PHYSICAL REVIEW A **67**, 056501 (2003)

Comments on the locality in density-functional theory

Ingvar Lindgren* and Sten Salomonson†

Department of Physics, Chalmers University of Technology and Göteborg University, SE-412 96 Göteborg, Sweden

(Received 8 July 2002; published 27 May 2003)

The "locality hypothesis" in density-functional theory (DFT), implying that the functional derivative is equivalent to a multiplicative local function, forms the basis of models of Kohn-Sham type. This has been generally accepted by the community since the advent of the model, and has later been formally proved for a large class of functionals. The hypothesis has recently been questioned by Nesbet [Phys. Rev. A **58**, R12 (1998) and Phys. Rev. A **65**, 010502 (2001)], who claims that it fails for the kinetic-energy functional for a system with more than two noninteracting electrons with a nondegenerate ground state. This conclusion has been questioned by Gál [Phys. Rev. A **62**, 044501 (2000)] and by Holas and March [Phys. Rev. A **64**, 016501 (2001)]. We claim that the arguments of Nesbet are incorrect, since the orbital functional used for the kinetic energy is not a unique functional of the total density in the domain of unnormalized orbitals. We have demonstrated that with a proper definition of the kinetic energy, which is a unique density functional also in the unnormalized region, the derivative can be represented by a single local multiplicative function for all v-representable densities. Therefore, we consider the controversy connected with the issue raised by Nesbet as resolved. We believe that the proof of the differentiability given here can be extended to larger groups of DFT functionals, and works along these lines are in progress

DOI: 10.1103/PhysRevA.67.056501 PACS number(s): 31.15.Ew, 31.15.Pf, 02.30.Sa

I. INTRODUCTION

There has for some time been a dispute in the literature about the so-called "*locality hypothesis*" of the density-functional theory (DFT), implying that the density-functional derivative is generally representable as a local multiplicative potential function. This hypothesis forms the foundation of DFT models of Kohn-Sham type [1,2]. Nesbet has in several papers argued that this hypothesis leads to inconsistencies for compact systems with more than two electrons [3,4]. This result has been questioned by Gál and by Holas and March [5,6]. Nesbet has recently responded to that criticism [7], and we shall here make a Comment on the issue.

In standard DFT a density functional $E[\rho]$ is set up for the energy, which is minimized under the constraint that the density $\rho(\boldsymbol{r})$ is normalized to the number of electrons. This requires that the functional is differentiable with respect to the density at the minimum. If the minimization is being performed inside the normalization domain, *Gâteaux* differentiablity [9] is sufficient. If, on the other hand, the Euler-Lagrange (EL) procedure is being used, then the functional has to be defined also outside the normalization domain and the functional has to be *Fréchet* [9] differentiable.

As Nesbet works with unnormalized wave functions, we shall here consider the Fréchet differentiability. Nesbet argues that the density functional is not Fréchet differentiable even for systems of noninteracting electrons with more than two electrons. We shall show here that such a derivative exists regardless of the number of electrons.

A density functional, $F[\rho]$, defined on a subset M of a Banach space E with the norm $||\cdot||$, is *Fréchet differentiable* at a density $\rho_0 \in M$, if there exists a *continuous and linear operator* $L(\cdot)$ such that [9]

$$F[\rho_0+\delta\rho]-F[\rho_0]=L(\delta\rho)+o(\rho_0,\delta\rho) \tag{1}$$

for all $\rho \in E$ and $\rho_0+\delta\rho \in M$, and where $o(\rho_0,0)=0$ and

$$\lim_{||\delta\rho||\to 0}\frac{o(\rho_0,\delta\rho)}{||\delta\rho||}=0. \tag{2}$$

The function L is then termed as the *Fréchet derivative* at the density ρ_0. Fréchet differentiability implies that the differential is to the leading order (in the sense above) of the form

$$\delta F[\rho_0,\delta\rho]=F[\rho_0+\delta\rho]-F[\rho_0]=\int d\boldsymbol{r}\, v([\rho_0];\boldsymbol{r})\,\delta\rho(\boldsymbol{r}), \tag{3}$$

where $v([\rho_0];\boldsymbol{r})$ is a single valued, bounded function of $\boldsymbol{r}$ that depends only on ρ_0. This function is conventionally referred to as the *functional derivative*

$$\left(\frac{\delta F[\rho]}{\delta\rho(\boldsymbol{r})}\right)_{\rho=\rho_0}=v([\rho_0];\boldsymbol{r}). \tag{4}$$

We shall assume here that the density ρ_0 is a ground-state density, corresponding to a Hamiltonian with an external potential v, i.e., a v-representable density. The modified density $\rho=\rho_0+\delta\rho$ on the other hand, is allowed to be in a much larger space ($\rho \in L^1 \cap L^3$ [14]), which includes also unnormalized densities.

