BEYOND DENSITY FUNCTIONAL THEORY:  
THE DOMESTICATION OF NONLOCAL POTENTIALS

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Due to efficient scaling with electron number N, density functional theory (DFT) is widely used for studies of large molecules and solids. Restriction of an exact mean-field theory to local potential functions has recently been questioned. This review summarizes motivation for extending current DFT to include nonlocal one-electron potentials, and proposes methodology for implementation of the theory. The theoretical model, orbital functional theory (OFT), is shown to be exact in principle for the general N-electron problem. In practice it must depend on a parametrized correlation energy functional. Functionals are proposed suitable for short-range Coulomb-cusp correlation and for long-range polarization response correlation. A linearized variational cellular method (LVCM) is proposed as a common formalism for molecules and solids. Implementation of nonlocal potentials is reduced to independent calculations for each inequivalent atomic cell.

1. Introduction

Hohenberg and Kohn\cite{1} (HK) proved for nondegenerate ground states that total electronic density determines the external potential acting on an interacting N-electron system. The constrained search procedure of Levy\cite{2} extends this proof to general variational forms of N-electron wave functions, easily extended to spin-dependent densities. Spin indices and summations are assumed here, but omitted from notation. HK theory defines a universal ground state density functional $F_s = E - V$, which reduces for noninteracting electrons to the kinetic energy functional $T_s$ of Kohn and Sham\cite{3} (KS). Implementation of the implied density-functional theory (DFT) followed only after introduction of the KS orbital mean-field model. In KS theory, the density function is $\rho(r) = \sum_i n_i \rho_i(r)$, a sum of orbital densities $\rho_i = \phi_i^* \phi_i$ for the model state, with occupation numbers $n_i$. The many review articles and monographs on DFT are exemplified by Parr and Yang\cite{4} and by Dreizler and Gross\cite{5}.
2. Motivation for an exact orbital theory

2.1. Can DFT with local potentials be an exact theory?

The relationship of DFT to many-body theory remains obscure, requiring quite different methodology for strongly-correlated systems. The KS construction is not easily related to strong-correlation theory, in which a Hubbard model is often introduced that has no relationship to the electronic density. There is no systematic way to improve model functionals. Nonphysical self-interaction produces incorrect ground states for magnetically ordered systems. Nonbonding interactions in molecules and optical potentials in electron scattering are not correctly described.

Numerous problems or paradoxes in DFT are associated with the assumption that exact mean-field theory requires only local one-electron potential functions. It is important to note that the mathematical issue here is not the existence of HK functionals as such, but rather the existence of the uniquely defined density functional derivatives required to determine variational Euler-Lagrange equations.

Quantitative tests show that an optimized effective potential (OEP local exchange) does not reproduce ground-state energies and densities in the unrestricted Hartree-Fock (UHF) variational model for atoms. Because the UHF energy functional is uniquely defined, and the accurately computable UHF ground-state density is both noninteracting and interacting v-representable, this textbook example of constrained variational theory is a rigorous consistency test for DFT. The exchange-only limit of DFT linear response theory is inconsistent with the time-dependent Hartree-Fock theory of Dirac, due to failure of locality. A postulated local kinetic energy would imply an exact Thomas-Fermi theory (TFT), in conflict with KS DFT and with the exclusion principle for more than two electrons.

In an orbital model, such as KS theory, the exclusion principle is imposed by independent variation and normalization of each occupied orbital of a model state. This logic produces an extended TFT when applied to orbital densities. This orbital-density theory is operationally equivalent to orbital functional theory (OFT), and reduces to KS DFT in the local density approximation (LDA). There is no conflict with rigorous theory. Confined to normalized total densities, functional analysis implies neither Thomas-Fermi nor KS equations.

2.2. OFT with nonlocal potentials can be an exact theory

For nondegenerate states, the KS Ansatz, $\rho = \sum_i n_i \rho_i$, expresses $\rho$ as a function of occupied orbitals of a Slater determinant model state $\Phi$. With this Ansatz, any well-defined density functional is also an orbital functional. If $F_\nu[\rho] = E - V$ is parametrized as an explicit functional of $\rho$, it defines an orbital functional $F[\{\phi_i\}]$ for all functions in the orbital Hilbert space. Schrödinger variational theory is expressed in terms of orbital functionals with functional differentials of the form

$$\delta F = \sum_i n_i \int d^3r \{ \delta \phi_i^* \frac{\delta F}{\delta \phi_i} + cc \}.$$
Beyond Density-Functional Theory: The Domestication of Nonlocal Potentials

This defines an orbital functional derivative of the general form \( \frac{\delta F}{\delta \phi_i} = \mathcal{F} \phi_i \), where \( \mathcal{F} \) is a linear operator. These functional derivatives determine orbital Euler-Lagrange (OEL) equations \( \mathcal{F} \phi_i = \{ \epsilon_i - v(r) \} \phi_i \). This is an exact theory if the true N-electron \( F = E - V \) can be expressed as an orbital functional\(^{17}\).

