

Does an exact local exchange potential exist?

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In Kohn–Sham density functional theory, equations for occupied orbital functions of a model state are derived from the exact ground-state energy functional of Hohenberg and Kohn. The exchange–correlation potential in these exact Kohn–Sham equations is commonly assumed to be a local potential function rather than a more general linear operator. This assumption is tested and shown to fail for the exchange potential in a Hartree–Fock model for atoms, for which accurate solutions are known.

1. Introduction

Hohenberg and Kohn [4] proved that an external potential function $v(\mathbf{r})$ is uniquely associated with the electron density function $\rho(\mathbf{r})$ for any N -electron ground state Ψ . A universal functional $F[\rho]$ is defined by subtracting $\int v\rho$ from ground-state energy $E[v]$. If ρ is arbitrary, $\int v\rho$ defines a functional $V[\rho]$. The energy functional $E_v = F + V$ is minimized by the ground-state density function ρ . In the density-functional theory (DFT) of Kohn and Sham [6], an N -electron model or reference state Φ is characterized by a set of orthonormal orbital wave functions $\{\phi_i\}$, with occupation numbers n_i . In the Kohn–Sham construction, Φ and a local potential function are determined by minimizing kinetic energy $(\Phi|T|\Phi)$ subject to the constraint that $\rho_\Phi = \sum_i n_i \phi_i^* \phi_i$ must be equal to the ground-state density function ρ_Ψ . Alternatively, exact Kohn–Sham equations are defined as the Euler–Lagrange equations for the occupied orbital functions that minimize the Hohenberg–Kohn energy functional. These equations contain functional derivatives $\delta E/\delta\rho$ and take the form

$$\left\{ \frac{\delta E}{\delta\rho} - \varepsilon_i \right\} \phi_i(\mathbf{r}) = 0. \quad (1)$$

The Thomas–Fermi equation can be derived if the functional derivative of the kinetic energy functional in exact Kohn–Sham equations is equivalent to a local potential function $v_T(\mathbf{r})$. It has recently been shown that the Thomas–Fermi equation is in general inconsistent with exact Kohn–Sham equations for the same Hohenberg–Kohn energy functional [9]. Hence an exact local effective potential does not exist for the ki-

netic energy functional. It cannot be assumed without proof that the correct variational expressions corresponding to functional derivatives of other nonlocal components of the energy functional in equation (1) are equivalent to local potential functions.

Payne [10] showed that unrestricted Hartree–Fock theory (UHF) for ground states satisfies Hohenberg–Kohn theorems, which establish the existence of an energy functional $E_v[\rho]$ of the reference-state electron density ρ . We use this UHF exact-exchange model of DFT, for which accurate energies and density functions can be computed, to examine the question of locality of the exchange potential in exact Kohn–Sham equations. The UHF energy mean value $\langle \Phi | H | \Phi \rangle$ is minimized without constraint other than normalization, so that Φ is identical to the minimizing state.

Exact Kohn–Sham equations for the occupied orbital functions of Φ are implied if these orbital functions can be freely varied about their ground-state values. Standard variational theory requires free variation of trial orbital functions within the relevant Hilbert space. This is a necessary condition for an integral of the form $\int \delta\phi_i^* \{ \mathcal{H} - \varepsilon_i \} \phi_i = 0$ to imply an effective Schrödinger (or Dirac) equation $\{ \mathcal{H} - \varepsilon_i \} \phi_i = 0$. In the UHF model, $E[\rho]$ is naturally expressed as a sum of component functionals that are explicit functionals of the occupied orbital functions $\{ \phi_i \}$. If v -representability fails for some perturbed density in an infinitesimal neighborhood of a given ground-state reference density, so that a corresponding perturbed external potential $v(\mathbf{r})$ and UHF ground state Φ do not exist, variations of an explicit functional $E[\rho]$ are constrained, and exact Kohn–Sham equations cannot be derived. However, the explicit orbital functionals of the UHF model and their variations remain well defined. Exact Kohn–Sham equations and UHF equations follow the same variational logic, using the same set of trial functions, and must determine the same UHF ground-state wave function and energy.

