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Kinetic energy as a density functional

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Whether or not kinetic energy can be represented in orbital Kohn-Sham equations by an effective local potential has been discussed in several recent publications, reaching conflicting conclusions. It is shown here that this conflict can be resolved by dropping the widespread but unjustified assumption that the existence of a ground-state density functional for the kinetic energy of an N-electron system implies the existence of a density-functional derivative equivalent to a local potential function. For more than two electrons, a density-functional derivative does exist, but has the mathematical character of a linear operator that acts on orbital wave functions.

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I. INTRODUCTION

The issue in dispute is whether an exact *ab initio* Thomas-Fermi theory (TFT) exists for ground states, equivalent to density-functional theory (DFT) [1,2]. This depends on the definition for N-electron ground states of a ground-state kinetic-energy functional $T_s[\rho]$ and of its density-functional derivative $\delta T_s/\delta\rho$, where ρ is the (spin-indexed) electron density. If $\delta T_s/\delta\rho$ is assumed to exist as a local function $v_T(\mathbf{r})$ it defines a Thomas-Fermi equation with the same physical content as the orbital equations of Kohn and Sham [3–5]. This ''locality hypothesis'' appears so intuitively obvious that it has tacitly been incorporated into arguments [4,5] purporting to refute a straightforward sum rule [3,6] that demonstrates incompatibility of the Thomas-Fermi (TF) and Kohn-Sham (KS) equations for systems with more than two electrons (more than one distinct orbital energy level).

It will be shown here that this functional derivative does indeed exist, but takes a mathematical form different from that assumed. More precisely, two kinds of functional derivatives are defined in functional analysis [7,8]. The functional derivative of Fréchet is the generalization to functional analysis of a total derivative, not depending on the ''direction'' of variation in the underlying function space. The functional derivative of Gâteaux is the generalization of a partial derivative, depending on the direction of variation. Analysis of the functional variation of the noninteracting ground-state kinetic energy, compatible with orbital Schrödinger equations, shows that the density-functional derivative is a Gâteaux derivative, having the character of a linear operator that acts on orbital wave functions, not a Fréchet derivative, equivalent to a local potential function [9,10]. A Gâteaux derivative does not define a Thomas-Fermi equation. This demonstration is summarized here for the simplest possible model, noninteracting electrons in a local external potential. In this model, all theoretical assertions can be tested for an atom composed of noninteracting electrons, using explicit hydrogenic orbital wave functions and the corresponding density functions.

The Kohn-Sham density function $\rho=\Sigma_i n_i \phi_i^* \phi_i$ implies that any functional of ρ is also a functional of the orbital functions ϕ_i. Hence DFT is also an orbital functional theory (OFT), for which the correct variational theory is well established and undisputed. Practical applications of DFT use the methodology of OFT, determining ground-state orbital wave functions and model density when an approximate exchange-correlation energy functional $E_{xc}[\rho]$ is specified. Hence a correct variational derivation of the appropriate Euler-Lagrange equations must satisfy consistency conditions between DFT and OFT representations of what should be the same theory for ground states. These consistency conditions, stated in the form of a chain rule, have been disputed by Gál [4] and by Holas and March [5]. This chain rule is rederived here in a way that makes no extraneous assumptions and can be verified for noninteracting electrons.

Holas and March [5] argue that ''the solution of the TF-like equation . . . and of the KS equations . . . should lead to the same results . . . ''. Their argument, however, invokes circular logic, and cannot reach a definite conclusion. The ''locality hypothesis'' is tacitly assumed and built into their notation. Their Eqs. (2.7) and (2.8) ignore the possibility that the functional derivative $\delta T_s/\delta\rho$ might be a linear operator rather than a local function. Equation (2.8) has no precise meaning unless this functional derivative is a multiplicative c number. Without this tacit assumption, one cannot conclude that the theory implies the existence of a ''TF-like equation.'' Their argument does not circumvent the sum rule [3] that implies violation of the exclusion principle for more than two electrons.

II. NONINTERACTING ELECTRONS

The mathematical issues involved in comparing ''exact'' Kohn-Sham equations with Thomas-Fermi theory, based on the same Hohenberg-Kohn ground-state theory, can be addressed in a model of N noninteracting electrons. Kinetic energy is defined exactly. A local external potential function $v(\mathbf{r})$ can be assumed, guaranteeing validity of Hohenberg-Kohn theorems [1] and of ''noninteracting v representability'' [11,12]. Limiting the discussion, for simplicity, to nondegenerate ground states, variational trial functions are unnormalized single Slater determinants Φ constructed from N spin-indexed occupied orbital wave functions ϕ_i for $i \leqslant N$. Total and orbital energies are Lagrange multipliers determined to enforce normalization. Spin indices and summations are implicit but are omitted in the simplified notation to be used here. $(\Phi|H|\Phi)$ is an explicit functional $T+V$ of trial orbital functions, where

$$T=\sum_i n_i(i|\hat{t}|i);\quad V=\sum_i n_i(i|\hat{v}|i), \tag{1}$$

expressed in terms of linear operators $\hat{t}=-(1/2)\boldsymbol{\nabla}^2$ and $\hat{v}$ for a general nonlocal potential. Occupation numbers $n_i=1$ for $i\leqslant N$ are not varied here. Matrix elements are defined by $(i|\ldots|j)=\int d^3\mathbf{r}\phi_i^*(\mathbf{r})\ldots\phi_j(\mathbf{r})$.

