Comment on "Kinetic energy as a density functional"

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In a recent paper, Nesbet [Phys. Rev. A **65**, 010502(R) (2001)] has proposed dropping "the widespread but unjustified assumption that the existence of a ground-state density functional for the kinetic energy, $T_s[\rho]$, of an N-electron system implies the existence of a density-functional derivative, $\delta T_s[\rho]/\delta\rho(\mathbf{r})$, equivalent to a *local potential* function," because, according to his arguments, this derivative "has the mathematical character of a *linear operator* that acts on orbital wave functions." Our Comment demonstrates that the statement called by Nesbet an "unjustified assumption" happens, in fact, to be a rigorously proven theorem. Therefore, his previous conclusions stemming from his different view of this derivative, which undermined the foundations of density-functional theory, can be discounted.

Nesbet has, in a recent paper [1], continued his previous efforts to reveal additional properties of the noninteracting kinetic energy functional $T_s[\rho]$, its functional derivative $\delta T_s[\rho]/\delta\rho(\mathbf{r})$, and related fundamental subjects of density-functional theory (DFT). In our present Comment, we are going to continue our previous dispute [2] with him (i.e., our Comment on his earlier paper [3]), because he refuted in [1] our argument [2] as "invoking circular logic:" according to his opinion, "the 'locality hypothesis' is tacitly assumed" by us, and our equations "ignored the possibility that the functional derivative $\delta T_s[\rho]/\delta\rho$ might be a linear operator rather than a local function." Since this blame for our tacit assumption in [2] of the locality hypothesis is so crucial for Nesbet that he sees no need to address in [1] our criticisms of his concrete statements in [3], we devote the present Comment mainly to the proof that $\delta T_s[\rho]/\delta\rho(\mathbf{r})$ does have the property of a local potential. This task is facilitated by the fact that, this time, Nesbet provides in [1] his own precise definition of $T_s[\rho]$, so our proof can be performed using his starting point.

Following Nesbet [1], let us consider a noninteracting N-electron system in an external *local* (multiplicative) potential $v(\mathbf{r})$, in its ground state (GS), which is assumed to be *nondegenerate*. Its total kinetic energy $T_{v,N}$ represents, by definition, the value of the single-particle kinetic energy functional corresponding to the actual electron density of this system:

$$T_s[\rho] = T_{v,N} \tag{1a}$$

for

$$\rho = \rho_{v,N}. \tag{1b}$$

By this construction, the domain of the definition of this functional is the functional space A_N^0 of "noninteracting v-representable densities" for N-electron systems with a nondegenerate GS, $\rho \in \mathsf{A}_N^0$. The kinetic energy, the electron density, and other characteristics of the system GS can be expressed in terms of orbitals and orbital energies, the eigensolutions of a one-electron Schrödinger equation:

$$\hat{t}\phi_i = \{\epsilon_i - v\} \phi_i, \quad i = 1, 2, \ldots, \tag{2a}$$

with energies ordered as

$$\epsilon_1 \leq \epsilon_2 \leq \cdots \leq \epsilon_N < \epsilon_{N+1} \leq \cdots \tag{2b}$$

(note a gap above the Nth-state level, which is connected with the nondegenerate GS of the system). Here $\hat{t}(\mathbf{r}) = -\frac{1}{2}\nabla^2(\mathbf{r})$ is the kinetic energy (differential) operator. Atomic units are used throughout. Spin indices and summations are implied but omitted for simplicity.

Being eigenfunctions of a Hermitian operator, the orbitals are orthogonal,

$$\langle \phi_i | \phi_m \rangle = 0 \tag{2c}$$

for $\epsilon_i \neq \epsilon_m$. In the case of d-fold degeneracy

$$\epsilon_j < \epsilon_{j+1} = \epsilon_{j+2} = \cdots = \epsilon_{j+d} < \epsilon_{j+d+1}, \tag{2d}$$

the set of independent eigenfunctions $\{\phi_{j+k}, k=1,\ldots,d\}$ can be orthogonalized to satisfy Eq. (2c) for $i=j+k$, $m=j+l$, $i \neq m$. Finally, all eigenfunctions are normalized,

$$\langle \phi_i | \phi_i \rangle = 1 \text{ for } i = 1, 2, \ldots. \tag{2e}$$

The orthonormal set of eigenfunctions (constructed in this way) corresponding to a degenerate level, Eq. (2d), $\langle \phi_{j+k} | \phi_{j+l} \rangle = \delta_{k,l}$ for $k,l=1,\ldots,d$, is not unique: an alternative set can be obtained by applying an arbitrary d-dimensional unitary transformation to the existing set.

