

Kinetic energy in density-functional theory

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(Received 9 December 1997)

While Kohn-Sham theory uses the quantum-mechanical operator for kinetic energy, Thomas-Fermi theory replaces this with an effective local potential. If both theories are based on the exact universal density functional defined by Hohenberg-Kohn theory, it is an interesting question whether they should give the same results for N -electron ground states. This question is examined and answered in the negative. The inconsistency is resolved only by extending the definition of functional derivatives to encompass linear operators. An exact theory must incorporate one-electron energies and occupation numbers derived from Kohn-Sham theory. [S1050-2947(98)50907-9]

PACS number(s): 31.10.+z

I. INTRODUCTION

Hohenberg and Kohn [1] proved the existence of a universal functional $F[\rho]$ equal to the mean value of the sum of kinetic energy T and two-electron Coulomb interaction U for an N -electron ground state whose electron density function is $\rho(\mathbf{r})$. The external potential function $v(\mathbf{r})$ that determines this ground state is uniquely associated with the specified density. The integral $\int v\rho$ defines a functional $V[\rho]$ in which $v(\mathbf{r})$ is considered to be fixed. Given $v(\mathbf{r})$, the total energy functional $E = F + V$ is minimized by the particular density ρ that corresponds to the N -electron ground state [1]. To avoid formal mathematical difficulties, both ρ and v are assumed here to correspond to physically realizable systems for integral N , and both are assumed to be spin-indexed scalar fields. Spin indices are suppressed in the notation used.

If the functional $E[\rho]$ can be defined for arbitrary variations $\delta\rho$ that do not conserve N , and if a functional derivative equivalent to a sum of local potential functions can be defined by $\delta E = \int (\delta E / \delta \rho) \delta \rho d^3\mathbf{r}$, the Thomas-Fermi equation is obtained by minimizing $E - \mu N$ for fixed v , where μ is the chemical potential [2]. Under the stated assumptions,

$$\delta\{E - \mu N\} = \int \left\{ \frac{\delta E}{\delta \rho} - \mu \right\} \delta \rho d^3\mathbf{r} = 0 \quad (1)$$

implies the Thomas-Fermi equation,

$$\frac{\delta E}{\delta \rho} = \mu. \quad (2)$$

Equation (2) determines $\rho(\mathbf{r})$ when μ is adjusted to give a specified value of N . This derivation can be questioned on several grounds. The parameter μ drops out of Eq. (1) for variations that conserve N . Separate assumptions are required to establish the meaning of functionals and functional derivatives for nonintegral N , and Fermi-Dirac statistics may impose severe restrictions [3].

The argument developed here will focus on the question as to whether the functional derivative for kinetic energy is equivalent to a local potential function. Substitution of an effective local potential $v_T = \delta T / \delta \rho$ for the kinetic-energy operator $\hat{v}_T = -\frac{1}{2}\nabla^2$ is implicit in the derivation and use of

the Thomas-Fermi equation. Kohn and Sham [4] found a way to use the kinetic-energy operator directly, by equating the true correlated ground-state density function to that of a noninteracting system of electrons moving in an effective potential field $w(\mathbf{r})$. The density function takes the form $\rho = \sum_i n_i \phi_i^* \phi_i$, expressed in terms of orthonormal orbital functions $\phi_i(\mathbf{r})$. The occupation numbers n_i are determined by Fermi-Dirac statistics at zero temperature, and can be assumed to have values limited to one or zero for a system with discrete one-electron energy levels or with an energy gap at the Fermi level. Through a derivation given in detail below, this leads to Kohn-Sham equations for the occupied orbital functions,

$$\left\{ \frac{\delta E}{\delta \rho} - \epsilon_i \right\} \phi_i = 0. \quad (3)$$

Here the kinetic energy part of $\delta E / \delta \rho$ is represented by the differential operator $-\frac{1}{2}\nabla^2$ and the remaining terms are assumed to define the local potential function $w(\mathbf{r})$.