The Schrödinger variational principle can be expressed in the form

$$\int d^3\mathbf{r}\sum_i n_i(\delta\phi_i^*\{\hat{t}+\hat{v}-\epsilon_i\}\phi_i+\text{c.c.})=0, \tag{2}$$

incorporating a diagonalized matrix of Lagrange multipliers for orthonormality constraints. If variations $\delta\phi_i$ are unconstrained in the orbital Hilbert space, this implies orbital Euler-Lagrange (OEL) equations,

$$\hat{t}\phi_i=\{\epsilon_i-\hat{v}\}\phi_i,\quad i=1,\ldots,N, \tag{3}$$

just Schrödinger equations for noninteracting electrons. This derivation uses orbital functional derivatives

$$\frac{\delta T}{n_i\delta\phi_i^*}=\hat{t}\phi_i,\quad \frac{\delta V}{n_i\delta\phi_i^*}=\hat{v}\phi_i, \tag{4}$$

defined such that

$$\delta T=\int d^3\mathbf{r}\sum_i n_i(\delta\phi_i^*\hat{t}\phi_i+\text{c.c.});$$

$$\delta V=\int d^3\mathbf{r}\sum_i n_i(\delta\phi_i^*\hat{v}\phi_i+\text{c.c.}). \tag{5}$$

When $\hat{v}$ is a local function $v(\mathbf{r})$, the equations solved for ground states in the Kohn-Sham construction (minimizing kinetic energy with fixed density) [2,13,14] are the same as these noninteracting OEL equations. The density function $\rho=\Sigma_i n_i\rho_i=\Sigma_i n_i\phi_i^*\phi_i$ is constructed as a sum of density components $\rho_i=\phi_i^*\phi_i$, with fixed occupation numbers n_i. If this noninteracting theory is extended as in the local-density approximation to include a model exchange-correlation energy determined by an explicit function of density, and hence of the occupied orbital functions, the orbital-functional derivation of the OEL equations given above produces the usual Kohn-Sham equations, using only standard variational theory. If nonlocal exchange is included and electronic correlation is neglected, this derivation follows exactly the logic of standard Hartree-Fock theory.

III. ORBITAL AND DENSITY-FUNCTIONAL DERIVATIVES

In deriving the OEL equations, one must consider infinitesimal variations of energy functionals of occupied orbitals $\{\phi_i\}$, or of the density function ρ constructed from such orbitals. Orbital-functional derivatives $\delta F/n_i\delta\phi_i^*=\hat{v}_F\phi_i$ of functional $F[\{\phi_i\}]$ are defined by

$$\delta F=\int d^3\mathbf{r}\sum_i n_i\left\{\delta\phi_i^*\frac{\delta F}{n_i\delta\phi_i^*}+\text{c.c.}\right\}. \tag{6}$$

The corresponding density variation is

$$\delta\rho=\sum_i n_i\{\delta\phi_i^*\phi_i+\text{c.c.}\}. \tag{7}$$

If F is also a density functional, $\delta F/\delta\rho$ can always be defined such that

$$\delta F=\int d^3\mathbf{r}\sum_i n_i\left\{\delta\phi_i^*\frac{\delta F}{\delta\rho}\phi_i+\text{c.c.}\right\}. \tag{8}$$

These equations make no unstated assumptions and are consistent if the orbital- and density-functional derivatives are related by the chain rule $(\delta F/\delta\rho)\phi_i=\delta F/n_i\delta\phi_i^*=\hat{v}_F\phi_i$. If the density-functional derivative $\delta F/\delta\rho$ were a Fréchet derivative, equivalent to a (spin-indexed) local function $v_F(\mathbf{r})$, Eq. (8) would reduce to $\delta F=\int d^3\mathbf{r}v_F(\mathbf{r})\delta\rho$. This formula is meaningful only if the linear operator $\hat{v}_F$ defined by the orbital-functional derivative is equivalent in the OEL equations to a multiplicative function $v_F(\mathbf{r})$. Assuming this to be true without proof [4,5] constitutes the "locality hypothesis." An existence proof is required to justify the "definition" $\delta F/\delta\rho=v_F(\mathbf{r})$ [11,12].

