Variational derivation of density functional theory

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It is shown here that Kohn-Sham equations cannot be derived from Hohenberg-Kohn theory without an additional postulate. Assuming that a functional derivative with respect to total electron density exists leads in general to a theory inconsistent with the exclusion principle. A mathematically and physically correct variational theory of the Kohn-Sham model can be developed using functional derivatives with respect to orbital densities. These partial (Gâteaux) derivatives can be constructed explicitly from general N-electron theory and are defined throughout the orbital Hilbert space. This theory is consistent with the local density approximation (LDA), but does not in general imply multiplicative local exchange-correlation potentials. Progress beyond the LDA in condensed-matter physics requires development of methodology for nonlocal exchange and correlation potentials.

I. INTRODUCTION

Hohenberg and Kohn\(^1\) proved, for nondegenerate states, that the ground-state total electronic density function determines the external potential function acting on an interacting N-electron system. This is easily extended to a spin-dependent density, so spin indices and summations are assumed here, but omitted from the notation. Implementation of the implied density-functional theory (DFT) followed only after introduction of the orbital model of Kohn and Sham\(^2\), who applied the Hohenberg-Kohn theory of the universal ground-state functional \(F_s = E - V\) to the kinetic energy functional \(T_s\), to which \(F_s\) reduces for noninteracting electrons. For noninteracting electrons, the density function \(\rho(\mathbf{r})\) is a sum of orbital densities \(\rho_i = \phi_i^*\phi_i\), one for each occupied orbital function of the Kohn-Sham model state. DFT is developed in many review articles and monographs, exemplified by\(^3,4\).

It is widely assumed that Hohenberg-Kohn theory implies the existence of an exact theory that can be represented by the Kohn-Sham model, using only multiplicative local potential functions. It is shown here that this assumption is based on a misconception of the implications of Hohenberg-Kohn theory. If the accepted interpretation were correct, an exact Thomas-Fermi theory (TFT) would exist, in conflict with Kohn-Sham DFT and with the exclusion principle for electrons. The assumed existence of exact local exchange-correlation potentials leads to several problems or paradoxes, resolved by the present analysis. Recent quantitative tests\(^5\) confirm a longstanding result of optimized effective potential (OEP) calculations, that the best possible local exchange potential does not reproduce unrestricted Hartree-Fock (UHF) ground-state energies and densities\(^6\). The exchange-only limit of DFT linear response theory\(^7\) is inconsistent with the time-dependent Hartree-Fock theory of Dirac\(^8\), due to failure of locality\(^9\).

The present analysis has important practical implications for computational methodology relevant to the electronic structure of large molecules and solids. In a formally exact theory, deduced directly from N-electron theory, nonlocal exchange-correlation potentials can be constructed that are free of electronic self-interaction and not inherently restricted to weak electronic correlation or to short-range interactions\(^10\). Progress beyond the local density approximation requires the timely development of computational methods appropriate to nonlocal potentials\(^11\).

II. DFT PRACTICE VERSUS DFT CONCEPTS

Practical applications of DFT use the Kohn-Sham Ansatz, \(\rho = \sum_i n_i \rho_i\), as a postulate for the density. Occupation numbers \(n_i\) are unity for occupied orbitals. Kinetic energy is defined (in the nonrelativistic limit) by the Schrödinger functional of occupied orbital functions, \(T = \sum_i n_i \langle i|\hat{T}|i\rangle\), where \(\hat{T} = -\frac{1}{2}\nabla^2\) in Hartree units. Given an external potential function \(v(\mathbf{r})\), the potential energy \(V = \sum_i n_i \langle i|v|i\rangle\) is an orbital functional, as is the Hartree energy \(E_h\). By the Kohn-Sham Ansatz, any assumed \(E_{xc}[\rho]\) is a functional of the occupied orbital functions. Given \(F = T + E_h + E_{xc}\) as an orbital functional, derivation of the orbital Euler-Lagrange (OEL) equations

\[
\mathcal{F}\phi_i = \{\epsilon_i - v(\mathbf{r})\}\phi_i
\]

is elementary, using Lagrange multipliers \(\epsilon_i\) for independent orbital normalization \(\langle i|i\rangle = 1\), \(i \leq N\). Linear operator \(\mathcal{F}\) is defined by the orbital functional derivative

\[
\mathcal{F}\phi_i = \frac{\delta F}{n_i \delta \phi_i^*}.
\]