A formal proof of the (Gâteaux) differentiability for a large class of density functionals has been given by Englisch and Englisch [10,11], based upon the works of Levy and Lieb [12–14]. The reader is also referred to a recent comprehensive review by van Leeuwen [8].

---

*Email address: ingvar.lindgren@fy.chalmers.se

†Email address: f3asos@fy.chalmers.se

The results of Nesbet are in conflict with well-established results in DFT. We have found that the main reason for the unexpected and erroneous result of Nesbet is that the expression he uses for the kinetic energy is not a well-defined density functional, when the condition of orbital normalization is relaxed. We shall demonstrate that with a proper definition of the kinetic-energy functional in the extended domain, the functional is Fréchet differentiable for any number of noninteracting electrons. This, we believe, will resolve the present controversy concerning the locality of density-functional derivatives.

II. NONINTERACTING ELECTRONS

A. General *N*-electron wave function

We consider a system of *N noninteracting electrons*, moving in an external potential $v(\boldsymbol{r})$, with the Hamiltonian (in Hartree atomic units, i.e., $m=e=\hbar=4\pi\epsilon_0=1$)

$$\hat{H}=\hat{T}+\hat{V}=\sum_{i=1}^{N}-\frac{1}{2}\nabla_i^2+\sum_{i=1}^{N}v(\boldsymbol{r}_i). \tag{5}$$

The kinetic-energy functional is defined by means of the constrained search [12–16]

$$T[\rho]=\min_{\Psi\to\rho}\langle\Psi|\hat{T}|\Psi\rangle, \tag{6}$$

where $\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)$ is an *N*-representable wave function, i.e., antisymmetrized and normalized. We shall also require that the kinetic energy is finite [8,14]. In the following we shall relax the normalization constraint but still use definition (6). The electron density is the diagonal of the first-order density matrix

$$\rho(\boldsymbol{r})=N\int d\boldsymbol{r}_2\int d\boldsymbol{r}_3\cdots\int d\boldsymbol{r}_N|\Psi(\boldsymbol{r},\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)|^2. \tag{7}$$

(The integration will include a sum over the spin coordinates.) This definition will be used also for unnormalized wave functions. The energy functional for the system is

$$E[\rho]=T[\rho]+V[\rho], \tag{8}$$

where

$$V[\rho]=\langle\Psi|V|\Psi\rangle=\int d\boldsymbol{r}v(\boldsymbol{r})\rho(\boldsymbol{r})$$

represents the interaction with the external field.

According to the Hohenberg-Kohn theorem [1], the infimum (which can be shown to be a minimum [10,14]) of the energy functional with respect to the density under the constraint of the density normalized to *N*, $\int d\boldsymbol{r}\rho(\boldsymbol{r})=N$, is the exact ground-state energy E_0 of the system, and the minimizing density is the exact ground-state density ρ_0,

$$E_0=\inf_{\rho\to N}\{T[\rho]+V[\rho]\}=T[\rho_0]+V[\rho_0]. \tag{9}$$

Originally, this theorem was shown for densities that are *v representable* with a nondegenerate ground state, i.e., corresponding to a nondegenerate ground state of a Hamiltonian with a local external potential, $v(\boldsymbol{r})$. Later the theorem has been extended to essentially all densities $(\rho\in L^1\cap L^3)$ [8,10–15]. Provided that the kinetic-energy functional is Fréchet differentiable, the minimization leads to the Euler equation

$$\left(\frac{\delta T[\rho]}{\delta\rho(\boldsymbol{r})}\right)_{\rho=\rho_0}+v(\boldsymbol{r})-\mu=0, \tag{10}$$

where μ is the Lagrange multiplier for the normalization constraint.