As is well known (see, e.g., [1]), the total kinetic energy and the electron-number density of the system can be calculated as

$$T_{v,N} = \sum_{i=1}^{N} \langle \phi_i | \hat{t} | \phi_i \rangle, \tag{3a}$$

$$\rho_{v,N} = \sum_{i=1}^{N} |\phi_i|^2. \tag{3b}$$

It should be noted that the normalization requirement (2e) is necessary for Eqs. (3) to be correct, and that these equations are invariant with respect to a unitary transformation applied to a set of degenerate level orbitals.

Next, consider the GS of the same system in a modified external potential $v(\mathbf{r}) + \lambda \, \delta v(\mathbf{r})$, again assumed to be local (multiplicative). The real parameter $\lambda > 0$ controls the strength of the perturbation. As previously, the total kinetic energy of the perturbed system defines a value of T_s corresponding to the perturbed electron density:

$$T_s[\rho + \lambda \, \delta\rho + O(\lambda^2)] = T_{v+\lambda \, \delta v, N} \tag{4a}$$

for

$$\rho + \lambda \, \delta\rho + O(\lambda^2) = \rho_{v+\lambda \, \delta v, N}. \tag{4b}$$

The perturbed orbital eigenfunction and energy of a nondegenerate ith state can be determined from the equation

$$\hat{t}\{\phi_i + \lambda \, \delta\phi_i + O(\lambda^2)\} = \{\epsilon_i + \lambda \, \delta\epsilon_i + O(\lambda^2) - v - \lambda \, \delta v\}$$
$$\times \{\phi_i + \lambda \, \delta\phi_i + O(\lambda^2)\}. \tag{5a}$$

Such an equation can also be used for states labeled by $i = j+k$, $k=1,\ldots,d$ that belong to a d-fold degenerate level, Eq. (2d), provided the opportunity of applying a unitary transformation to a set of d orbitals [mentioned just below Eq. (2e)] is exploited to obtain the perturbation matrix in the diagonal form

$$\langle \phi_{j+k} | \delta v | \phi_{j+l} \rangle = \delta_{k,l} \langle \phi_{j+k} | \delta v | \phi_{j+k} \rangle$$
$$\text{for } k,l = 1,\ldots,d. \tag{5b}$$

The normalization

$$\langle \phi_i + \lambda \, \delta\phi_i + O(\lambda^2) | \phi_i + \lambda \, \delta\phi_i + O(\lambda^2) \rangle = 1 \tag{5c}$$

is required to validate for the perturbed system the following analogs of Eq. (3):

$$T_{v+\lambda \, \delta v, N} = \sum_{i=1}^{N} \langle \phi_i + \lambda \, \delta\phi_i + \cdots | \hat{t} | \phi_i + \lambda \, \delta\phi_i + \cdots \rangle, \tag{6a}$$

$$\rho_{v+\lambda \, \delta v, N} = \sum_{i=1}^{N} |\phi_i + \lambda \, \delta\phi_i + \cdots|^2$$

$$= \rho_{v,N} + \lambda \sum_{i=1}^{N} \{\delta\phi_i^* \phi_i + \text{c.c.}\} + O(\lambda^2). \tag{6b}$$

According to Eqs. (4a) and (1a), the difference between Eqs. (6a) and (3a) represents a variation of the kinetic energy functional [use Eqs. (5a) and (2a) for its evaluation]:

$$\delta T_s \equiv T_s[\rho + \lambda \, \delta\rho + O(\lambda^2)] - T_s[\rho]$$

$$= \lambda \left(\sum_{i=1}^{N} \{\langle \delta\phi_i | \epsilon_i - v | \phi_i \rangle + \text{c.c.}\} + \sum_{i=1}^{N} \{\delta\epsilon_i \right.$$

$$\left. - \langle \phi_i | \delta v | \phi_i \rangle\} \right) + O(\lambda^2). \tag{7}$$

Obviously, the leading terms canceled out.