Equations (2) and (3) cannot both be generally true. On integrating the Thomas-Fermi formula,

$$\int \rho \frac{\delta E}{\delta \rho} d^3\mathbf{r} = N\mu, \quad (4)$$

where $N = \int \rho d^3\mathbf{r} = \sum_i n_i$. If the Kohn-Sham equations, Eq. (3), are multiplied on the left by $n_i \phi_i^*$, then integrated and summed, they produce

$$\sum_i n_i \int \phi_i^* \frac{\delta E}{\delta \rho} \phi_i d^3\mathbf{r} = \sum_i n_i \epsilon_i, \quad (5)$$

which should agree with Eq. (4) under the assumptions made. It is clear that these results are inconsistent. The chemical potential μ is not less than the highest value of ϵ_i for occupied orbital functions ($n_i = 1$). Hence $\sum_i n_i \epsilon_i < N\mu$ unless all ϵ_i are equal, generally possible for no more than two electrons. The present paper is concerned with the validity of and relationship between these apparently incompatible consequences of the same underlying theory.

II. EFFECTIVE LOCAL POTENTIALS

The functional derivative of a density functional F describes the change of F due to an arbitrary infinitesimal variation of ρ . This is usually defined by $\delta F = \int [\delta F / \delta \rho(\mathbf{r})] \delta \rho(\mathbf{r}) d^3 \mathbf{r}$, which requires the functional derivative to be a local function, as in the derivation of Eq. (2) in Thomas-Fermi theory. In Kohn-Sham theory, variations of the density are generated by variations of an orthonormal set of occupied orbital functions, for which $\rho = \sum_i n_i \phi_i^* \phi_i$. For variations generated in this way, the definition of a functional derivative can be generalized to

$$\delta F = \sum_i n_i \int \left\{ \delta \phi_i^*(\mathbf{r}) \frac{\delta F}{\delta \rho(\mathbf{r})} \phi_i(\mathbf{r}) + \text{c.c.} \right\} d^3 \mathbf{r}.$$

The functional derivative here can be a linear operator \hat{v}_F that acts on wave functions, but this reduces to the usual definition if the functional derivative is simply a local function $v_F(\mathbf{r})$. For a density functional that is also a functional of the orbital functions, orbital and density-functional derivatives are related by the chain rule $\delta F / \delta \phi_i^* = n_i (\delta F / \delta \rho) \phi_i$. As will be shown below, in Eqs. (8), the mean value of kinetic energy in the Kohn-Sham model state defines a kinetic-energy functional for which $\delta T / \delta \phi_i^* = n_i \{-\frac{1}{2} \nabla^2\} \phi_i$. The chain rule in this case defines the functional derivative $\hat{v}_T = \delta T / \delta \rho$ as a linear operator. It is used in this form in the Kohn-Sham equations, which will be shown below to be the correct result of variational theory.

It is possible for a linear operator to be equivalent to a local potential function in a set of differential equations. For any orbital functional that is also a density functional,

$$\begin{aligned} \sum_i \phi_i^* \frac{\delta F}{\delta \phi_i^*} &= \sum_i n_i \phi_i^*(\mathbf{r}) \frac{\delta F}{\delta \rho(\mathbf{r})} \phi_i(\mathbf{r}) \\ &= \sum_i n_i \phi_i^*(\mathbf{r}) \hat{v}_F \phi_i(\mathbf{r}). \end{aligned} \quad (6)$$

If the functional derivative $\delta F / \delta \rho$ defines a local potential $v_F(\mathbf{r})$, this function can be factored out of Eq. (6) and constructed from the formula

$$\sum_i \phi_i^* \frac{\delta F}{\delta \phi_i^*} = v_F(\mathbf{r}) \rho(\mathbf{r}). \quad (7)$$

In deriving the Thomas-Fermi equation, the functional derivative $\delta T / \delta \rho$ is assumed to define a local function $v_T(\mathbf{r})$. A derivation of the Kohn-Sham equations is given below that is valid whether or not local potentials $v_F(\mathbf{r})$ exist. Kinetic energy appears as the usual linear operator, $\hat{v}_T = -\frac{1}{2} \nabla^2$. The assumption that \hat{v}_T can be replaced by $v_T(\mathbf{r})$ is the principal difference between these theories. Their inconsistency for more than two electrons, as shown above, implies that this assumption fails, and that the Thomas-Fermi equation cannot be derived in an exact theory.