OFT is deduced from formally exact N-electron theory, and nonlocal exchange-correlation potentials are constructed. Quite explicitly, the exchange "potential" is the Fock exchange operator, and the correlation "potential" is determined by orbital functional derivatives of the linked-cluster expansion\(^7\). The implied OEL equations are a realization of "exact" KS equations. OFT implies a systematic refinement of the LDA based on implementation of nonlocal potentials. The theory is not density-dependent, bypassing questions of \( v \)-representability and of the convergence of density-gradient expansions. It is not restricted in principle to ground states, to weak correlation, or to short-range interactions\(^{17}\). It systematizes many alternatives currently being pursued in molecular DFT: the orbital-dependent exchange originally proposed by KS\(^3\), and the OEP approximation\(^7,8\), sometimes characterized as "exact KS"\(^{18}\). OFT nonlocal potentials are derived from functionals defined by antisymmetric wave functions. In principle, this eliminates self-interaction and the need for any \( \textit{ad hoc} \) correction\(^{19}\). In practice, computational methodology developed for the latter may be very useful in the context of the orbital-indexed potentials considered here. The present analysis has important practical implications for computational methodology relevant to the electronic structure of large molecules and solids. With a new theoretical basis embedded in N-electron theory, extension of current work on exact exchange in DFT to include electronic correlation requires timely development of efficient computational methods appropriate to nonlocal potentials\(^{20}\).

3. Orbital functional theory

3.1. \textit{An exact mean-field theory exists}

Specify any relationship \( \Psi \rightarrow \Phi \) that determines a model state \( \Phi \) for any N-electron state \( \Psi \), where \( \Phi \) is a Slater determinant for any nondegenerate state. This postulate implies the KS Ansatz in a variational theory of the model density. Imposing normalization \( (\Phi | \Psi) = (\Phi | \Phi) = 1 \), which causes no formal problems for a finite system, \( (H - E) \Psi = 0 \) implies that \( E = E_0 + E_c \), where \( E_0 = (\Phi | H | \Phi) \), and \( E_c = E - E_0 = (\Phi | H | \Psi - \Phi) \) defines the correlation energy. Since \( E_0 \) is an explicit orbital functional, an exact mean-field theory exists if \( E_c \) can be derived from many-body theory as an orbital functional. The linked-cluster expansion shows that this is possible. Exact OEL equations are defined formally by orbital functional derivatives of the linked-cluster expansion. An implicit closed form of the exact functional \( E_c \) has been derived\(^{21}\).
3.2. Kinetic energy and exact exchange

Using $\hat{t} = -\frac{1}{2} \nabla^2$ and $v = v(r)$, functional $E_0 = T + U + V$ is defined such that

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

for orthonormal orbital functions. The Coulomb interaction $u = 1/r_{12}$ defines orbital functional $U = E_h + E_x$, where

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

3.3. Variational equations for the orbitals

Orbital Euler-Lagrange (OEL) equations are derived using the orbital functional derivatives

$$\frac{\delta T}{n_i \delta \phi_i^*} = i\phi_i; \quad \frac{\delta U}{n_i \delta \phi_i^*} = \hat{u}\phi_i; \quad \frac{\delta V}{n_i \delta \phi_i^*} = v(r)\phi_i.$$  \hspace{1cm} (1)

Here $\hat{u} = v_h(r) + \hat{v}_x$, where $v_h$ is the Coulomb potential, and $\hat{v}_x$ is the Fock exchange operator. An orbital functional $E_c[\{\phi_i\}]$ defines

$$\frac{\delta E_c}{n_i \delta \phi_i^*} = \hat{v}_c\phi_i.$$  \hspace{1cm} (1)

An orbital functional $E_c$ is defined such that $\hat{v}_c$ is Hermitian. A Lagrange functional consistent with independent orbital normalization is defined by subtracting $\sum_i n_i (i|i) - 1\epsilon_i$ from the energy functional. Defining $F = E - V$, the OEL equations are

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

using the orbital functional derivative $\frac{\delta F}{n_i \delta \phi_i^*} = \mathcal{F}\phi_i = \{\hat{t} + \hat{u} + \hat{v}_c\}\phi_i$. Here $\hat{t}$ and $\hat{u}$ are explicitly nonlocal (linear operators), and there is no implication that $\hat{v}_x + \hat{v}_c$ is equivalent to a multiplicative local potential.