Within first-order perturbation theory, when the ith orbital level is nondegenerate, the perturbation of its energy is given simply by

$$\delta\epsilon_i = \langle \phi_i | \delta v | \phi_i \rangle. \tag{8}$$

However, this equation is valid also for $i = j+k$, belonging to the d-fold degenerate level, Eq. (2d), due to such a choice of a set of unperturbed orbitals that Eq. (5b) is satisfied. So from Eq. (8) follows the vanishing of the second sum in Eq. (7):

$$\delta T_s = \lambda \sum_{i=1}^{N} \{\langle \delta\phi_i | \epsilon_i - v | \phi_i \rangle + \text{c.c.}\} + O(\lambda^2) \tag{9a}$$

$$= \lambda \sum_{i=1}^{N} (\epsilon_i \{\langle \delta\phi_i | \phi_i \rangle + \text{c.c.}\}$$

$$- \{\langle \delta\phi_i | v | \phi_i \rangle + \text{c.c.}\}) + O(\lambda^2). \tag{9b}$$

From the terms linear in λ in the normalization Eq. (5c) it follows that

$$\langle \delta\phi_i | \phi_i \rangle + \text{c.c.} = 0. \tag{10}$$

Therefore the term proportional to ϵ_i in Eq. (9b) vanishes. However, it can also be replaced with a similar term of zero value, namely, $\mu\{\langle \delta\phi_i | \phi_i \rangle + \text{c.c.}\}$, where μ is an arbitrary real constant. After this substitution, Eq. (9) can be rewritten as

$$\delta T_s = \lambda \sum_{i=1}^{N} \{\langle \delta\phi_i | \mu - v | \phi_i \rangle + \text{c.c.}\} + O(\lambda^2). \tag{11}$$

Because of the locality of $\mu - v$, each term of the sum can be rewritten as $\int d^3r \, \{\mu - v\}\{\delta\phi_i^* \phi_i + \text{c.c.}\}$ and then the summation sign can be moved into the integrand. Therefore Eq. (11) leads to

$$\delta T_s = \lambda \int d^3r \{\mu - v\} \sum_{i=1}^{N} \{\delta\phi_i^* \phi_i + \text{c.c.}\} + O(\lambda^2), \tag{12}$$

and, after expressing the sum as $\delta\rho$ [compare Eqs. (4b) and (6b)], one finally reaches the result

$$T_s[\rho + \lambda \, \delta\rho + O(\lambda^2)] - T_s[\rho] = \int d^3r \{\mu - v\} \lambda \, \delta\rho + O(\lambda^2). \tag{13}$$

According to the commonly accepted definition of functional differentiation (see, e.g., [4,5]), Eq. (13) leads to the following value of the functional derivative:

$$\left.\frac{\delta T_s[\rho]}{\delta\rho(\mathbf{r})}\right|_{\rho=\rho_{v,N}} = \mu - v(\mathbf{r}). \qquad (14)$$

Since, by our construction, the density variations $\lambda\,\delta\rho$ in Eq. (13) integrate to zero, Eq. (14) represents the Gâteaux derivative of T_s rather than the Fréchet one [5] (the latter needs more general density variations, including those that do not integrate to zero). For the unperturbed density we have $\rho \in A_N^0$ by assumption, while the perturbed density belongs to A_N^0 because of Eq. (4b) and because the GS of the perturbed system is nondegenerate [for not too large λ, i.e., as long as the gap, seen initially in Eq. (2b), remains open, $\{\epsilon_N + \lambda\,\delta\epsilon_N + O(\lambda^2)\} < \{\epsilon_{N+1} + \lambda\,\delta\epsilon_{N+1} + O(\lambda^2)\}$]. Since δv is arbitrary, the perturbed density Eq. (4b) represents the most general neighborhood in A_N^0 of the unperturbed density Eq. (1b). Therefore the functional differentiation Eqs. (13) and (14) is performed within the functional space A_N^0. Let us note that the potential v occurs on both sides of Eq. (14): on the right, in a combination with an arbitrary constant μ it gives the value of the derivative; on the left, it characterizes the "point" $\rho = \rho_{v,N} \in A_N^0$ at which this derivative is calculated.