We assume here that the ground state is *nondegenerate*. The ground-state wave function, Ψ_0, obviously minimizes the kinetic energy of noninteracting electrons at the ground-state density ρ_0,

$$\begin{aligned}T[\rho_0]&=\min_{\Psi\to\rho_0}\langle\Psi|\hat{T}|\Psi\rangle\\&=\langle\Psi_0|\hat{T}|\Psi_0\rangle\\&=\langle\Psi_0|\hat{H}-\hat{V}|\Psi_0\rangle=\int d\boldsymbol{r}\left(\frac{E_0}{N}-v(\boldsymbol{r})\right)\rho_0(\boldsymbol{r}).\end{aligned} \tag{11}$$

According to the Hohenberg-Kohn theorem, this is a functional of the density for v-representable densities. In order to find out if this functional is Fréchet differentiable at such a density, we have to find the variation of the functional in the neighborhood of this density (i.e., all densities $\{\rho=\rho_0+\delta\rho\in L^1\cap L^3|\,||\delta\rho||<\varepsilon\}$). This includes densities not only outside the space of v-representable densities but also outside the normalization domain. Therefore, we shall have a closer look on the differential.

We return to definition (6), and want to find the variation of this quantity due to a small change of the ground-state density, $\rho=\rho_0+\delta\rho$,

$$T[\rho_0+\delta\rho]=\min_{\Psi\to\rho_0+\delta\rho}\langle\Psi|\hat{T}|\Psi\rangle. \tag{12}$$

We extend the definition by relaxing the normalization constraint on the wave function. This implies that the diagonal element of $\hat{T}$ is no longer the expectation value, but this is quite legitimate. For instance, normalizing the expression it by dividing it by the norm of the wave function, would not change the main result. We also use definition (7) of the density for unnormalized wave functions. Integration of the density then leads to

$$\int d\boldsymbol{r}\rho(\boldsymbol{r})=N\langle\Psi|\Psi\rangle, \tag{13}$$

which shows that normalizing the density to *N*, automatically implies that the wave function is normalized to unity.

We now write the wave function in Eq. (12) as $\Psi=\Psi_0+\delta\Psi$ with Ψ_0 being the normalized ground-state wave function. To begin with, we do not assume that $\delta\Psi$ has to be "small." We then have generally

$$\langle\Psi|\hat{T}|\Psi\rangle=\langle\Psi|\hat{H}-\hat{V}|\Psi\rangle=\langle\Psi|\hat{H}|\Psi\rangle-\int \mathrm{d}\boldsymbol{r}v(\boldsymbol{r})\,\rho(\boldsymbol{r}) \tag{14}$$

and

$$\begin{aligned}\langle\Psi|\hat{H}|\Psi\rangle&=\langle\Psi_0|\hat{H}|\Psi_0\rangle+\langle\delta\Psi|\hat{H}|\Psi_0\rangle+\langle\Psi_0|\hat{H}|\delta\Psi\rangle\\&\quad+\langle\delta\Psi|\hat{H}|\delta\Psi\rangle\\&=E_0\langle\Psi|\Psi\rangle+\langle\delta\Psi|\hat{H}-E_0|\delta\Psi\rangle.\end{aligned} \tag{15}$$

Using Eq. (13), the diagonal element of $\hat{T}$ becomes

$$\begin{aligned}\langle\Psi|\hat{T}|\Psi\rangle&=\langle\Psi|\hat{H}-\hat{V}|\Psi\rangle\\&=\int \mathrm{d}\boldsymbol{r}\left(\frac{E_0}{N}-v(\boldsymbol{r})\right)\rho(\boldsymbol{r})+\langle\delta\Psi|\hat{H}-E_0|\delta\Psi\rangle\end{aligned} \tag{16}$$

and the functional (12)

$$T[\rho]=\int \mathrm{d}\boldsymbol{r}\left(\frac{E_0}{N}-v(\boldsymbol{r})\right)\rho(\boldsymbol{r})+\inf_{\Psi\to\rho}\langle\delta\Psi|\hat{H}-E_0|\delta\Psi\rangle. \tag{17}$$

The differential then becomes, using Eq. (11),

$$\begin{aligned}\delta T[\rho_0]=T[\rho_0+\delta\rho]-T[\rho_0]&=\int \mathrm{d}\boldsymbol{r}\left(\frac{E_0}{N}-v(\boldsymbol{r})\right)\delta\rho(\boldsymbol{r})\\&\quad+\inf_{\Psi+\delta\Psi\to\rho_0+\delta\rho}\langle\delta\Psi|\hat{H}-E_0|\delta\Psi\rangle.\end{aligned} \tag{18}$$

The condition for Fréchet differentiability is then that the relation

$$\begin{aligned}&\inf_{\Psi_0+\delta\Psi\to\rho_0+\delta\rho}\langle\delta\Psi|\hat{H}_v-E_0|\delta\Psi\rangle/||\delta\rho||\to 0\\&\text{as }||\delta\rho||\to 0\end{aligned} \tag{19}$$

holds for all densities on the neighborhood of $\delta\rho_0$. This is plausible since the numerator is quadratic in $\delta\Psi$, while $\delta\rho$ has a linear part. But first it has to be shown that all densities in the neighborhood of ρ_0 can be generated by wave functions where $\delta\Psi$ is small.