4. OFT as an exact variational model

4.1. Correlation energy as an orbital functional

Unsymmetrical normalization $(\Phi|\Psi - \Phi) = 0$ defines an orthogonal projection, $P\Psi = \Phi$ and $Q\Psi = \Psi - \Phi$, where $P = \Phi\Phi^\dagger$ and $Q = I - P$. The N-electron Schrödinger equation can be partitioned by projection. In the limit $\eta \to 0+$,

$$Q\Psi = -[Q(H - E_0 - E_c - i\eta)Q]^{-1}H\Phi.$$  \hspace{1cm} (1)

Hence, for $\eta \to 0+$,

$$E_c = (\Phi|H|\Psi - \Phi) = (\Phi|H|Q\Psi) = -\langle \Phi|H[Q(H - E_0 - E_c - i\eta)Q]^{-1}H|\Phi \rangle.$$  \hspace{1cm} (1)

Because model state $\Phi$ determines $Q$, this exact expression for $E_c$ is an implicit orbital functional.

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4.2. Gâteaux functional derivatives

Suppose that an orbital functional $F$ is defined such that $\frac{\delta F}{\delta \phi_i} = \hat{v}_f \phi_i$ and $\hat{v}_f$ is Hermitian in the orbital Hilbert space. With no additional assumptions, the functional differential

$$\delta F = \sum_i n_i \int d^3 r \{ \delta \phi_i^* (r) \hat{v}_f \phi_i (r) + cc \} = \sum_i n_i \int d^3 r \frac{\phi_i^* \hat{v}_f \phi_i}{\phi_i^* \phi_i} \delta \rho_i$$

determines a density functional derivative. This derivative is an orbital-indexed local potential function

$$\frac{\delta F}{n_i \delta \rho_i} = \frac{\phi_i^* \hat{v}_f \phi_i}{\phi_i^* \phi_i} ,$$

defined throughout the orbital Hilbert space.

For unconstrained orbital variations about any stationary state, the functional differential of $F = E - V$ is determined by Eqs.(2), the OEL equations. In detail

$$\delta F = \sum_i n_i \int d^3 r \{ \delta \phi_i^* (r) F \phi_i (r) + cc \} = \sum_i n_i \int d^3 r \{ \epsilon_i - v_f (r) \} \delta \rho_i (r)$$

determines the density functional derivative

$$\frac{\delta F}{n_i \delta \rho_i} = v_f (r) = \epsilon_i - v(r).$$

Hence for any stationary state, $v_f (r)$ depends on the orbital subshell index unless all orbital energies are equal. Such dependence on a "direction" in the Banach space of densities defines a Gâteaux functional derivative, the generalization to functional analysis of an analytic partial derivative. The Gâteaux derivative expressed by an indexed local potential $v_f (r)$ is in general singular at nodes of the orbital function $\phi_i (r)$. A Fréchet derivative (multiplicative local potential) can exist only if $v_f$ is independent of its orbital index at all coordinate points, which requires elimination or exact cancellation of the orbital nodes. This condition is imposed by the construction of $vxc$ in the LDA, but cannot be assumed to be a general consequence of variational theory.

In order to generate Euler-Lagrange equations with a normalization constraint, a variational functional of total density must be defined for arbitrary infinitesimal variations about normalized densities. The HK functional $F_s$ is defined only for normalized ground states. No Euler-Lagrange equation is implied unless this definition can be extended to include infinitesimal neighborhoods of ground states. If a total (Fréchet) functional derivative were to exist, it would justify such an extension, implying an exact Thomas-Fermi theory. If the functional differential

$$\delta F = \int d^3 r \frac{\delta F}{\delta \rho} \delta \rho$$

is a unique functional of the total density variation $\delta \rho$, it defines a Fréchet functional derivative

$$\frac{\delta F}{\delta \rho} = v_f$$
as a multiplicative local potential function. Comparison of Eqs.(4) and (3) shows
that the total functional differential is not unique unless the corresponding Gâteaux
derivatives are all equal. For variations about a ground state, this requires all orbital
ergies to be equal, violating the exclusion principle for any compact system with
more than one electron of each spin. Hence exact TFT is not implied for more
than two electrons. In contrast, the Gâteaux derivatives are well-defined, and imply
modified Thomas-Fermi equations with orbital indices, consistent with the exclusion
principle, and with the general form of KS equations

Eqs.(3) and (4) cannot be reconciled for the HK functional $F_s$ unless all or-
bitral energy eigenvalues are equal$^{13,15}$. This difference is a consequence of different
normalization constraints in DFT or OFT and in TFT. That independent normal-
ization of orbital densities is physically correct, specifically enforcing the exclusion
principle in Hartree-Fock theory and KS DFT, is obvious for the example of an atom
with two noninteracting electrons of parallel spin. The ground state is $1s2s^3S^\pi$. 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 allows the nonphysical solution

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

which violates the exclusion principle.

