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Comment on ‘‘Kinetic energy in density-functional theory’’

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In a recent paper, R. K. Nesbet [Phys. Rev. A **58**, R12 (1998)] has compared the single-particle kinetic energy from the Kohn-Sham reference state theory with that of the Thomas-Fermi-like form of the density-functional theory. We argue that, contrary to his opinion, both theories should give the same results for N-electron ground-state density. We show also that there is no inconsistency between the kinetic-energy forms of the two theories, and no need to extend the definition of functional derivatives.

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I. INTRODUCTION

R. K. Nesbet, has in a recent paper [1], performed a comparison between two approaches to the density-functional theory (DFT) of an N-electron system: the Thomas-Fermi-like (TF) representation (formulated solely in terms of the electron density of the system), and the Kohn-Sham (KS) representation (formulated in terms of N one-electron spin orbitals). His conclusions seem to undermine the foundations of the DFT. Because there is no published reaction to the Nesbet's paper till now (to our best knowledge), we decided to clarify in our Comment the issues discussed by him, in order to assure all users of the DFT that this theory is fundamentally correct. As it will be shown, by using rigorous notation and precise definitions, and also clarifying semantics, all worrisome findings in Ref. [1] can be overcome.

II. THOMAS-FERMI-LIKE EQUATION

Similarly as in Nesbet's paper [1], we consider an N-electron system (like an atom, a molecule) described by the Hamiltonian $\hat{H}=\hat{T}+\hat{V}+\hat{U}$, where $\hat{T}=\Sigma_{i=1}^{N}\hat{t}(\mathbf{r}_i)$, $\hat{V}=\Sigma_{i=1}^{N}v(\mathbf{r}_i)$, and $\hat{U}=\Sigma_{1\leqslant i<j\leqslant N}u(\mathbf{r}_i,\mathbf{r}_j)$. Here $\mathbf{x}_i\equiv\{\mathbf{r}_i,s_i\}$ denotes the space-spin coordinate of ith electron, $\hat{t}(\mathbf{r})=-\frac{1}{2}\boldsymbol{\nabla}^2(\mathbf{r})$ is the kinetic energy (differential) operator, $v(\mathbf{r})$ is the local (multiplicative) external potential (due to clamped nuclei), and $u(\mathbf{r}_i,\mathbf{r}_j)=1/|\mathbf{r}_i-\mathbf{r}_j|$ is the local electron-electron interaction potential. Atomic units are used throughout. The ground-state (GS) energy E_{GS} of this system can be determined from the variational principle

$$E_{\mathrm{GS}}=\min_{\Psi}\langle\Psi|\hat{H}|\Psi\rangle=\langle\Psi_{\mathrm{GS}}|\hat{H}|\Psi_{\mathrm{GS}}\rangle, \tag{2.1}$$

where minimization goes in the Hilbert space of N-electron, antisymmetric, normalized, $\langle\Psi|\Psi\rangle=1$, wave functions $\Psi=\Psi(\mathbf{x}_1,\ldots,\mathbf{x}_N)$. Following Levy's constrained-search formulation [2] (see also Refs. [3] and [4]) the above minimization can be done in two steps, namely,

$$E_{\mathrm{GS}}=\min_{\rho\to N}\{\min_{\Psi\to\rho}\langle\Psi|\hat{T}+\hat{V}+\hat{U}|\Psi\rangle\}, \tag{2.2}$$

i.e., outer minimization over densities that lead to the given number of particles, $\rho\to N$, namely,

$$\int d^3r\,\rho(\mathbf{r})=N,\qquad \rho(\mathbf{r})\geqslant 0, \tag{2.3}$$

and the internal one over the wave functions that lead to the given density, $\Psi\to\rho$, namely,

$$N\sum_{s_1}\int d^4x_2\cdots d^4x_N|\Psi(\mathbf{x}_1,\ldots,\mathbf{x}_N)|^2=\rho(\mathbf{r}_1). \tag{2.4}$$

Here $\int d^4x_i$ means $\Sigma_{s_i}\int d^3r_i$. Using the property that for $\Psi\to\rho$ the expectation value $\langle\Psi|\hat{V}|\Psi\rangle$ can be expressed in terms of the density as $V[\rho]=\int d^3r\,v(\mathbf{r})\rho(\mathbf{r})$, Eq. (2.2) can be rewritten in a form

$$E_{\mathrm{GS}}=\min_{\rho\to N}E[\rho]=\min_{\rho\to N}\{F[\rho]+V[\rho]\}=E[\rho_{\mathrm{GS}}], \tag{2.5}$$

where the Hohenberg-Kohn (HK) [5] functional [2–4] is defined here by the internal minimization in Eq. (2.2)

$$F[\rho]=\min_{\Psi\to\rho}\langle\Psi|\hat{T}+\hat{U}|\Psi\rangle=\langle\ \ldots\ \rangle|_{\Psi=\Psi_{\min}[\rho]}. \tag{2.6}$$

