sigma(\mathbf{r})$  is the shape function with unit normalization  $\langle \sigma(\mathbf{r}) \rangle = 1$ . Consequently, any density functional  $A[\rho^N(\mathbf{r})]$  can be defined in terms of  $N$  and  $g(\mathbf{r})$ :

$$A[\rho^N(\mathbf{r})] = A[N\sigma(\mathbf{r})] = A[g(\mathbf{r}), N]. \quad (7)$$

It is straightforward to show that from the definition in Eq. (6) for a given  $\rho^N(\mathbf{r})$ , Gál's expression of the functional derivative with a fixed  $N$  is well defined without any arbitrary additive constant [10]:

$$\left. \frac{\delta A[\rho]}{\delta_N \rho(\mathbf{r})} \right|_{\rho=\rho^N} = \left. \frac{\delta A[\rho]}{\delta \rho(\mathbf{r})} \right|_{\rho=\rho^N} - \frac{1}{N} \left\langle \rho^N(\mathbf{r}) \left[ \frac{\delta A[\rho]}{\delta \rho(\mathbf{r})} \right]_{\rho=\rho^N} \right\rangle. \quad (8)$$

The symbol  $\delta A[\rho]/\delta_N \rho(\mathbf{r})$  in Gál's notation means that the density variation is such that it always lies within the space of densities normalized to  $N$  (see Ref. [10] for more details).

Led by the early success [9, 10], Gál and coworker have applied this line of treatment and shown that a first-degree homogeneous KS-type kinetic-energy functional can be defined and should be utilized in place of the conventional KS kinetic-energy functional [11], echoing the similar results advocated by Nguyen-Dang *et al.* [7], Bergmann and Hinze [8], Parr and Liu [12], and Lindgren and Salomonson [4, 5, 6].

It seems that Gál's proposal should be the canonical version to be adopted by the entire DFT community, provided that the definition in Eq. (6) is unique and genuine. Unfortunately, such an assessment cannot be substantiated, not only because Gál's proposal is in direct conflict with the latest results by Zahariev and Wang [16], but also because the definition in Eq. (6) is, in fact, not unique and genuine. With a little bit further generalization of the definition in Eq. (6), we write the normalized density as

$$\rho^{N,m}(\mathbf{r}) = g(\mathbf{r}) \left( \frac{N}{\langle g(\mathbf{r}) \rangle} \right)^{1+(m-1)\delta_{N,\langle g(\mathbf{r}) \rangle}} = \begin{cases} g(\mathbf{r}) \left( \frac{N}{\langle g(\mathbf{r}) \rangle} \right)^m, & \text{if } \langle g(\mathbf{r}) \rangle = N \quad ; \\ \rho^{N,1}(\mathbf{r}) \equiv \rho^N(\mathbf{r}), & \text{if } \langle g(\mathbf{r}) \rangle \neq N \quad . \end{cases} \quad (9)$$

Here,  $\delta_{N,\langle g(\mathbf{r}) \rangle}$  is the Kronecker delta, and  $m$  can be any real number. It is obvious that Eq. (9) coincides with Eq. (6) numerically:  $\rho^{N,m}(\mathbf{r}) = \rho^N(\mathbf{r})$ , but  $A[\rho^{N,m}(\mathbf{r})]$  and  $A[\rho^N(\mathbf{r})]$  do have different Gâteaux functional derivatives at fixed  $N$ .

Because of the directional nature of the Gâteaux differential, the density variation, once chosen, will not change its shape during the entire variational path. Moreover, if the variation  $\delta g(\mathbf{r})$  does not change the normalization of  $g(\mathbf{r})$ , say  $\langle \delta g(\mathbf{r}) \rangle = 0$ , the normalization of  $g(\mathbf{r}, \varepsilon) = g(\mathbf{r}) + \varepsilon \delta g(\mathbf{r})$  will remain the same throughout the entire variational process. Thus, for the set  $\{g(\mathbf{r}, \varepsilon) | g(\mathbf{r}, \varepsilon) = g(\mathbf{r}) + \varepsilon \delta g(\mathbf{r}), \langle g(\mathbf{r}, \varepsilon) \rangle \neq N\}$ , the Gâteaux functional derivative of a general functional  $A[\rho^{N,m}(\mathbf{r})]$  will be identical to that of  $A[\rho^N(\mathbf{r})]$ . However, for the set  $\{g(\mathbf{r}, \varepsilon) | g(\mathbf{r}, \varepsilon) = g(\mathbf{r}) + \varepsilon \delta g(\mathbf{r}), \langle g(\mathbf{r}, \varepsilon) \rangle = N\}$ , the Gâteaux functional derivative of a general functional  $A[\rho^{N,m}(\mathbf{r})]$  can be shown to be

$$\left. \frac{\delta A[\rho]}{\delta_N \rho(\mathbf{r})} \right|_{\rho=\rho^N} = \left. \frac{\delta A[\rho]}{\delta \rho(\mathbf{r})} \right|_{\rho=\rho^N} - \frac{m}{N} \left\langle \rho^N(\mathbf{r}) \left[ \left. \frac{\delta A[\rho]}{\delta \rho(\mathbf{r})} \right]_{\rho=\rho^N} \right\rangle, \quad (10)$$

which is different from that of  $A[\rho^N(\mathbf{r})]$  shown in Eq. (8). Just like that Eq. (9) is a generalization of Eq. (6), Eq. (8) becomes a special case of Eq. (10).

Moreover, because  $m$  is an arbitrary real number, Eq. (10) restores the ambiguity (of an arbitrary additive constant) associated with the Gâteaux functional derivative of a general functional in Hilbert space at a fixed  $N$ . It now becomes self-evident that the only physically meaningful way to resolve this ambiguity is through the extension based upon the statistical ensemble in Fock space and the key to unlock this ambiguity is by the careful inspection of the chemical potential at a fixed integral  $N$  [16].

### 3 Conclusions

In conclusion, among the numerous attempts to generalize the variational density domain of the HK universal density functional to unnormalized densities, the latest proposal by Lindgren and Salomonson [4, 5, 6] suffers from the same logical flaw of earlier works by Nguyen-Dang *et al.* [7], Bergmann and Hinze [8], and Parr and Liu [12]. Gál's proposal [9, 10, 11] is interesting in its own right, but the definition of the normalized density in terms of well-behaved positive functions [3, 17] is neither unique nor genuine, and hence should not be adopted in general.

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