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Tests of the locality of exact Kohn-Sham exchange potentials

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It is commonly assumed that exact Kohn-Sham theory implies a local exchange-correlation potential for ground states. Here we show that this is not true for the exchange potential in a Hartree-Fock model of density-functional theory, although Hohenberg-Kohn theorems can be proved for this model. It may not be possible to express exact Kohn-Sham equations in general in terms of density-functional derivatives that are equivalent to local potential functions.

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I. INTRODUCTION

Hohenberg and Kohn [1] proved that the external potential acting on an interacting N-electron system is uniquely associated with the electronic ground-state density function. Thus the ground-state energy is a functional of electron density. Kohn and Sham [2] introduced an orbital model or reference state. An exact Kohn-Sham theory is defined by varying the occupied orbital functions of this reference state so as to minimize the Hohenberg-Kohn ground-state energy functional. Alternatively, in the Kohn-Sham construction, the orbital functions are determined by minimizing the model kinetic energy over all sets of occupied orbital functions that produce the ground-state density.

Exact Kohn-Sham equations are defined as the Euler-Lagrange equations that determine occupied orbitals $\{\phi_i\}$ and the density function $\rho(\mathbf{r})$, expressed as $\Sigma_i n_i \phi_i^* \phi_i$, if the energy functional is known. The exchange-correlation energy functional $E_{\mathrm{xc}}[\rho]$ determines a functional derivative $\hat{v}_{\mathrm{xc}} = \delta E_{\mathrm{xc}}/\delta\rho$ in these equations. If the functional derivative $\hat{v}_{\mathrm{xc}}$ is equivalent to a local potential function $v_{\mathrm{xc}}(\mathbf{r})$, the Kohn-Sham construction and exact Kohn-Sham theory should give identical exact results for ground states. This is commonly assumed to be true as a matter of definition. Because we find that longstanding results in existing literature appear to contradict this assumption, we have set up a series of tests designed to examine its validity.

The standard variational derivation of the Schrödinger equation, valid for all stationary states, can be expressed in terms of functional derivatives in the form of linear operators acting on wave functions. Thomas-Fermi theory postulates that the kinetic-energy operator can be replaced by a local potential function, while Kohn and Sham (KS) [2] retain the kinetic-energy operator of Schrödinger. The empirical success of Kohn-Sham density-functional theory (DFT) indicates that this is the correct choice. It also indicates that variational theory does not imply that exact Kohn-Sham equations can be expressed in terms of density-functional derivatives equivalent to local potential functions (the locality hypothesis), contradicting the common assumption that validity of this hypothesis is implied by variational theory. This paradox might be resolved if Thomas-Fermi and exact Kohn-Sham theories were equivalent for ground states, using the exact Hohenberg-Kohn energy functional, but this has been ruled out by a recent demonstration of inconsistency for systems with more than two electrons [3].

Here we examine this hypothesis in a density-functional theory of the Hartree-Fock approximation, in order to clarify the relationship between a local exchange potential and a nonlocal exchange operator. The theory is developed in direct analogy to standard density-functional theory (DFT) [1,2,4], updating an earlier derivation by Payne [5]. We derive exact Kohn-Sham equations, equivalent to the Hartree-Fock equations of this model, but expressed in terms of functional derivatives of the Hartree-Fock energy functional. This provides a model problem for which exact results are known. A criterion for the existence of exact local potential functions is defined and tested in this model. It fails for the kinetic energy by a large margin over any possible numerical inaccuracy. This justifies the choice of the Schrödinger operator by Kohn and Sham, and verifies the inconsistency of Thomas-Fermi theory and exact KS equations. This and other tests of the exchange potential are considered here and lead to the conclusion that an exact local exchange potential does not exist for ground states of typical atoms.