III. REFERENCE STATES AND COMPONENT FUNCTIONALS

The postulate of Kohn and Sham [4] that the density function ρ is a sum of orbital densities is equivalent to assuming the existence of a reference state Φ defined by a normalized wave function that is a single Slater determinant. This can be put into a more general context by fixing the arbitrary normalization of the true correlated N -electron wave function Ψ so that $(\Phi | \Psi) = (\Phi | \Phi) = 1$. This unsymmetric normalization implies an unsymmetric energy formula for any energy eigenvalue $E = (\Phi | H | \Psi) = (\Phi | H | \Phi) + (\Phi | H | \Psi - \Phi)$. Because $\Psi - \Phi$ is orthogonal to Φ , the last term of this energy formula provides a natural definition of correlation energy $E_c = (\Phi | H | \Psi - \Phi)$ with respect to a given choice of the reference state. The universal functional $F[\rho] = E - \int v \rho d^3 \mathbf{r}$ is defined in ground states for which $\{T + U + V - E\} \Psi = 0$ and $E = E[v]$, a functional of the external potential. The universal functional takes the form $F[\rho] = (\Phi | T + U | \Phi) + (\Phi | T + U + V | \Psi - \Phi)$ using the Kohn-Sham ansatz, since $(\Phi | V | \Phi)$ is equal to the subtracted term $\int v \rho d^3 \mathbf{r}$.

If the reference state Φ is determined by ρ either directly or through the wave function Ψ , it becomes a functional $\Phi[\rho]$ and mean values evaluated in the reference state are functionals of the density. Under these conditions, the unsymmetric energy formula provides a natural decomposition of the universal functional into component density functionals, all defined by ground-state numerical values. These are

$$\begin{aligned} T[\rho] &= (\Phi | T | \Phi), \\ E_h[\rho] &= (\Phi | U_h | \Phi), \\ E_x[\rho] &= (\Phi | U_x | \Phi), \\ E_c[\rho] &= (\Phi | T + U + V | \Psi - \Phi). \end{aligned} \quad (8)$$

The notation here defines the Hartree or classical part of the reference-state energy (operator U_h), the exchange part (operator U_x), and a residual correlation term.

In the theory of Kohn and Sham [4], the reference state is determined by minimizing the kinetic energy while requiring the reference-state density ρ_Φ to be equal to the correlated density ρ_Ψ . This suffices to determine all of the component functionals listed in Eqs. (8). In reference-state density functional theory [5], the reference state Φ is determined by a condition of maximum overlap on the eigenstate Ψ . This eliminates the one-electron operator $T + V$ from the implied correlation part of the universal functional, but redefines the theory in terms of functionals of the reference-state electron density. In Hartree-Fock theory, the correlation term is absent and the reference state Φ is determined by minimizing $(\Phi | H | \Phi)$. This defines a universal functional $F_0[\rho]$ for single-determinant wave functions [6]. Component functionals are defined in Hartree-Fock ground states.

Except for E_c , each component functional defined by Eqs. (8) has an explicit representation as a functional of the occupied orbitals of the reference state. If an equivalent local potential exists for any of these functionals, including the kinetic energy, it can be extracted from Eqs. (6) and (7). For

the explicit density functional $E_h = \frac{1}{2} \sum_{i,j} n_i n_j (ij|u|ij)$, where $u = 1/r_{12}$, this construction gives the classical (Hartree) potential function,

$$\begin{aligned} v_h(\mathbf{r})\rho(\mathbf{r}) &= \sum_i n_i \phi_i^*(\mathbf{r}) \hat{v}_h \phi_i(\mathbf{r}) \\ &= \sum_i n_i \phi_i^*(\mathbf{r}) \sum_j n_j (j|u|j) \phi_j(\mathbf{r}). \end{aligned} \quad (9)$$

