Nonlocal potentials in independent-electron models

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This note summarizes the motivation for extending current density-functional theory to include nonlocal one-electron potentials, and proposes methodology for practical calculations. The theoretical model, orbital functional theory, has been shown to be exact in principle for the general N-electron problem, but must depend in practice on a parametrized correlation energy functional. The discussion here is intended to honor Lee Allen and to bring up to date some conversations that we began in 1954.

I. INTRODUCTION

The density functional theory (DFT) of Hohenberg, Kohn, and Sham [1,2] has become the method of choice for computation of electronic structure and properties of large molecules and of solids. This theory justifies an independent-electron model that is considered to be exact in principle for N-electron ground states [3,4]. It is widely assumed that such an exact model can be expressed in terms of local potential functions for exchange and correlation, although evidence to the contrary has existed for some time [5]. It has only recently been shown that this locality hypothesis is inconsistent with exact theory for more than two electrons [6]. The specific mathematical point is that density functional derivatives of the Hohenberg-Kohn universal functional cannot be equivalent to local potential functions, as assumed in established literature [3,4], for more than two electrons in a compact electronic system. These functional derivatives can be constructed explicitly [6,7], and are found to be Gâteaux derivatives, the generalization to functional analysis of analytic partial derivatives [8]. For more than two electrons, they do not reduce as commonly assumed to simpler Fréchet derivatives, equivalent to multiplicative local potential functions, the generalization to functional analysis of analytic total derivatives [8].

This mathematical development explains a number of inconsistencies or paradoxes that result from assuming the locality hypothesis [5]. Failure of locality for the exchange potential in a Hartree-Fock variational model of DFT is implied by results of optimized effective potential (OEP) calculations going back as far as Aashamar, Luke and Talman [9], confirmed by recent quantitative tests [10]. The resulting problems or paradoxes include failure of DFT linear response theory [11] to agree in the exchange-only limit with the time-dependent Hartree-Fock theory of Dirac [12]. This failure can be traced to the locality hypothesis [13].

The most striking paradox affects the kinetic energy. In contrast to the locality hypothesis, Kohn and Sham use the kinetic energy operator of Schrödinger for what should be the density functional derivative of a ground-state kinetic energy functional. If the locality hypothesis were a rigorous consequence of variational theory, it should be valid for the kinetic energy functional, implying for noninteracting electrons an exact Thomas-Fermi theory (TFT) equivalent to DFT. However, the variational equations of these theories are incompatible for more than two electrons [14]. The Kohn-Sham equations of DFT are correct for atomic shell structure, but the locality hypothesis in TFT is inconsistent with the exclusion principle [14]. This is evident for the lowest 1s2s3S state of an atom with two noninteracting electrons, perhaps the simplest unequivocal example of this inconsistency. Unless both 1s and 2s orbital densities are independently normalized, the lowest total energy is achieved for two electrons in the 1s state. Fermi-Dirac statistics require an independent Lagrange multiplier ǫi for each orbital, while TFT provides only a single parameter µ for the total density. An equivalent inconsistency is implied for interacting electrons. This conclusion has been disputed and defended in recent publications [15,16,7].

Given a choice between an exact theory and one that can be expressed entirely in terms of local potential functions, there are pragmatic arguments supporting either alternative. The existing computational methodology of DFT requires use of local potential functions. In the local-density approximation (LDA), which is entirely justified by variational theory [7], first-principles calculations for condensed matter have had a revolutionary impact on understanding physical properties due to electronic structure. However, for magnetically ordered materials, there is a persistent problem due to the nonphysical electronic self-interaction, which may require use of nonlocal potentials in a fully predictive theory. For molecules, long-range potentials due to polarization response can become significant in determining molecular conformations, but apparently cannot be modeled using only approximate local correlation potentials. The optical potentials required in electron scattering theory are not directly described by energy-independent local potentials.

With such applications or extensions of existing theory in mind, the present paper will consider practical issues that arise in extending existing local-potential methodology to the nonlocal potential functions appropriate to an ultimately exact independent-electron model.
II. VARIATIONAL THEORY

The variational theory of independent-electron models is most simply developed as an orbital functional theory (OFT) [17]. For an N-electron eigenstate such that \( (H - E)\Psi = 0 \) and any rule \( \Psi \rightarrow \Phi \) that determines a model or reference state \( \Phi \), unsymmetric normalization \( \langle \Phi | \Phi \rangle = 1 \) implies that \( E = \langle \Phi | H | \Psi \rangle = E_0 + E_c \), where \( E_0 = \langle \Phi | H | \Phi \rangle \) 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 orbi-tal 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

\[
T = \sum_i n_i \langle \hat{i} | \hat{i} \rangle; \quad V = \sum_i n_i \langle i | v | i \rangle, \quad (1)
\]

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

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

If \( Q = I - \Phi^\dagger \Phi \), \( E_c = \langle \Phi | H | \Psi - \Phi \rangle = \langle \Phi | H | Q \Psi \rangle \). This implies an exact but implicit orbital functional [17]

\[
E_c = -\langle \Phi | H | (Q | H - E_0 - E_c - i\eta) Q | -1 | H | \Phi \rangle, \quad (3)
\]

for \( \eta \rightarrow 0^+ \).