The assumption that an exact local exchange potential exists for ground states leads to several paradoxes in existing DFT literature. A very clear example is provided by comparing UHF ground-state energies of typical atoms with those computed in the optimized effective potential (OEP) model [11,13]. For the same N -electron Hamiltonian and set of variational trial functions (Φ), the OEP model constructs the best possible local exchange potential. OEP ground-state energies computed by Aashamar et al. [1], and with improved accuracy by Engel and Vosko [2], are -14.5724 for Be and -128.5455 for Ne in Hartree units, above the Hartree–Fock energies -14.57302 for Be and -128.54710 for Ne [3] by amounts greater than the expected residual numerical inaccuracy. The Kohn–Sham construction also posits a local exchange potential, but adds a constraint requiring the model density to equal the Hartree–Fock ground-state density. Hence variational theory implies that $E_{\text{KS}} \geq E_{\text{OEP}} \geq E_{\text{HF}}$. When $E_{\text{OEP}} > E_{\text{HF}}$, the OEP calculations imply that $E_{\text{KS}} > E_{\text{HF}}$, whereas exact minimization of the Hohenberg–Kohn energy functional would imply $E_{\text{KS}} = E_{\text{HF}}$. The way out of this paradox is to insist on a distinction between the “Kohn–Sham construction” (minimizing kinetic energy subject to a density constraint) and “exact Kohn–Sham equations” (minimizing the exact Hohenberg–Kohn energy functional), and to drop the assumption that the functional derivative of the exchange energy functional can be

equated to the necessarily local exchange potential derived in the Kohn–Sham construction.

In order to examine the question of locality of the effective exchange potential in exact Kohn–Sham equations, we extend the definition of functional derivatives to include linear operators that act on orbital wave functions. Thus in general for a functional $F[\rho]$, derivations given below assume only that the functional derivative $\delta F/\delta\rho$ is a linear operator \hat{v}_F , which may reduce to a local potential $v(\mathbf{r})$ in any particular case. We then examine consequences of such locality in the UHF model. The relationship between $\hat{v}_x = \delta E_x/\delta\rho$ and a local exchange potential $v_x(\mathbf{r})$ can be studied in this model without additional assumptions.

We show that certain inconsistencies between existing calculations can be traced to failure of the conventional assumption that \hat{v}_x is equivalent to a local potential function. We define and evaluate numerical criteria for the locality of functional derivatives of the ground-state kinetic energy and exchange energy functionals for He, Be, and Ne. Values of these criteria computed for Be and Ne are inconsistent with the existence of exact local potentials for either kinetic or exchange energy.

2. Variational theory

To avoid mathematical issues not relevant to the present argument, the local external potential $v(\mathbf{r})$ and the density function $\rho(\mathbf{r})$ normalized to N electrons are both assumed here to be spin-indexed scalar fields, realizable for physical systems. Spin indices and sums are suppressed in the notation. The N -electron Hamiltonian operator is $H_v = T + U + V$, where T is kinetic energy, U is the electronic Coulomb interaction, and V is the N -electron external potential constructed from $v(\mathbf{r})$.

In Kohn–Sham theory, $\rho = \sum_i n_i \phi_i^* \phi_i$, where occupation numbers n_i are determined by Fermi–Dirac statistics at zero temperature. Thus a density functional is also a functional of the orbital functions. Density variations are generated by varying the orthonormal set of occupied orbital functions $\{\phi_i\}$. In standard variational theory, as used here, derivation of differential equations requires free variation of trial orbital functions in the Hilbert space defined by bounded continuous functions with continuous gradients except for Coulomb cusp conditions. The variational derivations of Schrödinger and Fock, expressed in terms of functional derivatives of orbital functionals, lead to linear operators acting on wave functions. Functional derivatives that may be linear operators are related by the chain rule,

$$\frac{\delta F}{\delta \phi_i^*} = n_i \frac{\delta F}{\delta \rho} \phi_i.$$

Defining kinetic energy as the mean value in a model or reference state, standard variational theory for this orbital functional gives

$$\frac{\delta T}{n_i \delta \phi_i^*} = -\frac{1}{2} \nabla^2 \phi_i \quad \text{if } n_i \neq 0.$$

In a ground state, the orbital functional T is a density functional. Hence these formulas imply that the density functional derivative is the operator $-\frac{1}{2}\nabla^2$ derived by Schrödinger. The kinetic energy operator is used in this form in the Kohn–Sham equations [6]. This functional derivative is not equivalent to a local potential [9].