Thus $\Psi_{\min}[\rho_{\mathrm{GS}}]$ is the system GS function Ψ_{GS} seen in Eq. (2.1). The condition for the minimum in Eq. (2.5), $\delta E[\rho]=0$, can be achieved by solving a TF-like equation

$$\left.\frac{\delta F[\rho]}{\delta\rho(\mathbf{r})}\right|_{\rho=\rho_{\mathrm{GS}}}+v(\mathbf{r})=\mu. \tag{2.7}$$

Here $\delta F[\rho]/\delta\rho(\mathbf{r})$ is the functional derivative of $F[\rho]$, i.e., the function satisfying

$$F[\rho+\varepsilon\,\delta\rho]=F[\rho]+\varepsilon\int d^3r\frac{\delta F[\rho]}{\delta\rho(\mathbf{r})}\delta\rho(\mathbf{r})+O(\varepsilon^2). \tag{2.8}$$

It should be noted that the definition (2.6) holds for an integral, fixed N (which is involved in the definition of $\hat{T}$, $\hat{U}$ and Ψ). Thus allowed $\delta\rho(\mathbf{r})$, used in Eq. (2.8), cannot change the number of electrons in Eq. (2.3), $\int d^3r\ \delta\rho(\mathbf{r})=0$. Therefore, with μ an arbitrary constant, the function $(\delta F[\rho]/\delta\rho(\mathbf{r})-\mu)$ also represents the functional derivative of $F[\rho]$ because it satisfies Eq. (2.8) when inserted in the place of $\delta F[\rho]/\delta\rho(\mathbf{r})$. In this way, the presence of the parameter μ in Eq. (2.7) reflects the fact, that for variations that conserve N, functional derivatives are known with accuracy to an additive constant. Solving Eq. (2.7) means that $\rho(\mathbf{r})$ is varied until the sum on the left-hand side will become independent of $\mathbf{r}$. The value of μ has no physical meaning — it is connected with a particular numerical procedure [some implementation of the definitions (2.6) and (2.8)] used to evaluate $\delta F[\rho]/\delta\rho(\mathbf{r})$. With some procedure chosen, μ happens to be a sensitivity parameter of Eq. (2.7) — its concrete value as well as values of the function $\rho_{\mathrm{GS}}(\mathbf{r})$ for any $\mathbf{r}$, are determined by solving this equation. However, $\rho_{\mathrm{GS}}(\mathbf{r})$ of this solution is unique (independent of the choice of the procedure) and it leads, via Eq. (2.5), to the GS energy from $E_{\mathrm{GS}}=E[\rho_{\mathrm{GS}}]$.

There are known generalizations of the DFT (see, e.g., in Refs. [3] and [4]) which allow for arbitrary, nonintegral N in Eq. (2.5), but they involve an ensemble of systems (having different integral numbers of electrons) to define $F[\rho]$ more general than that in Eq. (2.6). In such case, the constant μ in Eq. (2.7) with the generalized $F[\rho]$, may be interpreted as the chemical potential of the ensemble. But such a generalization will not be considered in our paper.

We are ready now to comment on the Nesbet's statements in the paragraph surrounding Eqs. (1) and (2) of Ref. [1]. His supposition that the functional $E[\rho]$ can be defined for arbitrary variations of $\rho(\mathbf{r})$ that do not conserve N, was shown to be inconsistent with his earlier assumption about considering systems for integral N. Without this supposition, μ is not the chemical potential. We see also in Eq. (2.7) that, contrary to Nesbet's opinion, the parameter μ does not drop out of the TF-like equation for variations that conserve N.