The density belongs to the group $L^1\cap L^3$, and the corresponding norms are

$$||\delta\rho||_1=\int \mathrm{d}\boldsymbol{r}|\delta\rho(\boldsymbol{r})| \quad\text{and}\quad ||\delta\rho||_3=\left[\int \mathrm{d}\boldsymbol{r}|\delta\rho(\boldsymbol{r})|^3\right]^{1/3}. \tag{20}$$

The norm for the wave function is chosen to be $||\Psi||=\sqrt{\langle\Psi|\Psi\rangle}$. We consider now all densities in the neighborhood of ρ_0, $||\delta\rho||<\varepsilon$, and all wave functions generating these densities. Generally, there are several wave functions that generate a certain density, and we keep the function for which $||\delta\Psi||$ is the smallest. We now scale $\delta\Psi$ by a factor of λ $(0<\lambda<1)$, which means that $||\delta\Psi||\to\lambda||\delta\Psi||$ and to first order $||\delta\rho||\to\lambda||\delta\rho||$. By making λ sufficiently small, it then follows that all densities in a small neighborhood of ρ_0 can be generated by wave functions in a small neighborhood of Ψ_0.

Since each density in the neighborhood of ρ_0 can be generated by wave functions for which $\delta\Psi$ is small, it follows that condition (19) is fulfilled and the extended kinetic-energy functional (6) is Fréchet differentiable at any v-representable density, ρ_0, corresponding to a nondegenerate ground state. The functional derivative

$$\left(\frac{\delta T[\rho]}{\delta\rho(\boldsymbol{r})}\right)_{\rho=\rho_0}=\frac{E_0}{N}-v(\boldsymbol{r}) \tag{21}$$

is *equivalent to a single local multiplicative function*. The value of the constant in the derivative is the Lagrange multiplier in the EL procedure (10). It depends on the way the functional is extended into the domain of unnormalized densities and has no physical significance.

Instead of using the EL procedure, it is possible to perform the minimization entirely inside the domain of normalized densities, i.e., restricting the density variations to those fulfilling the condition $\int \mathrm{d}\boldsymbol{r}\delta\rho(\boldsymbol{r})=0$. In that case, one can only deduce the derivative up to an additive constant, i.e.,

$$\left(\frac{\delta T[\rho]}{\delta\rho(\boldsymbol{r})}\right)_{\rho=\rho_0}=-v(\boldsymbol{r})+\text{const.} \tag{22}$$

This is consistent with the results of Englisch and Englisch [10,11] and of van Leeuwen [8]. As mentioned, in that case the derivative is of the Gâteaux type.

It is expected that the method used here to investigate the differentiablity of the kinetic-energy functional for noninteracting electrons can also be used for more general functionals for *interacting electrons*, and work along these lines are now in progress [17].

B. Single determinant

The treatment above holds for any antisymmetric wave function. In order to make the comparison with Nesbet's treatment more transparent, we shall illustrate this by considering the special case of a system of two electrons (without spin) with the determinantal wave function

$$\Phi(\boldsymbol{r}_1,\boldsymbol{r}_2)=1/\sqrt{2}[\phi_1(\boldsymbol{r}_1)\phi_2(\boldsymbol{r}_2)-\phi_1(\boldsymbol{r}_2)\phi_2(\boldsymbol{r}_1)]. \tag{23}$$

The treatment could easily be generalized to a single Slater determinant of N electrons. The orbitals are assumed to be orthogonal but in order to be able to apply the EL procedure we shall, as before, relax the normalization constraint.

The density (7) now becomes

$$\rho(\boldsymbol{r})=|\phi_1(\boldsymbol{r})|^2\langle\phi_2|\phi_2\rangle+|\phi_2(\boldsymbol{r})|^2\langle\phi_1|\phi_1\rangle;$$

$$\int d\boldsymbol{r}\rho(\boldsymbol{r})=2\langle\phi_1|\phi_1\rangle\langle\phi_2|\phi_2\rangle, \tag{24}$$

and the diagonal element of the kinetic-energy operator

$$\langle\Phi|\hat{T}|\Phi\rangle=\int\int d\boldsymbol{r}_1 d\boldsymbol{r}_2\Phi^*(\boldsymbol{r}_1,\boldsymbol{r}_2)(\hat{t}_1+\hat{t}_2)\,\Phi(\boldsymbol{r}_1,\boldsymbol{r}_2)$$
$$=\langle\phi_1|\hat{t}|\phi_1\rangle\langle\phi_2|\phi_2\rangle+\langle\phi_2|\hat{t}|\phi_2\rangle\langle\phi_1|\phi_1\rangle. \tag{25}$$