Exact Kohn–Sham theory provides a model of noninteracting electrons in a potential field defined by the residual functional derivative $\delta(E - T)/\delta\rho$. We show here that assuming $\delta(E - T)/\delta\rho$ to be a local potential leads to contradictions that can be resolved as in the case of the kinetic energy by extending the definition of functional derivatives to include linear operators. It is commonly assumed that the functional derivative of a density functional F can be defined such that an arbitrary infinitesimal variation of ρ induces

$$\delta F = \int \frac{\delta F}{\delta\rho(\mathbf{r})} \delta\rho(\mathbf{r}) d^3\mathbf{r}.$$

For any density functional that is an explicit orbital functional,

$$\delta F = \sum_i \int \left\{ \delta\phi_i^* \frac{\delta F}{\delta\phi_i^*} + cc \right\} d^3\mathbf{r} = \sum_i n_i \int \left\{ \delta\phi_i^*(\mathbf{r}) \frac{\delta F}{\delta\rho(\mathbf{r})} \phi_i(\mathbf{r}) + cc \right\} d^3\mathbf{r}, \quad (2)$$

valid if $\hat{v}_F = \delta F/\delta\rho$ is a linear operator. Equation (2) reduces to the usual definition if a local function exists such that $\hat{v}_F = v_F(\mathbf{r})$.

3. Hartree–Fock as a density functional theory

In the UHF model, a functional of $\rho(\mathbf{r})$ is defined by restricting trial functions to be single Slater determinants [10]. This theory is a direct analog of standard DFT [4,6,7]. A universal functional $F_0[\rho]$ is defined by minimizing $(\Phi_t|T + U|\Phi_t)$ for given ρ . If a Lagrange-multiplier field $v(\mathbf{r})$ is specified,

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

where $E_0[v]$ is the ground-state Hartree–Fock energy in the external potential v . The electron density ρ_v is determined by the minimizing state Φ_v . Equation (3) defines a universal functional $F_0[\rho]$ when $v = v_\rho$ such that $\rho_v = \rho$ for $\Phi_v = \Phi_\rho$. The numerical value of F_0 in any Hartree–Fock ground state is specified by this equation.

Hohenberg–Kohn theorems for this model follow from this definition. When $\rho_v = \rho$,

$$F_0[\rho] = F_{0v}[\rho] = E_0[v] - \int v\rho d^3\mathbf{r}, \quad (4)$$

and the energy functional $E_{0v}[\rho] = F_0[\rho] + \int v\rho d^3\mathbf{r}$ takes its minimum value $E_0[v]$. If $F_0[\rho]$ corresponds to Φ_ρ but $v \neq v_\rho$, then

$$E_{0v}[\rho] = (\Phi_\rho|T + U + V|\Phi_\rho) \geq E_0[v]. \quad (5)$$

Equations (4) and (5) establish the variational property of the energy functional $E_{0v}[\rho]$.

The Hartree–Fock ground-state energy functional is subdivided into component orbital functionals $E_0[\rho] = T[\rho] + U[\rho] + V[\rho]$. Each of these functionals is a mean value evaluated in the reference state $\Phi = \Phi_\rho$, 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 , Coulomb minus exchange by \bar{u} , these component functionals are

$$\begin{aligned} T[\rho] &= (\Phi|T|\Phi) = \sum_i n_i \left(i \left| -\frac{1}{2}\nabla^2 \right| i \right), \\ V[\rho] &= (\Phi|V|\Phi) = \sum_i n_i (i|v|i), \\ U[\rho] &= (\Phi|U|\Phi) = \frac{1}{2} \sum_{i,j} n_i n_j (ij|\bar{u}|ij). \end{aligned}$$

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

$$E_h[\rho] = \frac{1}{2} \sum_{i,j} n_i n_j (ij|u|ij); \quad E_x[\rho] = -\frac{1}{2} \sum_{i,j} n_i n_j (ij|u|ji). \quad (6)$$

Assuming normalization $(\Phi|\Psi) = (\Phi|\Phi) = 1$, the correlation energy functional $(\Phi|U|\Psi - \Phi)$ defined in reference-state DFT (RDFT) [8] vanishes in the UHF model, because $\Psi = \Phi$. Euler–Lagrange equations for the occupied orbital functions are derived below. Because the UHF functional $E_{0v}[\rho]$ is an explicit functional of the occupied orbital functions, this derivation is valid for both Hartree–Fock and exact Kohn–Sham equations.