Orbital Euler-Lagrange (OEL) equations follow immediately from standard variational theory [18], in terms of the orbital functional derivatives

\[
\frac{\delta T}{n_i \delta \phi_i^*} = \hat{t} \phi_i; \quad \frac{\delta U}{n_i \delta \phi_i^*} = \hat{u} \phi_i; \quad \frac{\delta V}{n_i \delta \phi_i^*} = v(r) \phi_i; \quad \frac{\delta E_x}{n_i \delta \phi_i^*} = \hat{v}_x \phi_i, \quad (4)
\]

using \( \hat{u} = v_h(r) + \hat{v}_x \), where \( v_h \) is the classical Coulomb potential, and \( \hat{v}_x \) is the Fock exchange operator. For independent subshell normalization, Lagrange terms \( \langle i | i \rangle - 1 \rangle \phi_i \) are subtracted from the energy functional. Defining \( \delta \phi_i = \frac{\delta E}{n_i \delta \phi_i^*} \), the variational equation is

\[
\int d^3 r \sum_i n_i (\delta \phi_i^* \{ G - \epsilon_i \} \phi_i + cc) = 0, \quad (5)
\]

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

\[
\{ G - \epsilon_i \} \phi_i = 0, \quad i = 1, \cdots, N. \quad (6)
\]

Orbitals of different energy are orthogonal. Equivalently, the universal functional \( F = E - V \) defines

\[
\frac{\delta F}{n_i \delta \phi_i^*} = \mathcal{F} \phi_i = \{ \hat{t} + \hat{u} + \hat{v}_c \} \phi_i. \quad (7)
\]

and the OEL equations are

\[
\mathcal{F} \phi_i = \{ \epsilon_i - v \} \phi_i, \quad i = 1, \cdots, N. \quad (8)
\]

Overlap products in \( \langle \Phi | H | \Phi \rangle \) drop out of this argument, because they either produce a unit factor or are multiplied by a factor that vanishes. Explicitly, for non-interacting electrons, the same OEL equations are obtained if the simplified functional \( E_0 = T + V \) is replaced by \( \langle \Phi | \hat{T} + \hat{V} | \Phi \rangle \). The functional differential

\[
\sum_i n_i \int d^3 r | \delta \phi_i^* (r) \{ \hat{t} + v(r) - \epsilon_i \} \phi_i (r) + cc | \Pi_{j \neq i} (j | j) \rangle \]

\[
+ \sum_i n_i \langle i | \hat{t} + v(r) - \epsilon_i | i \rangle \delta \Pi_{j \neq i} (j | j) \rangle. \quad (9)
\]

must vanish for unconstrained orbital variations about a stationary state. It cannot do so unless all Lagrange multipliers \( \epsilon_i \) are included, precluding an equivalent Thomas-Fermi theory. Variations of the overlap product are multiplied by a factor that vanishes.

III. THE NEED FOR NONLOCAL POTENTIALS

Hohenberg-Kohn theory can be proven for a nondegenerate ground state of any version of OFT in which \( E_{xc} = E_x + E_c \) is approximated by a parametrized functional of \( \rho \) [19]. Model electronic density \( \rho = \sum_i n_i \rho_i \) is a sum of orbital subshell densities \( \rho_i = \phi_i^* (r) \phi_i (r) \). Defining \( \hat{v}_{xc} \phi_i = \delta E_{xc}/n_i \delta \phi_i^* \), the corresponding Kohn-Sham theory is determined by the OEL equations given above. The still controversial issue of whether or not the effective one-electron potentials in these equations can be expressed as multiplicative local potential functions depends on the relationship between the orbital functional derivatives of Eqs.(4) and the density functional derivatives needed for DFT.

Density functional derivatives must be consistent with the OEL equations. A crucial logical point is that because functional definitions must be extended to include variations that are not constrained by normalization [18], variational theory restricted to normalized ground states [20] cannot determine OEL equations. A variational derivation of the Kohn-Sham equations must extend the universal ground-state functional of Hohenberg and Kohn to density variations driven by unrestricted variations in the orbital Hilbert space. This extended functional is denoted here by \( F_\ast \). Orbital theory simplifies the mathematics, because such variations are necessary and sufficient to determine the Euler-Lagrange equations [18].