Note that the integration over the "passive" electron orbitals leads to normalization integrals, which are different from unity, when the orbitals are not normalized. If these integrals are left out, as Nesbet does, it is necessary to apply individual Lagrange multipliers for each orbital in the minimization process to preserve the normalization and to prevent the wave function from "collapsing" into a single orbital. By maintaining the normalization integrals, this is not needed—a single Lagrange multiplier is sufficient, in the same way as in the general case discussed in the preceding section. Density normalization then automatically implies wave-function normalization, as follows from Eqs. (13) and (24).

The expression in Eq. (25) is a functional of the density only in the v-representability domain. In order to demonstrate the Fréchet differentiability, we have, as before, to go outside this domain and study the behavior in the neighborhood of the ground-state density, also outside the normalization domain. The kinetic-energy functional is then defined by the constrained-search procedure (6)

$$T_s[\rho]=\min_{\Phi\to\rho}\langle\Phi|\hat{T}|\Phi\rangle, \tag{26}$$

this time with the function (Φ) restricted to a single determinant, which need not be normalized. From the result of the preceding section we know that in the neighborhood of the ground-state density the minimizing wave function is close to the ground-state function. Furthermore, we know that the differential of the kinetic energy in this neighborhood depends on leading order only on the density modification and *not* on the wave function that generates this density. This implies that *in the neighborhood of the ground-state density, expression (25) besides being an orbital functional is also a density functional*

$$\langle\Phi|\hat{T}|\Phi\rangle=T_s[\phi_1,\phi_2]$$
$$=T_s[\rho]$$
$$=\langle\phi_1|\hat{t}|\phi_1\rangle\langle\phi_2|\phi_2\rangle+\langle\phi_2|\hat{t}|\phi_2\rangle\langle\phi_1|\phi_1\rangle. \tag{27}$$

We consider now density variations due to the modifications $\delta\phi_1$ and $\delta\phi_2$ of the orbitals ϕ_1 and ϕ_2, respectively. Here, the normalization constraint is lifted but the orthogonality requirement is maintained. This leads to the density change

$$\delta\rho(\boldsymbol{r})=\delta\rho_1(\boldsymbol{r})+\delta\rho_2(\boldsymbol{r}), \tag{28}$$

where

$$\delta\rho_1(\boldsymbol{r})=\delta\phi_1^*(\boldsymbol{r})\phi_1(\boldsymbol{r})\langle\phi_2|\phi_2\rangle+|\phi_2(\boldsymbol{r})|^2\langle\delta\phi_1|\phi_1\rangle+\text{c.c.}, \tag{29}$$

leaving out the quadratic terms. $\delta\rho_2(\boldsymbol{r})$ is obtained from this expression by the exchange $(1\leftrightarrow2)$. This gives

$$\int d\boldsymbol{r}\delta\rho_1(\boldsymbol{r})=2\langle\delta\phi_1|\phi_1\rangle\langle\phi_2|\phi_2\rangle+\text{c.c.},$$

$$\int d\boldsymbol{r}\delta\rho_2(\boldsymbol{r})=2\langle\delta\phi_2|\phi_2\rangle\langle\phi_1|\phi_1\rangle+\text{c.c.} \tag{30}$$

The corresponding change in expression (27) is

$$\delta T_s=\langle\delta\phi_1|\hat{t}|\phi_1\rangle\langle\phi_2|\phi_2\rangle+\langle\phi_2|\hat{t}|\phi_2\rangle\langle\delta\phi_1|\phi_1\rangle+\text{c.c.}$$
$$+(1\leftrightarrow2), \tag{31}$$

which using the orbital equation

$$[\hat{t}+v(\boldsymbol{r})]\phi_i(\boldsymbol{r})=\varepsilon_i\phi_i(\boldsymbol{r}) \tag{32}$$