4. One-electron equations and energies

On introducing Lagrange multipliers λ_{ji} to enforce orthonormality of the orbital functions, first-order variations of the energy functional are given by

$$\begin{aligned} &\delta \left\{ E[\rho] - \sum_{ij} n_i n_j \left(\int \phi_i^* \phi_j d^3\mathbf{r} - \delta_{ij} \right) \lambda_{ji} \right\} \\ &= \sum_i n_i \left[\int \delta \phi_i^* \left\{ \frac{\delta E}{n_i \delta \phi_i^*} - \sum_j n_j \phi_j \lambda_{ji} \right\} d^3\mathbf{r} + cc \right] + \sum_i \delta n_i \int \phi_i^* \frac{\delta E}{\delta \rho} \phi_i d^3\mathbf{r}. \quad (7) \end{aligned}$$

Requiring this expression to vanish for unconstrained variations of the occupied orbital set ($n_i = 1$), with fixed occupation numbers, determines coupled Euler–Lagrange equations for the occupied orbitals,

$$\frac{\delta E}{n_i \delta \phi_i^*} = \sum_j n_j \phi_j \lambda_{ji}. \quad (8)$$

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 that diagonalizes the matrix $n_j \lambda_{ji} = \varepsilon_i \delta_{ij}$. The energy functionals T, V, E_h, E_x defined above are invariant under unitary transformation of the occupied orbitals of Φ . External and Coulombic potentials v and v_h are determined as local potentials consistent with the chain rule for functional derivatives,

$$\frac{\delta F}{\delta \phi_i^*} = n_i \frac{\delta F}{\delta \rho} \phi_i.$$

The implied functional derivative $\delta T / \delta \rho$ is the linear operator $-\frac{1}{2} \nabla^2$. The Euler–Lagrange equations for the canonical occupied orbitals $\{\phi_i\}$ of Φ are the exact Kohn–Sham equations

$$\frac{\delta E_x}{n_i \delta \phi_i^*} = \frac{\delta E_x}{\delta \rho} \phi_i = \left(\varepsilon_i + \frac{1}{2} \nabla^2 - v(\mathbf{r}) - v_h(\mathbf{r}) \right) \phi_i(\mathbf{r}). \quad (9)$$

For the exchange energy functional E_x ,

$$\hat{v}_x \phi_i = \frac{\delta E_x}{n_i \delta \phi_i^*} = - \sum_j n_j (j|u|i) \phi_j(\mathbf{r}),$$

and these equations are identical to the Hartree–Fock equations. If occupation numbers are varied in a basis of canonical Kohn–Sham eigenfunctions, only the final term in equation (7) is nonzero, and the equation implies Janak’s theorem [5]

$$\frac{\partial E}{\partial n_i} = \int \phi_i^* \frac{\delta E}{\delta \rho} \phi_i \, d^3 \mathbf{r} = \int \phi_i^* \frac{\delta E}{n_i \delta \phi_i^*} \, d^3 \mathbf{r} = \varepsilon_i. \quad (10)$$

In the Kohn–Sham construction [6], a kinetic energy functional is defined 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 equation (3),

$$T_w[\rho] = \min_{\Phi_t} \left[(\Phi_t | T | \Phi_t) + \int w(\rho_t - \rho) \, d^3 \mathbf{r} \right] = E_w[w] - \int w \rho \, d^3 \mathbf{r}. \quad (11)$$

$E_w[w]$ here 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 occupied orbital functions in the noninteracting model state are

$$v_x(\mathbf{r})\phi_i(\mathbf{r}) = \left(\varepsilon_i^{\text{KS}} + \frac{1}{2}\nabla^2 - v(\mathbf{r}) - v_h(\mathbf{r}) \right) \phi_i(\mathbf{r}), \quad (12)$$

where v_h is the classical Coulomb (Hartree) potential, and the exchange potential is defined by $v_x = w - v - v_h$. In the exact Kohn–Sham equations (9), $v_x(\mathbf{r})$ is replaced by the functional derivative $\delta E_x[\rho]/\delta\rho(\mathbf{r})$. If this is a local function, these equations are identical.