A universal Hohenberg-Kohn functional is defined for Hartree-Fock ground states. We carry out the Kohn-Sham construction directly, minimizing the kinetic energy subject to constrained density, and report calculations of comparable high accuracy using the optimized effective potential (OEP) method [6,7], in which a local potential function is constructed that minimizes the mean total energy of the reference state, without constraining the density. Calculations comparing the Hartree-Fock model with the Kohn-Sham construction and with the OEP method were carried out for atomic He, Be, and Ne. Details will be published elsewhere, but relevant results are summarized here. Both OEP and the KS construction posit a local exchange potential, but the KS construction also constrains the density function. This implies $E_{\mathrm{KS}} \geqslant E_{\mathrm{OEP}}$, so that $E_{\mathrm{KS}} \geqslant E_{\mathrm{OEP}} \geqslant E_{\mathrm{HF}}$ [8]. If the locality hypothesis were valid, OEP, the KS construction, and exact Kohn-Sham theory would be equivalent for Hartree-Fock ground states and give the Hartree-Fock energy and wave function. A well-established counterexample is provided by comparing HF ground-state energies with the OEP method [6,7]. The ground-state energies E_{OEP} [9,10] are -14.5724 for Be and -128.5455 for Ne, in Hartree units, above the Hartree-Fock energies [11] -14.5730 for Be and -128.5471 for Ne by amounts greater than the expected residual computational errors. Energies very close to OEP are obtained using the Kohn-Sham construction [8]. These results are confirmed by new calculations reported here. Total energies are obtained with sufficient accuracy to remove any doubt that E_{KS} and E_{HF} differ significantly except for He. $E_{\mathrm{OEP}}(\leqslant E_{\mathrm{KS}})$ is greater than E_{HF}, which is the exact Kohn-Sham energy for this model. This tests the hypothesis that the exact Kohn-Sham exchange potential must be a local function and indicates that it is not true.

A criterion parameter is defined here whose vanishing is a necessary but not sufficient condition for locality of an effective potential function. For He, Be, and Ne, this test fails by a wide margin for the kinetic energy but is satisfied to computational accuracy for the Hartree potential. For the exchange potential, we prove that this parameter must vanish as a consequence of the OEP integral equation, and verify this by calculations. When computed for the Kohn-Sham exchange potential for Be and Ne, this parameter is small but significantly larger than in the OEP calculations. Comparisons of data in existing literature show inconsistencies that are confirmed by the present tests. These results negate the assumption that variationally correct exact Kohn-Sham equations can always be expressed in terms of functional derivatives in the form of local potential functions, and hence that the Kohn-Sham construction for ground states is equivalent to exact Kohn-Sham theory based on the Hohenberg-Kohn energy functional.

One motivation for the present study is that Hartree-Fock theory can be extended to include electronic correlation by adding an approximate correlation energy functional [12] to the Hartree-Fock total-energy expression [13,14]. The Kohn-Sham construction for such models can be derived from a constrained search procedure [4] following the logic of the Hartree-Fock model considered here. The proposed approximate correlation energy functional [12] is, like the ordinary exchange energy of the reference state, an explicit functional of the occupied orbital set, and only implicitly a functional of the density. It is important to understand the implications of exact theory regarding an effective potential derived from such an orbital functional. In applications to large molecules or solids, it would be advantageous to replace the nonlocal part of these modified Hartree-Fock equations by an equivalent local potential function, if such a potential exists.

II. HARTREE-FOCK AS A DENSITY-FUNCTIONAL THEORY

Consider an interacting nonrelativistic N-electron quantum system described by wave functions restricted to the form of single Slater determinants. A ground-state wave function Φ is a single Slater determinant with orthonormal occupied spin-indexed orbital functions $\{\phi_i\}$ and spin-indexed electron density $\rho(\mathbf{r})$. Specific spin indices are omitted in derivations here. These definitions correspond to the unrestricted Hartree-Fock approximation for a ground state. If an N-electron reference state is defined by the criterion of maximum projection on Φ, as in reference-state density-functional theory (RDFT) [15], this reference state is identical to the Hartree-Fock ground state and the two spin-indexed densities coincide. It follows from theorems proved in RDFT that the ground-state Hartree-Fock theory is equivalent to a density-functional theory based on spin-indexed density ρ. Theorems that establish this analogy to standard DFT [1,2] are derived here in the Hartree-Fock context.

Consider the constrained-search derivation of Levy [4], applied within the restricted set of single-determinant variational trial functions. The universal functional $F_0[\rho]$ is defined by the minimum of $(\Phi|T+U|\Phi)$ over the set of all normalized Slater determinants Φ that produce the density ρ. Here T and U are, respectively, the N-electron kinetic-energy operator and the Coulomb interaction. An equivalent definition is obtained by introducing a spin-indexed external potential $v(\mathbf{r})$ as a Lagrange multiplier field. A functional of $\rho(\mathbf{r})$ is defined by

$$\begin{aligned} F_{0v}[\rho] &= \min_{\Phi_t}\left((\Phi_t|T+U|\Phi_t) + \int v(\rho_t-\rho)\, d^3\mathbf{r} \right) \\ &= E_0[v] - \int v\rho\, d^3\mathbf{r}. \end{aligned} \tag{1}$$