\(\mathcal{F}\) is assumed to be defined such that \(\mathcal{F}\) is hermitian. For noninteracting electrons, and also in the local-density approximation (LDA), when \(E_{xc}\) is the integral of a local function of \(\rho\), the OEL equations (1) reduce explicitly to Kohn-Sham equations\(^2\) with local potentials.
Eqs.(1) imply equivalent equations\textsuperscript{12}
\[ \frac{\delta F}{\delta \phi_i} = \epsilon_i - v(r), \] (3)
to be solved for the orbital density functions \( \rho_i \). The Lagrange multipliers \( \epsilon_i \) are to be determined so that independent normalization conditions \( \langle i | i \rangle = \int \rho_i d^3r = 1 \) are satisfied. These modified Thomas-Fermi equations are operationally equivalent to the Kohn-Sham or OEL equations, consistent with the exclusion principle.

This practical derivation makes no use of Hohenberg-Kohn theory except to justify particular approximations to \( E_{xc} \). The density function is constructed after the fact from solutions of the variational equations. To define the model state, some rule \( \Psi \rightarrow \Phi \) must be postulated to supplement the Kohn-Sham Ansatz for the density. Examples are \( \rho_\Phi = \rho_\Psi \) (Kohn-Sham), \( \Psi = \Phi \) (unrestricted Hartree-Fock), and \( \langle \delta \Phi | \Psi \rangle = 0 \), the Brueckner-Brenig condition that selects the model state of greatest weight in \( \Psi \). A derivation starting from Hohenberg-Kohn theory is more problematic, since a formal theory of allowable densities is required\textsuperscript{15}. In the orbital theory described above, this is avoided by recognizing that densities freely constructed from orbital functions in the usual Hilbert space suffice for a valid N-electron theory.

**III. INCOMPLETENESS OF HOHENBERG-KOHN THEORY**

The Hohenberg-Kohn ground-state functional \( F \) is defined only for normalized total densities, \( \int \rho = N \). Standard variational theory constrains normalization using the modified Lagrange functional \( F + V - \mu(\int \rho - N) \), which is to made stationary by varying \( \rho \) with unconstrained normalization\textsuperscript{16}. \( \mu \) is adjusted to satisfy the normalization constraint. This requires the definition of \( F_\mu \) to be extended into all infinitesimal neighborhoods of normalized densities consistent with the orbital Hilbert space. Without such an extended definition, Hohenberg-Kohn theory is incomplete: it cannot determine the variational Euler-Lagrange equations for \( \rho \).

This point is evident in the rigorous derivation of English and English\textsuperscript{17}. In their Eq.(4.1) they propose to complete their derivation by inserting a single constant, which would play the role of the usual chemical potential \( \mu \) if the implied Euler-Lagrange equations were valid. However, comparison with Eqs.(3), implied by physically correct Kohn-Sham equations, indicates that a single constant does not suffice to enforce the exclusion principle\textsuperscript{18}. Independent normalization of each orbital density is required. The derivation in\textsuperscript{17}, restricted to normalized total densities, cannot distinguish between one or several constants, all of which drop out of the variational integrals. As shown here, this is a crucial limitation of Hohenberg-Kohn theory.

If the functional differential
\[ \delta F_\mu = \int d^3r v_F(r) \delta \rho(r), \] (4)
is uniquely defined for unrestricted variations, it determines a total (Fréchet\textsuperscript{19}) density functional derivative
\[ \frac{\delta F_\mu}{\delta \rho(r)} = v_F(r). \] (5)
This is stated as the unique definition of a density functional derivative in standard DFT literature\textsuperscript{3,4}. If such a Fréchet derivative exists, varying the Lagrange functional using standard variational theory\textsuperscript{16} implies the Euler-Lagrange equation
\[ v_F(r) = \mu - v(r). \] (6)
This is a Thomas-Fermi equation, to be solved by varying a trial density for specified \( \mu \), then adjusting \( \mu \) to satisfy the normalization condition. It is inconsistent with Eqs.(3) unless all \( \epsilon_i \) are equal\textsuperscript{18,20}.