It is worth noting that the expression in the second line of Nesbet's Eq. (9) of [1] is equivalent to our Eq. (9a) if his $\delta\phi_i$ plays the role of our $\lambda\,\delta\phi_i$; however, these $\lambda\,\delta\phi_i$ and $\delta\phi_i$ denote, in fact, quite different objects. Our $\lambda\,\delta\phi_i$ satisfies Eq. (5a), i.e., the Schrödinger equation describing the motion in a perturbed potential $v(\mathbf{r}) + \lambda\,\delta v(\mathbf{r})$, and also satisfies the normalization Eq. (5c), while Nesbet's $\delta\phi_i$ represents a variation of an occupied orbital "in any infinitesimal function neighborhood of a solution of the GS equations," "restricted only by orthogonality to all other occupied orbitals." Therefore, his modified density $\rho + \delta\rho$ [where the density variation $\delta\rho$ in terms of these $\delta\phi_i$ is given in Eq. (7) of [1]] does not belong to the domain of v-representable densities. This is the reason why completely different conclusions are drawn by us and by Nesbet from seemingly the same equations.

The main result of our present Comment, Eq. (14), demonstrates that the locality of $\delta T_s[\rho]/\delta\rho(\mathbf{r})$ is not a hypothesis but a rigorously proven fact, thus refuting Nesbet's opposite opinion [1]. Our proof of the locality of the functional derivative has been performed here for a particular functional $T_s[\rho] \in R^1$, defined in a particular domain $\rho \in A_N^0$, i.e., for the functional considered by Nesbet in [1]. The mathematical tools applied by us are just as simple as those used by him. But, in fact, our result happens to be a special case of a general result about the locality of the functional derivative of an arbitrary real functional on $L^p(R^3)$ (provided such a derivative exists); see, e.g., Eq. (5.51) in the monograph [5] cited by Nesbet [1]. However, for the proof of the locality in this case much more advanced mathematics needs to be involved. The mentioned topic represents an ingredient of a rigorous formulation of DFT foundations given by Lieb [6] and Englisch and Englisch [7]. As shown by them, the electron density ρ of the DFT belongs to the space $B = L^1(R^3) \cap L^3(R^3)$. The Lieb functionals $F_L[\rho]$ and $T_{s,L}[\rho]$, defined for $\rho \in B$ (the generalizations of the basic Hohenberg-Kohn functionals for interacting and noninteracting N-electron systems, respectively, written as Legendre transforms of the energy functionals) exhibit the property of being convex and lower semicontinuous. Therefore their functional derivatives (in the Gâteaux sense) exist for $\rho \in \tilde{A}_N \subset B$ and $\rho \in \tilde{A}_N^0 \subset B$, respectively. Here $\tilde{A}_N$ is the space (the set) of interacting ensemble–v-representable densities $\tilde{A}_N^0$—the noninteracting analog. These functional derivatives belong to the Banach space of *local potentials* $B^* = L^{3/2}(R^3) + L^{\infty}(R^3)$, dual to B. Because the exchange-correlation potential of the Kohn-Sham (KS) equations involves simultaneously $\delta F_L[\rho]/\delta\rho(\mathbf{r})$ and $\delta T_{s,L}[\rho]/\delta\rho(\mathbf{r})$ with $\rho \in \tilde{A}_N \subset B$ and $\rho \in \tilde{A}_N^0 \subset B$, respectively, it is important to know whether $\tilde{A}_N$ and $\tilde{A}_N^0$ have an overlap. While the precise answer to this question is unknown to us, we can apply the following reasoning. The sets $\tilde{A}_N$ and $\tilde{A}_N^0$ can be shown to be dense subsets of each other (as follows from application of Lemma 6.3 of [7] to the interacting and noninteracting cases); therefore the density of an interacting system, $\rho \in \tilde{A}_N$, can, to arbitrary accuracy, be reproduced by the ensemble density ρ_{KS} of the GS of a system of N noninteracting electrons moving in the local effective KS potential, $\rho_{KS} \in \tilde{A}_N^0$. In this way, the validity of the KS equations can be settled.

In light of the above mentioned rigorous results, our previous Comment [2], which involved local functional derivatives of various functionals important for DFT, cannot be refuted by the argument of a "tacitly assumed locality hypothesis" [1]; all conclusions drawn by us in [2] remain valid, thus showing that DFT is fundamentally correct and internally consistent, despite Nesbet's worrisome claims in [3] and [1] to the contrary.

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