$E_0[v]$ here is the ground-state Hartree-Fock energy in the given potential v. The minimizing state Φ_v determines electron density ρ_v. When $v=v_\rho$ such that $\rho_v=\rho$ for $\Phi_\rho=\Phi_v$, Eq. (1) determines the universal functional $F_0[\rho]=(\Phi_\rho|T+U|\Phi_\rho)$. The numerical value of this functional in any Hartree-Fock ground state is given explicitly by this equation.

Generalized Hohenberg-Kohn theorems follow immediately from this definition. When $\rho=\rho_v$ and $v=v_\rho$,

$$F_0[\rho]=F_{0v}[\rho]=E_0[v]-\int v\rho\, d^3\mathbf{r}, \tag{2}$$

and the energy functional $E_{0v}[\rho]=F_0[\rho]+\int v\rho\, d^3\mathbf{r}$ takes its minimum value $E_0[v]$. Since ρ determines Φ_ρ, when $\rho\neq\rho_v$ and $v\neq v_\rho$, then $F_0[\rho]=(\Phi_\rho|T+U|\Phi_\rho)$ and $\int v\rho\, d^3\mathbf{r}=(\Phi_\rho|V|\Phi_\rho)$. Hence

$$E_{0v}[\rho]=(\Phi_\rho|T+U+V|\Phi_\rho)\geqslant E_0[v]. \tag{3}$$

Equations (2) and (3) establish the variational property of the energy functional $E_{0v}[\rho]$.

The Hartree-Fock ground-state energy functional is subdivided into component functionals defined as mean values in the reference state $\Phi=\Phi_\rho$. The energy functional is $E_0[\rho]=T[\rho]+U[\rho]+V[\rho]$, where the individual functionals can be expressed in terms of the occupied orbital functions $\{\phi_i\}$ of Φ. Introducing occupation numbers n_i, and denoting the two-electron Coulomb interaction by u and Coulomb minus exchange by $\overline{u}$, these component functionals are

$$T[\rho]=(\Phi|T|\Phi)=\sum_i n_i(i|-\tfrac{1}{2}\nabla^2|i),$$

$$U[\rho]=(\Phi|U|\Phi)=\frac{1}{2}\sum_{i,j} n_i n_j(ij|\overline{u}|ij),$$

$$V[\rho]=(\Phi|V|\Phi)=\sum_i n_i(i|v|i).$$

Here $U[\rho]=E_h[\rho]+E_x[\rho]$, where

$$E_h[\rho]=\frac{1}{2}\sum_{i,j} n_i n_j(ij|u|ij),$$

$$E_x[\rho]=-\frac{1}{2}\sum_{i,j} n_i n_j(ij|u|ji). \qquad (4)$$

Assuming normalization $(\Phi|\Psi)=(\Phi|\Phi)=1$, the correlation energy functional $(\Phi|U|\Psi-\Phi)$ defined in RDFT [15] vanishes in the present case.

III. FUNCTIONAL DERIVATIVES AND LOCAL POTENTIALS

The change of a density functional F due to an arbitrary infinitesimal variation of ρ is usually expressed in the form $\delta F=\int[\delta F/\delta\rho(\mathbf{r})]\delta\rho(\mathbf{r})d^3\mathbf{r}$, defining the functional derivative $\delta F/\delta\rho$. Exact Kohn-Sham equations for the occupied orbital functions of Φ can only be derived if these orbital functions can be freely varied about their ground-state values, within the relevant Hilbert space. This is a necessary condition for the integral $\int\delta\phi_i^*\{\mathcal{H}-\epsilon_i\}\phi_i=0$ to imply an effective Schrödinger (or Dirac) equation $\{\mathcal{H}-\epsilon_i\}\phi_i=0$. In Hartree-Fock or Kohn-Sham theory, the spin-indexed local-density function $\rho=\Sigma_i n_i\phi_i^*\phi_i$ is constructed from orbital functions in this Hilbert space. Functional derivatives of an orbital functional follow from $\delta F=\Sigma_i\int\{\delta\phi_i^*(\mathbf{r})\times[\delta F/\delta\phi_i^*(\mathbf{r})]+\text{c.c.}\}d^3\mathbf{r}$ and take the form of a linear operator acting on an orbital function, $\delta F/\delta\phi_i^*(\mathbf{r})=n_i\hat{v}_F\phi_i(\mathbf{r})$. For consistency with the use by Kohn and Sham [2] of the kinetic-energy operator of Schrödinger, functional derivatives of an orbital functional that is also a density functional must be related by the generalized chain rule $\delta F/\delta\phi_i^*=n_i(\delta F/\delta\rho)\phi_i$, which maintains the correct order of symbols in case the functional derivative $\hat{v}_F=\delta F/\delta\rho$ is not equivalent to a local function $v(\mathbf{r})$. This reduces to the usual definition if the functional derivative is equivalent to a local function.