All considerations can be repeated for a system of N noninteracting electrons, moving in the external potential $v_{\mathrm{s}}(\mathbf{r})$. The corresponding Hamiltonian is $\hat{H}_{\mathrm{s}}=\hat{T}+\hat{V}_{\mathrm{s}}$, where $\hat{V}_{\mathrm{s}}=\sum_{i=1}^{N}v_{\mathrm{s}}(\mathbf{r}_i)$. Now the role of $F[\rho]$, Eq. (2.6), is played by the noninteracting kinetic-energy functional

$$T_{\mathrm{s}}[\rho]=\min_{\Phi\to\rho}\langle\Phi|\hat{T}|\Phi\rangle=\langle\ \dots\ \rangle|_{\Phi=\Phi_{\min}[\rho]}, \tag{2.9}$$

where the trial functions Φ belong to the same Hilbert space as defined previously for functions Ψ [below Eq. (2.1)]. Equation (2.5) is replaced now by

$$E_{\mathrm{GS}}^{\mathrm{s}}=\min_{\rho\to N}E_{\mathrm{s}}[\rho]=\min_{\rho\to N}\{T_{\mathrm{s}}[\rho]+V_{\mathrm{s}}[\rho]\}=E_{\mathrm{s}}[\rho_{\mathrm{GS}}^{\mathrm{s}}], \tag{2.10}$$

where $V_{\mathrm{s}}[\rho]=\int d^3r\ v_{\mathrm{s}}(\mathbf{r})\rho(\mathbf{r})$, which leads to the TF-like equation

$$\left.\frac{\delta T_{\mathrm{s}}[\rho]}{\delta\rho(\mathbf{r})}\right|_{\rho=\rho_{\mathrm{GS}}^{\mathrm{s}}}+v_{\mathrm{s}}(\mathbf{r})=\mu_{\mathrm{s}}. \tag{2.11}$$

The GS function of the noninteracting system is $\Phi_{\mathrm{GS}}=\Phi_{\min}[\rho_{\mathrm{GS}}^{\mathrm{s}}]$.

III. KOHN-SHAM EQUATIONS

The KS [6] representation of the density-functional theory is formulated in terms of the exchange-correlation energy functional $E_{\mathrm{xc}}[\rho]$ defined by the relation

$$F[\rho]=T_{\mathrm{s}}[\rho]+E_{\mathrm{es}}[\rho]+E_{\mathrm{xc}}[\rho], \tag{3.1}$$

in which $E_{\mathrm{es}}[\rho]=\frac{1}{2}\int d^3r_1\,d^3r_2\,u(\mathbf{r}_1,\mathbf{r}_2)\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)$ is the classical electrostatic energy of the system, while $F[\rho]$ and $T_{\mathrm{s}}[\rho]$ are defined by the means of Eqs. (2.6) and (2.9). After inserting $F[\rho]$ in the form (3.1) into Eq. (2.5) we obtain

$$E_{\mathrm{GS}}=\min_{\rho\to N}\{T_{\mathrm{s}}[\rho]+V_{\mathrm{KS}}[\rho]\}=\{\cdots\}|_{\rho=\rho_{\mathrm{GS}}}, \tag{3.2a}$$

where $V_{\mathrm{KS}}[\rho]=V[\rho]+E_{\mathrm{es}}[\rho]+E_{\mathrm{xc}}[\rho]$ is the KS effective potential-energy functional, and, next, a TF-like equation

$$\left\{\frac{\delta T_{\mathrm{s}}[\rho]}{\delta\rho(\mathbf{r})}+v_{\mathrm{KS}}(\mathbf{r};[\rho])\right\}_{\rho=\rho_{\mathrm{GS}}}=\mu_{\mathrm{KS}}, \tag{3.2b}$$

where $v_{\mathrm{KS}}(\mathbf{r};[\rho])=\delta V_{\mathrm{KS}}[\rho]/\delta\rho(\mathbf{r})=v(\mathbf{r})+v_{\mathrm{es}}(\mathbf{r};[\rho])+v_{\mathrm{xc}}(\mathbf{r};[\rho])$ is the KS potential, with $v_{\mathrm{es}}(\mathbf{r};[\rho])=\delta E_{\mathrm{es}}[\rho]/\delta\rho(\mathbf{r})=\int d^3r'\ u(\mathbf{r},\mathbf{r}')\rho(\mathbf{r}')$ and $v_{\mathrm{xc}}(\mathbf{r};[\rho])=\delta E_{\mathrm{xc}}[\rho]/\delta\rho(\mathbf{r})$. For the reasons discussed earlier, $v_{\mathrm{KS}}(\mathbf{r};[\rho])$ is known with the accuracy to an additive constant, which is represented in Eq. (3.2b) by μ_{KS} — a sensitivity parameter of this equation.