A density functional T_s is defined by the orbital functional T evaluated for ground-state occupied orbital functions ϕ_i. In order to conform to the standard variational theory of the Schrödinger equation, the notation T_s here extends this definition to all density functions generated by orbital variations in any infinitesimal function neighborhood of a solution of the ground-state equations. For variations about ground-state solutions of Eqs. (3), assuming a local external potential $v(\mathbf{r})$,

$$\delta T_s=\int d^3\mathbf{r}\sum_i n_i(\delta\phi_i^*\hat{t}\phi_i+\text{c.c.})$$

$$=\int d^3\mathbf{r}\sum_i n_i(\delta\phi_i^*\{\epsilon_i-v\}\phi_i+\text{c.c.}). \tag{9}$$

Variation of a specified occupied ϕ_i in the orbital Hilbert space, restricted only by orthogonality to all other occupied orbitals, defines a partial density-functional derivative $\delta T_s/n_i\delta\rho_i$ such that

$$\delta T_s=\int d^3\mathbf{r}\sum_i n_i\left(\delta\phi_i^*\frac{\delta T_s}{n_i\delta\rho_i}\phi_i+\text{c.c.}\right). \tag{10}$$

The partial functional derivatives implied by Eqs. (9) and (10) are local functions

$$\frac{\delta T_s}{n_i\delta\rho_i(\mathbf{r})}=\epsilon_i-v(\mathbf{r}). \tag{11}$$

For fixed orbital normalization, the eigenvalues ϵ_i drop out of the variational equations and cannot be determined. This constraint is explicitly relaxed in the variational derivation of the orbital Schrödinger equation. If $\epsilon_i - v$ were the same function $v_T(\mathbf{r})$ for all i, a Fréchet derivative $\delta T_s/\delta\rho$ would be defined such that $\delta T_s = \int d^3\mathbf{r}(\delta T_s/\delta\rho)\delta\rho$. This function could replace the linear operator $\hat{t}$ in the orbital Schrödinger equations.

Equation (11) implies that such a unique local function does not exist unless all one-electron energies ϵ_i are equal. This confirms the implication of the sum rule derived previously [3]. However, Eq. (11) does define a functional derivative that differs depending on the eigenvalues ϵ_i, characteristic of different partial densities. Such a dependence on direction in the density-function space defines a Gâteaux functional derivative [7,8]. Since $\rho = \Sigma_i n_i \rho_i$, if $\delta T_s/\delta\rho$ exists, the partial functional derivatives

$$\frac{\delta T_s}{n_i \delta\rho_i} = \epsilon_i - v(\mathbf{r}) \tag{12}$$

must satisfy the elementary chain rule

$$\frac{\delta T_s}{n_i \delta\rho_i} = \frac{\partial\rho}{n_i \partial\rho_i}\frac{\delta T_s}{\delta\rho} = \frac{\delta T_s}{\delta\rho}. \tag{13}$$

Defining $\mathcal{H} = \hat{t} + v$, an explicit orbital index is not needed if Eq. (12) is interpreted to define a linear operator acting on orbital wave functions, $\delta T_s/\delta\rho = \mathcal{H} - v = \hat{t}$. This confirms the chain rule for functional derivatives, and can be verified explicitly in the noninteracting atom model.

IV. CONCLUSIONS

There is no conflict between standard variational theory in the orbital-functional derivation and formal results of functional analysis [15,16], when the theory is restricted to normalized orbitals and density [9]. It has been shown here that for a system of noninteracting electrons in an external potential field $v(\mathbf{r})$, variations of ground-state kinetic energy T_s, induced by variation of any occupied orbital function with fixed normalization, define a density-functional derivative as a local function plus an undetermined constant. In order to define a Thomas-Fermi equation this undetermined constant must have a specific value. Extension of this derivation to unconstrained orbital variations shows that this ‘‘constant’’ has different values for different orbital components of the electron density. Hence the implied functional derivative is a Gâteaux derivative, whose value depends on a direction in the function space [8] (p. 123). For a partial density ρ_i this direction is defined by variations of orbital ϕ_i that are orthogonal to all other occupied orbital functions. The existence of a local functional derivative in any particular direction in the function space does not imply that a unique local function exists that can replace the kinetic-energy operator $\hat{t}$ in Kohn-Sham equations. Assuming the existence of such a local potential leads to a contradiction for $N > 2$.

The Hohenberg-Kohn theorems ensure that variational energy is minimized by the ground-state density associated with a given external potential. This density is uniquely determined by variational theory. Because of the ‘‘directional’’ nature of the density-functional derivative, exact TFT equations must be operationally equivalent to the OEL equations, which explicitly use the nonlocal Schrödinger operator $\hat{t}$. This is consistent with an extended definition of the density-functional derivative $\delta T_s/\delta\rho = \mathcal{H} - v = \hat{t}$. Hence it is variationally correct to use $\hat{t}$ in Kohn-Sham equations. The problem with TFT for more than two electrons is that the orbital structure of the density function must also be determined, in order to define the kinetic energy. Semiclassical TFT becomes a quantum theory of electrons only on replacing the *c*-number function v_T by the *q*-number operator $\hat{t}$.

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