Each of the ground-state density functionals defined by Eqs. (4) is an explicit functional of the occupied orbitals of the reference state. If the functional derivative $\hat{v}_F=\delta F/\delta\rho$ reduces to a local potential $v_F(\mathbf{r})$ for any such orbital functional that is also a density functional, then the definition of orbital functional derivatives implies a sum rule,

$$\sum_i \phi_i^*\frac{\delta F}{\delta\phi_i^*}=\sum_i n_i\phi_i^*(\mathbf{r})\hat{v}_F\phi_i(\mathbf{r})=v_F(\mathbf{r})\rho(\mathbf{r}). \qquad (5)$$

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

$$v_h(\mathbf{r})\rho(\mathbf{r})=\sum_i n_i\phi_i^*(\mathbf{r})\sum_j n_j(j|u|j)\phi_i(\mathbf{r}). \qquad (6)$$

Given $E_x=-\frac{1}{2}\Sigma_{i,j}n_i n_j(ij|u|ji)$ for a ground state, Eq. (5) implies

$$v_x(\mathbf{r})\rho(\mathbf{r})=-\sum_i n_i\phi_i^*(\mathbf{r})\sum_j n_j(j|u|i)\phi_j(\mathbf{r}), \qquad (7)$$

equivalent to the local exchange potential of Slater [16]. For the kinetic-energy functional $(\Phi|T|\Phi)$,

$$v_T(\mathbf{r})\rho(\mathbf{r})=\sum_i n_i\phi_i^*(\mathbf{r})\{-\tfrac{1}{2}\nabla^2\}\phi_i(\mathbf{r}). \qquad (8)$$

IV. ONE-ELECTRON EQUATIONS AND ENERGIES

For an orthonormal set of orbital functions ϕ_i, the density function $\rho=\rho_\Phi$ takes the form $\Sigma_i n_i\phi_i^*\phi_i$. The occupation numbers n_i for ground states are determined by Fermi-Dirac statistics at zero temperature. For a system with discrete one-electron energy levels or with an energy gap at the Fermi level, occupation numbers can be assumed to have values one or zero only. For consistency with the Hohenberg-Kohn theorems, the energy functional must be minimized with respect to variations of the orbital functions. In the Hartree-Fock model, the energy mean value $(\Phi|H|\Phi)$ is an explicit functional of the occupied orbital functions. The Euler-Lagrange equations generated by minimizing this functional, subject to orthonormality of the orbital functions, define exact Kohn-Sham equations for the occupied orbitals. Hartree-Fock equations follow from the same derivation.

Kohn and Sham [2] define a kinetic-energy functional by minimizing the kinetic energy of a reference state under the constraint that $\rho_\Phi=\rho$ for an exact ground state. This construction defines an effective local potential as a Lagrange multiplier field $w(\mathbf{r})$, in analogy to Eq. (1),

$$\begin{aligned} T_w[\rho]&=\min_{\Phi_t}\left((\Phi_t|T|\Phi_t)+\int w(\rho_t-\rho)d^3\mathbf{r}\right)\\ &=E_w[w]-\int w\rho\,d^3\mathbf{r}. \end{aligned} \qquad (9)$$

Here $E_w[w]$ is the noninteracting ground-state energy of N electrons in an external potential field w. If $w=w_\rho$ is chosen so that the minimizing Φ_w gives $\rho_w=\rho_{\text{HF}}$, the equations for the noninteracting electronic orbitals occupied in Φ in the Hartree-Fock model are

$$v_x(\mathbf{r})\phi_i(\mathbf{r})=[\epsilon_i^{\mathrm{KS}}+\tfrac{1}{2}\nabla^2-v(\mathbf{r})-v_h(\mathbf{r})]\phi_i(\mathbf{r}), \qquad (10)$$

where $v_x=w-v-v_h$ and $E_w=\Sigma n_i\epsilon_i$. In the exact Kohn-Sham equations, derived below, the local exchange potential $v_x(\mathbf{r})$ here is replaced by the functional derivative $\hat{v}_x=[\delta/\delta\rho(\mathbf{r})]E_x[\rho]$. If an equivalent local exchange potential exists, these equations are identical.