By comparing the TF-like equation for the noninteracting system (2.11) and the KS TF-like equation for the interacting system (3.2b), we see that the interacting GS density ρ_{GS} can be determined by solving the equivalent noninteracting problem with the potential $v_{\mathrm{s}}(\mathbf{r})=v_{\mathrm{KS}}(\mathbf{r};[\rho_{\mathrm{GS}}])$. However, since ρ_{GS} is not known in advance, an iterative method of solution, which leads to self-consistency, is to be applied, starting from some guessed initial approximation ρ_{ini} for the density to evaluate the initial v_{s} as $v_{\mathrm{KS}}[\rho_{\mathrm{ini}}]$. Equation (3.2) tells us that, provided the exact exchange-correlation energy functional $E_{\mathrm{xc}}[\rho]$ and its functional derivative $v_{\mathrm{xc}}(\mathbf{r};[\rho])$ are available ($V[\rho]$ and $E_{\mathrm{es}}[\rho]$, and their derivatives are known), the model noninteracting N-electron system can be introduced, which leads to the true correlated GS density $\rho_{\mathrm{GS}}(\mathbf{r})$. Various approximate forms of E_{xc} and $v_{\mathrm{xc}}(\mathbf{r})$, as *explicit* functionals of the density ρ, are known (e.g., in the so-called generalized gradient approximation (GGA) of Perdew and Wang [7]) with accuracy sufficient for many applications (note that the dominant two remaining terms of V_{KS} and v_{KS} are *exact* and *explicit* functionals of ρ). But, in order to exploit Eq. (3.2) for a numerical determination of $\rho_{\mathrm{GS}}(\mathbf{r})$ and E_{GS}, one also needs reliable approximations for $\delta T_{\mathrm{s}}[\rho]/\delta\rho(\mathbf{r})$ and $T_{\mathrm{s}}[\rho]$. Known in the literature, various *explicit* forms of these functionals (like in GGA) are not accurate enough to produce reasonable results for systems where $\rho(\mathbf{r})$ is far from homogeneous, although the corresponding calculational schemes are highly efficient. Besides approximate forms for these functionals, there are available procedures calculating them accurately for an arbitrary input $\rho(\mathbf{r})$, e.g., one developed by Zhao, Morrison, and Parr [8]. However, these procedures are so ''expensive'' computationally, that it would be impractical to solve Eq. (3.2b) for $\rho_{\mathrm{GS}}(\mathbf{r})$ with their help [see also comments below Eq. (4.3)].

This difficulty can be circumvented, because the GS problem of a noninteracting system can be addressed alternatively by solving the Schrödinger equation

$$\hat{H}_{\mathrm{s}}\Phi_{\mathrm{GS}}=E^{\mathrm{s}}_{\mathrm{GS}}\Phi_{\mathrm{GS}}. \tag{3.3a}$$

Since the N-electron Hamiltonian is a sum of one-electron Hamiltonians, each depending on the coordinate $\mathbf{r}_i$ of a separate electron

$$\hat{H}_{\mathrm{s}}=\sum_{i=1}^{N}\,[\hat{t}(\mathbf{r}_i)+v_{\mathrm{s}}(\mathbf{r}_i)], \tag{3.3b}$$

the method of separation of variables can be applied. Thus the eigenfunction Φ_{GS} can be written as a product of one-electron functions (spin orbitals) $\phi_i(\mathbf{x})$, the solutions of

$$[-\tfrac{1}{2}\boldsymbol{\nabla}^2(\mathbf{r})+v_{\mathrm{s}}(\mathbf{r})]\phi_i(\mathbf{r},s)=\epsilon_i\,\phi_i(\mathbf{r},s),\qquad i=1,2,\ldots, \tag{3.4}$$

with ϵ_i being the separation constants. It will be convenient to choose real orbitals, $\phi_i^*=\phi_i$, which is possible due to the real nature of the Hamiltonian. After ordering the orbital energies $\epsilon_1\leqslant\epsilon_2\leqslant\cdots\leqslant\epsilon_N<\epsilon_{N+1}\leqslant\cdots$ and normalizing the orbitals, $\langle\phi_i|\phi_i\rangle=1$, the Slater determinant (D)

$$\Phi_{\mathrm{D}}[\phi_1,\ldots,\phi_N]\equiv(N!)^{-1/2}\det\{\phi_i(\mathbf{x}_j)\}_{i,j=1,\ldots,N} \tag{3.5}$$

is the N-electron GS eigenfunction Φ_{GS}, while $E^{\mathrm{s}}_{\mathrm{GS}}=\epsilon_1+\cdots+\epsilon_N$ is the eigenenergy (for simplicity, a nondegenerate GS is assumed, otherwise, Φ_{GS} may be a linear combination of a few Slater determinants). When $v_{\mathrm{KS}}(\mathbf{r})$ is substituted for $v_{\mathrm{s}}(\mathbf{r})$, then Eq. (3.4) represents the system of KS equations [6] for the KS spin orbitals and orbital energies.