The rigorous theory of Englisch and Englisch [20] proves the existence of a generic density functional derivative for a nondegenerate ground state. Although
not considered in the original derivation, it is clear from the OEL Eqs. (8) that the undetermined constant in [20], Eq. (4.1), must have orbital indices in order to be consistent with the electronic subshell structure implied by Fermi-Dirac statistics [7]. This is made explicit by Eqs. (7, 8) here, which imply that a functional derivative exists that depends on an orbital subshell index. Evaluated for a ground state [6, 21], the functional differential

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

\[ = \sum_i n_i \int d^3r \{ \epsilon_i - v(r) \} \delta \rho_i(r) \] (10)
determines the functional derivative

\[ \frac{\delta F_s}{n_i \delta \rho_i} = \epsilon_i - v(r). \] (11)

Because this depends on an orbital index, it defines a Gâteaux derivative [6, 8]. If a Fréchet derivative were to exist, equivalent to a multiplicative local potential function, it would imply the Thomas-Fermi equation,

\[ \frac{\delta F_s}{\delta \rho} = \mu - v(r). \] (12)

Because all \( \delta F_s/n_i \delta \rho_i \) must equal \( \delta F_s/\delta \rho \) if the latter exists, these equations are inconsistent unless all \( \epsilon_i \) are equal. Hence a Fréchet derivative cannot exist for more than one electron of spin without violating the exclusion principle. This result is not in conflict with rigorous analysis [20], which establishes the existence of Gâteaux derivatives in general, but cannot distinguish between Gâteaux and Fréchet derivatives because normalization is constrained [6]. For noninteracting electrons, this analysis applies to the Kohn-Sham kinetic energy functional \( T_s \) [7]. If independent subshell normalization is enforced, using Gâteaux derivatives and the set of Lagrange multipliers \( \{ \epsilon_i \} \), a generalized Thomas-Fermi theory can be expressed in terms of partial densities and is equivalent to the orbital functional theory of Eqs. (8) [21].

The mathematical situation is that for more than one electron of either spin, the functional \( F_s \) cannot be extended to derive Euler-Lagrange equations for an unstructured total density \( \rho \), because a Fréchet functional derivative does not exist. However, because Gâteaux derivatives exist, an extended functional of orbital subshell densities does exist. Independent subshell variations imply Euler-Lagrange equations equivalent to the OEL equations, valid for electronic subshell structure and for the exclusion principle. For noninteracting electrons, \( F_s \) reduces to the Kohn-Sham functional \( T_s \), with the same mathematical properties. There is no implication that the density functional derivative of \( E_{xc} \) must be a local potential function \( v_{xc}(r) \), unless this is mandated by the simplified functional dependence assumed in the local density approximation (LDA).

### IV. NONLOCAL POTENTIALS

The concept of a Gâteaux functional derivative establishes a direct relationship between orbital-indexed local potential functions and nonlocal potentials defined by orbital functional derivatives. Using exchange energy as an example, the orbital functional derivative is \( \delta E_x/n_i \delta \phi_i = \tilde{v}_x \phi_i \), and the functional differential can be expressed as

\[ \delta E_x = \sum_i n_i \int d^3r \{ \delta \phi_i^* \tilde{v}_x \phi_i + cc \} \]

\[ = \sum_i n_i \int d^3r \frac{\phi_i^* \tilde{v}_x \phi_i}{\phi_i^* \phi_i} \delta \rho_i. \] (13)

This determines a Gâteaux derivative

\[ \frac{\delta E_x}{n_i \delta \rho_i} = \frac{\phi_i^* \tilde{v}_x \phi_i}{\phi_i^* \phi_i} = v_{xi}(r), \] (14)

valid for arbitrary variations in the orbital Hilbert space. The technical problem of generalizing Kohn-Sham methodology to an exact theory reduces to methodology for such indexed local potentials. The occurrence of different potentials for different orbital indices can be compensated during self-consistent iterations by using off-diagonal Lagrange multipliers for orthogonalization. These parameters must vanish on convergence for closed-shell OEL equations. In the case of exchange in atoms, this is a variant of well-established methodology for iterative solution of the Hartree-Fock equations [22]. Inclusion of an indexed correlation potential, derived from any parametrized functional \( E_c \)

\[ v_{ci}(r) = \frac{\phi_i^* \tilde{v}_x \phi_i}{\phi_i^* \phi_i} \] (15)
is a straightforward generalization.