Because Thomas-Fermi theory (TFT) enforces only total density normalization, it can determine only a single Lagrange multiplier \( \mu \). This does not exclude solutions that violate the exclusion principle. The example of the lowest \( 1s^2 2s^3 S \) state of an atom containing two noninteracting electrons is discussed below. In this example, two independent orbital energies \( \epsilon_1 \) and \( \epsilon_2 \) are required, not just the single parameter \( \mu \). The conclusion is that the required Fréchet density functional derivative cannot exist in a physically correct theory for any compact system with more than one electron of each spin.

**IV. THE EXCLUSION PRINCIPLE IN DFT**

In any independent-electron orbital model, the exclusion principle requires independent normalization of each orbital density. This is explicit in any physically correct theory of noninteracting electrons, implicit in the Kohn-Sham equations, and is a standard aspect of Hartree-Fock equations. If the Kohn-Sham density decomposition is added as a postulate to the analysis of English and English, the constraint of independent orbital normalization requires independent variation of the orbital partial densities. Such density variations, driven by free (unnormalized) variations of occupied orbital functions, determine Eqs.(3) as Euler-Lagrange equations for the orbital densities\textsuperscript{12}. These equations are expressed in terms of partial (Gâteaux\textsuperscript{19}) functional derivatives of the universal functional \( F=E-V \). Independent normalization of each orbital density introduces independent Lagrange multipliers, which are the one-electron energies in the corresponding orbital Eqs.(1).

Eqs.(3) and (6) can be reconciled only if all orbital energy eigenvalues are equal\textsuperscript{18,20}. This is seen here to be a direct consequence of the different normalization constraints. That independent normalization of the orbital densities is physically correct, specifically enforcing
the exclusion principle in Hartree-Fock theory and Kohn-Sham DFT, is obvious in the example of an atom with two noninteracting electrons of parallel spin. The ground state is 1s2s $^3S$. The density constraints are:

\[ \text{DFT} : \int \rho_{1s} = 1, \int \rho_{2s} = 1 \]

\[ \text{TFT} : \int (\rho_{1s} + \rho_{2s}) = 2. \]

This TFT constraint does not exclude the nonphysical solution

\[ \text{TFT} : \int \rho_{1s} = 2, \int \rho_{2s} = 0, \]

which violates the exclusion principle.

V. GÅTEAUX FUNCTIONAL DERIVATIVES

Euler-Lagrange equations are implied for interacting and noninteracting electrons, respectively, only if the definitions of $F_s$ and $T_s$ can be extended to unnormalized densities generated by infinitesimal variations unconstrained in the orbital Hilbert space. Given $F_s$ as a functional of total density, it is also an orbital functional as a result of the Kohn-Sham Ansatz. The orbital functional derivative in the OEL Eqs.(1) exists if

\[ \delta F_s = \sum_i n_i \int d^3r \{ \delta \phi_i^* (r) \mathcal{F} \phi_i (r) + cc \} \]

defines a unique functional of the occupied orbital functions. For variations about a stationary state, Eqs.(1) imply that

\[ \delta F_s = \sum_i n_i \int d^3r \{ \epsilon_i - v(r) \} \delta \rho_i (r), \]

since $\delta \rho_i = \{ \delta \phi_i^* \phi_i + cc \}$. This proves, by construction, the existence of a Gâteaux functional derivative whose value for such variations is

\[ \frac{\delta F_s}{n_i \delta \rho_i} = \epsilon_i - v(r), \]

for $i \leq N$. A total (Fréchet) derivative is defined only if these partial functional derivatives are all equal, which requires all $\epsilon_i$ to be equal.