for the ground state, becomes

$$\delta T_s=\langle\delta\phi_1|\varepsilon_1-v(\boldsymbol{r})|\phi_1\rangle\langle\phi_2|\phi_2\rangle+\langle\phi_2|\varepsilon_2-v(\boldsymbol{r})|\phi_2\rangle$$
$$\times\langle\delta\phi_1|\phi_1\rangle+\text{c.c.}+(1\leftrightarrow2)$$
$$=(\varepsilon_1+\varepsilon_2)\langle\delta\phi_1|\phi_1\rangle\langle\phi_2|\phi_2\rangle+\text{c.c.}-\int d\boldsymbol{r}v(\boldsymbol{r})\delta\rho_1(\boldsymbol{r})$$
$$+(1\leftrightarrow2)$$
$$=\int d\boldsymbol{r}(E_0/2-v(\boldsymbol{r}))(\delta\rho_1(\boldsymbol{r})+\delta\rho_2(\boldsymbol{r})) \tag{33}$$

with $E_0=\varepsilon_1+\varepsilon_2$. This confirms the fact that to leading order this depends only on the density, and no minimization in Eq. (26) is needed in the neighborhood of the ground-state density. The result also confirms that the functional is Fréchet differentiable at the ground-state density and that the functional derivative can be represented by a *single* local multiplicative function,

$$\left(\frac{\delta T_s[\rho]}{\delta\rho(\boldsymbol{r})}\right)_{\rho=\rho_0}=\left(\frac{\delta T_s[\rho]}{\delta\rho_1(\boldsymbol{r})}\right)_{\rho=\rho_0}$$
$$=\left(\frac{\delta T_s[\rho]}{\delta\rho_2(\boldsymbol{r})}\right)_{\rho=\rho_0}$$
$$=E_0/2-v(\boldsymbol{r}). \tag{34}$$

As before, we could confine the variations to those that preserve the density normalization, and we would retrieve result (22).

We can now confirm our results by means of the *chain rule*, which is used by Nesbet to illustrate the breakdown of the locality hypothesis. We evaluate first the orbital derivative, considering expression (27) as an *orbital functional*,

$$\frac{\delta T_{\mathrm{s}}[\phi_1,\phi_2]}{\delta\phi_1^*}=\hat{t}|\phi_1\rangle\langle\phi_2|\phi_2\rangle+\langle\phi_2|\hat{t}|\phi_2\rangle\phi_1$$
$$=[(E_0-v(\boldsymbol{r}))\langle\phi_2|\phi_2\rangle-\langle\phi_2|v(\boldsymbol{r})|\phi_2\rangle]\phi_1(\boldsymbol{r}). \tag{35}$$

Here, *the orbitals are regarded as independent*.

Next, we evaluate the orbital derivative from the same expression, considering it as a *density functional*. In order to do so, we have to *disregard that fact that the orbital might be interconnected*, otherwise the result will become meaningless,

$$\frac{\delta T_{\mathrm{s}}[\phi_1,\phi_2]}{\delta\phi_i^*(\boldsymbol{r})}=\int \mathrm{d}\boldsymbol{r}'\frac{\delta T_{\mathrm{s}}[\rho]}{\delta\rho(\boldsymbol{r}')}\frac{\delta\rho(\boldsymbol{r}')}{\delta\phi_i^*(\boldsymbol{r})}. \tag{36}$$

With the expression for density (24) this yields

$$\frac{\delta T_{\mathrm{s}}[\phi_1,\phi_2]}{\delta\phi_1^*(\boldsymbol{r})}=\int \mathrm{d}\boldsymbol{r}'\frac{\delta T_{\mathrm{s}}[\rho]}{\delta\rho(\boldsymbol{r}')}[\delta(\boldsymbol{r}-\boldsymbol{r}')\langle\phi_2|\phi_2\rangle$$
$$+|\phi_2(\boldsymbol{r}')|^2]\phi_1(\boldsymbol{r})$$
$$=\left[\frac{\delta T_{\mathrm{s}}[\rho]}{\delta\rho(\boldsymbol{r})}\langle\phi_2|\phi_2\rangle+\left\langle\phi_2\left|\frac{\delta T_{\mathrm{s}}[\rho]}{\delta\rho}\right|\phi_2\right\rangle\right]\phi_i(\boldsymbol{r}). \tag{37}$$

Identification with orbital derivative (35) then leads immediately to

$$\frac{\delta T_{\mathrm{s}}[\rho]}{\delta\rho(\boldsymbol{r})}=E_0/2-v(\boldsymbol{r}), \tag{38}$$

which is identical to our previous result (34). The same result is obtained if we consider the derivative with respect to the second orbital.