Given $E_x = -\frac{1}{2} \sum_{i,j} n_i n_j (ij|u|ji)$ for a ground state, Eq. (7) implies

$$\begin{aligned} v_x(\mathbf{r})\rho(\mathbf{r}) &= \sum_i n_i \phi_i^*(\mathbf{r}) \hat{v}_x \phi_i(\mathbf{r}) \\ &= -\sum_i n_i \phi_i^*(\mathbf{r}) \sum_j n_j (j|u|i) \phi_j(\mathbf{r}), \end{aligned} \quad (10)$$

equivalent to the local exchange potential of Slater [7]. For the kinetic energy of the reference state, $T = \sum_i n_i (i|-\frac{1}{2}\nabla^2|i)$, Eq. (7) gives a formula assumed in deriving Eq.(3),

$$\begin{aligned} v_T(\mathbf{r})\rho(\mathbf{r}) &= \sum_i n_i \phi_i^*(\mathbf{r}) \hat{v}_T \phi_i(\mathbf{r}) \\ &= \sum_i n_i \phi_i^*(\mathbf{r}) \left\{ -\frac{1}{2}\nabla^2 \right\} \phi_i(\mathbf{r}). \end{aligned} \quad (11)$$

IV. ONE-ELECTRON EQUATIONS

For consistency with the Hohenberg-Kohn theorems, the energy functional must be minimized with respect to variations of the orbital functions, subject to orthonormality. The Kohn-Sham equations are the Euler-Lagrange equations generated by this minimization condition. First-order variations of the energy functional, modified using Lagrange multipliers λ_{ji} to enforce orthonormality of the orbital functions, are given by

$$\begin{aligned} &\delta \left\{ E[\rho] - \sum_{ij} n_i n_j \left(\int \phi_i^* \phi_j d^3\mathbf{r} - \delta_{ij} \right) \lambda_{ji} \right\} \\ &= \sum_i n_i \left[\int \delta \phi_i^* \left\{ \frac{\delta E}{n_i \delta \phi_i^*} - \sum_j n_j \phi_j \lambda_{ji} \right\} d^3\mathbf{r} + \text{c.c.} \right] \\ &+ \sum_i \delta n_i \int \phi_i^* \frac{\delta E}{\delta \rho} \phi_i d^3\mathbf{r}. \end{aligned} \quad (12)$$

Euler-Lagrange equations follow on requiring this expression to vanish for unconstrained variations of the occupied orbital set, with fixed occupation numbers ($n_i = 1$). The coupled equations for the occupied orbitals are

$$\frac{\delta E}{n_i \delta \phi_i^*} = \sum_j n_j \phi_j \lambda_{ji}. \quad (13)$$

As in Hartree-Fock theory, a canonical form is obtained by diagonalizing the matrix of Lagrange multipliers. The kinetic-energy term here is $\delta T/n_i \delta \phi_i^* = -\frac{1}{2}\nabla^2 \phi_i$. From the

chain rule for orbital functional derivatives of density functionals, $\delta F/n_i \delta \phi_i^* = (\delta F/\delta \rho) \phi_i$, the remaining operator terms are $[\delta(E-T)/\delta \rho] \phi_i$. Assuming that this functional derivative defines a local potential $w(\mathbf{r})$, this gives the usual form of the Kohn-Sham equations, Eq. (3). If occupation numbers are varied in a basis of Kohn-Sham eigenfunctions, only the final term in Eq. (12) is nonzero. On introducing the chemical potential μ as a Lagrange multiplier for the constraint $\sum_i n_i = N$, the variational equation takes the form

$$\sum_i \left\{ \frac{\partial E}{\partial n_i} - \mu \right\} \delta n_i = \sum_i \{ \epsilon_i - \mu \} \delta n_i = 0, \quad (14)$$

where $\epsilon_i = \int \phi_i^* (\delta E/\delta \rho) \phi_i d^3\mathbf{r}$, in the canonical orbital basis. The first equality here implies Janak's theorem [8], $\epsilon_i = \partial E/\partial n_i$. The second equality is consistent with Fermi-Dirac statistics. At zero temperature, variations δn_i must vanish except at the Fermi level, $\epsilon_i = \mu$.