Gâteaux functional derivatives exist in general throughout the orbital Hilbert space. They can be constructed from any well-defined density functional, using the Kohn-Sham orbital decomposition of the total model density function. They define local potentials indexed by orbital subshells, in general not a global local potential unless the orbital index drops out. For example, for any orbital functional $F[\{\phi_i\}]$, the functional differential

\[ \delta F = \sum_i n_i \int d^3r \{ \delta \phi_i^* \mathcal{F} \phi_i + cc \}
= \sum_i n_i \int d^3r \frac{\phi_i^*}{\phi_i^* \phi_i} \delta \rho_i, \]

is uniquely defined for $i \leq N$ throughout the orbital Hilbert space if the orbital functional derivative $\mathcal{F} \phi_i$ exists. This determines the Gâteaux derivative

\[ \frac{\delta F}{n_i \delta \rho_i} = \frac{\phi_i^*}{\phi_i^* \phi_i} \mathcal{F} \phi_i = v_{Fi}(r), \]

valid for arbitrary variations in the orbital Hilbert space. This logic validates Eqs.(3) in a density-based theory. Because this orbital-indexed multiplicative local potential is singular at any node of $\phi_i$, these Gâteaux derivatives can only be equal for all index values if the nodes exactly cancel. A Fréchet derivative can occur only in such a special case, which is very difficult to construct unless the functional is defined as in the local density approximation.

Hence extending the definition of $F_s[\rho]$ so as to determine TFT equations conflicts in general with the exclusion principle. In contrast, an extended functional $F_s[\{\rho_i\}]$ and its Gâteaux derivatives exist, implying Eqs.(3). The corresponding OEL equations reduce to Kohn-Sham equations in the LDA, but locality of kinetic, exchange, and correlation potentials is not implied for more general energy functionals. The mathematical statement of this situation is that the Hohenberg-Kohn argument does not imply the existence of a Fréchet functional derivative, equivalent to a multiplicative local potential function, for any system with more than one Fermi-Dirac electron of each spin. This conclusion does not conflict with the rigorous theory of Englisch and England. Their argument, restricted to normalized ground-state total densities, cannot distinguish between Fréchet and Gâteaux functional derivatives.

VI. ORBITAL FUNCTIONALS IN AN EXACT THEORY

Formally exact orbital functionals for kinetic, exchange, and correlation energy can be deduced from standard N-electron theory. They can be incorporated into a formally exact mean-field theory in which the OEL equations extend Kohn-Sham theory to nonlocal potentials (orbital-indexed local potentials). Progress beyond the local-density approximation requires development of computational methodology for such nonlocal potentials.

The variational theory of independent-electron models is most simply developed as an orbital functional theory (OFT). For an N-electron eigenstate such that $(H - E)|\Psi\rangle = 0$ and any rule $\Psi \rightarrow \Phi$ that determines a model or reference state $\Phi$, unsymmetrical normalization $(\Phi|\Psi\rangle = (\Phi|\Phi\rangle = 1$ implies that $E = (\Phi|H|\Phi\rangle = E_0 + E_c$, where $E_0 = (\Phi|H|\Phi\rangle$ is an explicit orbital functional,
and \( E_c = \langle \Phi | H | \Psi - \Phi \rangle \) defines the correlation energy. Restricting the discussion to nondegenerate states, \( \Phi \) is a Slater determinant constructed from occupied orbital functions \( \{ \phi_i \} \), with occupation numbers \( n_i = 1 \). Spin indices and sums are assumed here but are suppressed in the notation. For orthonormal orbital functions, \( E_0 = T + U + V \), where

\[
T = \sum_i n_i (\hat{\phi}_i | i \hat{\phi}_i) \quad ; \quad V = \sum_i n_i (i | \phi_i) ,
\]

(12)

for \( \hat{\phi}_i = -\frac{1}{4} \nabla^2 \). Two-electron functionals are defined for \( u = 1/r_{12} \) by \( U = E_h + E_x \), where

\[
E_h = \frac{1}{2} \sum_{i,j} n_i n_j (\hat{\phi}_i | \hat{\phi}_j) \quad ; \quad E_x = -\frac{1}{2} \sum_{i,j} n_i n_j (\phi_i | \phi_j) .
\]

(13)

If \( Q = I - \Phi \Phi^\dagger \), \( E_c = \langle \Phi | H | \Psi - \Phi \rangle = \langle \Phi | H | Q | \Psi \rangle \). This implies an exact but implicit orbital functional

\[
E_c = -\langle \Phi | H | (Q (H - E_0 - E_c - i \eta) Q)^{-1} H | \Phi \rangle ,
\]

(14)

for \( \eta \to 0 + \). Because \( E_c \) is determined by the antisymmetric model function \( \Phi \), its functional derivatives cannot introduce spurious electronic self-interaction.