First-order variations of the energy functional, modified using Lagrange multipliers λ_{ji} to enforce orthonormality of the orbital functions, are given by

$$\delta\left\{E[\rho]-\sum_{ij} n_i n_j\left(\int \phi_i^*\phi_j d^3\mathbf{r}-\delta_{ij}\right)\lambda_{ji}\right\}$$
$$=\sum_i n_i\left[\int \delta\phi_i^*\left\{\frac{\delta E}{n_i\delta\phi_i^*}-\sum_j n_j\phi_j\lambda_{ji}\right\}d^3\mathbf{r}+\text{c.c.}\right]$$
$$+\sum_i \delta n_i\int \phi_i^*\frac{\delta E}{\delta\rho}\phi_i d^3\mathbf{r}. \qquad (11)$$

Euler-Lagrange equations follow on requiring this expression to vanish for unconstrained variations of occupied orbitals of Φ with fixed occupation numbers $n_i\neq 0$. The coupled equations for the occupied orbitals are

$$\frac{\delta E}{n_i\delta\phi_i^*}=\sum_j n_j\phi_j\lambda_{ji}. \qquad (12)$$

The functional derivative $\delta T/n_i\delta\phi_i^*$ is the differential term $-\frac{1}{2}\nabla^2\phi_i$. The energy functionals T,V,E_h,E_x defined above are invariant under unitary transformation of the occupied orbitals. In Hartree-Fock theory without symmetry constraints, variational theory determines Φ but not the particular orbital basis. It is customary to select a *canonical* orthonormal basis which diagonalizes the matrix $n_j\lambda_{ji}=\epsilon_i\delta_{ij}$. The Euler-Lagrange equations for the canonical occupied orbitals $\{\phi_i\}$ of Φ are the Hartree-Fock equations

$$-\sum_j n_j(j|u|i)\phi_j(\mathbf{r})=[\epsilon_i^{\mathrm{HF}}+\tfrac{1}{2}\nabla^2-v(\mathbf{r})-v_h(\mathbf{r})]\phi_i(\mathbf{r}). \qquad (13)$$

The external and Coulombic potentials v and v_h are determined by the chain rule for functional derivatives, $\delta F/n_i\delta\phi_i^*=(\delta F/\delta\rho)\phi_i$. On applying this formula to the functional E_x, the exchange term on the left here becomes $(\delta E_x/\delta\rho)\phi_i$, giving the exact Kohn-Sham equations. Equation (10) is obtained if this functional derivative defines a local exchange potential v_x. If energy formulas are interpolated using fractional occupation numbers and occupation numbers are varied in a basis of canonical Kohn-Sham eigenfunctions, only the final term in Eq. (11) is nonzero, and the equation implies Janak's theorem [17],

$$\frac{\partial E}{\partial n_i}=\int \phi_i^*\frac{\delta E}{\delta\rho}\phi_i d^3\mathbf{r}=\int \phi_i^*\frac{\delta E}{n_i\delta\phi_i^*}d^3\mathbf{r}=\epsilon_i. \qquad (14)$$

Since the left-hand members of Eqs. (10) and (13) are different, the two equations in general produce different sets of occupied orbital functions. However, if the functional derivative $\hat{v}_x=\delta E_x/\delta\rho(\mathbf{r})$ reduces to a local exchange potential $v_x(\mathbf{r})$, the proof that the Hartree-Fock ground-state energy is a functional of the density implies that both equations produce the same ρ and Φ_ρ. The occupied orbital functions determined by the local-potential equation must be solutions of the general (noncanonical) Hartree-Fock equations. If Eqs. (10) and (13) are each summed and integrated as indicated by $\Sigma_i n_i\int\phi_i^*\{\cdots\}d^3\mathbf{r}$, then Eq. (7) and the invariance of such trace sums under unitary transformations of the occupied orbitals imply that the sum of eigenvalues $\Sigma_i n_i\epsilon_i$ must be the same for both equations. Individual components of the total energy must also be identical.