This derivation involves no assumptions beyond standard variational theory. The exact Hohenberg-Kohn energy functional leads to exact Kohn-Sham equations. These equations follow from expressing the energy functional as a sum of component functionals defined, except for the residual correlation energy, as reference-state mean values. Density-functional derivatives of these component functionals define linear operators that may be equivalent to local potentials. The functional derivative of the kinetic-energy functional is obtained explicitly as a linear operator. It cannot be identified with a local potential function without an additional hypothesis or proof. The hypothesis that this operator is equivalent to a local potential function is tested by the Thomas-Fermi formalism. As indicated in comparing Eqs. (4) and (5), the Thomas-Fermi equation is inconsistent with the Kohn-Sham equations for more than two electrons. This inconsistency negates the stated hypothesis.

If an effective local potential $v_T(\mathbf{r})$ is substituted for the one-electron kinetic-energy operator in the Kohn-Sham equations, as it is in Thomas-Fermi theory, these equations change character drastically. Individual orbital energies ϵ_i are replaced by the chemical potential μ . Since the local potential is independent of index i , the equations cannot determine the orbital substructure of the density function. Even if all components of $\delta E/\delta \rho$ were local functions, and an equation analogous to the Thomas-Fermi equation were defined by a weighted sum of the Kohn-Sham equations,

$$\frac{\delta E}{\delta \rho} = \frac{\sum_i n_i \phi_i^* \epsilon_i \phi_i}{\sum_i n_i \phi_i^* \phi_i} = \bar{\epsilon}(\mathbf{r}), \quad (15)$$

the theory still would require Kohn-Sham eigenvalues and occupation numbers.

It can easily be shown that Hohenberg-Kohn theory applies to the model of Hartree-Fock ground-states [9]. A direct test of locality is provided by considering variations of ground-state Hartree-Fock ρ and E induced by varying the nuclear charge Z [6]. From Eq. (11), $v_T(\mathbf{r})$ is the mean local kinetic energy, such that $T = \int v_T \rho d^3\mathbf{r}$. If v_T is equivalent to the functional derivative $\delta T/\delta \rho$, then Z derivatives of ρ and

of the kinetic-energy functional T must be related by $\delta T/\delta Z = \int v_T(\partial\rho/\partial Z)d^3\mathbf{r}$. Hence the existence of a local functional derivative requires that

$$Q_T = \int \frac{\partial v_T}{\partial Z} \rho d^3\mathbf{r} = 0. \quad (16)$$

In recent work to be published elsewhere [6], this quantity has been computed for atomic He, Be, and Ne, giving the values $Q_T(\text{He}) = -0.494 \times 10^{-5}$, $Q_T(\text{Be}) = 0.812$, and $Q_T(\text{Ne}) = 6.849$ in Hartree atomic units. For the typical atoms Be and Ne, the criterion parameter Q_T differs from zero by an amount much greater than any possible computational inaccuracy. This indicates that it cannot generally be valid to assume that the functional derivative $\delta T/\delta\rho = \hat{v}_T$ defines a local potential $v_T(\mathbf{r})$.

V. DISCUSSION

It has been shown here that the Thomas-Fermi equation is inconsistent with the variational equations that determine orbital structure of the density function in Kohn-Sham theory. To compute this orbital structure, it is necessary to describe kinetic energy by the linear operator $-\frac{1}{2}\nabla^2$ rather than by an effective local potential v_T . An important implication of this result is that Fermi-Dirac statistics, involving occupation numbers for normalized orbital functions, cannot be implemented in Thomas-Fermi theory. This is consistent with the well-known failure of this theory to describe atomic shell structure. The essential conclusion of this analysis is that for ground states Thomas-Fermi theory is not equivalent to Kohn-Sham theory, even if the exact Hohenberg-Kohn universal density functional were known and used.

ACKNOWLEDGMENTS

The author is grateful to R. Colle for discussions, and to the Scuola Normale Superiore (Pisa) for financial support.

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