Orbital Euler-Lagrange equations follow immediately from standard variational theory\(^{16}\), in terms of the orbital functional derivatives

\[
\frac{\delta T}{n_i \delta \phi_i^*} = \frac{\delta U}{n_i \delta \phi_i^*} = \hat{u} \phi_i ; \\
\frac{\delta V}{n_i \delta \phi_i^*} = v(\mathbf{r}) \phi_i ; \\
\frac{\delta E_c}{n_i \delta \phi_i^*} = \hat{v}_c \phi_i ,
\]

(15)

using \( \hat{u} = v_h(\mathbf{r}) + \hat{v}_x \), where \( v_h \) is the classical Coulomb potential, and \( \hat{v}_x \) is the Fock exchange operator. Defining \( F = E - V = T + U + E_c \), its orbital functional derivative is

\[
\frac{\delta F}{n_i \delta \phi_i^*} = \mathcal{F} \phi_i = \{ \hat{u} + \hat{v}_x \} \phi_i ,
\]

(16)

For independent subshell normalization, Lagrange terms \( \epsilon_i [(i | i) - 1] \) are subtracted from the energy functional. The variational condition is

\[
\int d^3 \mathbf{r} \sum_i n_i (\delta \phi_i^* \{ \mathcal{F} + v - \epsilon_i \} \phi_i + cc) = 0 ,
\]

(17)

for unrestricted orbital variations in the usual Hilbert space. This implies the OEL equations

\[
\mathcal{F} \phi_i = \{ \epsilon_i - v \} \phi_i , \quad i = 1, \ldots, N .
\]

(18)

These equations reproduce Eqs.(3), derived directly from the OEL equations. This derivation generalizes Eq.(6) of Ref.5 to incorporate the exclusion principle\(^{12}\). Orthogonality constraints consistent with independent variation of orbital densities follow from the operationally equivalent OEL equations.

\[
\frac{\delta_i^* \mathcal{F} \phi_i}{\delta \phi_i^*} = v_{Fi}(\mathbf{r}) = \epsilon_i - v(\mathbf{r}) , \quad i = 1, \ldots, N .
\]

(19)

1. P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).
2. W. Kohn, W. and L. J. Sham, Phys. Rev. 140, A1133 (1965).
3. R. G. Parr and W. Yang, Density-Functional Theory of Atoms and Molecules; Oxford Univ. Press, New York, 1989.
4. R. M. Dreizler and E. K. U. Gross, Density functional theory, Springer, Berlin, 1990.
5. R. Colle and R. K. Nesbet, J. Phys. B 34, 2475 (2001).
6. K. Aashamar, T. M. Luke and J. D. Talman, At. Data Nucl. Data Tables 22, 443 (1978).
7. M. Petersilka, U. J. Gossmann and E. K. U. Gross, Phys. Rev. Lett. 76, 1212 (1996).
8. P. A. M. Dirac, Proc. Camb. Phil. Soc. 26, 376 (1930).
9. R. K. Nesbet, Phys. Rev. A 60, R3343 (1999).
10. R. K. Nesbet, Int. J. Quantum Chem. 85, 405 (2001).
11. R. K. Nesbet, Int. J. Quantum Chem. 95, xxx (2003), published online 12 June, 2003.
12. R. K. Nesbet, Int. J. Quantum Chem. 90, 262 (2002).
13. K. A. Brueckner and W. Wada, Phys. Rev. 103, 1008. (1956).
14. W. Brenig, Nucl. Phys. 4, 363 (1957).
15. E. H. Lieb, Int. J. Quantum Chem. 24, 243 (1983).
16. R. K. Nesbet, Variational principles and methods in theoretical physics and chemistry, Cambridge Univ. Press, New York, 2003.
17. H. Englisich and R. Englisich, phys.stat.sol.(b) 123, 711-721; 124, 373-379 (1984).
18. R. K. Nesbet, Phys. Rev. A 58, R12 (1998).
19. P. Blanchard and E. Brüning, Variational Methods in Mathematical Physics: A Unified Approach, Springer, Berlin, 1992.
20. R. K. Nesbet, Phys. Rev. A 65, 010502(R) (2002).