Equation (7) implies if $\hat{v}_x=v_x(\mathbf{r})$ that v_x must be the Slater exchange potential. This result follows whenever E_x is defined by Eq. (4). It clearly carries over to the situation of nonzero correlation energy in RDFT [15]. In standard DFT, it is implied if correlation energy is defined in a separate postulate as the difference between total energy and reference-state energy $(\Phi|H|\Phi)$ [18]. Since the assumed local exchange potential is defined for the true model ground state, it should agree with that computed in the OEP method. In fact, characteristic differences between Slater and OEP exchange potentials are well established [7,9,10]. Since Hartree-Fock minimizes the sum of two nonlocal energies, kinetic and exchange, while the Kohn-Sham construction selectively minimizes the kinetic energy, the possibility that ground-state Hartree-Fock kinetic energy is greater than that obtained by the Kohn-Sham construction cannot be excluded. When this is true, the argument given above implies that an exact local exchange potential does not exist. In this case, the reference state Φ determined by the Kohn-Sham construction, minimizing total kinetic energy for a specified density, cannot be identical with the ground-state Hartree-Fock wave function. The difference of total energies defines an artificial correlation energy inherent in the Kohn-Sham construction.

To summarize, assuming that the ground-state functional derivative $\delta E_x/\delta\rho$ is a local function implies several exact results in the Hartree-Fock model theory. If the ground state is not degenerate, Eqs. (13) and (10) must produce occupied orbital sets that transform into each other and give the same reference state Φ. The sum $\Sigma_i n_i\epsilon_i$ of occupied orbital energies must be the same for Hartree-Fock, exact Kohn-Sham, and OEP. The local exchange potential v_x must be the Slater potential, Eq. (5). The OEP equations must produce the same local potential as the Kohn-Sham construction, in which total kinetic energy is minimized for a fixed density function. This requires the ground-state Hartree-Fock kinetic energy to be a minimum among states Φ that produce the same density function ρ. Conversely, failure of any of these consequences of exact Kohn-Sham theory implies that the functional derivative $\delta E_x/\delta\rho$ is not a local function.

V. RESULTS OF CALCULATIONS

The Kohn-Sham construction defines a variational procedure using trial functions in the usual Hilbert space. The KS

TABLE I. Criteria for local functional derivatives (hartree units; signed integers indicate powers of 10).

Atom	P_h^{HF}	P_x^{HF}	P_x^{KS}	P_T^{HF}	P_T^{KS}
He	−0.347−9	0.174−9	0.174−9	−0.606−5	−0.606−5
Be	−0.316−9	0.126	−0.1−3	0.812	0.815
Ne	0.152−8	0.442	−0.3−4	6.859	6.862

model potential w determines the local exchange potential v_x in Eq. (10). If ρ is obtained by solving the Hartree-Fock Eqs. (13), an iterative process can be set up, similar to that proposed by Zhao *et al.* [19]. Starting with the Slater potential, v_x is built up by solving the Poisson equation for successive iterates of the residual density error $\rho_t-\rho$. This iterative algorithm will be described in detail elsewhere. The incremental exchange potential is a solution of a Poisson equation, which makes it a radially smooth function. Calculations using this algorithm have been carried out for atomic He, Be, and Ne. Computed total energies agree closely with prior results [8].

Ground-state wave functions calculated as parametric functions of the nuclear charge Z determine ground-state densities and values of each of the component energy functionals considered here. The relationship of these quantities is determined by the definition of density-functional derivatives appropriate to Hohenberg-Kohn theory. A necessary condition for a local potential function $v_F(\mathbf{r})$ to be equivalent to a functional derivative $\delta F/\delta\rho$ in exact Kohn-Sham equations is that the criterion defined by [18]

$$P_F=\frac{\partial}{\partial Z}F[\rho]-\int d^3\mathbf{r}\,v_F(\mathbf{r})\frac{\partial\rho}{\partial Z} \tag{15}$$

should vanish to the accuracy of the wave-function calculation.