Hartree-Fock methodology based on expansion in atomic Gaussian basis orbitals is valid in principle, but becomes impractical for large molecules and solids. For solids, multiple scattering theory (MST) [23] has been the method of choice for DFT calculations. It provides a common methodology for molecules, based on variational treatment of space-filling atomic cells [24]. In MST, the principal calculation over a range of orbital energies is to solve the OEL equations within each local atomic cell, or within the enclosing sphere of each such cell. Independent representations of a wave function within each cell are matched across intercell boundaries using variational formalism [24]. Generalization of the intracell calculations to nonlocal potentials is straightforward, simply including an indexed parametrized exchange-correlation potential while integrating Schrödinger or semirelativistic equations at specified energy. The practical technical problem is thus reduced to the treatment of the long-range tails of indexed local potentials defined within each cell. In MST, the formalism is greatly simplified by the
fact that atomic basis functions are literally truncated at cell boundaries [24]. This means that there are no intercell overlap contributions.

An approximation that may turn out to be both efficient and accurate is suggested by the MST formalism. This is a "local nonlocal" (LNL) model. True indexed potentials are to be used only within atomic cells, but are replaced by their asymptotic forms in external cells. In general, these asymptotic forms arise from electrostatic multipole potentials, and can be represented as long-range local potentials. If this is valid, the indexed potentials in each cell are augmented by an external field potential that is summed over all other cells. As in the well-known Ewald expansion, this implies substantial cancellation of fields, including electrostatic screening, and may justify neglecting such terms during self-consistent iterations, including them as first-order perturbations after convergence.

An important step toward practical methodology for long-range correlation has been proposed, and tested in an electron scattering model [25]. In a general context, the method is to compute, for each atomic cell, the first-order perturbed orbital functions due to external multipole fields. Intercell correlation energy then can be formulated in terms of these polarization pseudostates, and response potentials can be constructed that are correct at long range, but vanish smoothly at the cell origin. An example of dipolar response has been carried out in detail. The implied polarization potential is used to calculate polarization response effects in e – He scattering cross sections [25].

[1] Hohenberg, P. and Kohn, W., Phys.Rev. 1964, 136, B864.
[2] Kohn, W. and Sham, L.J., Phys.Rev. 1965, 140, A1133.
[3] Parr, R.G. and Yang, W., Density-Functional Theory of Atoms and Molecules; Oxford University Press: New York, 1989.
[4] Dreizler, R.M. and Gross, E.K.U., Density functional theory; Springer-Verlag: Berlin, 1990.
[5] Nesbet, R.K., First Annual John C. Slater Lectures, Univ. of Florida, 2001; Adv. Quantum Chem., in the press.
[6] Nesbet, R.K., Int.J.Quantum Chem. 2001, 81, 384.
[7] Nesbet, R.K., Phys.Rev.A 2002, 65, 010502(R).
[8] Blanchard, P. and Brüning, E., Variational Methods in Mathematical Physics: A Unified Approach; Springer-Verlag: Berlin, 1992.
[9] Aashamar, K., Luke, T.M. and Talman, J.D., At.Data Nucl.Data Tables 1978, 22, 443.
[10] Colle, R. and Nesbet, R.K., J.Phys.B 2001, 34, 2475.
[11] Petersilka, M., Gossmann, U.J. and Gross, E.K.U., Phys.Rev.Lett. 1996, 76, 1212.
[12] Dirac, P.A.M., Proc.Camb.Phil.Soc. 1930, 26, 376.
[13] Nesbet, R.K., Phys.Rev.A 1999, 60, R3343.
[14] Nesbet R.K., Phys.Rev.A 1998, 58, R12.

[15] Gál, T., Phys.Rev.A 2000, 62, 044501.
[16] Holas, A. and March, N.H., Phys.Rev.A 2001, 64, 016501.
[17] Nesbet, R.K., Int.J.Quantum Chem. 2001, 85, 405.
[18] Nesbet, R.K., Variational principles and methods in theoretical physics and chemistry; Cambridge Univ. Press: New York, 2002.
[19] Nesbet, R.K., Int.J.Quantum Chem. 2000, 77, 521.
[20] Englisch, H. and Englisch, R., phys.stat.sol.(b) 1984, 123, 711; ibid. 1984, 124, 373.
[21] Nesbet, R.K., Int.J.Quantum Chem. 2002, 90, 262.
[22] C. Froese Fischer, The Hartree-Fock Method for Atoms; Wiley: New York, 1977.
[23] Gonis, A. and Butler, W.H., Multiple Scattering in Solids; Springer: New York, 2000.
[24] Nesbet, R.K., Int.J.Quantum Chem. 2002, 91, 46.
[25] Nesbet, R.K., Phys.Rev.A 2000, 62, 040701(R).