5. How to do it

The technical problem of generalizing KS DFT to an exact theory reduces to
methodology for indexed local potentials. For atoms or local atomic cells, this just
adds an indexed correlation potential $v_{ci}(r) = \frac{\phi_i^* \phi_i}{\phi_i^* \phi_i}$ to standard Hartree-Fock
methodology for the Fock exchange potential$^{24}$. Off-diagonal Lagrange multipliers
can be used to constrain orbital orthogonality during self-consistent iterations. For
closed-shell systems, these Lagrange multipliers must vanish on convergence.

5.1. Energy-linearized variational cellular method

Basis-set expansion becomes impractical for large molecules and solids. The alterna-
tive methodology of multiple scattering theory, used in many variants for the
electronic structure of condensed matter$^{25}$, can be formulated as a variational cel-
lar method (VCM)$^{26,7}$. In full-potential MST, local basis functions are computed
numerically in each atomic cell of a space-filling Voronoi lattice. These functions
are truncated at local cell boundaries, and linear combinations are matched varia-
tionally across cell interfaces$^7$. The logical structure and inherent efficiency of the
VCM emulate a tight-binding model. It can be linearized in energy and adapted to a general variational method for solids and molecules\textsuperscript{27}. Using numerical basis functions in local cells validates semirelativistic calculations for heavy atoms, and validates frozen-core approximations. These features are exploited in condensed-matter methodology. Truncating basis functions at cell boundaries removes intercell overlap and multicellular Coulomb integrals from the methodology. Local cells interact through boundary matching and through extended potential functions that act as an external field in each cell. As in quantum field theory, the essential physics is that of quasiparticles interacting through effective mean fields.

5.2. The local nonlocal (LNL) model

Intracell calculations including an indexed correlation potential are just like Hartree-Fock for atoms, not a practical problem. Indexed local potentials are consistent with MST, which simply uses a different orbital basis in each local cell. The residual practical problem is the treatment of long-range tails of the indexed potentials. The truncated basis removes all intercell overlap contributions to these potentials. Electronic correlation arises from two distinct causes. The short-range effect of the Coulomb cusp is significant for intracellular correlation, while the long-range effect of polarization is expected to be the principal intercellular correlation effect. In the case of metals, long-range correlation is required for dynamical exchange screening, needed to eliminate nonphysical behavior of exact exchange at the Fermi surface. The long-range asymptotic form of the indexed potentials for exchange and correlation is electrostatic, modified by polarization response. The significant success of DFT and of model theories suggests that, not far outside a source charge density, the asymptotic potentials in general reduce to nonindexed collective fields. If this is valid, it would justify a ”local nonlocal” (LNL) model, in which true indexed potentials are used only within local cells, while asymptotic forms of the extracellular fields are combined as an effective mean field in each such cell. As in the Ewald expansion, this implies significant cancellation or screening of fields. This may justify neglecting the multipole part of the effective field in each cell during self-consistent iterations, including it as a first-order perturbation after convergence.

5.3. Coulomb-cusp correlation

Short-range correlation is dominated by the Coulomb pole $u = 1/r_{12}$, requiring a $1 + \frac{1}{2}r_{12}$ cusp in the wave function. The Colle-Salvetti (CS) Ansatz\textsuperscript{28} imposes this cusp condition, multiplying model state $\Phi$ by a symmetrical factor $\Pi_{i<j}[1 - \xi(r_i, r_j)]$, where, in relative coordinates $q = r_i - r_j$ and $r = \frac{1}{2}(r_i + r_j)$, $\xi(r, q) = \exp(-\beta^2 q^2)[1 - \Gamma(r)(1 + \frac{1}{2}q)]^2$. Correlation energy can be expressed exactly as a sum of pair-correlation energies, $E_c = (\Phi|H|\Psi - \Phi) = \sum_{i<j} n_i n_j \epsilon_{ij}^c$. This can be parametrized, in analogy to CS, by $\epsilon_{ij}^c = -(ij|\tilde{u}\xi_{ij}(q)|ij)$, where $\tilde{u} = u(1 - \mathcal{P}_{12})$, $\mathcal{P}_{12}$ is the 2-electron exchange operator, and $\xi_{ij}(q) = \exp(-\beta^2 q^2)[1 - \gamma_{ij}(1 + \frac{1}{2}q)]$. 
The normalization condition \( (\Phi|\Psi - \Phi) = 0 \) determines