5. Functional derivatives and local potentials

Each of the ground-state density functionals defined by equations (6) is an explicit functional of the occupied orbitals of the reference state. If a local potential $v_F(\mathbf{r}) = \delta F/\delta\rho$ exists for a density functional that is also an orbital functional, functional derivatives of $F[\{\phi_i\}]$ with respect to the orbital functions used to construct ρ give a sum rule that determines v_F ,

$$\sum_i \phi_i^* \frac{\delta F}{\delta \phi_i^*} = \sum_i n_i \phi_i^*(\mathbf{r}) \frac{\delta F}{\delta \rho(\mathbf{r})} \phi_i(\mathbf{r}) = \frac{\delta F}{\delta \rho(\mathbf{r})} \rho(\mathbf{r}) = v_F(\mathbf{r}) \rho(\mathbf{r}). \quad (13)$$

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 formula gives the classical Coulomb potential function,

$$v_h(\mathbf{r})\rho(\mathbf{r}) = \sum_i n_i \phi_i^*(\mathbf{r}) \sum_j n_j (j|u|j) \phi_j(\mathbf{r}). \quad (14)$$

Given $E_x = -\frac{1}{2} \sum_{i,j} n_i n_j (ij|u|ji)$ for a ground state, equation (13) implies

$$v_x(\mathbf{r})\rho(\mathbf{r}) = - \sum_i n_i \phi_i^*(\mathbf{r}) \sum_j n_j (j|u|i) \phi_j(\mathbf{r}), \quad (15)$$

equivalent to the local exchange potential of Slater [12]. This result follows whenever E_x is defined by equation (6). It clearly carries over to the situation of nonzero correlation energy in RDFT [8]. 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 $(\Phi|H|\Phi)$. For the kinetic energy functional $(\Phi|T|\Phi)$,

$$v_T(\mathbf{r})\rho(\mathbf{r}) = \sum_i n_i \phi_i^*(\mathbf{r}) \left\{ -\frac{1}{2}\nabla^2 \right\} \phi_i(\mathbf{r}). \quad (16)$$

6. Criteria for locality

Since the left-hand members of equations (12) and (9) are different, the two equations in general produce different sets of occupied orbital functions. However, if a local exchange potential $v_x(\mathbf{r}) = \delta E_x / \delta \rho(\mathbf{r})$ exists, the proof that the Hartree–Fock ground state energy is a functional of the (reference-state) 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 equations (12) and (9) are each summed and integrated as indicated by $\sum_i n_i \int \phi_i^* \{ \dots \} d^3 \mathbf{r}$, then equation (15) and the invariance of such trace sums under unitary transformations of the occupied orbitals imply that the sum of eigenvalues $\sum_i n_i \varepsilon_i$ must be the same for both equations. Individual components of the total energy must also be identical.

If the ground-state functional derivative $\delta E_x / \delta \rho$ is a local function several exact results are implied in the Hartree–Fock model theory. If the ground state is not degenerate, equations (12) and (9) must produce occupied orbital sets that transform into each other and give the same reference state Φ and ground-state energy, and the same sum $\sum_i n_i \varepsilon_i$ of orbital energies for Hartree–Fock, OEP, and the Kohn–Sham construction. The OEP equations must produce the same local exchange potential v_x as the Kohn–Sham construction, and v_x must be the Slater potential, equation (13). The ground-state Hartree–Fock kinetic energy must be a minimum among states Φ that produce the same density function ρ . 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.

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 . For a local functional derivative, Z -derivatives of E_h and ρ would be related by

$$\frac{dE_h}{dZ} = \int v_h(Z; \mathbf{r}) \frac{\partial \rho(Z; \mathbf{r})}{\partial Z} d^3 \mathbf{r}. \quad (17)$$

As defined by equation (14), v_h is twice the Coulomb energy density. From this definition,

$$\frac{dE_h}{dZ} = \frac{1}{2} \int \left(v_h \frac{\partial \rho}{\partial Z} + \frac{\partial v_h}{\partial Z} \rho \right) d^3 \mathbf{r}, \quad (18)$$

so that the relationship to be tested is

$$Q_h = \frac{1}{2} \int \left(v_h \frac{\partial \rho}{\partial Z} - \frac{\partial v_h}{\partial Z} \rho \right) d^3 \mathbf{r} = 0. \quad (19)$$

A similar formula is obtained for the exchange potential,

$$Q_x = \frac{1}{2} \int \left(v_x \frac{\partial \rho}{\partial Z} - \frac{\partial v_x}{\partial Z} \rho \right) d^3 \mathbf{r} = 0. \quad (20)$$

If Q_x is nonzero, a local functional derivative does not exist. For the kinetic energy the locality criterion is

$$Q_T = \int \frac{\partial v_T}{\partial Z} \rho d^3\mathbf{r} = 0. \quad (21)$$

7. Calculations and conclusions

Calculations for most atoms find $E_{\text{OEP}} > E_{\text{HF}}$ [1,2]. Characteristic differences between Slater and OEP exchange potentials indicate that an exact local exchange potential consistent with equation (15) does not exist.