For the density $\rho(\mathbf{r})$ which is necessary to evaluate

$$v_{\mathrm{s}}(\mathbf{r})=v_{\mathrm{KS}}(\mathbf{r};[\rho]), \tag{3.6}$$

one uses the density derived from the function $\Phi_{\mathrm{GS}}=\Phi_{\mathrm{D}}[\phi_1,\ldots,\phi_N]$, namely [compare Eq. (2.4)]

$$\rho(\mathbf{r})=\tilde{\rho}(\mathbf{r};[\phi_1,\ldots,\phi_N])\equiv\sum_{i=1}^{N}\sum_{s}\phi_i^2(\mathbf{r},s). \tag{3.7}$$

At self-consistency, this density is the true correlated GS density, because the two alternative methods that solve the GS *density problem* of the N-noninteracting-electron system, via Eq. (3.4) with Eqs. (3.6) and (3.7), or via Eq. (3.2b), must give the same result. The interacting electron energy is calculated as $E_{\mathrm{GS}}=E[\rho_{\mathrm{GS}}]$ in Eq. (3.2a), using

$$\langle\Phi_{\mathrm{D}}|\hat{T}|\Phi_{\mathrm{D}}\rangle=\tilde{T}[\phi_1,\ldots,\phi_N]\equiv\sum_{i=1}^{N}\int d^4x\,\phi_i(\mathbf{x})(-\tfrac{1}{2}\boldsymbol{\nabla}^2(\mathbf{r}))\phi_i(\mathbf{x}) \tag{3.8}$$

for the noninteracting kinetic energy T_{s} in the KS approach, while using Eq. (2.9) in the TF-like approach, and, in practice, applying some approximation for $E_{\mathrm{xc}}[\rho]$. Thus the question raised in the Abstract of Ref. [1], whether the solution of the KS equations and the solution of the TF-like equation should give the same results for the GS (if both are based on the same universal functional defined by the HK theory) is seen to be answered in the positive.

We can comment now on Eq. (3) in Ref. [1], named by Nesbet the KS equations. When his explanation, written just below the mentioned equation, is taken into account, and for $w(\mathbf{r})$ we understand $v_{\mathrm{KS}}(\mathbf{r})$, his equation coincides with our Eqs. (3.4) with (3.6). But we disagree with denoting the sum $\hat{t}(\mathbf{r})+v_{\mathrm{KS}}(\mathbf{r})\equiv\hat{v}_T(\mathbf{r})+w(\mathbf{r})$ by $\delta E[\rho]/\delta\rho(\mathbf{r})$. The object $\delta E[\rho]/\delta\rho(\mathbf{r})$ enters the KS TF-like equation (3.2b), because this equation can be written equivalently as $\delta E[\rho]/\delta\rho(\mathbf{r})|_{\rho=\rho_{\mathrm{GS}}}=\mu_{\mathrm{KS}}$ by noting that $E[\rho]=T_{\mathrm{s}}[\rho]+V_{\mathrm{KS}}[\rho]$ [see Eqs. (2.5) and (3.2a)]. The first term of $\delta E[\rho]/\delta\rho(\mathbf{r})$, namely, $\delta T_{\mathrm{s}}[\rho]/\delta\rho(\mathbf{r})$ [denoted as $v_T(\mathbf{r})$ by Nesbet] is a local potential, therefore the sum of it and another local potential $v_{\mathrm{KS}}(\mathbf{r};[\rho])$ may be required in Eq. (3.2b) to be a constant (at the solution $\rho=\rho_{\mathrm{GS}}$). Thus the inconsistency of Eqs. (5) and (4) in Ref. [1], pointed out by Nesbet, is only apparent; his Eq. (5) contains, in fact, $\{\hat{t}(\mathbf{r})+v_{\mathrm{KS}}(\mathbf{r})\}$, although denoted (incorrectly, in our opinion,) as $\delta E[\rho]/\delta\rho(\mathbf{r})$. Additional arguments in favor of this opinion can be found in the next section.