\[
\gamma_{ij} = \frac{(ij|\exp(-\beta \epsilon q^2)[ij])}{(ij|\exp(-\beta \epsilon q^2)(1 + \frac{1}{2q})[ij])},
\]

such that \( (ij|\xi_{ij}[ij]) = 0 \) for each pair. The free parameter \( \beta_{ij} \) can be chosen to minimize the Bethe-Goldstone (independent electron pair model) energy for each orbital pair. The nonlocal correlation potential is defined by \( \hat{v}_c \phi_i = \frac{\delta E_i}{n_i\delta\phi_i} = -\sum_j n_j (j|\bar{u}\xi_{ij}|j)\phi_i \). Antisymmetry is built in. Terms \( j = i \) vanish, so there is no self-interaction. The indexed local correlation potential is

\[
v_c(r) = -\phi^{-1}_i(r) \sum_j n_j (j|\bar{u}\xi_{ij}|j)\phi_i(r).
\]

### 5.4. Multipole response correlation

If the mapping \( \Psi \rightarrow \Phi \) is determined by the Brueckner-Brenig condition\(^{29,30}\), \( (\delta\Phi|\Psi) = 0 \), so that \( \Phi \) is the reference state of maximum weight in \( \Psi \), this removes all single virtual excitations \( \Phi^a \) from \( \Psi \). Then the leading terms of \( Q\Psi \) are double virtual excitations \( \Phi^{ab} \) with coefficients \( c_{ij}^{ab} \). Higher-order terms do not interact with \( \Phi \) through the Coulomb interaction. Thus \( E_c = (\Phi|H|Q\Psi) \) is a sum of pair correlation energies\(^7\),

\[
\epsilon_{ij} = \sum_{n<\beta}(1 - n)(1 - n_\beta)(ij|\bar{u}|ab)c_{ij}^{ab}.
\]

The expression \( (a|\hat{v}_c|i) = (a|\delta E_c|n_i\delta\phi_i^a) \) can be evaluated, treating the coefficients \( c_{ij}^{ab} \) as constants in the current cycle of an iterative loop\(^{21}\). These matrix elements

\[
(a|\hat{v}_c|i) = \sum_j n_j \sum_{c<\beta}(1 - n_c)(1 - n_\beta)(aj|\bar{u}|cb)(cb|\bar{c}|ij)
- \sum_{k<j} n_kn_j \sum_b (1 - n_k)(kj|\bar{u}|ib)(ab|\bar{c}|kj),
\]

agree with the leading self-energy diagrams in many-body perturbation theory. This determines the kernel of the linear operator \( \hat{v}_c \).

As an illustrative example, this formula has been simplified and applied to the leading long-range term in an iterative expansion of the multipole polarization potential implied by bound-free correlation between a scattered electron and a polarizable target\(^{21}\). This analysis introduces a polarization pseudostate \( \phi_{pj} \), computed as the normalized first-order response of an occupied orbital \( \phi_j \) of the target system to an external multipole field. For multipole index \( \lambda \), transition matrix elements \( (p_j|u|j) \) vary as \( r^\lambda \) for small \( r \) and as \( 1/r^{\lambda+1} \) for \( r \gg r_0 \). The implied multipole polarization potential is quadratic in these transition elements and varies as \( r^{2\lambda} \) and \( 1/r^{2\lambda+2} \), respectively, in these limits. Hence, unlike earlier models from purely asymptotic theory, this potential vanishes as \( r \rightarrow 0 \). When applied for \( \lambda = 1 \) to variational calculations of low-energy e-He scattering, this polarization potential produced scattering phase shifts in good agreement with earlier variational calculations that incorporated dipole polarization response. The indicated general methodology is to compute first-order multipole pseudostates within each atomic
cell, and then use them to construct the multipole polarization potentials that contribute to the mean external field in all other cells.

6. Conclusions

This brief review is intended to motivate and to outline methodology that should be implemented in order to get beyond current practical limitations of density-functional theory. It is a call to the condensed-matter community to move beyond DFT by extending current methodology for nonlocal potentials. It is a call to the theoretical chemistry community, concerned with the electronic structure of large molecules, to set aside CI methods and restricted DFT in favor of an efficient, practicable, and ultimately exact ab initio mean-field theory.

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