For exchange energy, it is important to note that the vanishing of P_x is a necessary but not sufficient condition for locality of an effective exchange potential. In the Hartree-Fock (UHF) model of DFT [5], an effective local exchange potential can be obtained either by the Kohn-Sham construction (KSC) or by minimizing the variational energy $(\Phi|H|\Phi)$ for a model state Φ whose occupied orbital functions are determined by a local optimized effective potential (OEP). In OEP theory [6,7], the local exchange potential $v_x(\mathbf{r})$ is determined by an integral equation deduced from the variational condition, for arbitrary $\delta v(\mathbf{r})$,

$$\sum_i n_i\int d^3\mathbf{r}\,\phi_i^*(\mathbf{r})\,\delta v(\mathbf{r})\sum_a(1-n_a)\,\phi_a(\mathbf{r})(\epsilon_a-\epsilon_i)^{-1}\times(a|v_x-\hat{v}_x|i)=0, \tag{16}$$

where $\hat{v}_x$ is the Fock exchange operator. Indices $i\leqslant N$ and $a>N$ here denote occupied and unoccupied orbitals of the model state with orbital energies ϵ_i and ϵ_a, respectively. This equation is derived by requiring $(\Phi|H|\Phi)$ to be stationary for restricted orbital variations

$$\delta\phi_i(\mathbf{r})=-\int g_i(\mathbf{r},\mathbf{r}')\,\delta v(\mathbf{r}')\,\phi_i(\mathbf{r}')\,d^3\mathbf{r}' \tag{17}$$

driven by $\delta v(\mathbf{r})$, where

$$g_i(\mathbf{r},\mathbf{r}')=\sum_a(1-n_a)\,\phi_a(\mathbf{r})(\epsilon_a-\epsilon_i)^{-1}\phi_a^*(\mathbf{r}').$$

Because of the Green's-function weighting in Eq. (16), it does not imply that $(a|v_x-\hat{v}_x|i)=0$ for all $i\leqslant N<a$, a condition for equivalence to UHF. If this condition is not satisfied, the OEP model state differs from the UHF ground state, and $E_{\mathrm{OEP}}>E_{\mathrm{UHF}}$. However, the OEP integral equation implies that the linear operator $\hat{v}_x$ is equivalent to the local potential v_x for all orbital variations generated by a local potential function. Since this includes variations of a nuclear charge, the OEP integral equation implies that the locality criterion P_x for the OEP exchange energy must vanish by construction. This provides a numerical test of the accuracy of an OEP calculation. The Kohn-Sham construction obtains a local exchange potential subject to the additional constraint that $\rho_{\mathrm{KSC}}=\rho_{\mathrm{UHF}}$ in the Hartree-Fock model. If $\rho_{\mathrm{OEP}}\neq\rho_{\mathrm{UHF}}$, then the KSC and OEP model states must differ, and P_x does not necessarily vanish for the KS construction.

Table I lists computed values of P_h, P_x, and P_T for He, Be, and Ne. In the Hartree-Fock model of DFT, components of the ground-state energy functional are defined by Eqs. (4). Z derivatives of the HF density function and of these components of the ground-state HF energy are used in Eq. (15) to test the locality hypothesis for several effective local potentials. P_x^{HF} tests the Slater exchange potential and P_x^{KS} tests the local exchange potential computed by the Kohn-Sham construction. P_T, defined for the local potential computed from Eq. (8), is large except for He. As expected, P_h vanishes to within computational accuracy in all cases. Its value is a measure of the numerical accuracy of the calculations. In these calculations, P_x^{OEP} vanishes to computational accuracy and P_x^{HF} fails this test by a large margin. P_x^{KS} is nonzero for Be and Ne, but is quite small. Since $P_x=0$ is a necessary but

TABLE II. HF and OEP energies and eigenvalues for Be and Ne: total energy (E), exchange energy (E_x), kinetic energy (E_T), eigenvalues ($\epsilon_{1s},\epsilon_{2s},\epsilon_{2p}$) (hartree units).

	E	E_x	E_T	ϵ_{1s}	ϵ_{2s}	ϵ_{2p}
Be (HF)	−14.57302	−2.66691	14.57302	−4.73267	−0.30927	
Be (OEP)	−14.57256	−2.66609	14.573	−4.123	−0.311	
Ne (HF)	−128.54709	−12.10835	128.54709	−32.7724	−1.9304	−0.8504
Ne (OEP)	−128.54563	−12.10551	128.546	−30.710	−1.602	−0.733

TABLE III. One-electron energies (hartree units).