IV. HARTREE-FOCK-LIKE APPROACH

To address the problem, raised by Nesbet, whether functional derivatives should be understood as linear operators, let us apply the Hartree-Fock (HF) approach to the solution of the GS problem for a *noninteracting* system. Because the GS function of such system is a Slater determinant, this approach gives the exact GS energy rather than the upper bound:

$$\begin{aligned}E^{\mathrm{s}}_{\mathrm{GS}}&=\min_{\Phi_{\mathrm{D}},\langle\Phi_{\mathrm{D}}|\Phi_{\mathrm{D}}\rangle=1}\langle\Phi_{\mathrm{D}}|\hat{H}_{\mathrm{s}}|\Phi_{\mathrm{D}}\rangle\\&=\min_{\phi_1,\ldots,\phi_N,\langle\phi_i|\phi_i\rangle=1}\Big\{\tilde{T}[\phi_1,\ldots,\phi_N]\\&\quad+\int d^3r\,v_{\mathrm{s}}(\mathbf{r})\tilde{\rho}(\mathbf{r};[\phi_1,\ldots,\phi_N])\Big\},\end{aligned} \tag{4.1}$$

see Eqs. (3.5), (3.8), and (3.7) for the definitions of Φ_{D}, $\tilde{T}$, and $\tilde{\rho}$. The Euler-Lagrange equations, which correspond to the minimization (4.1)

$$\frac{1}{2}\,\frac{\delta}{\delta\phi_i(\mathbf{r},s)}\bigg\{\tilde{T}[\phi_1,\ldots,\phi_N] + \int d^3r'\,v_{\mathrm{s}}(\mathbf{r}')\tilde{\rho}(\mathbf{r}';[\phi_1,\ldots,\phi_N]) - \epsilon_i\bigg(\int d^4x'\,\phi_i^2(\mathbf{x}')-1\bigg)\bigg\}=0,\qquad i=1,\ldots,N, \tag{4.2}$$

lead immediately to Eq. (3.4). Now, ϵ_i plays the role of the Lagrange multiplier connected with the normalization constraint for the orbital $\phi_i(\mathbf{x})$ [there is no need to impose the orthogonality constraints, because the Hermicity of the resulting one-electron Hamiltonian in Eq. (3.4) leads to orthogonal eigenfunctions].

When the minimization (4.1) is performed in two steps, similarly as in Eq. (2.2), it leads to Eq. (2.10) again, but with $T_{\mathrm{s}}[\rho]$ defined now by

$$\begin{aligned} T_{\mathrm{s}}[\rho] &= \min_{\Phi_{\mathrm{D}}\to\rho}\langle\Phi_{\mathrm{D}}|\hat{T}|\Phi_{\mathrm{D}}\rangle \\ &= \min_{\{\phi_1,\ldots,\phi_N\}\to\rho}\tilde{T}[\phi_1,\ldots,\phi_N] \\ &= \tilde{T}[\phi_1^{\min}[\rho],\ldots,\phi_N^{\min}[\rho]], \end{aligned} \tag{4.3}$$

where $\{\phi_1,\ldots,\phi_N\}\to\rho$ denotes a set of N spin orbitals that satisfy the constraints $\{\langle\phi_i|\phi_i\rangle=1$ for $i=1,\ldots,N$ and $\tilde{\rho}(\mathbf{r};[\phi_1,\ldots,\phi_N])=\rho(\mathbf{r})\}$. For densities $\rho(\mathbf{r})$, which are noninteracting v representable, the definition (4.3) of $T_{\mathrm{s}}[\rho]$ is equivalent [4] to the more general definition (2.9). Zhao *et al.* [8] have used the definition (4.3) to construct an algorithm that gives the value of $T_{\mathrm{s}}[\rho]$ and $\delta T_{\mathrm{s}}[\rho]/\delta\rho(\mathbf{r})$ for an arbitrary noninteracting v-representable $\rho(\mathbf{r})$ as an input; in an intermediate step, N orbitals are to be determined self-consistently. The present authors have shown earlier [9] that the same definition can be used to construct a different algorithm for the same purpose, in which a system of $(N-1)$ second-order differential coupled equations must be solved in an intermediate step. Therefore, such algorithms remain rather impractical for application in Eq. (3.2).