We have here demonstrated that it is possible to evaluate the orbital derivative from a density functional, using the chain rule, and that knowledge about the orbital derivative can be used to deduce the density derivative. *A prerequisite is here that the expression used is simultaneously an orbital and a density functional*. The last point is crucial, because *it is prisicely at this point that the approach of Nesbet fails*, as we shall demonstrate below. Although, his expression is a density functional at the ground-state density, this is *not* the case in the neighborhood, which is needed in order to define the density derivative.

III. COMMENTS ON THE TREATMENT OF NESBET

We shall now comment in more detail on the treatment of Nesbet [3,7] and start by reproducing his main results, restricting ourselves for simplicity again to two electrons with no spin. Nesbet defines the kinetic-energy functional by $T_{\mathrm{s}}[\rho]=\langle\Phi|\hat{T}|\Phi\rangle$ *without* the constraint search (26). As before, Φ is here a single Slater determinant of spin orbitals ϕ_i, which are orthogonal but not necessarily normalized. Nesbet emphasizes the importance of going outside the domain of normalized orbitals in applying the EL procedure, but nevertheless leaves out the normalization integrals and uses instead of (25) the expression

$$T_{\mathrm{s}}=\langle\phi_1|\hat{t}|\phi_1\rangle+\langle\phi_2|\hat{t}|\phi_2\rangle \tag{39}$$

throughout the domain. Similarly, instead of the density expression (24), he applies

$$\rho(\boldsymbol{r})=|\phi_1(\boldsymbol{r})|^2+|\phi_2(\boldsymbol{r})|^2 \tag{40}$$

also in the extended domain. It can be shown that *leaving out the normalization integrals in Eqs.* (24) *and* (25) *causes the kinetic energy, seen as a functional of the total density, to be multivalued outside the domain of normalized orbitals.*

Making the same orbital modifications as in the preceding section, keeping the orbitals orthogonal but relaxing the normalization condition, leads to

$$\delta\rho_1(\boldsymbol{r})=\delta\phi_1^*(\boldsymbol{r})\phi_1(\boldsymbol{r})+\mathrm{c.c.},\quad \delta\rho_2(\boldsymbol{r})=\delta\phi_2^*(\boldsymbol{r})\phi_2(\boldsymbol{r})+\mathrm{c.c.}, \tag{41}$$

which for the ground state becomes

$$\delta T_{\mathrm{s}}=\langle\delta\phi_1|\varepsilon_1-v(\boldsymbol{r})|\phi_1\rangle+\langle\delta\phi_2|\varepsilon_2-v(\boldsymbol{r})|\phi_2\rangle+\mathrm{c.c.} \tag{42}$$

or

$$\delta T_{\mathrm{s}}=\int \mathrm{d}\boldsymbol{r}[\varepsilon_1-v(\boldsymbol{r})]\delta\rho_1(\boldsymbol{r})+\int \mathrm{d}\boldsymbol{r}[\varepsilon_2-v(\boldsymbol{r})]\delta\rho_2(\boldsymbol{r}). \tag{43}$$

This should be compared with our equation (33), where δT_{s} depends only on the *total density* $\rho(\boldsymbol{r})=\rho_1(\boldsymbol{r})+\rho_2(\boldsymbol{r})$. Nesbet's procedure leads—in contrast to our result (34)—to an *orbital dependence* of the derivative

$$\frac{\delta T_{\mathrm{s}}}{\delta\rho_1}=\varepsilon_1-v(\boldsymbol{r})\neq\frac{\delta T_{\mathrm{s}}}{\delta\rho_2}=\varepsilon_2-v(\boldsymbol{r})\quad \varepsilon_1\neq\varepsilon_2, \tag{44}$$

corresponding to Eq. (12) in Nesbet's paper [7].

We can also see the effect of the omission of the normalization integrals on the application of the chain rule (36), which with expression (40) for the density simplifies to

$$\frac{\delta T_{\mathrm{s}}[\phi_1,\phi_2]}{\delta\phi_i^*(\boldsymbol{r})}=\frac{\delta T_{\mathrm{s}}[\rho]}{\delta\rho(\boldsymbol{r})}\frac{\delta\rho(\boldsymbol{r})}{\delta\phi_i^*(\boldsymbol{r})}=\frac{\delta T_{\mathrm{s}}[\rho]}{\delta\rho(\boldsymbol{r})}\phi_i(\boldsymbol{r}). \tag{45}$$

When this is compared with the orbital derivative

$$\frac{\delta T_{\mathrm{s}}[\phi_1,\phi_2]}{\delta\phi_i^*(\boldsymbol{r})}=\hat{t}\,\phi_i(\boldsymbol{r})=[\varepsilon_i-v(\boldsymbol{r})]\phi_i(\boldsymbol{r}), \tag{46}$$

we retrieve the orbital-dependent derivative (44), which evidently cannot be represented by a single local function and only as a *linear operator*.