Atom	Level	$-I$ [a]	$\epsilon^{(\mathrm{HF})}$ [b]	$\epsilon^{(\mathrm{OEP})}$	$\epsilon^{(\mathrm{KS})}$	$\epsilon^{(\mathrm{XS})}$
He	$1s$	-0.903	-0.918		-0.918	-0.918
Be	$1s$		-4.733	-4.123	-4.125	-4.624
	$2s$	-0.343	-0.309	-0.311	-0.309	-0.326
Ne	$1s$		-32.772	-30.710	-30.821	-32.076
	$2s$		-1.931	-1.602	-1.720	-1.751
	$2p$	-0.792	-0.850	-0.733	-0.852	-0.912

[a] Moore [20].

[b] Froese Fischer [11].

not sufficient condition for locality, this result does not conflict with other data cited here.

Table II lists total and orbital energies obtained in new variational HF and OEP calculations. The expected accuracy is within one unit in the final figure quoted. Details of these calculations will be published elsewhere. They verify or refine the results of earlier OEP calculations [9,10]. Table III lists $-I$, where I is the experimental ionization potential, canonical Hartree-Fock orbital energies ϵ_i^{HF}, self-consistent orbital energies ϵ_i^{XS} obtained from Eq. (10) using the Slater exchange potential of Eq. (7), Kohn-Sham orbital energies ϵ_i^{KS} obtained as described above, and OEP eigenvalues. Table IV lists total energy, kinetic energy, exchange energy, and eigenvalue sums from the same calculations. Except for He, all of these results differ. As discussed above, this implies for Be and Ne that the functional derivative $\delta E_x/\delta\rho = \hat{v}_x$ is not equivalent to a local exchange potential in the Hartree-Fock model of DFT.

VI. DISCUSSION

Common assumptions about Kohn-Sham density-functional theory have been tested here by numerical calculations. These calculations test rigorous theoretical consequences of assuming that a local function exists equivalent to the density-functional derivative of a ground-state exchange energy. The tests clearly succeed for He but fail for both Be and Ne. Since these are typical atoms, similar tests are expected to fail in general for atoms or molecules with more than two electrons.

Practical results that support this conclusion have been known for some time. While an exact Kohn-Sham theory with a local potential is expected to reproduce energy and density-dependent properties of the true ground state, this has never been achieved for real systems with more than two electrons. If electronic correlation is omitted, such an exact theory should coincide for Hartree-Fock ground states with the OEP method, and both should be equivalent to exact Hartree-Fock for closed-shell atoms. But characteristic differences are well-established, especially in the one-electron energies. Sums of OEP orbital energies are significantly different from the corresponding Hartree-Fock sums. The present analysis identifies the cause of these discrepancies.

TABLE IV. Total energies and eigenvalue sums (hartree units).

Atom	Method	E (total)	E (kinetic)	E_x	$\Sigma\epsilon$
He	HF [a]	-2.8617	2.8617	-1.0258	-1.8359
	OEP [b]	-2.8617		-1.0258	-1.8359
	KS	-2.8617	2.8616	-1.0258	-1.8359
	XS	-2.8617	2.8616	-1.0258	-1.8359
Be	HF	-14.5730	14.5730	-2.6669	-10.0839
	OEP	-14.5724		-2.6658	-8.8683
	KS	-14.5724	14.5724	-2.6658	-8.8696
	XS	-14.5614	14.9513	-2.7155	-9.9015
Ne	HF	-128.5471	128.5471	-12.1083	-74.5081
	OEP	-128.5455		-12.1050	-69.0184
	KS	-128.5454	128.5451	-12.1050	-70.1940
	XS	-128.5007	131.6979	-12.3075	-73.1273

[a] Froese Fischer [11].

[b] Engel and Vosko [10], present results for $\Sigma\epsilon$.

Although limited to a theory without electronic correlation, so that accurate calculations can be carried out, the present results have profoundly unsatisfactory implications for several practical aspects of density-functional theory. The full theory, including electronic correlation, can hardly be expected to have a simpler mathematical structure than the explicit exchange energy treated here. It may not be possible to construct a theory that realizes the goal of an exact local exchange-correlation potential for more than two electrons.

Note added in proof. In refining our OEP calculations, we find that orbital energies are more sensitive to the variational basis than is indicated here. Total OEP energies, however, are variationally stable and appear to be numerically accurate as stated. Our KSC results are cross-checked between independent algebraic and numerical programs, but this was not possible for the OEP results. OEP calculations in which the basis sensitivity has been reduced will be reported in a later publication. We are grateful to J. B. Krieger for calling this problem to our attention.

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