Nevertheless, Eq. (4.3) will be helpful in discussing Eq. (6) of Nesbet's paper [1]. We rewrite his equation in application to $F=T_{\mathrm{s}}[\rho]$, using our notation and the convention about real orbitals:

$$\sum_{i=1}^{N}\sum_{s}\phi_i(\mathbf{r},s)\frac{1}{2}\frac{\delta\tilde{T}[\phi_1,\ldots,\phi_N]}{\delta\phi_i(\mathbf{r},s)} \tag{4.4a}$$

$$=\sum_{i=1}^{N}\sum_{s}\phi_i(\mathbf{r},s)\frac{\delta T_{\mathrm{s}}[\rho]}{\delta\rho(\mathbf{r})}\phi_i(\mathbf{r},s) \tag{4.4b}$$

$$=\sum_{i=1}^{N}\sum_{s}\phi_i(\mathbf{r},s)\hat{t}(\mathbf{r})\phi_i(\mathbf{r},s). \tag{4.4c}$$

To facilitate the interpretation, we distinguished here two functionals, $T_{\mathrm{s}}[\rho]$ and $\tilde{T}[\phi_1,\ldots,\phi_N]$, in the place of one functional F in Nesbet's Eq. (6). By direct functional differentiation in the definition (3.8), one verifies that the expression (4.4c) is equal to the expression (4.4a). On the other hand, the expression (4.4b) can be obtained directly from the expression

$$\sum_{i=1}^{N}\sum_{s}\phi_i(\mathbf{r},s)\frac{1}{2}\frac{\delta T_{\mathrm{s}}[\tilde{\rho}[\phi_1,\ldots,\phi_N]]}{\delta\phi_i(\mathbf{r},s)}, \tag{4.4d}$$

{it is only similar to (4.4a), because $\tilde{T}$ is replaced by $T_{\mathrm{s}}[\tilde{\rho}]$} by applying to it the chain rule for the functional differentiation

$$=\sum_{i=1}^{N}\sum_{s}\phi_i(\mathbf{r},s)\frac{1}{2}\int d^3r'\frac{\delta T_{\mathrm{s}}[\rho]}{\delta\rho(\mathbf{r}')}\frac{\delta\tilde{\rho}(\mathbf{r}';[\phi_1,\ldots,\phi_N])}{\delta\phi_i(\mathbf{r},s)} \tag{4.4e}$$

and the result $\delta\tilde{\rho}(\mathbf{r}')/\delta\phi_i(\mathbf{r},s)=2\phi_i(\mathbf{r},s)\delta(\mathbf{r}'-\mathbf{r})$ of the functional differentiation in Eq. (3.7). So, in order to have the expression (4.4b) equal to the expression (4.4c), the relation $T_{\mathrm{s}}[\tilde{\rho}(\phi_1,\ldots,\phi_N)]=\tilde{T}[\phi_1,\ldots,\phi_N]$ should hold for an *arbitrary* set of orthonormal spin orbitals $\{\phi_1,\ldots,\phi_N\}$. But, it is not true. As we see from Eq. (4.3), this relation is satisfied only by a *special* ρ-dependent set $\{\phi_1^{\min}[\rho],\ldots,\phi_N^{\min}[\rho]\}$, determined in the process of the minimization with constraints. Therefore, Eqs. (6), (7), and (11) in Ref. [1] are not true; the kinetic-energy operator $\hat{t}(\mathbf{r})\equiv-\frac{1}{2}\boldsymbol{\nabla}^2(\mathbf{r})\equiv\hat{v}_T$ is involved in Eq. (4.3) in $\tilde{T}$ *during* the minimization [see also Eq. (3.8)], while the local potential $v_T(\mathbf{r})\equiv\delta T_{\mathrm{s}}[\rho]/\delta\rho(\mathbf{r})$, arises from the functional differentiation of $T_{\mathrm{s}}[\rho]$, which is the *result of* the minimization in Eq. (4.3).

Similarly, the relation between the nonlocal operator $\hat{v}_{\mathrm{x}}[\phi_1,\ldots,\phi_N]$ of the HF theory and the local exchange potential $v_{\mathrm{x}}(\mathbf{r};[\rho])=\delta E_{\mathrm{x}}[\rho]/\delta\rho(\mathbf{r})$ of the DFT, cannot be written in the form of Nesbet's Eq. (10) in Ref. [1]. Moreover, this local v_{x} involves, besides the Slater potential, also other terms. The detailed discussion of these problems can be found in our papers [10,11].