The reason for the strange result of Nesbet is that *the quantity T_{s} is not a density functional in the neighborhood of the ground-state density*. It can easily be shown that this quantity, regarded as a functional of the total density (40), becomes *multivalued* outside the domain of normalized orbitals. Then it cannot be a density functional, which by definition has to be unique in the entire domain. The multivaluedness is a consequence of the omission of the normalization integrals.

From the fact that Nesbet finds functional derivatives that have an apparent orbital dependence, he draws the conclusion that they can be interpreted as *Gâteaux derivatives*. This conclusion is not correct either, simply because his kinetic-energy expression is not a density functional.

IV. CONCLUSIONS

We have shown that for a system of noninteracting electrons, the kinetic-energy functional is Fréchet differentiable at the ground-state density, if the normalization constraint is relaxed, and that the functional derivative at this density can be represented by a single local multiplicative function. This is in conflict with the result of Nesbet, who, using different expressions for the kinetic energy and the density in the unnormalized domain, finds that the derivative has an orbital dependence and can only be represented by a linear operator. According to Nesbet, this demonstrates a failure of the locality hypothesis.

We claim—in accordance with the previous commentators [5,6]—that the results of Nesbet are erroneous. In our opinion, the main reason for the failure of the procedure used by Nesbet is that the density functionals are extended into the domain of unnormalized densities in an incorrect way, which leads to multivaluedness. This effect, however, shows up only in the Fréchet derivative. Inside the normalization domain, where it is sufficient to work with the Gâteaux derivative, all results agree.

Note added in proof. Since this manuscript was submitted, we have studied the differentiability of density functionals further [18]. We have found that defining the Gâteaux differentiability as often used in the DFT literature [8], requiring the differential to be linear and continuous, the difference between the Gâteaux and Fréchet differentiabilities is quite subtle and hardly of any practical importance. We have also found that large classes of density functionals are under general circumstances Gâteaux differentiable in this sense, which is sufficient for DFT purposes. Strict Fréchet differentiability does not seem to be needed here. This does not change the main outcome of this Comment, though, that the kinetic-energy functional is differentiable for noninteracting electrons, regardless of the number of electrons—in contrast to the claims of Nesbet.

ACKNOWLEDGMENTS

Communications with Robert Nesbet as well as with Andreas Görling, Vincent Ortez, Erkki Bröndas, Evert Jan Baerends, Robert van Leeuwen, and Andrzej Holas are acknowledged. This work was supported by the Swedish Research Council (S.S.) and the Alexander von Humboldt Foundation (I.L.).

---

[1] P. Hohenberg and W. Kohn, Phys. Rev. B **136**, B864 (1964).
[2] W. Kohn and L.J. Sham, Phys. Rev. **140**, A1133 (1965).
[3] R.K. Nesbet, Phys. Rev. A **58**, R12 (1998).
[4] R.K. Nesbet and R. Colle, Phys. Rev. A **61**, 012503 (1999).
[5] T. Gál, Phys. Rev. A **62**, 044501 (2000).
[6] A. Holas and N.M. March, Phys. Rev. A **64**, 016501 (2001).
[7] R.K. Nesbet, Phys. Rev. A **65**, 010502 (2001).
[8] R. van Leeuwen, Adv. Quantum Chem. **43** (2003).
[9] P. Blanchard and E. Brüning, *Variational Methods in Mathematical Physics. A Unified Approach* (Springer-Verlag, Berlin, 1992).
[10] H. Englisch and R. Englisch, Phys. Status Solidi A **123**, 711 (1984).
[11] H. Englisch and R. Englisch, Phys. Status Solidi A **124**, 373 (1984).
[12] M. Levy, Proc. Natl. Acad. Sci. U.S.A. **76**, 6062 (1979).
[13] M. Levy, Phys. Rev. A **26**, 1200 (1982).
[14] E.H. Lieb, Int. J. Quantum Chem. **24**, 243 (1983).
[15] R.M. Dreizler and E.K.U. Gross, *Density Functional Theory* (Springer-Verlag, Berlin, 1990).
[16] R.G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).
[17] L.A. Lusternik and V.J. Sobolev, *Elements of Functional Analysis* (Wiley, N.Y., 1961).
[18] I. Lindgren and S. Salomonson, Adv. Quantum Chem. (to be published).