Table 1 compares total energies, exchange energies, and eigenvalue sums obtained for He, Be, and Ne by Hartree–Fock and OEP calculations. As argued above, these results should agree if a local exchange potential exists. The differences apparent in these results indicate that this is not true except for He.

The locality criteria defined by equations (19)–(21) have been computed and cross-checked using independent variational and numerical Hartree–Fock programs. Table 2 lists values computed for He, Be, and Ne. As expected, Q_h vanishes to within computational accuracy in all cases, Q_x is nonzero for both Be and Ne, and Q_T is small only for He. This implies that an exact local exchange potential does not exist for Be or Ne.

Since these are typical atoms, there is no reason to expect a simpler result for any atom or molecule with more than two electrons. It can hardly be expected that exact cancellation would occur between nonlocal exchange and correlation terms so as to simplify the theory when correlation is included. Thus it is unlikely that the local

Table 1
Total energies and eigenvalue sums (Hartree units).

Atom	Method	E_{total}	E_x	$\sum \varepsilon$
He	HF [3]	−2.8617	−1.0258	−1.8359
	OEP [1,2]	−2.8617	−1.0258	−1.8359
Be	HF	−14.5730	−2.6669	−10.0839
	OEP	−14.5724	−2.6658	−8.8728
Ne	HF	−128.5471	−12.1083	−74.5081
	OEP	−128.5455	−12.1050	−70.1293

Table 2
Criteria for local functional derivatives (Hartree units,
signed integers indicate powers of 10).

Atom	Q_h	Q_x	Q_T
He	0.131−8	−0.657−9	−0.494−5
Be	0.334−9	−0.126	0.812
Ne	0.963−6	−0.442	6.849

exchange–correlation potential anticipated in exact Kohn–Sham theory exists except for two-electron systems.

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References

- [1] K. Aashamar, T.M. Luke and J.D. Talman, Optimized central potentials for atomic ground-state wavefunctions, *At. Data Nucl. Data Tables* 22 (1978) 443.
- [2] E. Engel and S.H. Vosko, Accurate optimized-potential-model solutions for spherical spin-polarized atoms: Evidence for limitations of the exchange-only local spin-density and generalized-gradient expansions, *Phys. Rev. A* 47 (1993) 2800–2811.
- [3] C. Froese Fischer, *The Hartree–Fock Method for Atoms* (Wiley, New York, 1977).
- [4] P. Hohenberg and W. Kohn, Inhomogeneous electron gas, *Phys. Rev.* 136 (1964) B864–B871.
- [5] J.F. Janak, Proof that $\partial E/\partial n_i = \varepsilon_i$ in density-functional theory, *Phys. Rev. B* 18 (1978) 7165–7168.
- [6] W. Kohn and L.J. Sham, Self consistent equations including exchange and correlation effects, *Phys. Rev.* 140 (1965) A1133–A1138.
- [7] M. Levy, Universal variational functionals of electron densities, first-order density matrices, and natural spin-orbitals and solution of the v -representability problem, *Proc. Natl. Acad. Sci.* 76 (1979) 6062–6065.
- [8] R.K. Nesbet, Alternative density functional theory for atoms and molecules, *J. Phys. B* 29 (1996) L173–L179.
- [9] R.K. Nesbet, Kinetic energy in density-functional theory, *Phys. Rev. A* 58 (1998) R12–R15.
- [10] P.W. Payne, Density functionals in unrestricted Hartree–Fock theory, *J. Chem. Phys.* 71 (1979) 490–496.
- [11] R.T. Sharp and G.K. Horton, A variational approach to the unipotential many-electron problem, *Phys. Rev.* 90 (1953) 317.
- [12] J.C. Slater, A simplification of the Hartree–Fock method, *Phys. Rev.* 81 (1951) 385–390.
- [13] J.D. Talman and W.F. Shadwick, Optimized effective atomic central potential, *Phys. Rev. A* 14 (1976) 36–40.