Our next comment concerns the last paragraph of Sec. IV of Ref. [1]. The expression $T=\int\tilde{v}_T\rho\,d^3r$ represents the global kinetic energy in terms of the local kinetic-energy density $\tilde{v}_T(\mathbf{r})\,\rho(\mathbf{r})\equiv\Sigma_i\Sigma_s\phi_i(\mathbf{r},s)\hat{t}(\mathbf{r})\phi_i(\mathbf{r},s)$ [the right-hand side of Eq. (11) of Ref. [1], rewritten in our convention, see also Eq. (3.8) here]. Since T is a universal functional of ρ, this property is conveyed to $\tilde{v}_T$, so $\tilde{v}_T=\tilde{v}_T(\mathbf{r};[\rho])$. Considering an atom of the nuclear charge Z, the dependence on Z enters its GS kinetic energy via the GS density ρ depending on Z. Therefore, for the Z derivative we have

$$\frac{\partial T[\rho]}{\partial Z} = \int d^3r \frac{\partial}{\partial Z}\{\tilde{v}_T(\mathbf{r};[\rho])\,\rho(\mathbf{r})\}$$
$$= \int d^3r \left\{ \frac{\partial \tilde{v}_T(\mathbf{r};[\rho])}{\partial Z}\rho(\mathbf{r}) + \tilde{v}_T(\mathbf{r};[\rho])\frac{\partial \rho(\mathbf{r})}{\partial Z} \right\}, \tag{4.5}$$

where

$$\frac{\partial \tilde{v}_T(\mathbf{r};[\rho])}{\partial Z} = \int d^3r' \frac{\delta \tilde{v}_T(\mathbf{r};[\rho])}{\delta \rho(\mathbf{r}')} \frac{\partial \rho(\mathbf{r}')}{\partial Z}, \tag{4.6}$$

or, alternatively to Eq. (4.5),

$$\frac{\partial T[\rho]}{\partial Z} = \int d^3r \frac{\delta T[\rho]}{\delta \rho(\mathbf{r})} \frac{\partial \rho(\mathbf{r})}{\partial Z}. \tag{4.7}$$

Since $\tilde{v}_T(\mathbf{r}) \neq \delta T/\delta\rho(\mathbf{r})$ [as we have shown, Eq. (11) in Ref. [1] is incorrect], we see from the comparison of Eq. (4.5) with Eq. (4.7) that there is no reason for the first term on the right-hand side of Eq. (4.5) — the quantity

$$Q_T = \int d^3r \, \frac{\partial \tilde{v}_T(\mathbf{r};[\rho])}{\partial Z}\rho(\mathbf{r}), \tag{4.8}$$

Eq. (16) of Ref. [1]—to be zero. Thus, Nesbet's numerical results, showing finite values of Q_T for a few atoms, confirm our conclusion that the local kinetic energy per particle $\tilde{v}_T(\mathbf{r})$ is not the functional derivative $\delta T[\rho]/\delta\rho(\mathbf{r}) \equiv v_T(\mathbf{r})$.

Commenting on Sec. V of Ref. [1] we agree with Nesbet's statement about the well-known failure of the genuine TF theory to describe the atomic shell structure. This fact indicates that $T_s[\rho] \approx c_{\mathrm{TF}} \int d^3r\, \rho^{5/3}$ — the local density approximation (LDA) for the kinetic energy — is too crude an approximation (although LDA is quite reasonable in the case of the exchange-correlation energy functional). If some algorithm that implements the definition (4.3) of $T_s[\rho]$ (e.g., from Ref. [8]) was used in Eq. (3.2b), the TF-like method should give the atomic shell structure, because, as it was shown, it leads to the exact GS density, the same as one obtained in an alternative way by solving the KS equations.

V. CONCLUSIONS

We have shown that two DFT approaches to the GS density problem, namely, via the solution of the TF-like equation (3.2b) or the self-consistent solution of the KS equations (3.4) with (3.6) and (3.7), should lead to the same results, because they represent two equivalent quantum-mechanical methods to solve the GS problem of the reference noninteracting system, either by applying the variational principle, Eq. (4.1), or by solving the Schrödinger equation (3.3a). Therefore the corresponding kinetic-energy contributions are represented in two *different* forms: as a local potential $v_T(\mathbf{r}) \equiv \delta T_s[\rho]/\delta\rho(\mathbf{r})$, in Eq. (3.2b), and as a differential operator $\hat{v}_T(\mathbf{r}) \equiv -\frac{1}{2}\boldsymbol{\nabla}^2(\mathbf{r})$ in Eq. (3.4). The Nesbet's argumentation in Eq. (6) of Ref. [1] that these two forms may be identical [his Eq. (11)] is incorrect, because he does not take into account that the equality $T_s[\tilde{\rho}[\phi_1,\ldots,\phi_N]] = \tilde{T}[\phi_1,\ldots,\phi_N]$ holds only for the set $\{\phi_1^{\min}[\rho],\ldots,\phi_N^{\min}[\rho]\}$ [the result of minimization (4.3)] rather than for an arbitrary set of orthonormal spin orbitals $\{\phi_1,\ldots,\phi_N\}$.

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